Université d'Ottawa • University of Ottawa

Factors Affecting Collaboration Among Learners in a Web-based Learning (WBL) Environment

By

Deborah E.Tiwari

Faculty of Education

School of Graduate Studies and Research

A thesis submitted in conformity with the requirements of the Degree of Doctor of Philosophy in the University of Ottawa

Abstract

Because Web-based Learning (WBL) is a relatively new educational environment, limited research has been undertaken in exploring the factors that affect learners and instructors in WBL. (Trentin, 2001; Muirhead, 2001; Sloffer, Dueber & Duffy, 1999; Gabriel, 1999; Land & Hannafin, 1997; Mayer, 1997; Newman, Webb & Cochrane, 1996). How WBL learners co-construct knowledge through collaboration with each other under the guidance of an instructor has not been examined in-depth. Although there is literature that examines general factors affecting learners in the WBL environment, there is little research that reveals why these factors are significant to the process of constructing learning, or how they impact learners' ability to collaborate in a WBL environment (Trentin, 2001; Carstens & Worsfold, 2000; Sloffer, Dueber & Duffy, 1999; Gabriel, 1999; Edelson, Pia, & Gomez, 1996; Silva & Breuleux, 1994).

This qualitative single case study was comprised of a WBL course delivered to a group of public sector employees in various locations around the world, and focused on their WBL experiences. An instructor, a course administrator, a Website manager, and eight learners volunteered to participate in the case study. Data from the study were analyzed in order to provide in-depth descriptions of factors affecting collaboration among learners in a course delivered solely through WBL.

This study revealed factors that primarily prevented learners from collaborating among themselves as they constructed their learning in a Web-based environment. Some factors that could have facilitated collaboration were evident; however, the barriers to it were insurmountable in this case. The findings of this study have illuminated findings of previous studies, and contributed new understandings. Recommendations for WBL

processes and components will assist WBL instructors and designers to facilitate collaboration and knowledge co-construction among learners.

Dedication

I dedicate this thesis to my Grandmothers:

Georgina Maude Graham McNamee

and

Dorothy Ladubec Bjerke Lemko.

Their intelligence, creativity and
work ethic continue to inspire me,
though they have long since gone.

Acknowledgements

I want to thank my thesis director, Dr. Colla Jean MacDonald, for her encouragement and guidance throughout my program and the writing of my thesis. Her candid, constructive advice was invaluable. I also want to thank my internal committee members, Dr. Janice Ahola-Sidaway, Dr. Cheryl Duquette and Dr. Raymond LeBlanc, for their comments and suggestions for the thesis. Their contributions made it stronger.

Deep gratitude and appreciation go to my son, Sasha, and my husband, Adrian, for their support, and for the sacrifices they made along the way so that mommy could work on her "book".

I need to thank my family and friends for their support. Their confidence in me during this process helped me immensely, and especially at times when my own confidence faltered. Special thanks go to my parents, Ron and Peggy Bjerke, who celebrate their golden anniversary in December 2002, and to my best buddy, Julie Duff, for helping me keep my goals in sight.

Finally, I must not forget my appreciation for Oliver and little Angel, our miniature schnauzers, who loyally kept me company during long days of writing.

****

I stepped from plank to plank
So slow and cautiously;
The stars about my head I felt,
About my feet the sea.

I knew not but the next
Would be my final inch,-
This gave me that precarious gait
Some call experience.

Emily Dickinson

TABLE OF CONTENTS

List of Tables

List of Figures

OVERVIEW OF THE STUDY

Web-based Learning (WBL) is one educational environment where learning is constructed (Burge, 2000; Wilson & Lowry, 2000; Gabriel, 1999; Edelson, Pia, & Gomez, 1996; McIssac & Gunawardena, 1996; Lebow, 1993; Duffy & Jonassen, 1992; Jonassen, 1991). In WBL, instructors guide, mentor and facilitate interaction among learners. The degree to which participants interact in a WBL course may also be integral to the perceived success or failure of WBL, and to its potential as an effective educational venue. An integral component of a social constructivist learning environment, collaboration may also be essential for successful WBL. Although some research points to general factors affecting learners in the WBL environment, there is limited research which reveals why they are significant to the process of constructing learning online (Muirhead, 2001; Mayer, 1997).

There is little research to date which reveals how these factors impact learners' ability to collaborate among themselves in this environment. This study contributes to an understanding of WBL, a learning environment where research and theory building about it are relatively young (Merriam, 1998). It addresses a gap in the literature by revealing the barriers and facilitators that either prevent or encourage learners to collaborate among themselves as they co-construct their learning in a solelyWeb-based environment (Muirhead, 2001). Moreover, it also provides poignant insight into the effect of these barriers on learners' perceptions. The understandings and recommendations of this study

provide educators with insight into improving the design and delivery of courses through WBL, and for facilitating collaboration among learners.

This thesis is comprised of six chapters. Chapter One introduces the study by describing the problem, the purpose of the study, and the conceptual framework that guided and provided the study's structural integrity. Definitions of terms generally found in the WBL environment are included. Chapter Two provides a context for the study through a comprehensive review of the literature, beginning with the general discussion about WBL and its orientation as a constructivist learning environment. Social constructivist theory and collaboration theory are reviewed, followed by the literature that explores interaction in WBL environments. Chapter Three examines the gap in the literature and presents the research questions that guided the present study. The research methodology is discussed from the governing research paradigm through data collection, data analysis and data management. Chapter Four reveals the findings by theme, from major themes to lesser themes. The findings are then discussed within the context of current WBL research in Chapter Five. The latter chapter concludes with recommendations for facilitating collaboration in WBL courses, based on the findings of the study. Chapter Six presents the implications of the study, conclusions, and suggestions for further research. The implications of the findings and recommendations for teaching and learning in the WBL environment are discussed. The thesis concludes with some reflections and thoughts about the development of WBL pedagogy.

Chapter 1

An Introduction

My interest and motivation for pursuing a doctorate in Education, within the discipline of Psychopedagogy, and focussing on Web-based Learning (WBL), has been to contribute to the creation of pedagogically grounded WBL environments. Because WBL is still very new and undeveloped as an educational venue, it is important to me, as an educator and educational researcher, that sound teaching theory underlies WBL development.

Working professionally within the Canadian telecommunications industry for ten years, I witnessed tremendous change over a relatively short period of time. As a participant in an environment that both developed and marketed innovative technology, I closely observed the evolution of technology from teleconference to Internet. As a marketing manager, I conducted market research and advised on its results for the development of products and services for business and general consumers. I often noted, much to my chagrin as a consumer and as an educator, that the implementation of technology was often led by the technology itself rather than the need it might serve. This sometimes resulted in a "square peg meets round hole" scenario, where users of technology were unable to use it effectively because the technology was not designed to match their needs or capabilities.

In this environment that I observed the evolution of the Internet itself into multi-faceted venues for doing business, for providing entertainment, and for delivering education. It is the latter venue, and the scores of educational Websites and course

providers that it spawned, which captured my interest and imagination. I was excited by the possibilities that WBL presented, but I was also concerned about the learners and instructors who would be adopting WBL as their classroom. It became obvious that, despite best efforts to the contrary, many learners and instructors were struggling with the challenges presented by the WBL environment. My intuition and experience influenced my suspicion that technology was driving pedagogy rather than the reverse (Breithaupt, MacDonald, Stodel & Farres, 2002; Jung, 2000; Carr & Carr, 2000, Mayer, 1997).

I do believe that WBL will evolve as a sound educational environment as educational researchers contribute to the development of WBL pedagogy. This study focuses on what I think is an important and vital element to the process of learning, and its facilitation in WBL. When learners are provided with the opportunity and capability to collaborate with each other through discussion in WBL, the experience can go beyond simply learning course content to greater depths of understanding. When collaboration is achieved, learners become members of a community that may persist after their WBL course is over.

Statement of the Problem

Web-based Instruction (WBI) as a pedagogically sound, educational environment is in its infancy (Trentin, 2000; Wilson & Lowry, 2000; Gabriel, 1999; Mitchell, Kerr & DiPetta, 1998; Hill, 1997; Mayer, 1997). A thorough understanding of the issues that impact on instructors and learners when they interact in this environment is needed for the development of viable WBI pedagogy. In particular, there is a need for a theoretical underpinning in order to ground WBI pedagogy (Burge, 2000; Wilson & Lowry, 2000;

Kent & McNergney, 1999; Mayer, 1997; Lebow, 1993). Current research reveals that WBI may be inherently aligned with constructivist learning theory (Burge, 2000; Wilson & Lowry, 2000; Gabriel, 1999; Edelson, Pia, & Gomez, 1996; Jonassen, Peck & Wilson, 1999; Jonassen, 1991; McIssac & Gunawardena, 1996), where the onus for learning shifts from instructor to learner in knowledge construction. As the body of research literature related to WBI continues to grow, researchers, including myself, are re-naming WBI as Web-based Learning (WBL) in order to more accurately reflect the constructivist nature of this learning environment. In the present study, therefore, I use the term Web-based Learning (WBL) to reflect the learning activities, pedagogical strategies and discussions that take place in Web-based environments.

Research also shows that WBL holds promise for a social constructivist venue where a high degree of collaboration may occur among learners (Gabriel, 1999; MacDonald & Gabriel, 1999; Mitchell, Kerr & DiPetta, 1998; Edelson, Pia, & Gomez, 1996; Newman, Webb & Cochrane, 1995; Yakimovicz & Murphy, 1995; Eastmond & Rohfeld, 1993), under the guidance and mentorship of their WBL instructors. The degree to which collaboration is possible in a WBL course may also be integral to the perceived success or failure of WBL for the delivery of education, and to its potential as an effective educational venue. As an integral component of a social constructivist learning environment (Schwandt, 1994; Moyse & Elsom-Cook, 1992; Lave & Wenger, 1991), collaboration may also be the integral component of successful WBL.

Because WBL is a relatively new educational venue, limited research has been undertaken in exploring the factors that affect learners and instructors in a WBL environment (Trentin, 2001; Sloffer, Dueber & Duffy, 1999, Gabriel, 1999; Land &

Hannafin, 1997; Newman, Johnson, Cochrane, & Webb, 1996). How learners construct knowledge through collaborating with each other under the guidance of an instructor, who collaborates with them, has not been examined in-depth (Hara & Kling, 2000; Kitchen & & McDougall, 1999; Holt, 1998; Davis, 1997). Although some research points to general factors affecting learners in the WBL environment, there is little research revealing why these factors are significant to the process of constructing learning (Trentin, 2001; Hara & King, 2000; Sloffer, et al., 1999; Gabriel, 1999; Davis, 1997; Edelson, Pia, & Gomez, 1996; Silva & Breuleux, 1994). Moreover, there is no research to date which reveals how or why these factors impact WBL learners' perceptions and ability to collaborate among themselves in this environment. Finally, few qualitative studies have been conducted in a course where learners meet solely online. While quantitative research has revealed factors that enhance or impede learning in a strictly WBL environment, there is a gap in the research literature that describes why or how these factors affect learners (Muirhead, 2001; Carstens & Worsfold, 2000; Gabriel & MacDonald, in press).

An opportunity for conducting an investigation to address this gap in the literature presented itself during a discussion with the manager of a learning Website for a Government of Canada federal department. Both of us were speakers at a high-tech conference and noticed the other's presentation abstract in the conference handbook. I had been working as a senior consultant to the federal government for several years, and was speaking about my research in WBL. She was presenting an overview of her department's creation of a WBL Website.

This departmental learning Website provides employees with distance learning services both at headquarters in Ottawa and abroad. Launched in the late nineties, the learning Website is evolving as technological advances are implemented within the department's infrastructure. Of specific interest to me were the WBL venues provided for learners to collaborate with each other. Currently the departmental learning Website uses a bulletin board feature where learners may post text. To date, this has not been well utilized by learners, despite promotion by the learning Website manager. When she discovered that I was looking for a research site to study collaboration among learners in WBL, she suggested the study would be of interest and potential benefit to her department. She also was concerned about the factors that impacted on collaboration among learners, and wanted to know how to improve WBL for the learners. Since an asynchronous venue for learner collaboration was planned for an upcoming course, I agreed with her that this course was a mutually beneficial research site for my study.

Purpose of the Study: Discovering factors that enabled or impeded collaboration

The purpose of this study was to investigate the factors that facilitated or created barriers to collaboration among course participants, and how this affected their perceived ability to construct learning. A new frontier for education, WBL is, perhaps, a new educational institution for this century.

The intent of this study was to contribute to WBL pedagogy by constructing an understanding that furthers WBL theoretical development and uncovers particular needs for developing WBL pedagogy. In particular, I wanted to discover and examine specific barriers, and some facilitators, that affect the ability of WBL learners to co-construct

learning through effective collaboration among themselves. By understanding the nuances of both the barriers and the facilitators that impacted collaboration among learners in a WBL course, educators will be better equipped to design and deliver courses through this medium.

Research approach and conceptual framework: guiding the study

The research approach illustrated in Figure 1 shows the governing research paradigm and research activity of the study. The first, second and third planes reveal a qualitative, Constructivist research approach. The first plane depicts the research paradigm and the overarching ontology and epistemology that guided this qualitative single case study. Because WBL is an inherently social constructivist learning environment where learners co-construct knowledge with other course participants, many WBL researchers have invoked a constructivist paradigm as an appropriate theoretical framework to guide their studies (Burge, 2000; Wilson & Lowry, 2000; Land & Hannafin, 1997; Edelson, Pia & Gomez, 1996; McIssac & Gunwardena, 1996; Jonassen, Myers & McKillop, 1996; Jonassen, 1991). All participants, including myself as researcher, were sources of data.

The nature of reality for WBL learners is that they construct it themselves, both alone and in concert with other course participants. WBL is a research environment where multiple realities (Creswell, 1998) exist for learners, instructors and researchers. It is these multiple realities that have been collected as data resulting in rich descriptions which were further refined and interpreted to create understandings.

Conceptual Framework and Research Activities of The Study

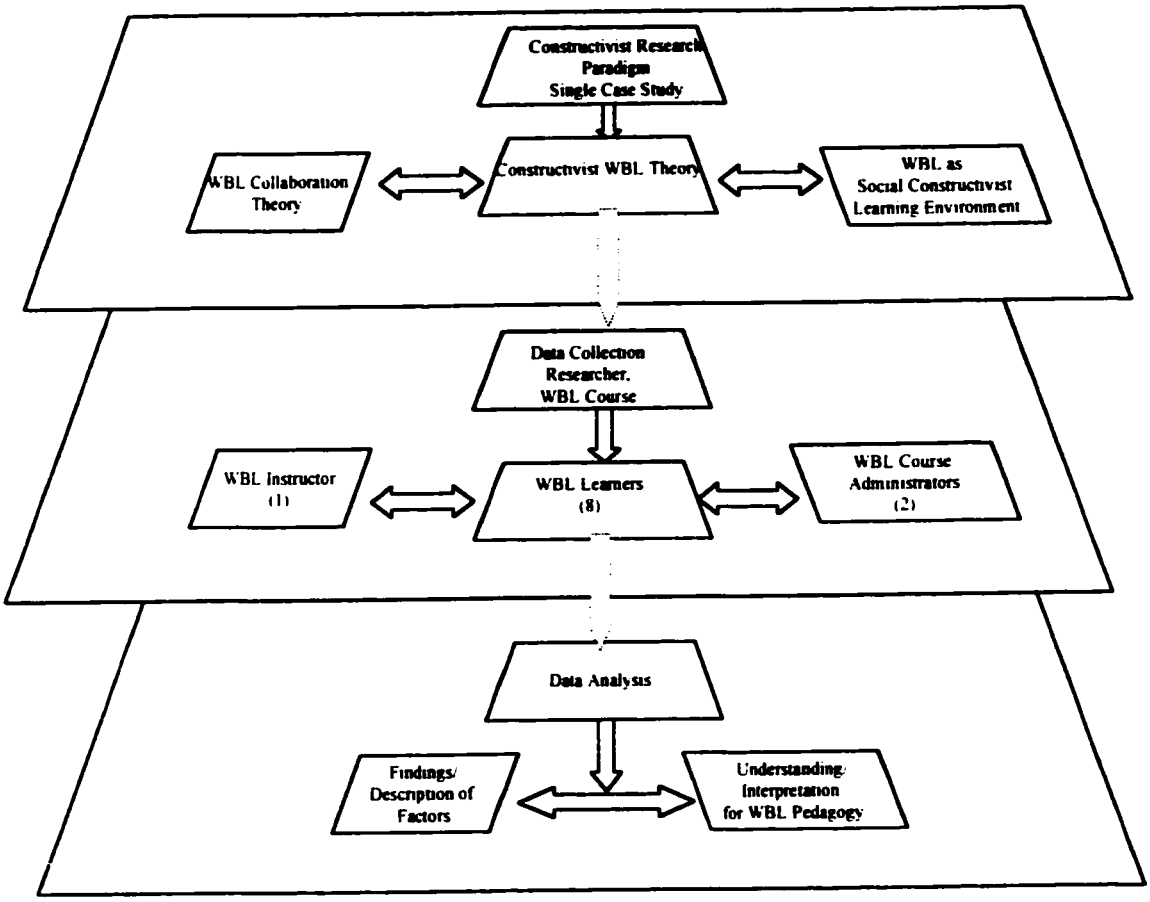


Figure 1. Conceptual framework and research activities of the study.

Theoretical underpinnings

The first plane of Figure 1 illustrates the theoretical underpinnings of the study. Developers of WBL pedagogy may anchor it within constructivist theory (Oliver & Omari, 2001; Carr-Chellman & Duchastel, 2000; de Caprariis, 2000; Westera & Sloep, 1998; Dede, 1995; El-Tigi & Branch, 1997; Spiro, Feltovich, Jacobson, & Coulson, 1991; Jonassen, Myers & McKillop, 1996; Jonassen, 1991). The very nature and context of WBL courses is such that learners must often, if not always, construct their own learning, individually, with their instructor and, at times, through collaboration with other learners (Hung & Nichoui, 2001; Logan, 2000, Lauzon, 1999; Jonassen, Dyer, Peters, Robinson, Harvey, Kling & Loughner, 1997; Silva & Breuleux, 1994).

The tenets of constructivist learning theory suggest that learners bring their past learning and experiences to every learning situation, where they incorporate new information and socially-mediated knowledge as they construct new knowledge for themselves (Dalgarno, 2001; Lauzon, 1999; Morrison & Collins, 1996; Westera & Sloep, 1998; Gruender, 1996; Ahola-Sidaway, MacLean, & Treuhaft, 1990). In the constructivist environment, learners are primary stakeholders in the success of the learning process. Optimal results of this process are learners who, through individual and collaborative efforts, have achieved new learning and understanding of a particular subject or topic and its place within the world. Along the way, they may have also developed new sources of information and collaborative partners for constructing future learning (Westera & Sloep, 1998; Gruender, 1996).

In a constructivist learning environment, collaboration occurs when there is social interaction between learners which will "...enhance the learning that students achieve

through the transformative process of communication" (Edelson, et al., 1996). Key to that transformation is the interdependence of individual and social processes when learners co-construct knowledge (John-Steiner & Meehan, 2000; Logan, 2000). When learners commence activity in a learning venue, they may initially depend on other more experienced participants to lead the way. Once they know more and are more secure or self-efficacious in the environment, they also become more responsible and participatory in the learning process (John-Steiner & Meehan, 2000; Lave & Wenger, 1991).

Context of Data Collection

The second plane of Figure 1 illustrates the research environment. A WBL course and its participants comprised this single case study. The writing skills course was the case as it was delivered through the departmental learning Website. The course participants included eight learners and three non-learners. Five learners accessed the course Website from foreign locations, and three learners were based in Ottawa. The non-learners included the instructor and two course administrators located in Ottawa.

Results of Data Analysis

The third plane shown in Figure 1 reveals the final stages of research activity. The findings of this study provided the kind of insight required for creating WBL environments where learners can collaborate unimpeded by perceived barriers. I had expected to locate the facilitators and barriers to collaboration in WBL within the course delivery as it was affected by course organization, administrative support, and delineation of the roles of learners and instructors in WBL. What I also learned was that course

participants' experiences, expectations, and personality characteristics also had a direct influence on how learners interacted and learned in this environment, and whether or not interactions could be described as collaborative discussion.

Understandings constructed from the findings of the study contribute to the development of WBL pedagogy. Particular needs are identified and recommendations are made for improving WBL so that collaboration among learners leads to optimum learning for them. Interpretations of the findings are offered as a lens through which to view other WBL environments.

Definition of Terms

The following definitions are provided for understanding terms that appear throughout the thesis, some of which are particular to WBL.

Web-based Learning (WBL)

Web-based Learning (WBL) is learning that is facilitated through an Internet Website, where learners access courses and learning materials, and communicate with instructors and other learners through the Website. WBL may reflect its constructivist nature as an environment where learners construct knowledge on their own and with other learners under the guidance of an instructor or facilitator. In this case, WBL was achieved through a departmental learning Website, in a writing skills course. The learning materials and Website tools were self-contained in the course site, and participants could interact with each other asynchronously through the "bulletin board", where they could post text and read text posted by others.

Web-based Instruction (WBI)

Web-based Instruction (WBI) holds the same definition as WBL; however, it implies an instructor-led learning environment. Educational researchers are moving to re-describe the Web-based learning environment as WBL to denote its constructivist nature as learners construct and co-construct knowledge together in WBL courses. To date, WBI has been used to describe WBL activities in most of the research literature. In this study, Web-based Learning (WBL) will be used in reference to Web-based learning activity and related research literature.

Internet

The Internet is the technological network infrastructure that facilitates the exchange and the dissemination of information. The Internet is the support mechanism for the Web.

The Web

The Web is the repository of information on the Internet, including voice, video and data.

Synchronous Communication

Synchronous communication refers to online communication that takes place between participants at the same time from different locations within a Website venue. Internet "chat rooms" are examples of synchronous, online communication venues. In

this case, there was no synchronous, online venue where course participant could meet for discussions.

Asynchronous Communication

Asynchronous communication refers to online communication that takes place between participants at different times from different locations within a Website venue provided for that purpose. Internet "listservs" are examples of asynchronous, online communications venues. In this case, asynchronous, online communication was achieved through the bulletin board where course participants could post comments and read the comments of others.

Online Conferencing

Online conferencing describes formal occasions when course participants communicate with each other using the Internet, either in asynchronous or synchronous Website venues.

Bulletin board

The bulletin board is the Website tool on the departmental learningWebsite that is provided for course participants to communicate with each other. Communication on the bulletin board is asynchronous, with participants posting messages to and in response to each other.

Posting

Posting refers to the activity of writing comments on a computer screen and then using Website tools provided to place the comments within the desired Website venue, such as the bulletin board.

Learners

Learners in this study were course participants who registered for the Writing skills course, and completed the requirements of the course. Eight learners participated in the study. Three learners were based in Ottawa, and five learners were based in various locations around the world.

Non-Learners

Non-learners in the study describe the participants who were responsible for delivery of the course, and included the instructor and two course administration participants. The instructor was a retired teacher who had taught in traditional and distance venues for many years. Her role was to deliver the course to learners, to guide their discussion on the bulletin board, and to evaluate their assignments as they were submitted. The course administration participants included the departmental learning Website manager, who was responsible for the overall implementation and maintenance of the Website and its courses, and the course manager, whose role was to design and administer the courses and to address learners' administrative and technical concerns.

Chapter 2

A Context: Review of the Literature

Introduction

This review provides a current and historical perspective on the development of WBL. It generally supports an emerging constructivist, learner-focused paradigm with WBL (Wilson & Lowry, 2000; Reigeluth and Squire, 1998; Lebow, 1993; Jonassen, 1991). The research presented in this review falls under the following general headings: Distance Learning Through WBL; WBL as a Constructivist Learning Environment; WBL Models; Teaching and Learning in the WBL Environment; Self-efficacy in WBL; and Collaborative Learning in WBL.

Distance Learning through WBL

Distance learning environments have evolved from written, pen and paper correspondence to include radio, television and computer based instruction, computer mediated communications, and the Internet (Marina, 2001; MacDonald & Gabriel, 1999; Schrum, 1998; Hill, 1997; Bates, 1995). Instructional methods that use computer technology, the Internet and the Web, may have the greatest potential for promoting the interaction and engagement of distance learners. Passerini & Granger (2000) suggest that "...it is only with the use of the Internet, and the World Wide Web, that distance education moves away from an objectivist approach to education to a constructivist environment" (p.4). The Web has not yet evolved to its full potential for instruction and learning (Trentin, 2001; Logan, 2000; Wilson & Lowry, 2000; Hill, 1997; Mayer, 1997;

Jonassen, 1991; Lebow, 1993). Distance education through the Internet is mainly asynchronous as Websites become repositories for information, supplied by instructors and learners at different times, and then accessed at different times (Morrison, 2001). WBL has substantial potential for extending distance instruction from this kind of model to one that includes active asynchronous and synchronous learning (Muirhead, 2001; Trentin, 2001; Burge, 2000; Wilson & Lowry, 2000; Berge, 2000; MacDonald & Gabriel, 1999; Hill, 1997).

There are technological, organizational, institutional, ethical, and pedagogical considerations and issues for distance learning in the Internet environment. The creation of Web-based learning environments, and with it a complete reliance on technology, presents a new set of challenges for institutions, instructional designers, the instructors themselves, and learners (Breithaupt, et. al., 2002; Kang, 2001; Luker, 2000; Lauzon, 1999; Driscoll, 1998; Hill, 1997; Bates, 1995; Shimabukuro, 1995; Jonassen, 1991). The impact of technology and WBL on distance learners has spawned the development of research and pedagogy that is learner-centred (Burge, 2000; Ely, 1999). However, there are improvements to be made to help WBL participants achieve success. Feelings of isolation and disconnection, information overload, and a sense of being overwhelmed seem to plague learners and prevent them from becoming actively engaged in WBL (Christensen, 2001; Huang, 1997; Hill, 1997). Costs related to acquiring the necessary technology in order to engage in WBL are also a consideration (Hill, 1997). Overcoming a fear of how to use technology and software is an issue for many people. For instructors and administrators, course planning, technical support, payment, evaluation, and course validity provide organizational challenges (Breithaupt, et. al., 2002; Hill, 1997; Jonassen,

et al., 1997). Willis and Dickinson (1997) note that extensive effort is involved in the creation of the Web-based, distance education environment, and usually requires a multi-faceted team of professionals, in addition to the instructor, to produce quality educational materials for the site. As is the case with other distance learning venues, the medium often drives the methodology and, in turn, may constrain instruction (Wilson & Lowry, 2000; Simonson, 2000). However, there are pedagogical methodologies and strategies which can lessen the constraints of this medium, and involve the incorporation of a venue to allow for interaction between course participants (Wilson & Lowry, 2000; Simonson, 2000; Jung, 2000; Newman et al., 1995).

Technological considerations for Web-based distance learning

Technological considerations for distance learning through the Internet include the purchase and support for computer hardware and software, and, of course, the Internet connection for access to the Web (Hill, 1997). The initial cost associated with these items remains substantial for many learners. Some learners may also require training on how to use the equipment and the Internet to access the World WideWeb (WWW) and Web-based libraries.

In an asynchronous WBL environment, the technological components generally consist of: (a) a server housing the WBL Website, links to the WWW, and access by registering learners; (b) a Website and pages containing the instructional materials to guide learners; (c) e-mail capability for individual interaction with instructors and fellow learners; (d) a computer conferencing venue where group postings may be made and read

by all learners in a course; and, if desired, (e) a CD Rom with additional course readings or required materials (Driscoll, 1998; Hill, 1997).

In the cases where a synchronous venue is included, it generally takes the form of simultaneous. Web-based, desktop conferencing where a number of learners in various locations share a visible workspace on their respective computer screens. Where Web-based, desktop video-conferencing is a capability, they may also be able to see each other as they talk. Usually, this kind of synchronous interaction is accessed through a corporate Intranet, accessible only to employees and housed within a company's dedicated technology server. The costs involved when video capability comes into play are usually prohibitive for both the WBL course provider and the average learner.

There are technological challenges peculiar to distance education offered through the Internet via the Web. These include the manipulation of WBL interactive methods and tools to ensure involvement of learners in this venue (Shotsberger, 1997). The appropriate blend of asynchronous and synchronous interaction between learners and instructors in order to achieve learning and a sense of community or belonging to a class continues to be studied by educational researchers (Burge, 2000; Newman, et. al., 1996).

The advantage that technology provides to learners is immediate access to information and contact with communities of expertise. Time and distance are of no consequence in either seeking out desired information, in performing course-related activities, and in connecting with others (Kearsley, 2000; Garmer & Firestone, 1996; Shimabukuro, 1995). It is possible that solely asynchronous WBL courses are more advantageous than when there is a synchronous component, strictly because there is less consequence if technology fails. Asynchronous learners may access and upload or

download information and assignments, e-mail or post comments to a listserv at their convenience; whereas, synchronous learners must be online with either their instructor or peers, or both, in "real-time" which puts them at the mercy of technological malfunction.

The disadvantages of technology-driven "classrooms" are often issues of cost, fear of technology, computer malfunction, and feelings of alienation when working alone at the computer (Wilson & Lowry, 2000; Hill, 1997; Jonassen, et al., 1997; Huang, 1997). There is the possibility that many learners may not have access to or cannot afford to buy computers, let alone pay for an Internet connection in order to access WBL (McCormack & Jones, 1998). This is usually not a concern for learners in corporate or public sector environments where most have desktop computer systems and access to Internets and Intranets. Some learners may also fear a technology because they have not had much exposure to it. Learners in this situation may be intimidated by using the equipment, software, and navigational tools required by WBL (Hill, 1997). Frustration comes fairly easily when difficulties arise with connecting to the Internet and, depending on modem capabilities, speed of access and navigation (Harmon & Jones, 1999; Forman, 1994). Again, these issues are not as prevalent in corporate or government settings where learners have ready, high-speed access to the Internet and the latest in computer equipment and software, and have some experience using them. The importance of access to technical support in WBL is a key issue for WBL instructors to address (Muirhead, 2001; Kearsley, 2000).

Organizational considerations for Web-based distance learning

Organizational considerations are magnified in a Web-based, asynchronous distance venue because a Website, related materials, and enabling the access to them must be done months ahead of the course commencement date (Trentin, 1999; Hill, 1997; Willis & Dickinson, 1997). Ongoing support in the event of technical failure is a constant and costly requirement. A mechanism to ensure cohesiveness and a sense of continuity in the course is another organizational challenge (Hill, 1997), and presently takes the form of daily updates and revisions to the Website itself in the asynchronous environment. Initially cumbersome, these tasks, and using technology itself, will be less burdensome and difficult as instructors make the transition to the WBL environment and become comfortable and adept within it (Harasim, Hiltz, Teles, & Turoff, 1995).

Course planning and organization is important for all classroom and distance education, and critical in WBL (Ruokamo & Pohjolainen, 2000; Kearsley, 2000; Hill, 1997; Jonassen, et. al., 1997). In addition to course materials and administrative issues, the WBL site must be designed to house all course-related information and interaction, including links to other WWW sites. Instructors must also, as in any class, provide clear directions and guidelines to deal with grading and participation issues and expectations (Benigno & Trentin, 2000). This is particularly important in a venue where learners are "invisible" and are only seen as participating when they submit assignments and contribute text-based commentary (Muirhead; 2001; Harasim, Hiltz, Teles & Turoff, 1995).

Once the course commences, ongoing support, both technological and instructor-based, is necessary. Learners require support and guidance when they run into real or

perceived technological difficulties. Instructor support, in the forms discussed previously, is critical to creating a sense of continuity and community (Kearsley, 2000; Schrum, 1998; Hill, 1997; Harasim, et al., 1995), and to guiding and facilitating individual and group reflection and collaboration, as learners construct knowledge in this environment (Wilson & Lowry, 2000).

Institutional considerations for Web-based distance learning

First and foremost, institutions need to take care when planning and implementing technological change; just as they would for any major institutional change (Marina, 2001, Ruakamo & Pohjolainen, 2000). The learning objectives and the technological infrastructure required to support WBL must be sound in order for it to be successfully implemented:

> Most traffic wrecks that take place on the e-learning highway are due to omission rather than commission-institutional partnerships that are keen on technology have a tendency to become caught up in the fast-paced nature of technological change and perceive time spent on laying the groundwork to be time wasted....the technology, not the need, is driving the change. (Hezel & Dominguez, 2001, p.2.)

All aspects of facilitating WBL, from an institutional perspective, must be clearly envisioned and planned prior to invoking the technology (Marina, 2001, Ruokamo & Pohjolainen, 2000). Institutions who neglect to do this in a rush to be competitive are

doomed to "seat-of-the-pants" management and successes (Knowlton, 2000; Furnell. Evans & Bailey, 2000; Turoff, 1997).

Another consideration is that WBL instructors, as part of higher-learning institutions such as universities and colleges, are rarely compensated for the enormous. additional tasks and responsibilities that come with the design and delivery of WBL (Trentin, 1999). This is a distinct disadvantage in that there is little motivation to move learning into this realm. As well, issues of security of transactions, security of information provided by the institution and learners, equity of access. issues around learner evaluation and course credits are primary institutional concerns (Benigno & Trentin. 2000; Schrum, 1998; Shimabukuro, 1995). Fortunately, rapid advances in secure technology are reducing these obstacles.

Despite a daunting plethora of obstacles to overcome in WBL, many institutions are striving to adopt it as a learning environment. A vision of its potential along with the convenience of access seem to overcome the detractions of WBL for learners and instructors.

Ethical issues for Web-based distance learning

Ethical issues underlie Web-based distance education concerns, in the same way that they do in other distance venues. These are present in: admission; intake and retention of learners; course development and presentation; evaluation; program and course marketing and administration; and facilitator/instructor/learner interaction (Hill. 1997). These issues need to be dealt with early in the planning stages (Willis & Dickinson. 1997). Effective distance education programs require very careful planning

and a close understanding of course and learner requirements (Driscoll, 1998; Willis & Dickinson, 1997). This is no less the case when distance education is offered through the Internet (Benigno & Trentin, 2000; MacDonald & Gabriel, 1999).

Pedagogical considerations for Web-based distance learning

Dependence on asynchronous communication in distance education creates a transactional distance between learners and instructors, and among learners (Christensen, 2001; Shotsberger, 1997). An environment that promotes collaborative communication may result in learners taking part-ownership in the instruction (Kearsley, 2000; Shotsberger, 1997; Newman et al., 1995), which may increase their motivation, and create a sense of belonging to a class or community. Sharing of ideas and concerns among all participants involved in the learning, leads to improved instructional practices and learning strategies (Wilson & Lowry, 2000; Logan, 2000; MacDonald & Gabriel, 1999; Shotsberger, 1997; Jonassen, 1991). Design of WBL may incorporate both asynchronous and synchronous options, to give learners access to the course materials, to electronic libraries, to the instructor, and to each other, as well as to their individual progress through learning objectives (Lewis, Whitaker & Julian, 1995).

Anderson and Joerg (1996) concur in their review of the challenges WBL presents to instructors. Particularly critical is the linking of text, graphics, audio, video files and executable programs which may be located anywhere on the Internet. The linking structure must be conceptually organized and interrelated, and visually appealing (Muirhead, 2001; Kearsley, 2000; Alexander, 2000; Lebow, 1993; Jonassen, 1991). WBL studies point to the necessity for studies which contribute to the development of

organizing models which capture the constructivist nature of WBL (Burge, 2000; Wilson & Lowry, 2000; Jonassen, et. al., 1996; Lebow, 1993). When this is achieved, WBL will fulfill its potential as a learner-centred educational venue where participants construct knowledge through collaboration and negotiation (Carr-Chellman & Duchastel, 2000; Hickey, 1997).

WBL as a Constructivist Learning Environment

Constructivisim represents a major shift away from a dominant objectivist pedagogy. In this shift, the focus moves from instructor to learner (Burge, 2000; Wilson & Lowry, 2000; Lebow, 1993; Jonassen, 1999, 1991). Objectivism denotes the existence of a real world that is structured and must be revealed, interpreted, and "mapped" onto learners by instructors (Jonassen, 1991). Constructivism, on the other hand, begins from the premise that learners construct their own learning, or "realities" by interpreting their own perceptions of information presented to them. Influencing their interpretations are learners' previous experiences in the world, experience with the particular subject being studied, personal beliefs, and their existing cognitive structures, along with the social context within which the information is presented (Wilson & Lowry, 2000; Jonassen, et. al., 1999; Saye, 1997; Hill Duin & Hansen, 1994; Lebow, 1993; Jonassen, 1991). As a result, external reality is unique for each learner, although, through collaboration, learners may find they have common understandings and views regarding particular learning or understanding.

Instructors in the constructivist learning environment act as guides or coaches to direct and redirect learners in their quest for knowledge, and to help learners analyze their

own learning and problem-solving strategies (Wilson & Lowry, 2000; Wilson, 1996; Lebow, 1993; Jonassen, 1991; White, 2000). Instructors may provide individualized response to their learners' particular needs, learning skills, and quests, and help to create, but not control, interest and engagement with the subject matter (Lebow, 1993). By also providing a venue for learners to communicate with each other, constructivist instructors encourage knowledge negotiation and construction, and cooperative learning (Lauzon, 1999; Lebow, 1993; Jonassen, et. al., 1999, Jonassen,1991).

According to many scholars, WBL environments may offer an optimal venue for constructivist learning for a number of reasons, not the least of which is its inherent situated nature for learners. Because WBL learners are situated in physical isolation from their instructor and other learners, they must, to a greater degree, construct and be responsible for their own learning (Kearsley, 2000). WBL may also be particularly suited to adult learners who are often experienced learners and workers, and may be better able to collaborate in a social constructivist environment because they may be used to engaging in collaborative discussion in the performance of their work-related duties (Yakimovicz & Murphy, 1995). In the process of determining the meaning of what they are learning, learners interpret, problem-solve, and integrate information into understanding which is relative to their personal contexts (Oliver & Omari, 2001; Carr-Chellman & Duchastel, 2000; Jonassen, et. al., 1999; Jonassen, 1991).

Another reason why WBL may provide the ideal constructivist learning environment is its facility and opportunity for externalized reflection and collaboration among learners (Oliver & Omari, 2001; de Caprariis, 2000; Lebow, 1993;). One of the underlying tenets of social constructivism is the idea that understanding and knowledge is

socially negotiated when individuals become aware of others' understandings of the same topic (Hung & Nichani, 2001; Lauzon, 1999; Jonassen, et. al., 1999). Since WBL learners come from different "realities", they approach their learning from various perspectives and construct knowledge through negotiation and collaboration (Lauzon, 1999; Harasim, et. al., 1998). Passerini & Granger (2000) suggest that "Asynchronous discussions, moderated and summarized by the instructor, become the 'live' textbook where students learn from each other" (p.4). Further studies are needed to explore the opportunity for how online reflection and collaboration can contribute to honing critical and higher-order thinking skills in WBL (Benson Soong, et. al., 2001; Newman, et. al., 1996).

WBL Models

Relan and Gillani (1997) characterize the traditional classroom model as instructor-centred with a one-way transmission of information from the instructor, and with instructor and learners physically co-located. The instructor disseminates knowledge, usually in a lecture format, while learners listen and reflect on the information presented (Knowlton, 2000). WBL, on the other hand, is described as a collaborative learning environment in which cognitive instructional strategies are applied (Newman, et. al., 1995; Jonassen, 1991). Learners use the vast resources of the Internet, independently, to support their "classroom" learning. Hiltz (1994) concludes that learners must spend more time doing coursework in WBL than they do in many traditional class. They are forced to play a more active role in their learning by virtue of the medium (Trentin, 1999; Lebow, 1993, Jonassen, et. al., 1999, Jonassen, 1991);

whereas, in the traditional classroom, they may passively take notes (Relan & Gillani, 1997).

Presently, researchers are developing models for designing WBL. Some organize venues and material according to the subject matter, while some pattern tools and content in a structure which reflects learners' mental conceptions (Anderson and Joerg, 1996). Others are developing models to address a unique learning environment where a diversity of capabilities of mainly adult learners must be supported and managed (MacDonald, Breithaupt, Stodel, Farres & Gabriel, 2001; McConnell, 2000; Passerini & Granger, 2000). Learners may hail from anywhere in the world and come together in a WBL course. The structures and pedagogy that support WBL must be flexible (Frost & Taylor, 2001; Passerini & Granger, 2000). In implementing WBL models, it is incumbent upon instructors in WBL to sort materials and information into units of knowledge and activities, based on course content, which they can guide their learners through asynchronously (Dowling, 1997). When learners engage in the activities to construct their knowledge, it has also been suggested that a mechanism be in place so that instructors can sense when learners are having difficulty navigating their way through these units (McConnell, 2002; Knowlton, 2000; Hill & Hannafin, 1997).

Jonassen et. al. (1997) suggest the Cognitive Flexibility Theory as the most likely adaptable model to the hypertext environment of the Web. Based on cognitive learning theory, it is a conceptual model for the design of learning environments developed to simplify concepts in order to make them understandable by learners. It focuses on the role of context, with the underlying theory that learning acquired in a real-world context is better retained and built-upon. It seems to be further suggested that a WBL model

based on this theory will move WBL from a strictly "pre-packaged" venue, into one where the best of what is pre-packaged is combined with interaction among learners to create an environment where "advanced knowledge acquisition" may occur (Jonassen, et. al., 1997; Dalgarno, 2001). An advantage to using this model, perhaps as a template for developing others, is that when learners reconcile a number of perspectives about a particular subject, they are forced to take the next step and construct their own knowledge or meaning. The implications of this for learning and retention are extremely positive, moving learners beyond simply regurgitating subject matter absorbed in a one-way transmission from the instructor. WBL necessitates that learners take responsibility for both what they learn and the level to which they take that information (Wilson & Lowry, 2000; Lebow, 1993; Jonassen, et. al., 1999; Jonassen, 1991). WBL design must acknowledge learners' life situations and experiences, as well as provide a venue for interaction in order to promote a high level of knowledge construction and learning (Knowlton, 2000; Burge, 2000; Canada; 2000; Weiss, 2000). Development of WBL models should reflect these considerations for optimum learning (Hamilton, 1994; Moyse & Elsom-Cook, 1992).

Driscoll (1998) notes that juxtaposing learning objectives with the cognitive domain is a recommended beginning for choosing WBL. Driscoll suggests "Bloom's Taxonomy of Educational Objectives in the Cognitive Domain" as a guide for determining appropriate WBL. The Taxonomy denotes six progressively more complex levels of educational objectives within structured and unstructured cognitive domain. Knowledge, comprehension and application fall within the structured cognitive domain and constitute lower levels of learning:

> Knowledge can be defined as the recall of specific and isolated bits of information, methods, sequences, and principles....Comprehension is the ability to use knowledge without necessarily relating it to other material or seeing its fullest impact at the time....Application is the ability to abstract information such as rules, general methods, and procedures, and to apply them. (Driscoll, 1998, p.50)

Taking learners through analysis to synthesis and evaluation levels of knowledge construction lies within the ill-structured cognitive domain and results in higher levels of learning (Driscoll, 1998):

> Analysis is the ability to break down an item into its constituent elements or parts....Synthesis is the ability to put together elements and parts to form a whole....Evaluation is the ability to apply judgment about the value of materials or methods for a given purpose. (Driscoll, 1998, p.51)

It is also important for instructors to be able to assess the collaborative activity and levels of co-achievement of learners in a course "...without sacrificing individual accountability" (Cramer, 1994, p. 80).

While learners engaged in WBL must learn independently of their instructor and other learners, it is important for them to feel that they are not lost and alone in the Internet environment when they encounter navigational or content-based problems. Learners need to know that there is a real person, an instructor or facilitator, whom they may contact for guidance to overcome difficulties encountered with course materials, or

problems with using the medium itself (Hacker & Niederhauser, 2000; Hill & Hannafin, 1997). The design of WBL must resolve these issues in order to be effective, and one way to do that is to involve instructors and learners in the process (Burge, 2000; Oliver, 2000; Saye, 1997; Newman et al., 1995; Burge, 1994; Eastmond & Rohfeld, 1993).

Instructing and Learning in the WBL Environment

WBL poses many challenges and opportunities for instructors and learners (Barone & Luker, 2000; Burge, 2000; Jonassen, et. al., 1999; Blanton, Moorman & Trathen, 1997; Shimabukuro, 1995; Newman, et. al., 1995; Marcinkiewicz, 1994; Hiltz, 1994; Albright & Graf, 1992). Often, instructors, curriculum designers, and instructional designers use the latest technology without careful consideration given to basic issues of learner instruction, equity of access to interactive learning systems, and the roles which must be assumed by instructors and learners (Trentin, 2001; Hezel & Dominguez, 2001; Burge, 2000; Glassman, 2000; Gray, 1997; Mayer, 1997; Hill, 1997). Lack of attention to these factors may have negative consequences (Trentin, 2001; Hezel & Dominguez, 2001; Shotsberger, 1997; Anderson & Joerg, 1996; Lohr, Ross, & Morrison, 1995).

In addition to implementing technology into course delivery without consideration for the impact on learners, researchers have suggested there is a lack of confidence and skill on the part of educators for using technology as part of course delivery (Trentin, 2001; Marcinkiewicz, 1994). Instructors need to become experts in their own right in using computers, the Internet and the WWW in order to impart knowledge and guidance to their learners (Trentin, 2001; Gray, 1997; Valde, et. al., 1996; Marcinkiewicz, 1994). In a 1994 study, Marcinkiewicz recommended that technology be

implemented across teacher education courses, no matter how painful. The finding that learners' perceived ability in using computers and the Internet is directly related to their instructors' demonstrated competence with technology, underpins the necessity for change in this direction (Marcinkiewicz, 1994). It must also extend beyond teacher education to other instructional venues where technology-assisted learning is offered. At issue is how it becomes the learning environment itself as in WBL.

WBL research literature reveals many positive outcomes and possibilities when a Web-based environment becomes a learning environment (Kearsley, 2000; Reigeluth & Squire, 1998; Dowling, 1997; Freitag & Sullivan, 1995; Jonassen, 1991; Lebow, 1993). A vital, potential learning outcome of WBL is that it may readily support the development of higher-order and critical thinking abilities when venues are provided for asynchronous reflection and collaboration (Kearsley, 2000; Newman, et. al., 1996; Lebow, 1993; Jonassen, 1991).

Some researchers point to the fact that WBL has been technology-driven, instead of being used as the tool it is to empower learning (Trentin; 2001; Shotsberger, 1997). Many of the challenges facing the integration of technology into learning, in general, are the same as those found in WBL. It cannot be said that technology has been fully integrated into or across the curriculum to date, at any level (Barone & Luker, 2000; Valde, et. al., 1996). Elements that deter or even prevent the use of technology in the classroom, are often repeated in the development and use of WBL environments. Valde, et. al. (1996) conducted a survey of teacher education graduates and found that there was a perceived need for computer technology instruction and that use of computers in the classroom needed to be modeled in the courses they took. Instructors need to realize that

computers don't "teach", they "respond", and that computer use is not taught, rather, it is learned (Valde et al., 1996). Technology does not replace instructors (Kent & McNergney, 1999; Bates, 1995). This realization is a vital beginning for both the integration of computer technology into classrooms, and for WBL. The instructor-learner relationship in the classroom is affected by learners' playing a more active role in their learning through computer use (Barone & Luker, 2000; Glassman, 2000).

Appropriate instructor training is critical to the success of WBL (Chaffee, 2000; White, 2000; Gray, 1997; Shimabukuro, 1995; Marcinkiewicz, 1994). Instructors in this environment need to feel comfortable with using computer technology and believe in its role in enhancing learning; it is likely that attaining that comfort level precedes such a belief. Computers can be used as more than just delivery systems for computer-based instruction and WBL. Instructors need to view them as cognitive tools for individual and collaborative learning, which provide access to a wealth of information and expertise available all over the world via the Internet (Jonassen, 1999; Driscoll, 1998; Gray, 1997). Access to the Internet and the Web is required because it links individuals and institutions around the world.

Instructors require the time to familiarize themselves with both the technology and the Internet (White, 2000). Once they feel competent in these areas, training in developing WBL and the sites where courses will be delivered is an appropriate next step (Gray, 1997; Albright & Graf, 1992). It is advantageous for them to be able to create or to be able to supervise the creation of visually effective graphics and text, and to be able to organize and manage their learners at a distance. However, as Burge (1999) emphasizes, the good design of WBL courses requires a team which includes expertise in

content, editing, graphic design, Web design, and, possibly, audio and video. Making WBL effective also means that an understanding of the role of computers in instruction, access issues, and training requirements is key (White, 2000). This includes the ability to determine whether or not the subject content and the learning objectives are appropriate for WBL (Bagi & Crooks, 2001).

Logan (2000) adds that designers of WBL sites should also keep in mind that the importance of visual appeal is secondary to a site's capability for facilitating interaction among course participants as:

> Visual richness does not guarantee learning; interactivity does....low-tech, 'less is more' style of creating online courses and learning environments makes use of a minimum amount of memory, which permits rapid access and downloading of the course material (Logan, 2000, p. 280).

Visual effectiveness does not infer "razzle-dazzle" or "bells and whistles". Clarity is of utmost importance, and simple, effective design is less taxing on the supporting technology infrastructure. These are important learner-centred considerations for site design. Instructors need to work closely with designers of WBL sites to ensure their learner-centredness.

Usually, site information consists of the content of the course, and may take the form of printed text, lectures, videos, demonstrations or simulations (Hansen and Frick, 1997) in hypertext or hypermedia formats. The act of clicking on icons associated with each area takes learners to pertinent reference materials where they may also, if it is available, make notes about their reactions to the content, and read the reactions of fellow

learners to the same content (Dowling, 1997; Newman, et. al., 1995). Instructors may also add to the commentary found in these locations, and in this way, albeit asynchronously, guide and facilitate real debate, which results in learning and new understanding.

A venue for interaction between instructors and individual learners is a necessary component. Presently in WBL, this is mainly accomplished through e-mail. Synchronous interaction among all course participants through a chat-room type of venue is seen as logical next step in WBL design (Ingram, Hathon & Evans, 2000; Newman, et al., 1995) if further studies determine that it significantly contributes to learning. The role of instructors in a synchronous forum will be similar to the asynchronous venue; however, guidance and discussion facilitation is provided during the interaction among learners at the same time.

Learner role in WBL

There are questions about whether or not the structural cues of a WBL site are enough to support learning to the extent where learning actually results in meaning-making (Jonassen, et. al., 1997; Newman et al., 1995). Two of the most important elements of any learning environment are integration and comprehensiveness, and in order to ensure learners' opportunity to learn within WBL, the site requires the facility to achieve both. Learners must be able to integrate what they find on the WBL site with what they know already, in order to achieve a new understanding. There is a need for better models to be developed which will support meaningful learning in WBL (Logan, 2000; MacDonald & Gabriel, 1999; Jonassen, et. al., 1997).

Even in a solely asynchronous mode, WBL may be used to support a number of valuable activities for learners in this environment (Hill, 1997; Newman et al., 1995). Given that the WBL site is constructed to do so, the possibilities for enhanced communications between learners and their instructor and their peers may be seen as an improvement over the traditional classroom venue. Virtual office hours, learner-to-learner and learner-to-instructor e-mail, Web-based testing and evaluation, and inter-institutional communication are means for interaction to take place. Some researchers have suggested that the setback of WBL may be found in the lack of synchronous interaction between instructor and learners, and between learners; however, improving interactive capabilities is an imminent next step in WBL (Newman, et. al., 1996). Others have argued that it is the convenience flexibility of asynchronous interaction that appeals to many WBL learners.

In WBL, learners play an active role in their pursuit of knowledge. It is the autonomous nature of their participation that encourages learners to take more responsibility for their learning in a WBL course, than they might in a traditional classroom (Kearsley, 2000). Initiative and self-discipline are absolutely necessary to achieve learning beyond simple knowledge acquisition in the WBL classroom. Many online courses suffer a high drop-out rate because learners are not prepared for the responsibilities of this medium. Kearsley (2000) proposes that learners need to be taught "...how to be better learners" (p.62). He suggests teaching them skills of time management and basic study skills, and learning to use software and the Internet. Ensuring they know how to use WBL Website tools such as e-mail and discussion forums is vital for interaction and potential collaboration. Increasing learner motivation to use

the tools provided is something that WBL instructors must address. The importance of communications and writing skills are underscored in this environment (Kearsley, 2000).

Instructor role in WBL

The role of WBL instructors is threefold: to formally organize an environment where both synchronous and asynchronous interaction may take place; to facilitate an appropriate blend of synchronous and asynchronous communication; and to create a sense of community and collaboration among learners (Shotsberger, 1997; Edelson, Pea & Gomez, 1996; Flannery, 1994).

Honebein (1996) suggests seven pedagogical goals when developing constructivist learning environments:

1. Provide experience with the knowledge construction process.
2. Provide experience in and appreciation for multiple perspectives.
3. Embed learning in realistic and relevant contexts.
4. Encourage ownership and voice in the learning process.
5. Embed learning in social experience.
6. Encourage the use of multiple modes of representation.
7. Encourage self-awareness of the knowledge construction process. (Honebein, 1996, p.11-12)

Honebein sees the seven goals as essential to the design of constructivist learning environments, whether they espouse traditional or WBL pedagogy.

Poole (2000) suggests that verbal interactions among discussion participants can be monitored by instructors according to categories developed by Bellack, Kliebard, Hyman & Smith in 1966, called pedagogical moves:

- Structuring: Setting the context for behavior by initiating or stopping interaction. An example is to begin class by focusing on a topic or problem.

- Soliciting: Verbal prompts designed to elicit a verbal response. Questions, commands, imperatives and requests fall under this category.

- Responding: Addressing soliciting moves.

- Reacting: Responses caused indirectly by structuring, soliciting, or responding. Clarification, synthesis, and expanding on ideas serve as reacting moves, while a responding move is always elicited by a solicitation. (Poole, 2000)

Poole points out that by being aware of learners' participation, according to the categories, online designers can improve conferencing venues. Taking this a step further, it could be argued that the categories can assist WBL instructors in managing and facilitating collaborative discussion to meet the objectives of the course. In WBL, discussion among participants can be observed to ensure learning objectives are being met. Instructors and designers can intervene if a problem is detected, or track the success of a WBL model for facilitating collaboration (Moyse & Elsom-Cook, 1992).

Because successful WBL environments include and promote self-directed learning, pedagogical goals need to be considered as an integral component of the site

design. Research into the incorporation of the Web into teaching and learning echoes the findings of previous research into the integration of technology, specifically computers, into the classroom. In a 1996 study, Anderson & Joerg found that learners display a lower rate of adoption of Web into their learning when they confront technical difficulties and do not feel confident in the Web environment. A careful balance of instructor and learner control must be achieved so that learners do not get lost and frustrated (de Caprariis, 2000; Ebersole; 1997; Anderson & Joerg, 1996).

A challenge for those who wish to integrate the Web into their teaching is to ensure learners understand and achieve confidence about using the tools at their disposal for searching and finding information on the Web. If course delivery is at a distance, then the Website design becomes crucial to learners' success at accessing and sending information, and for synchronous and asynchronous communication. Self-efficacy, of both instructors and learners, influence the success or failure of the integration of the Internet into course delivery (Hill & Hannafin, 1997; Saye, 1997).

Hansen and Frick (1997) divide WBL into four areas: the presenting of information; the provision of human interaction; the assessment of learning; and the management of the course and its materials. With adult learners, instructors may also act as mentors for their learners (Cohen, 1995). Instructors involved in WBL undertake the responsibility for delivering the course in this environment. If they are competent in creating, designing and authoring the materials themselves, they may choose to do so. If not, it means coordinating the efforts of professionals for the different requirements of a WBL site. To date, these sites have been designed for, mainly, asynchronous WBL.

Driscoll (1998) suggests that the role of WBL instructors who teach asynchronously encompasses five responsibilities:

- Facilitating learning - creating a safe environment; asking students to contribute to online conferences; asking them to describe both positive and negative online experiences.

- Guiding instruction - providing a flexible outline with clear goals; encouraging learners to manage learning and establish objectives; helping them to recognize voids; motivating them to explore related topics.

- Providing resources - providing online and off-line resources related to course content; encouraging learners to tap experience and knowledge of experts worldwide.

- Evaluating outcomes - evaluating assignments, discussions and interactions; responding quickly with assessments; monitoring discussion forum and suggesting themes for dialogue; testing to identify problems; providing learners with self-assessment tools and reflection exercises to assess progress.

- Communicating with learners - assigning individual, reflective and group projects; asking learners to develop solutions to problems.

> test them and reflect on outcomes, using academic and commercial resources and subject experts. (Driscoll, 1998, p.86-87)

Driscoll stresses the importance of monitoring and facilitating learner interactions so they go beyond simple information exchange, to the exchange and sharing of ideas and knowledge in order to build new knowledge and perspectives about a subject (Gerlach, 1994). Brookfield (1986) argues that this may be particularly important for adult learners where in "...the most effective learning groups, facilitating behaviors are assumed by various members of these groups at different times" (p. 286).

Instructors and learners also need to know how well the material is being learned, and a mechanism for evaluation or assessment of learning and of WBL learning models is required (MacDonald et al., 2001; Driscoll, 1998). The mode for assessment in this environment is computer-based or computer-mediated (Driscoll, 1998; Hansen and Frick, 1997) and can occur asynchronously at a distance through the Internet. Shotsberger (1997) sees this as contributing to the importance of the instructor's role as facilitator of computer conferencing that creates a sense of community and collaboration. Shotsberger refers to three basic tenets for instructors in WBI: responsiveness, online competence, and the organization of venues for the exchange of ideas as critical to effective WBL(Shotsberger, 1997). The interaction and subsequent discussions facilitated by instructors must also be guided by them so that they become discussions with purpose (White, 2000; Lougher, 1980).

The role of instructors is to ensure learners are situated in a "...rich and sufficiently complex learning environment..." (Westera & Sloep, 1998, p. 33), which also supports collaboration among learners. Authentic problems which generate intrinsic

motivation (1998) will catapult learners to construct what they learn through an active process which includes social construction of knowledge. Learners who succeed in a constructivist learning environment are usually "...autonomous, self-supporting, and responsible individuals who are capable of managing their own objectives, and of determining which learning activities are useful [for them]" (Westera & Sloep, 1998, p.33).

Administrative tasks associated with course management for instructors may actually be made somewhat easier in WBL because it is computer-assisted. When learners register for a course, the mechanism is likely there to automatically enroll them in the instructor's e-mail list for the course that would include grade distribution, and asynchronous course interaction (Driscoll, 1998). Naturally, access must be protected with passwords, and confirmed against learner rosters associated with a course to ensure confidentiality and reliability (Zellner, 1997).

Self-efficacy in WBL

Instructor and learner self-efficacy may be particularly critical in WBL because they are separated from each other by time and space. In their 1997 study, Hill and Hannafin found that self-efficacy in WBL is necessary on two levels: learners and instructors must feel confident in their ability to use computers and the Internet, and they must also feel secure in their ability to learn while physically isolated from other learners and their instructor. WBL, as a successful learning environment where learning objectives are achieved, may be directly reflective of the self-efficacy of instructors and, especially, learners in WBL environments (Hill & Hannafin, 1997; Saye, 1997).

Bandura's theory of self-efficacy may be readily applied to learners in the Internet environment. He proposes that people's self-efficacy beliefs can be developed in four ways, the most effective of which is found in what he calls "mastery experiences" (Bandura, 1995). When people develop self-efficacy through mastery experiences, they are developing affective, cognitive and behavioural tactics for determining and following through with task-appropriate actions. As self-efficacy develops, so does resiliency to changing circumstances and environments (1995). In studies conducted within the Internet environment, degree of self-efficacy is evident when people adopt various navigational tactics to achieve their objectives, and do not simply quit or become discouraged when initial tactics do not work (Hill & Hannafin, 1997; Saye, 1997). The mastery of these learning experiences in an Internet medium can also increase self-confidence in pursuing unexplored Internet territory (Yakimovicz & Murphy, 1995).

Learner self-efficacy in WBL

It could be argued that learners who enroll in WBL courses should already possess a good degree of self-efficacy because they know they will be physically isolated from their instructor, and from other learners. They also know that they must have some competence in using a computer and, at the very least, an acquaintance with the Internet environment. It would seem logical that WBL learners are self-motivated, a key outcome of self-efficacy, as they must set their own objectives, guide themselves within the Internet environment, and produce the level of effort required to achieve their objectives (Schrum, 1998). The nature of theWBL environment would seem to require that learners also be self-motivated to succeed within it.

A perception of anonymity may influence learners' self-efficacy in Web-based communications. Some researchers suggest that asynchronous interaction may be a blessing for shyer, types of learners who may hesitate to, if ever, participate in class discussion out of shyness or fear:

> ...the nature of online communication is such that all can have their say. In the face-to-face encounter those on the margins are often left there - on the margins. Afraid to engage, or if they do engage, afraid of retribution and being challenged by others.... (Lauzon, 1999, p.274).

These types of learners also have time to compose their contributions to discussions; whereas, in a face-to-face situation, their fear may make them nervous and their contributions somewhat incoherent as a result. The fear of this happening often may be what renders them silent (Lauzon, 1999). There is a need for studies which explore the reasons for learners' silence in WBL where venues for interaction are included and expected as part of the course.

Research conducted in Open-ended Learning Environments (OELEs), where participants learned through computers and the Internet examined factors likely to affect the success or failure of open-ended learning. Perceived self-efficacy in the use of computer equipment and the Internet provided a distinct advantage for learners who had previous experience using the technology (Hill & Hannafin, 1997). Those who had no or limited previous experience felt disoriented and lost (Hill & Hannafin, 1997). An interesting and perhaps telling discovery is that when they experienced navigational difficulties on the Internet, both efficacious and non-efficacious learners in the OELE

study failed to invoke techniques and directions provided to them prior to commencing the learning task. Instead, the learners in the study either resorted to other, random methods for seeking out the prescribed information, or they gave up altogether and reported feelings of being lost and frustrated (Hill & Hannafin, 1997).

WBL instructors and designers need to consider incorporating appropriate mechanisms and venues for feedback and assessment in an attempt to eliminate the sense of isolation and self-doubt experienced by some learners in Internet-based learning (Hill and Hannafin, 1997, Saye, 1997, Lebow, 1993). This sort of experience contributes to learners' lack of self-efficacy which directly influences their ability and motivation to learn in a particular setting (Bandura, 1995) and to enter into collaborative knowledge construction with other learners.

It is critical for learners to have a sense that they are not lost in cyberspace when they run into difficulties, and that there is a real entity - an instructor or facilitator - there to rely upon for guidance. This is necessary for overcoming difficulties with both the course content and the technology (Hill & Hannafin, 1997; Saye, 1997). Through guidance, and experience with the medium and the environment, learners will develop self-efficacy.

Instructor self-efficacy in WBL

The level of instructor self-efficacy in WBL may contribute to the level of self-efficacy experienced by their learners. The more comfortable and proficient the instructor is with using technology will influence learners' confidence and security in their use of it (Saye, 1997; Marcinkiewicz, 1994). More research into exactly how and

why instructor self-efficacy influences learner self-efficacy is necessary. Studies to date have shown that instructors' demonstrated actions and thinking about technology are related to the varying degrees to which it is incorporated into learning (Saye, 1997; Marcinkiewicz, 1994). In a study of a technology-driven course, van den Berg found that instructors' perceptions of innovations and perceived problems with innovations will directly affect the success or failure of the implementation of that innovation (van den Berg, 1999).

Appropriate training will promote self-efficacy in WBL instructors. They need to be comfortable both with using computers and teaching in an Internet environment before they can attain a sense of self-efficacy (Gray, 1997; Saye, 1997). It is self-efficacy that will move instructors from feeling forced into incorporating technology-driven learning objectives into their instruction, to setting learning objectives which will incorporate appropriate technology to best attain them (Gray, 1997). It is important to involve instructors in the full process of planning and implementing innovation to increase the success of that innovation (van den Berg, 1999).

Collaborative Learning in WBL

Building on Vygotskian theories about human development and learning, Lave and Wenger (1991), and Rogoff (1997) have extrapolated the implications of socio-cultural significance for learners both when they are participating alone and in groups. Learners adopt certain roles and working methods, and display certain patterns of behaviour and values en route to achieving their collaborative objectives. Issues of trust, flexibility and internalization are integral to moving through the stages of collaborative

activities. As learners trust each other they become more open and flexible in their acceptance of alternative ideas. They also internalize new understandings throughout the process. It is this simultaneous internalization of individual beliefs with socially negotiated understandings which characterizes the co-construction of new knowledge, and is a result of collaboration. Through this experience, learners may find their individual voices or sense of expertise on the subject at hand (Johnson-Eilola, 1994).

Collaboration among learners is not a new phenomenon; however, the Web brings a whole new meaning and perspective to the way in which learners, and others, may collaborate to advance understanding of a subject under study (Kearsley, 2000; MacDonald & Gabriel, 1999; Newman, et. al., 1995; King, 1994; Maule, 1993; Greller & Barnes, 1993). Inherent in collaboration is the individual reflection of each participant/learner.

Collaboration in learning and other situations takes place when individuals externalize their own constructions of knowledge, and contribute to and imbibe the knowledge and experience of others. Brookfield (1986) reflects on the writings of earlier adult education pedagogists such as E. C. Lindeman, and notes that including group discussion as part of a course "...is regarded as the pedagogic setting uniquely suited to adult education because it allows for collaborative reflection on the meaning of the group members' experiences." (Brookfield, 1986, p. 137). Learners internalize what they have learned in a process that involves the larger community of practice (Hung & Nichani, 2001). In the case of WBL, this is a community of learners who come together for a course. When individuals come together in a learning situation, it makes sense to encourage the externalization of differing and similar viewpoints as a focus for discussion

(Moyse & Elsom-Cook, 1992). Ideally, this results in refinement and understanding and, ultimately, in new knowledge (Garmer & Firestone, 1996).

Collaboration through the Web most often takes the form of asynchronous, individual reflections via e-mail, listservs and electronic bulletin boards. Members of a group with a common interest collaborate with each other in an online venue set-up for that particular purpose. Collaboration among the group hinges on their sense of responsibility toward each other in achieving the common goal at hand (Trentin, 1999). In WBL, the allowance for collaborative learning is usually made within an asynchronous venue (Muirhead, 2001; MacDonald & Gabriel, 1999; Maule, 1993; King, 1994; Davis, 1997; Silva & Breuleux, 1994). Collaboration may take place when there is interaction between WBL learner and instructor, learner and other learners, and all course learners and their instructor (Trentin, 1999; Dede, 1996; Greller, 1993; Maule, 1993; Newman, et al., 1995; Cutler, 1995; Blanton, Moorman, & Trathen, 1997; Jonassen, 1996). A criticism of online courses centres on the quality of the interaction and whether the interaction leads to collaboration and learning (Muirhead, 2001). Some researchers have argued that collaboration cannot occur when learners are isolated from each other as it is, by definition, a social activity (Marjanovic, 1999). Because WBL is mainly conducted asynchronously, collaboration generally takes place through e-mail and computer conferencing (Edelson, Pea & Gomez, 1996) where learners may contribute their reflections on a particular topic. Asynchronous social interaction can ensue as learners provide further reflections in the form of comments on others' reflections. Learners integrate their own understandings with those of their peers in a reciprocal process of asynchronous verbalization. This could be described as a process of both "reflection in

action" and "reflection on action" (Schon, 1987) which often results in collaboration. WBL proponents suggest that online collaboration may be more effective than that achieved in the traditional classroom (Muirhead, 2001). Others contend that there has been little success in achieving the kind of interaction where collaboration occurs, and this is frustrating for WBL instructors (Marjanovic, 1999). In a study where online collaboration was a course component, and despite encouragement from their instructors, learners' contributions were negligible and of a non-collaborative nature (Marjanovic, 1999).

Jonassen et. al. (1999) note that " Collaboration most often requires conversation among participants" (p.10). In WBL, the 'conversation' among learners is usually asynchronous. Through collaborative conversation, learners may construct knowledge through a process Dunlap and Grabinger (1996) called "generative learning". This process also finds a home in the theory of "active learning" (Harasim, et. al., 1995). The tacit expectation of learners in a constructivist environment, such as WBL, is that they will "...deliberately take action to create meaning from what they are studying..." (Harasim, et al., p.67). Learners must engage in further collaboratory reflective discussion to refine and integrate varying points of view in order to negotiate concurrence, including that of the instructor, about learning and new knowledge derived from the process (McConnell, 2002; Trentin, 1999; Moyse & Elsom-Cook, 1992). Inherent in this activity is learners' individual reflection about new understandings, and their ongoing contributions to the discussion at hand. It is a cyclical process of individual and collective reflection and collaboration (Oliver, 2000; Jonassen, et. al., 1999).

In WBL, the instructor's role in this process is vital without being intrusive as subject matter experts. Instructors are simultaneously: online information consultants, interaction and discussion facilitators, team collaborators, role models for online participation, and academic advisors (Muirhead, 2001; Stathakos & Davie, 2000; Kearsley, 2000; Kent & McNergney, 1999; Jonassen, et. al., 1999; Trentin, 1999; Kook, 1997; Mitchell & DiPetta, 1998; Harasim, et. al., 1995). The instructor's role in WBL underlies and facilitates the success of learners' individual and collaborative activities within the course.

A community of learners provides their individual reflections, and then responds to those reflections in an ongoing, reflective, asynchronous dialogue (Jonassen, et. al., 1999; Lave & Wenger, 1991). In studies on asynchronous collaboration in WBL, researchers found that encouraging learners to provide their reflections in a venue provided for that purpose, creates opportunity for refinement of those reflections (Sloffer, et. al., 1999; Newman, et. al., 1996; Newman, et. al., 1995). This occured when learners and instructors discussed the reflections and refined understandings and learning of course material (Moyse & Elsom-Cook, 1992). Extending what is known as "knowledge negotiation" to learning on the Internet, allows for knowledge to be jointly constructed by instructors and learners (Moyse & Elsom-Cook, 1992). It also promotes consideration of other perceptions of the same issue or subject, and sometimes from different cultural perspectives, which often results in learners' being forced to consider a topic outside of the perceptions or beliefs they may have had previously (Kearsley, 2000; Jonassen, et. al., 1999; Hill Duin & Hansen, 1994; Moyse & Elsom-Cook,1992; Lave & Wenger, 1991). This not only may enhance their learning of a particular subject; it may also expand their

cognitive abilities (Jonassen, et. al., 1999; Driscoll, 1998; Lave & Wenger, 1991). An added advantage in the WBL environment is that learners and instructors may come together from all parts of the world in order to achieve a common goal: the making of learning and, hopefully, the creation of knowledge to benefit others (Lave & Wenger, 1991). The benefits may go beyond the WBL classroom to influence the daily lives of participants as they work and communicate with each other on a professional level (Trentin, 2001; Jonassen, et. al., 1999; Hill Duin & Hansen, 1994).

The potential benefit of including venues for synchronous and asynchronous collaboration in WBL needs to be studied further (Newman, et. al., 1996). There is limited research that demonstrates the benefit of asynchronous collaboration in WBL (Schrum, 1998), and particularly in courses that are conducted solely online (Newman, et. al., 1996). Albeit beyond the focus of the present study, the literature also points to a need for research to determine whether synchronous collaboration among learners in WBL enhances learning (Martin, 1997; Newman, et. al., 1995). The rationale for exploring the benefits of synchronous collaboration includes the value of spontaneous response to other's perceptions and understanding of the same issue or topic (Newman, et. al., 1996).

Within the Internet environment, collaborative, spontaneous response may be somewhat different than spontaneous response within a discussion where people are literally face-to-face. The difference is that the response is written, as opposed to spoken and, therefore, may be somewhat more careful and reflective, despite the fact that it is immediate (Logan, 2000; Newman, et al., 1996). "Forced by the technology not to interrupt one another's interventions...the voice of each participant is heard" (Logan,

2000, p. 267). Currently, WBL collaboration taking place asynchronously could be described as "collaborative reflection", which may be extremely valuable to learners in WBL in terms of achieving understanding of a given subject. Among professionals, collaboration is "...an important venue for new ideas....new insights....and opportunities for professional generativity" (Henderson, 1996, p. 188). At its best, collaborative reflection could produce invention and new understanding, (Schrum, 1998; Newman, et. al., 1995).

In their study, Newman, et. al. (1996) found an intensity of thoughtfulness and collaboration in all stages of asynchronous electronic conferencing within educational Internet venues (p.11). They discovered that "...the [asynchronous] computer conference discussions showed a significantly deeper overall critical thinking ratio than the face-to-face seminars...independent of group differences". This may be because learners reflect upon their written contributions and, perhaps, rewrite them prior to posting them (Cahoon, 1998). Whether this phenomenon would carry over into courses that are conducted strictly online, or in synchronous computer conferencing requires exploration (Newman, et. al., 1996; Newman, et. al., 1995).

Reflection as a catalyst for collaboration

There seem to be two schools of thought regarding the essence of how reflection is manifested. Donald Schon's (1987) theory of reflection embodies a self-directed, individual, internal process. It could be said that individual reflection is the starting point for entrance into collaboration with others. In preparation for collaboration, individuals usually will have reflected on a subject matter at hand in order to develop their individual

perspectives. Others see collaboration as the catalyst which propels individuals to engage in reflection as a cyclical act of revisiting and reworking beliefs alone and with others (Glassman, 2000; Clift, Houston & Pugach, 1990). Captured in the development of their perspectives or opinions as a result of reflections are the doubts or questions that may arise as a result of direct experience with the subject matter or topic (Grimmett & Erickson, 1988). Schon's (1987) view of the reflective instructor sees the instructor as a kind of "coach" who listens, responds, and guides learners to discovery and articulation of their discoveries. In this activity there is an inherent collaboration going on between instructor and learners. Collaboration also incorporates a continuous process of reflection, understanding and action that can ignite and hone critical thinking skills.

WBL environments usually house an asynchronous means for learners and instructors to converse in order to achieve understanding and course objectives. Within asynchronous interaction are the individual reflections of course participants as they contribute to an ongoing discussion through text (Cutler, 1995). The potential for learning and sharpening critical thinking skills through reflective, asynchronous communication is evident to many instructors involved in WBL (Harasim, et. al., 1995; Silva & Breuleux, 1994; Newman, et al., 1996, 1995). The important point here is that WBL environments need to include venues for social and instructor/learner interaction, and venues where individual reflections may be externalized (Clift, et. al., 1990). Further investigation will help determine what kinds of venues are required, and what is necessary to inspire learners to participate in them in the desired manner.

Critical Thinking

Critical thinking is a human response to inquiry. It is "...a questioning that derives from puzzlement....learners must generate hypotheses, gather evidence, consider alternatives, and come to a reasoned position on the issue" (Sloffer, et. al., 1999, p. 1). In doing so, learners move through stages of: problem identification, problem definition, problem exploration, problem applicability and problem integration (Newman et al., 1996; Bates, 1995). Critical thinking is integral to a learner-centred, constructivist environment, is inquiry-based, and, in WBI, begins with the individual learner. In a continuous process of reflection and collaboration, learners construct their own interpretations and understandings (Jonassen, et. al., 1997). Jonassen, et al. promote rich environments for learning where learners are confronted with a problem and must seek to solve it by invoking the "...knowledge they need to learn, which requires that they seek out information, differing interpretations, or a variety of support systems" (p.120). Through activities of researching, organizing and collaborating to construct knowledge, learners must engage in higher-order critical thinking (Muire, Nazarian & Gilmer, 1999; Cahoon, 1998; Jonassen, et. al., 1996; Bates, 1995).

Newman, et al. (1996) compared levels of attainment of critical thinking between face-to-face and WBI venues in an experiment, which utilized theories of critical thinking stages and skill development. They espouse five stages of skills in the critical thinking process: (a) Level 1: Problem identification – elementary clarification and identification; (b) Level 2: Problem definition – in-depth clarification through analysis of values, beliefs and assumptions; (c) Level 3: Inference – admitting or proposing an idea based on links to true propositions; (d) Level 4: Judgement – making decisions, evaluations

and criticisms; and (e) Level 5: Strategies – for applications of solutions. The premise for the experiment was that a WBL venue would not facilitate critical thinking to the degree of face-to-face interaction. In fact, the opposite was concluded. Asynchronous individual and collaborative reflections of learners revealed more statements indicating deeper critical thinking occurred throughout each level and skill stage than those documented from the face-to-face situations (Newman, et al., 1996). Lee (1999) argues that asynchronous conferencing fosters critical thinking skills through collaborative, albeit written, brainstorming. Driscoll (1998) suggests invoking "Bloom's Taxonomy of Educational Objectives in the Cognitive Domain" to denote levels of learning reached by WBL learners from lower domain levels of knowledge acquisition, comprehension and application, to higher domain levels of learner-applied analysis, synthesis and evaluation.

Further investigation is required to determine if these higher levels are consistently present in WBL conferencing venues. Kearsley (2000) stresses the difference between participation and interaction, and notes that learners may participate in online discussions simply by providing commentary; whereas interaction entails their visibly active presence in providing response or feedback to posted commentary. Gilbert & Moore (1998) caution that without proper guidance, interactivity designed to meet course objectives can devolve into social interactivity.

Newman et al. (1996) voiced another concern that the kind of critical thinking resulting from face-to-face "brainstorming" exercises is not attainable in an asynchronous environment. Other researchers have noticed a decline in interactivity when learners become frustrated by delayed feedback in asynchronous conferencing (Lee, 1999). Perhaps there may be stages of asynchronous collaboration among learners which could

be described as "reflective brainstorming". An argument could be made that this indeed could exist and may be linked to Schon's theory of reflection-in-action and reflection-on-action, but this requires investigation to be substantiated.

Again, the role of WBL instructors is crucial to the creation and support of an environment where individual and group critical thinking may occur, whether it be asynchronous or synchronous. Marchese (2000) suggests that "...'deep learning,' as the Europeans dub it" (p.4), is possible when instructors encourage and guide online conferencing. As facilitators, instructors need to strike a delicate balance between guiding discussions without influencing them (Cahoon, 1998). Ensuring all learners in a course contribute to the process also requires monitoring the participants as well as their discussions (Driscoll, 1998).

Meaningful Discussion and Learning

The potential for meaningful discussion that enhances learning in WBL may be key to its viability as an educational environment. Through discussion, learners are often able to go beyond learning course content to greater depths of understanding. Jenlink and Carr (1996) identify conversations common to educational venues. A "Dialogue" conversation occurs between two or more people; however, individuals may engage in self-dialogue which, for example, may present itself in a reflective journal. Individuals engaged in dialogue may suspend their own points-of-view in order to examine others, which allows the group (consisting of two or more participants) to "...become aware of the diversity of assumptions..." (Jenlink & Carr, 1996, p. 33). This may result in a collective consciousness about a particular topic; at other times, participants do not

immediately reach agreement. The goal is to listen to and respect all thoughts and opinions in order to realize a shared understanding and knowledge construction (Lauzon, 1999). "Design" conversation contributes to new understandings about topics being discussed. Working in tandem with dialogue, design conversation moves participants from a shared understanding to the development of new directions of that understanding. Engaging in both dialogue and design conversation facilitates the construction of meaning and, with guidance,"...unconceal the hidden tacit understandings..." (Jenlink & Carr, 1996, p.37).

Meaningful learning ensues as a level of understanding is achieved which provides learners entry into a "community of practice" where they possess the required knowledge to solve problems and make decisions within that practice (Sloffer, et al., 1999; Lave & Wenger, 1991). Generally, those who participate in these types of discussions look forward to connecting with peers from other communities in creative and fruitful conversation (Jenlink & Carr, 1996). This can contribute to a "...cross-pollination of ideas...." (Seely Brown, 2000, p.19).

Ultimately, this learning extends into and improves other facets of learners' lives and communities. Necessary to the achievement of learning is the mentorship and guidance of experienced practitioners such as instructors. Sloffer, et al. (1999) note that:

> An attempt to conduct meaningful discussion under normal classroom conditions—a group of thirty people, together for fifty-minute blocks which are interspersed with lectures and administrative details—would be ridiculed anywhere but in an academic setting (p. 1).

Sloffer, et al. (1999) attempted to determine the potential of Web-based, asynchronous conferencing for "...inquiry-driven critical thinking in a collaborative inquiry environment..." (p. 1). They found that each component of collaborative discussion activity required very specific directions and support from instructors in order for meaningful discussion and learning to take place. The structure of both environment and activities must be pedagogically rigorous so that learners are not distracted or feel lost-in-space, which can lead to a lack of self-efficacy and, in turn, lack of participation. This finding echoes throughout WBL research (Ellis & Phelps, 2000; Sloffer, et. al., 1999; Allegra, 1997).

The recurring theme throughout the literature is the significance of the role of WBL instructors. As in any educational setting, it underlies all learning activities. It is the skillful and mindful (Langer, 1997) design and construction of learning venues and activities that facilitates learners' abilities, individually and as groups. It supports problem solving and knowledge seeking through collaboration, critical thinking, meaningful discussion and, ultimately, construction of learning (Moller, Harvey, Downs & Godshalk, 2000). The results of this sort of "mindful learning" (Langer, 1997) that is found in constructivist learning environments contributes to learners' retention of knowledge, and possibly to a process of lifelong learning.

Summary of WBL Research Literature

Developers and implementors of WBL pedagogy may anchor it within constructivist theory (Oliver & Omari, 2000; Carr-Chellman & Duchastel, 2000; de Caprariis, 2000;Westera & Sloep, 1998; Dede, 1997; El-Tigi & Branch, 1996; Spiro, et.

al., 1991; Jonassen, et. al., 1996; Jonassen, 1991). The very nature and context of WBL courses is such that learners must often construct their own learning, individually, with their instructor and, at times, through collaboration with other learners (Hung & Nichoui, 2001; Logan, 2000, Lauzon, 1999; Jonassen, et. al., 1997; Silva & Breuleux, 1994).

The tenets of constructivist learning theory suggest that learners bring their past learning and experiences to every learning situation, where they incorporate new information and socially-mediated knowledge as they construct new knowledge for themselves (Lauzon, 1999; Morrison & Collins, 1996; Westera & Sloep, 1998; Gruender, 1996). In the constructivist environment, learners are the primary stakeholders in the success of the learning process and assessment. As such, they may also be active negotiators with their instructors in determining both (Reeves & Okey, 1996; Duffy & Jonassen, 1992; Jonassen, 1991). Within the constructivist learning context, learners choose from an instructor-provided set of activities in order to facilitate their own knowledge construction (Jonassen, et. al., 1996; Jonassen, 1991) and to meet learning objectives. Optimal results of this process are learners who, through individual and collaborative efforts, have achieved new learning and understanding of a particular subject or topic and its place within the world. Along the way, they may have also developed new sources of information and collaborative partners for constructing future learning (Westera & Sloep, 1998; Gruender, 1996).

The potential also exists, and, in fact, is recommended, for learners to participate in determining the design of WBI learning sites and "tools" if at all possible (Trentin, 2001; Erskine, Carter-Tod & Burton, 1997; Silva & Breuleux, 1994). This helps to ensure that the technology does not drive the instructional objectives, as often happens

(Hill, 1997), but rather is driven by the objectives of instructors and learners in the environment (Lawless & Brown, 1997). Two primary reasons for including learners in WBL design is to determine what learners want or need in a WBL site, and to develop profiles of learners most likely to succeed in this environment. Further investigation is required into WBL learner personality characteristics and motivation will assist in designing sites that are conducive to the learners who choose WBL (Dede, 1995; Spiro, et. al., 1991).

WBL learners who are usually physically isolated from their instructor and from each other must be able to function in a more structured but less supervised educational environment than they may have previously experienced (Glassman, 2000). Cognitive and meta-cognitive factors influence learners' capabilities to construct knowledge in this type of situation (Spiro, et al., 1991; Jonassen, 1991). Learners must be able to function in an isolated situation from instructors and other learners in performing course related activities (Kearsley, 2000). They must also be able to identify and use Website tools to navigate their ways to information and Web venues required by a course. In an ideal constructivist WBL site, the components and tools therein may be adjusted to suit the needs and preferences of instructors and learners throughout the duration of a course. To date, this type of WBL venue has not been attempted or tested (Lawless & Brown, 1997). On the positive side, WBL may invoke "...a whole new dimension of learning styles..." (Dede, 1996, p.167). Forms of delivery for WBL are unique to each course, as there is no universally prescribed format or curricular context. However, WBL courses are usually offered asynchronously, which means that learners can participate anytime. Very few provide a venue for synchronous interaction where learners must participate at a

particular time. Whether or not this is a disadvantage has yet to be determined (Newman, et. al., 1996).

Issues of pedagogy relate to both teaching and learning. Disadvantages of WBL centre on assumptions that learners may feel isolated, unconnected and overwhelmed by information (Hill, 1997). Alternatively, the advantage of asynchronous interaction in terms of learners' feelings of self-efficacy and empowerment in a Web-based environment stems from being "invisible" and isolated from other learners. WBL research shows that many previously shy learners will more readily contribute to and online discussion than a face-to-face one (de Caprariis, 2000; Sloffer, et. al., 1999; Jonassen, 1996; Newman, et al., 1996;). Further instructor and peer response to their contributions and collaborations help to build confidence and self-efficacy of these kinds of learners.

In a constructivist learning environment, collaboration occurs when there is social interaction between learners that enhances learning through the process of communicating with each other, and leads to a new awareness or understanding (Logan, 2000; Kearsley, 2000; Edelson, et. al., 1996). Key to a transformation of understanding is the interdependence of individual and social processes when learners co-construct knowledge. When learners commence activity in a learning venue, they may initially depend on other more experienced participants to lead the way. Once they know more and are more secure or self-efficacious in the environment, they also become more responsible and participatory in the learning process (Lave & Wenger, 1991).

Higher-order thinking and collaboration is, indeed, attainable through asynchronous communication in the WBL environment (Kearsley, 2000; Sloffer, et. al.,

1999; Newman, et al., 1996), and, perhaps, to a higher degree than in face-to-face situations (Haughey & Anderson, 1998; Newman, et al., 1996). Asynchronous interaction supports critical and reflective thinking because learners have the time to do both before they contribute to a discussion (Haughey & Anderson, 1998). The fact that they contribute to a collaboration in writing also means they have an opportunity to critically reflect on their words and the words of their peers prior to posting commentary. Linked to this is the advantage of "active learning" which is, by necessity, required in WBL (Harasim, et. al., 1995). Learners must actively participate through their e-mailed or posted commentary in order to be "present". A caveat to this is that instructors must ensure that parameters for learner participation are clearly outlined, defined and acknowledged by their WBI learners for issues of grading and class participation.

Development of a sound WBL theoretical framework and pedagogy is critical to ensure all types of learners, who access WBL from a variety of institutions and venues, are able to learn collaboratively and evolve their learning into professional communities of practice (Trentin, 2001; Lave & Wenger, 1991). Identification and illumination of the barriers and facilitators to collaboration in WBL is essential in order to achieve an understanding and evolve WBL toward its potential.

The findings of the present study provide validation of and further insight into previously identified barriers and facilitators to collaboration. The study also contributes new findings to address gaps in the research literature by revealing the factors that directly affect learners' participation in asynchronous, online course conferencing.

In addition to explicating the study's methodology, the following chapter reveals a study that is unique from other WBL studies on collaboration in both its context, and in

the execution of some of the research methodology. From a research perspective, the methodology of this study may also contribute to the literature about conducting Web-based research.

Chapter 3: Methods

Introduction

Pedagogical development in Web-based Learning (WBL) is in its infancy (Trentin, 2000; Wilson & Lowry, 2000; Gabriel, 1999; Mitchell, et. al., 1998; Hill, 1997; McIsaac & Gunawardena, 1996; Land & Hannafin, 1997; Newman, et. al., 1995; Jonassen, 1991). WBL researchers are struggling to find theoretical underpinnings for research, which examine pedagogical issues in this environment (Burge, 2000; Wilson & Lowry, 2000; McIssac & Gunawardena, 1996: Lebow, 1993). There is a strong movement toward the constructivist paradigm as an appropriate, theoretical framework within which WBL research may find integrity and viability (Burge, 2000; Wilson & Lowry, 2000; Gabriel, 1999; Land & Hannafin, 1997; Edelson, Pia & Gomez, 1996; McIssac & Gunawardena, 1996; Jonassen, et. al.,1996; Jonassen,1991). A variety of qualitative, and quantitative, research methodologies have been employed by WBL researchers, depending on the objectives of their studies (Savenye & Robinson, 1997). This study is grounded and executed within a qualitative, constructivist paradigm, using case study methodology.

Research Design

The study is informed by research that suggests WBL may provide an ideal venue for collaboration among learners which results in critical thinking, meaningful discussion and effective learning (Gabriel, 1999; MacDonald & Gabriel, 1999; Mitchell, et. al., 1999; Newman, et. al. , 1995; Edelson, et. al., 1996). In order to fully grasp how learners

function within WBL "classrooms", researchers are increasingly looking to a constructivist research paradigm to anchor their studies, and invoking a range of qualitative methodologies (Sexton, 1997; Land & Hannafin, 1997; McIsaac & Gunawardena, 1996; Mitchell, et. al., 1998).

Epistemology

Creswell (1998) notes that epistemology reveals the relationship between the researcher and the researched. The epistemology of researchers who frame their research within a constructivist paradigm reflects their conviction that they are co-participants in their studies. Constructivist researchers actively participate in the research setting and observe activities within the setting. Like their participants, constructivist researchers are also sources of data. They are the orchestrators, facilitators and participants in the inquiry (Guba & Lincoln, 1994). As data are generated, interpretation and meaning are created by the researcher in concert with the participants.

In this study, data were mainly generated through in-depth interviews, and text as participants communicated asynchronously through e-mail messages. Since there was no synchronous component to the WBL course, meanings and communications between and among participants were extensively derived from written text.

The theory of social constructivism supports a constructivist research stance, data collection and interpretation. Based on the premise that knowledge is a process of construction (Eisner, 1991; Schwandt, 1994), social constructivists take this further when they purport that meaning is shaped by "...conventions of language and other social processes" (Schwandt, 1994, p. 127). Radical constructivists focus on individual

knowledge construction, whereas social constructivists see it collectively constructed in the social arena (Schwandt, 1994; Sexton, 1997). Both theories may find validation within the WBL environment in the same way that they do in traditional classrooms. This depends on the particular context of a course, and on the text that results from interaction between participants.

Ontology

Intimately connected to epistemological considerations is the ontology of the research stance. On a philosophical level, constructivist researchers support the belief that "...reality is constructed by individuals involved in the research situation" (Creswell, 1998, p. 76). From this stance, the nature of reality for WBL learners is believed to be one of constructing their learning in an Internet environment. The creation of communities of practice within the world of the Internet is a topic for research in its own right. For the purpose of this study; however, it warranted mention because it is part of what may inspire the construction of "reality" by learners, instructors and researchers during a WBL course.

Ontologically, a constructivist research paradigm is conducive to qualitative inquiry in WBL. It is a research environment where "multiple realities" (Creswell, 1998) exist for learners, instructors and researchers. Focusing on emerging data through the lens of constructivism, these multiple realities may be collected as data:

> ...in the form of multiple, intangible mental constructions, socially and experientially based, local and specific in nature...and dependent for their form and content on the individual persons or groups holding

the constructions (Guba & Lincoln, 1994, p. 110).

Researchers in WBL may gather tangible mental constructions as data, through text-based, individual and group work. From the data, they may construct interpretations and explanations, which provide insight into the dynamic manifestations of knowledge and social construction occurring in WBL. The data may also be found in the lived, Web-based experiences of the participants, including the researcher (Sexton, 1997), and reveal much about social and communication strategies developed or not developed in a particular WBL course.

The focus of this qualitative research study was to collect and interpret the data of a particular case. Adopting an ontological stance that knowledge and truth are created and not discovered provided a natural and coherent approach to collecting and analyzing data within a constructivist orientation (Bogdan & Biklen, 1998). The premise that data are constructions of the participants in particular settings at particular times, provided opportunity for the effective use of case study methodology in WBL (van Manen, 1990) where the context for learning requires that it be constructed by learners, individually and together (Jonassen, 1991; Land & Hannafin, 1997).

Case Study Methodology

The choice of research methodology reflects constructivist epistemology and ontological stance, and allows for fluid interpretation within the context of the research setting. Stake (1995) captures the essence of case study research when he says:

> Because it is an exercise in such depth, the [case] study is an opportunity to see what others have not yet seen, to reflect the uniqueness of our own lives, to engage the best of our interpretive powers... (Stake, 1995, p.136).

Central to the selection of methodology is the researcher's "...general orientation to life, the view of knowledge, and the sense of what it means to be human..." (van Manen, 1990, p. 150). I believe that to derive a whole and complete understanding of the factors which affect learners in WBL includes an understanding of the context. Merriam (1998) notes that "...case study is a design particularly suited to situations in which it is impossible to separate the phenomenon's variables from their context" (Merriam, 1998, p.29). In WBL, the factors include the context, as learners become part of that context when they interact and communicate through text-based e-mails or computer conferencing. Burge (1994) argues that "A qualitative approach has to be context-specific, occur in a way that reduces the intrusiveness of the researcher, focus on the wholeness of a phenomenon and the experience as lived by the persons involved...." (p.25). Context is an ever-present issue in WBL as all participants are at the mercy of technological foibles and system failure.

The governing methodological choice drove the methods selected for data collection. Purpose played a significant role in selection of methodology. The ultimate purpose of the study was to contribute to the development of WBL pedagogy. In order to contribute to the development of pedagogy, van Manen (1990) proposes that pedagogical theory "...has to be theory of the unique, of the particular case....[it] starts with and from the single case, searches for universal qualities, and returns to the single case" (p. 150).

Case study research has been used to "unobtrusively learn more about students, teachers, and trainers who use a new technology" (Savenye & Robinson, 1997, p. 1173). Qualitative methods employed have included "...surveys, interviews, and observations during the front-end analysis and evaluation stages..." (p. 1173). Often, a case study has been invoked by educational technologists to find answers to particular questions, rather than to provide a description of the group or the context. It is important, however, that educators involved in using the newer technologies, such as WBL, "...study learners and learning processes in new ways" for deeper understandings (Savenye & Robinson, 1997, p. 1174). Merriam (1998) notes that a case study may assist in advancing understanding of the dynamics of a particular program. If conducted with a closer regard for the tenets of its practice, a case study may provide rich, thick descriptions of issues that affect particular learning activities and processes in WBL. The data mined from these descriptions assist researchers in the construction of knowledge about the particular case, which may contribute to theory-building, as opposed to generalization (Yin, 1984). This is a needed component of WBL theoretical development (McIssac & Gunawardena, 1996).

Stake (1995) notes that the role of qualitative researchers in knowledge construction as interpreter and "...gatherer of interpretations, is central" (p.99). The emphasis is on "vigorous interpretation", as case study researchers gather data through observation and other methods (p.9). Interpretations, rather than conclusions (p. 12), are facilitated through careful reflection on the data, from the perspectives of both participant and researcher. In choosing to do a case study for research in WBL, my role as researcher was that of participant and data gatherer. This allowed for inductive, detailed

interpretations of rich, thick data from all perspectives: learners, instructor, course administrators, and researcher. It is essential to have these perspectives for contributing to understandings of how WBL contextual factors affect the learning process (Land & Hannafin, 1997; Mitchell, et. al., 1998).

Single-Case Study Considerations

Merriam (1998) describes three main types of case study research: descriptive, interpretive and evaluative. The choice depends on the purpose of the case study and on the issue or issues which have inspired research questions. The nature of my study is best served by both the descriptive and the interpretive. The choice of a descriptive case study is useful for contributing to an understanding of areas where research and theory-building are relatively young (Merriam, 1998), as in WBL. Rich, thick descriptions of data convey more than simple information; they also provide insight into the nuances and the context where data are constructed by participants in a study. The interpretive study requires a theoretical base in order to challenge or support existing theory (Merriam, 1998), as the data reveal contrasts and comparisons. Because WBL is a relatively new learning venue, compared to more traditional venues, it presented a challenge to do either. However, some interpretation was required for theory-building; therefore, there is a blend of the descriptive and the interpretive. I am aware that care must be taken not to mix traditions; however, there is a movement by researchers in technology-driven environments to "...establish theoretical frameworks as a basis for research and...examine the interactions of technology with teaching and learning" (McIsaac &

Gunawardena, 1996, p. 431). This may involve creating "hybrid" research methodology in order to perform research in Web-based settings.

Focus for Research

The purpose of the study was to reveal the factors that either discouraged or enabled learners to collaborate among themselves as they constructed their learning in WBL. Exposing the influence these factors have on learners' perceptions of their ability to construct knowledge in WBL provides insights into particular successes and failures of existing WBL pedagogy.

Research Questions

The study was guided by the following research questions:

1. What facilitates collaboration in Web-based Learning?
2. What are the barriers to collaboration in Web-based Learning?
3. How do the facilitators and barriers affect learners' perceived ability to construct knowledge in Web-based Learning?
4. What evidence is there that learners are or are not collaborating?

Site and Participants

Site

The research site was the departmental learning Website of a Canadian federal government department. Operated out of Ottawa, it provides WBL courses for employees in headquarters and one hundred and fifty-eight locations around the world.

The courses currently available range from language training to instruction in sustainable development and negotiation skills. Some courses are strictly related to job skills, while others are college and university-level skills content. All courses support the goal of providing employees with the means to upgrade or, perhaps, to change their professional focus.

The departmental learning Website was an excellent site for my case study for several reasons. Firstly, prior to the start of data collection for this study, it had approximately two years to establish itself with employees as a learning centre, and it had worked out many of the technological "bugs" that can cause distraction for WBL learners. Secondly, the venue made it possible to gather data both online through the departmental learning Website, and in interviews with WBL learner and non-learner participants. This contributed to the validity of the study through triangulation as some factors discovered in data collected in interviews and reflective journals were also observed (Maxwell, 1996).

Participants

The sample size included twelve participants: eleven from the federal department, and myself as the researcher-participant (Appendix B). The sampling was purposeful, with a goal of "...achieving representativeness or typicality of the settings, individuals, or activities selected" (Maxwell, 1996, p. 71). The participants were unknown to me prior to the study.

The participants for this case study involved employees of a Canadian federal department who enrolled in a course offered through its departmental learning Website.

Seven were located in Ottawa, including myself, and five were located at various department locations around the world. Of the twelve employees who actually took the course, out of an original enrollment of eighteen, eight also participated in the case study. In addition to the learner participants, the course instructor, administrator, the departmental learning Website manager, and researcher also participated. Three of the four male participants and five of the eight female participants were learners. All of them had significant experience using computers and technology. Everyone used e-mail on a daily basis. The learner participants had taken at least one previous course through the departmental learning Website. Of the eight learner participants, six were taking the course voluntarily, and two at their managers' request. The ages of the participants ranged from twenty-five to sixty.

A WBL business writing skills course was purposely selected as an appropriate setting for the study. The course was being offered over the summer months, which is traditionally a less busy time for employees in the local and foreign locations. Summer courses and winter courses are usually more popular among these employees, based on enrollment history. The learners who enrolled in this course had completed a prerequisite writing skills WBL course and, thus, met my criterion of having had experience taking at least one, previous WBL course. The learners also met the criterion of having daily experience using computers, e-mail and the Internet. The eight learner participants enrolled in the course who also volunteered for the case study, did so based on their availability and willingness to participate. Enrollment in the departmental learning Website course sizes is typically small in number (three to ten). This course was exceptional in its roster of twelve learners who actually took the course, out of an original

enrollment of eighteen (six who had enrolled did not follow through to take the course. and there was no follow-up with them to determine why they had dropped-out).

Other participants in the case study included the course instructor, the departmental learning Website manager who designs, administrates and manages the site itself, and the course administrator, all based in Ottawa. These participants also met the criteria of having had experience with the delivery of previous WBL courses. All of them used computers, e-mail and the Internet in their daily activities. They were particularly committed to the incorporation of an asynchronous venue for collaboration in the writing skills course, and adamant about its importance to enhancing course content through the opportunity for collaborative discussion among learners. The learning Website manager and course administrator were keen to have learners discuss their writing challenges and experiences with each other, based on each learner's unique perspective and situation. Because learners were based in different locations, and faced the communications challenge of varying cultural protocols, the manager and course administrator felt strongly that collaboration among learners would lead to the sharing of ideas for business writing requirements. The course would give learners the theory; the collaboration would provide them with an opportunity for sharing ideas for applying what they had learned.

All participants were generally aware of informal, Web-based online Internet chatrooms and listservs as venues for communicating with others about particular topics; however, none of the participants in the study had actively participated in these venues, and all stated that they had no interest in engaging in this type of general, informal, online communication on the Web.

Profiles of the Participants

The following brief profiles of the participants, given pseudonyms, are presented to provide a snapshot of their individual contexts and experiences related to their participation in the delivery of WBL. It is important to have some sense of this so that the experiences described in Chapter Four may be better appreciated. While some of their experiences are similar, they are each unique in their approach to WBL, and this is sometimes related to the physical context from which they access WBL. The profiles help to "set the stage" for understanding the WBL experiences in this case.

The profiles include little if any personal information. At times, personal information was shared with me; however, for ethical reasons, I have not included information that was not provided as part of a response to an interview question. Where personal information was provided as part of a response to an interview question, it is included.

Christine

Christine is an administrative officer and a learner participant. Her job is mainly to provide information, and to direct employees (she refers to them as clients) to other sources of information beyond the scope of what she provides. This is accomplished over the telephone and through e-mail, to employees at headquarters and at locations around the world. At times she functions as a receptionist for her area, when the incumbent in the position is ill or on holidays. Christine had taken a number of computer-based, word processing tutorials prior to the WBL courses undertaken through the departmental learning Website.

Christine is hoping to advance in the administration hierarchy and views her WBL courses as a means to achieve this. She is a gentle and somewhat timid person who displayed more confidence as she moved through the WBL course. Initially, she felt very insecure and uncomfortable about not being in a classroom where she could be with other learners and an instructor; she misses the interaction. While she says she prefers to be face-to-face during a course, she is discovering what she considers to be advantages of WBL. She said that taking WBL courses has helped her to become more confident in other areas of her work because WBL required her to be independent and responsible for learning the course material. Christine provided an example of this by explaining how, since taking courses through WBL, she had taken the initiative to devise a project plan for her supervisor, something she previously would have done only upon request from her supervisor. Christine also finds that she thinks of more possibilities for sources of information for her clients because her WBL course links have taken her to information resources around the world.

Adrian

Adrian has been with the same office division for nine years. She is an information and administration officer and generates reports and statistics for her clients. She acts as supervisor in her area when her supervisor is away, and hopes to achieve that position someday. She is very computer literate and uses a wide range of programs in her daily work. Like many government employees, she is busy to the exclusion of breaks and extraneous activities. It was difficult for her to find the time to be interviewed for the study. I sensed that she was constantly anxious and stressed about time.

Adrian stated a preference for the traditional classroom because of her time pressures, which are constant, when she is at her workplace. She felt that going away from the job site was the only way she could concentrate on a course. She liked WBL because of its flexibility of time and access; however, she found it nearly impossible to fit it into her work day, and she resented having to do it outside of work hours when that became necessary.

Since most of Adrian's communication with her clients has migrated to e-mail, she wanted to improve her writing skills and, therefore, enrolled in the writing skills courses. While she describes herself as not being shy about asking questions in a classroom with others, she finds she is hesitant to use an online bulletin board. She misses the interaction and collaboration of the traditional classroom. Despite this, Adrian is enthusiastic about WBL and says she enjoys learning this way.

Fiona

Fiona is a community college graduate and took a number of computer programming courses during her studies. She has been out of school for awhile and wanted to take a course that would be directly relevant to her job as an information officer. She sees it as professional development, and something that will help in her work appraisal. She, like the other participants, is very busy in her job and has very little time to spare. I sensed that she was pressed for time during the interview process.

Fiona describes herself as self-disciplined, an attribute she says she has developed as a result of WBL. She is also confident about her ability to learn and to manage her time at work and at home so that she can complete her WBL coursework. She noted that

she made use of the departmental learning Website "Do Not Disturb" sign (see Appendix E) given to her when she began the course.

Fiona misses having an instructor and classmates "in front of her". She does not mind working on her course from home if necessary, although she prefers to work from the office to avoid Internet charges, and interruptions at home. Fiona made a point of telling me that she feels WBL should not be restricted to "working people or students", and that it should be introduced to housewives who are at home with babies, and to the physically disabled.

Lynn

Lynn is a university graduate who planned to begin part-time graduate studies in the fall of 2000. She is an information officer. She describes herself as a fast learner and highly adaptable. She says her workload is manageable and finds time to for WBL during her office hours. Lynn finds it difficult to close her door and decline colleagues' requests of her at the office, when she is doing her coursework. She likes to do her assignments at home where she will not be interrupted.

One complaint Lynn has about WBL is the fact that it requires looking at a computer screen, which makes her eyes sore. Because she spends much of her time at work on the computer, she often prefers to print course materials so that she can read hardcopy. Lynn is an ESL learner, and is also studying French, as well as improving her English writing skills. Her objective is to improve her writing style so that she can "...present something carrying negative meanings in a positive and acceptable manner.

This includes making complaints, turning down suggestions, and appraising under-performing staff." (Lynn, interview 1)

Lynn enjoys learning and has consistently taken courses in her spare time. She finds WBL "...a bit cold and non-human", but sees it as "...the trend to deliver courses" (Lynn, interview 1).

Oliver

Oliver is an administrative officer and describes himself as having no problem using the computer for work or for WBL, although he says he is not an "IT fan" (Oliver, interview 1). He is an ESL learner and was not enthusiastic about taking the course, and as a result spends as little time as possible doing the required activities. Oliver's supervisor asked him to take the course as part of his work duties. He sits in a workstation in an open office layout, and is interrupted fairly often. Despite this, he works on the course only at the office because he was required to take it by his supervisor. For this reason, he considers doing course assignments as a part of his job as well.

Oliver says he prefers "...this type of 'on your own' learning" (Oliver, interview 3) because he can adapt WBL to his own schedule and pace. In past courses he has found it stressful when he knows he is "behind other learners" (Oliver, interview 3); so he is less anxious in WBL because "...this way I do not need to worry as I will not know anyway" (Oliver, interview 3).

Maria

Maria is an information officer and provides information and support to visiting dignitaries. She uses a computer daily in the performance of her job and is comfortable participating in WBL, although she finds it difficult to find time for it. She is an ESL learner, and her objective for taking this course was to "...refresh my writing skills and to acquaint myself with the latest writing techniques" (Maria, interview 1).

Maria is also often interrupted at work and WBL is "...always ranked with the lowest priority in my daily work" (Maria, interview 2). She attends many meetings within and outside of the office, and she often has to respond to urgent requests. She has children at home, and she says doing her coursework there is not an option for her. I sensed that Maria felt pressured for time in responding to my interview questions. She was very direct and succinct in her answers.

Michael

Michael is a computer technician and often travels to foreign locations to set-up and test computer equipment. He can be on location for months at a time. He enjoys taking courses through WBL because of the flexibility and ease of access from most of the foreign locations. He was less enthusiastic about taking this particular course because he had been asked to enroll by his supervisor. At times during the three interviews, I had to carefully steer Michael away from complaining about his work environment and colleagues, and back to the topic of our discussion. He did say that his colleagues did not interrupt him when he was doing coursework and, in that sense, he was in an environment supportive of WBL.

Michael described himself as having been identified with a learning disability when he was at university. He did not graduate from university and is bitter about his experience there. He felt that as soon as he was labeled with the disability, his marks dropped significantly. He said he did not get any additional help for his disability, which he described as dyslexia. Based on his experience, Michael also feels that universities are inflexible when it comes to course times, deadlines for assignments and exam timing. He has not had any recent experience of this perceived inflexibility, but he hasn't pursued courses through a university because of his past experiences. Alternatively, he is enthusiastic about his experience with WBL, as he is able to complete assignments and courses according to his schedule, and he appreciates the anonymity of asynchronous attendance.

Michael also described himself as a lifelong learner, and believes it is important "...to keep the brain active. If you don't, you start on that long decline...." (Michael, interview 1). He feels it is particularly important to keep abreast of the latest developments in his field. Michael was confident in his professional abilities but lacked self-confidence in his learning abilities, despite the fact that he has "...a stack this deep of certificates...." (Michael, interview 2). Michael is unhappy and cynical about younger, certified technicians being promoted ahead of him because he has not graduated from a certified program. He wants the departmental learning Website to offer certified programs of study so that he can graduate from a program.

At first Michael scoffed at the idea of online conferencing with other learners, but he later attempted to get some discussion going on the bulletin board. He also said that it was a lack of time, not interest, which kept him from online conferencing activity.

although I suspected it may also be due to a fear of expressing himself in writing. He seemed cynical about the quality of discussion that had or could take place on the bulletin board.

Sean

Sean is a university graduate and in a public affairs management position. He began but did not finish a master's degree. He describes himself as a "Superuser of computers" (Sean, interview 1) and uses a wide array of programs. Sean sometimes finds it difficult to find time during his workday to do his coursework. He feels that WBL from home is not an option for him as he has a young child who requires his attention.

Sean misses what he calls "visual and audio contact" (Sean, interview 2) with other course participants. Until venues such as the bulletin board are made user-friendlier for interaction, he would prefer to have a Web-based component as part of a course delivered in a traditional classroom. Sean describes WBL as a "solitary experience" (Sean, interview 2). He feels that WBL requires "...a lot more self-discipline than actually going to a campus, sitting in a classroom and learning" (Sean, interview 3).

Julie

Julie is a mid-level manager, and responsible for the departmental learning site. At the time of the study, she had been in her current position for the past two years. Her role in the delivery of WBL courses was to, in her words, "...create the environment for the course to happen and, once a course is up and running... to be a third eye " (Julie, interview 1). She was committed to "...maximizing the possibilities of the medium."

(Julie, interview 1), and she felt it was very important that course delivery be designed for the medium of the Internet. She came to her current job from previous jobs in corporate training, where she was a trainer in the private sector, and she had worked as a graphic designer prior to that position.

When Julie began this job, there were two courses offered through the departmental learning Website. She found that these courses had simply been taken from their paper-based format and put up in the same format on the Website, so that there were, simply, typed pages on the screen. She was also surprised to find that assignments continued to be sent by regular mail, and communication was through e-mail only. She was learning about WBL at the same time as she was tasked with redesigning the departmental learning Website. She felt it was important to put herself in the position of users of the site in order to determine the venues and features that would become part of the Website. She felt encumbered by the technology architecture that was already in place, but had to work within its parameters.

Julie was sure about a few things in terms of the site design: she wanted the learning Website to be very professional looking, and she wanted the site and venues within it to simulate the experience of being in a university campus. She also wanted the site to be seen as inclusive in order to reflect the diversity of the learners who would be accessing courses from various locations around the world.

Julie also stressed her belief in the importance of collaboration for learning, and she had made many efforts to create venues where course participants could engage in discussion. She was frustrated by the lack of use of these venues in the majority of

courses, and found it difficult to obtain feedback from learners as to why they were not using the discussion venues, such as the bulletin board.

Since Julie's redesign of the departmental learning Website, more courses were being offered and the population of learners had grown. Despite its statistical success, she faced constant criticism of the site from colleagues offering courses through traditional classroom and distance venues. Some of this was fueled by the fact that the learning Website users communicated only to notify course administrators of problems, or to complain about something, and there has been little response to feedback forms where learners could describe both negative and positive experiences. Nonetheless, the course and learner numbers continued to grow.

When I first met her, Julie impressed me as a dedicated and driven professional, and someone who was determined to make her WBL site the absolute best it could be for learners. She was a bright, energetic woman committed to using every moment of her workday, and beyond, to improve the departmental learning Website. Sadly, the last time I spoke with Julie, she was actively looking for another position as she was feeling worn out by having to constantly defend the effectiveness of WBL, and go to battle for budget to implement improvements to the departmental learning Website.

Bill

Bill is a mid-level manager. One of his responsibilities is to deliver and manage the instruction and administration of the writing skills courses. He had been in this job for a number of years, and has overseen the delivery of courses through traditional

classroom and distance venues, as well as some through the departmental learning Website.

In his view, Bill's role was to hire a consultant (instructor) to deliver the course, and to notify department locations about course availability, start dates, and course expectations. He made decisions about course extensions, and liaised with the instructor and departmental learning Website manager when learners raised issues about technology or course timeframes.

I sensed that Bill was somewhat skeptical about the effectiveness of WBL; however, he viewed the transition of course delivery to WBL as inevitable, particularly given the nature of the department's working environment. His workload was also immense, and he was doing the best he felt he could to support his WBL participants.

Like Julie, Bill was disappointed that learners were not using the online bulletin boards for collaborative discussion in WBL courses. He also felt that it was valuable for learning the course material, for sharing ideas and experiences of how learning could be applied to work situations, and for developing professional, collaborative relationships that would last beyond the course. He thought that WBL might help people in the foreign locations to feel less isolated from each other, and from headquarters (which has been an ongoing complaint).

Bill readily agreed to participate in the study, but I found it challenging to obtain interview time. His schedule was also extremely busy, and it seemed difficult for him to make time for something extra. When we did meet; however, Bill was forthcoming with his views and descriptions of his experience with WBL. He seemed dedicated to

ensuring his clients (learners) are meeting their learning objectives through the departmental learning Website.

Angela

Angela described herself as a retired English schoolteacher whom, since retirement several years ago, has continued to teach adults on a contract basis for educational institutions and private and public sector organizations. She was one of the non-learner participants. She taught in traditional classroom and distance venues, and, recently, through WBL as well. Angela's role in this course was to be the instructor. In the execution of her role she provided guidance on course materials and assignments, marked assignments and made suggestions for improvements, and encouraged and reminded learners to use the bulletin board.

Angela was enthusiastic about the potential for WBL and enjoyed her instructing role in this environment. She particularly liked the flexibility of time, and that she could instruct without having to leave her home. She experienced frustration about her perceived lack of control over learner activities, particularly when it was obvious that they had not done required reading or research prior to submitting their assignments. Angela noted that her frustrations should be taken "with a grain of salt" as she experiences good days and bad days in her role as WBL instructor. She felt she had to hide her "irritation" when learners seemed to ignore clear instructions and guidance, or registered for a course and then did not follow through and take it. Nonetheless, Angela's approach with learners was gentle and encouraging, and she had a great sense of humour,

which helped her to maintain perspective. Her learners commented on how nice and funny she seemed.

Angela, like the other non-learner participants, greatly wanted to see WBL learners enter into collaborative discussion about what they were learning in the course. Based on past teaching experience, she felt discussion helps learners to reinforce what they are learning with new perspectives gained from other course participants. She felt helpless and frustrated when her efforts at instigating discussion on the bulletin board evoked little or no response from the learners.

Researcher

I have been working as a Senior Consultant in the private and public sector for eight years. My work has consisted mainly of devising strategies and providing advice and analysis to senior government and private sector officials on various issues that impact their portfolios. Prior to this, I had worked in the telecommunications industry, and had also taught English at college and university levels. My teacher's perspective has always influenced how I perform my work, and I attribute many work-related achievements to this. In fact, it was my intrinsic educator-self that became both intrigued and concerned as I witnessed the influence of technology and the Internet on all aspects of our lives, and on education.

Like my participants in the study, I used computers, e-mail and the Internet in my daily activities. In preparation for the study, and a few weeks before it commenced, I audited a two-week, WBL pilot course being offered to public servants by the Public Service Commission. I wanted to explore a WBL course from a learner's perspective.

Although I did not do the course assignments, I thoroughly reviewed the Website and links, and read learners' commentaries on the bulletin board venue provided for learner interaction. Despite a written request to participate in discussion with each other on the course Website, only two learners (out of an enrollment of eight) posted a few comments consisting of questions about the course. I was disappointed to see the lack of interest in the bulletin board. I asked a learner enrolled in the course about the reason for his non-participation. He told me that while he would like to engage in an online debate about course content, he did not have time for it. This made me think about the learners who would be participating in my study. I wondered if they would have difficulty finding time to interact. I was anxious to begin the study and collect the data that would answer my research questions.

About the same time as I began the data collection for my study, I became a founding member (volunteer) of a government committee that we subsequently named the "Distance Learning Network" (DLN). There were about six people in our founding group, from various federal departments, who created the constitution and mandate for this committee in an effort to effect collaboration among federal departments with regard to the delivery of "e-learning". The DLN has expanded to include representation from almost every federal entity. Presently, the group meets once every two months, and shares information and resources, and has collaborative dialogue about their experiences.

The issues and challenges discussed at these sessions echoed some of the discoveries I made as I collected and analyzed the data from my study. As the researcher in my case study (see Appendix A), I enjoyed taking part in the course from my researcher's perspective. It was fascinating and exhilarating for me to interact with the

course participants, who did not hesitate to describe what they thought, felt and experienced in WBL.

The Course

The departmental learning Website's writing skills courses were similar to courses I had previously taught at Ottawa's Algonquin College, entitled "English I and II for Business". The objectives of the course in this study, as outlined on the course Website, are to have learners:

- assess their level of knowledge about writing
- become familiar with common writing structures
- explore techniques for improving writing style
- practice techniques for editing and proofreading
- review practices of clear and simple business writing
- examine structure for writing reports
- experiment with "brainstorming" as a technique for getting started on a writing task
- ensure written work meets highest standards

The course itself (see Appendix D, Course Map) was designed to be delivered over a six to eight week timeframe, and commenced the first week of July, 2000, with a targeted closure by the end of August, 2000. In fact, in response to learners' requests, the course was extended twice, each time by three weeks, and did not actually conclude until midway through October, 2000. The writing skills course consists of five main modules, each of which includes the following:

- The learning objectives for the module, along with related topics to outline what learners may expect from the course;
- A scenario which provides an illustration of the topic, and asks learners for their reflections on questions about the scenario;
- Background information on the module's topic;
- Practice exercises, with suggested answers, in preparation for doing the formal assignment.

The formal requirement for course credit included the submission of three assignments to the instructor. The original due dates were, respectively, July 5, 2000; July 17, 2000; and August 4, 2000. These dates due dates were extended for some learners who could not meet the deadlines. Other, informal requests of the learners included asking for their reflections on course content, and for them to participate in collaboration on the bulletin board.

Learners were required to complete and submit an assignment at the beginning, middle and end of the course. The first assignment was due one week after the course commenced, the second at four weeks, and the third due date was one week prior to the end of the course.

The course assignments varied in length and difficulty level. For example, the first assignment required learners to use the hyperlinks on the course site to research some media sites on the Internet. The second assignment required that they write a brief report on what they found using a particular style of business writing. The third assignment involved preparing a work-related report and incorporate a series of writing

steps from the planning of the first draft, and revising their reports, using writing skills and brainstorming skills they were learning, until they handed in their final copies at the conclusion of the course. Learners were required to initiate work on this latter assignment almost as soon as they began the course.

Within the text of each module, links were highlighted words or phrases that, when clicked upon, would link learners to sites for information to help them understand concepts in the course. "Frequently Asked Questions (FAQ)" also appeared throughout the text and took learners to answers to help them get started on assignments, or to overcome a difficulty they were experiencing with an assignment. A listing of online documents, which were hyperlinked to the course site, and a list of recommended hardcopy books, CD's and videos provided learners with suggested materials to enhance their learning.

Other Website tools that learners were directed to use were "my notepad" and the "bulletin board". The notepad tool provided learners with a place to save their ongoing work, and to keep track of questions, problem areas, test results, and Website addresses they wanted for future reference. They were encouraged, with written comments on the bulletin board from the learning Website manager and the instructor, to use it as a venue for sharing information and resources, for asking questions, and for discussing what they were learning with other course participants. A "Help" tool allowed learners to quickly access general information about the course, as well as information about site navigation. A "Course Map" (Appendix D) provided a hyperlinked overview of each module and its related information and assignments, and worked as a course outline for learners to

follow. Instructions on how to use each Website tool were provided on their respective pages.

When learners had submitted their last assignments, they were asked to do the "Post Course Quiz", also located on the course site. The quiz consisted of an editing exercise. Learners were not required to submit their answers, but to compare their revisions with a few provided by the instructor.

A "Course Evaluation" tool provided learners with an evaluation form to assess the writing skills course and the departmental learning Website. This tool is a component of every Departmental learning Website course, but is rarely completed and submitted by the learners.

Data Collection

While I had a design for my case study, as a qualitative researcher, I was flexible and open to the unexpected. Issues, case boundaries and arrangements were renegotiated as required to meet the needs of the participants (Stake, 1995). Data collection and analysis was an interactive, simultaneous activity (Merriam, 1998). For example, the departmental learning Website courses are usually eight to ten weeks in duration; however, the deadline for completing this course was extended twice, and each extension comprised three weeks for a total course length of fourteen weeks. I adjusted my scheduling of interviews accordingly. I began collecting data through my own reflective journal, one week prior to the beginning of the course, and completed data collection five weeks after the course was finished. I wrote my thoughts in my reflective journal on a daily basis during the first week of data collection. I continued to write my reflections in

my journal on an "as they came to me" basis throughout the study. Sometimes this meant writing on a daily basis, or doing a lengthy reflection a couple of times during a week. Quite often, it meant getting up in the middle of the night as something struck me as significant to write down. Data collection took place over a timeframe of twenty weeks, from the last week of June 2000, to the last week of November 2000.

I had to adjust my methodology for in-depth interviewing according to the preferences of the participants. I was able to conduct and tape-record live, in-depth interviews with the six local participants. My plan for in-depth interviewing of the five foreign-based participants was to make an appointment with each of them for a phone interview that I would tape-record and then transcribe. In order to do this, given their time zones, I was prepared to conduct this activity in the middle of the night. However, all of the foreign-based participants vigorously declined this methodology and stated a preference for it to be done via e-mail. They felt that they would be constantly interrupted during a phone interview, and that this would be inconvenient for them and for me. I agreed to conduct the interviews through e-mail, and this procedure is described in detail later in this chapter. Although I was initially apprehensive about doing this, I consulted research literature on online date collection (Merriam, 1998; Land & Hannafin, 1997) and verified that it was an effective, and accepted method. This proved true as I found interviewing participants by e-mail garnered rich data, and was a very satisfying process of ongoing dialogue between myself and the individual learners in foreign locations.

Data Collection Methods

Case Study data collection methods may include all or a selection of: participant observation; non-participant observation, in-depth interviews, focus group interviews, and document and artifact analysis, including reflective journals and field notes (Savenye & Robinson, 1997). In the study, I used three of these methods in order to provide rich, thick descriptions of the data (Bogdan & Biklen, 1998). The collection of data from three sources - the in-depth interviews, reflective journals by the researcher and participants, and participant observation - contributed to the trustworthiness of the findings. I also collected course materials and communications between participants on the course Website and included these as supplementary data for the study.

At the commencement of the course, I sent the participants an "e-mail of introduction and invitation to participate in the study" (Appendix A). One of the eight learner participants dropped-out of the course and the study, midway, citing time constraints as the cause. The remaining seven learner participants completed the course and continued to participate in the case study.

I felt strongly that it was invaluable to have those responsible for the delivery of the course also participate in the study in order to garner the experiences of both learners and those responsible for delivering the course. The learning process in this Web-based environment was analyzed from both learning and course delivery perspectives. As well, my participation in the study as a constructivist researcher provided an additional perspective on what I observed and heard. An interesting juxtaposition of learner perspective with course delivery perspective soon became apparent between the data generated from the non-learner participants and those of the learner participants. This

juxtaposition provided further insight and valuable perspective through which to view data from the study in answer to the research questions.

In-depth Interviews

I conducted three in-depth interviews, using open-ended questions (Appendix F), with each learner participant at the beginning, midway and near the conclusion of the study (and the course). The goal of the first interview was to collect data on their general experiences, attitudes, and expectations regarding taking courses through WBL, and to gather some information for their profiles. The second and third interviews focused on the learner participants' experiences with WBL collaboration among themselves during this study.

Originally, I had planned to conduct two interviews with learner participants, one at the beginning of the course and one at the end of the course. Due to the sporadic nature of the reflective journal activity from some of the learners; however, I decided to conduct an additional set of interviews. This was done at the mid-point of the study in order to capture their thoughts and feelings as they reflected on the course as they progressed through the course.

I conducted two in-depth interviews, using open-ended questions, with each of the WBL Instructor, the course administrator, and departmental learning Website manager, near the beginning and at the end of the study. The goal of these interviews was to gather data on their experiences with collaboration among WBL learners from instructional and administrative perspectives. At the beginning of the study, I had planned to conduct only one interview with these participants; however, because their reflective journal activity

was sparse, I decided to conduct a second interview near the end of the study. This was done in order to capture their thoughts and feelings as they reflected on the course, the learners and their own roles and activities during course delivery.

Reflective journals

I asked each learner participant to keep a reflective journal during the study (Appendix C). In general, I asked them to write down their thoughts and feelings about taking a WBL course. Specifically, I asked them to comment on the interactions between participants on the bulletin board.

I asked the course instructor, the learning Website manager and the course administrator to each keep a reflective journal during the study. I asked them to document their reflections on the course delivery from instructional and administrative perspectives, as well as their thoughts about perceived or real difficulties experienced by the learners, particularly when they participated in bulletin board activity.

As researcher, I kept a reflective journal immediately prior to, during, and immediately following the study. I continuously documented my reflections on all aspects of the study and the participants, as I commenced, conducted and concluded the study.

Participant observation

I observed course participants' interactions through asynchronous text posted to the bulletin board, the WBL tool provided for that purpose. Course participants were aware that I would be accessing the course Website and bulletin board to observe and collect

their written interactions. I observed the bulletin board on a daily basis; however, minimal interaction took place during the course. Nevertheless, my observations were recorded, and I further reflected upon both the interaction I had observed and on the silence of the bulletin board in my journal.

Archival Data

I collected all course Website information and included it as data for the study. Website information ranged from directions on navigating the Website and related links, using the Website tools, and directions and guidelines for the completing the assignments and related activities.

Procedure

When employees registered for the course, the learning Website manager contacted each of them to notify possible participants about the study. I then sent an e-mail to prospective participants for the study once the manager notified me of their interest (Appendix A). I outlined the nature and extent of participation, and arranged a time for an interview. I made appointments to meet with each of the local non-learner and learner participants, to explain the study, the nature of their involvement in the study, and to obtain informed consent prior to conducting the interview (see Appendix B). In the case of consent for the five learner participants located in foreign offices, I sent an e-mail to prospective participants to explain the study and their role as participants, and obtain informed consent by faxing the consent form to those who agreed to participate.

Once participants and consent were established, and the course began, I proceeded to arrange the first set of in-depth interviews (see Appendix C). For the local interviews, held during the first two weeks of July 2000, I asked permission to tape-record the discussion, and informed the participants that a transcript would be provided for their verification of accuracy, prior to data analysis. The interviews took from one and one-half to two hours each and were tape-recorded and transcribed.

In the case of the foreign-based learners, I was forced to adjust my methodology in deference to their expressed preference for online communication with me. All of the foreign-based learners requested that their interviews be conducted through e-mail. I researched recent literature on e-mail interviewing and checked with others who were conducting research into Internet entities. I found that interviewing through e-mail can be as effective as in-person interview because while there may be less spontaneity, interviews conducted through e-mail have tended to be more reflective (Bauer & Anderson, 2000). I proceeded with the e-mail interviews in the second week of July 2000, by sending each foreign-based participant one question, with several related sub-questions at a time. What ensued was an ongoing e-mail dialogue between myself and each learner that spanned over several days until responses had been received for the questions for each interview.

I had included a template for the reflective journals when I sent a note to arrange the first interviews (Appendix C). It was a guide to record their thoughts and feelings, as described previously, and asked them to commence this activity. In the case of the locally based participants, they received their templates in the first and second weeks of July 2000. I then began to analyze the data from the first interviews by first listening

carefully to the tapes, and then transcribing the tape recordings verbatim. The transcribed interviews were then sent to the participants for verification. In the case of the foreign-based learners, I printed their e-mail responses to my questions as they responded to each question. I sent them the electronic template for their reflections after they had responded to the first interview questions, and all received the template by the first week of August 2000. While engaged in the latter activities, I made notes on my perceptions and ideas about what I heard and saw in the interviews and reflections (Maxwell, 1996; Bogdan & Biklen, 1998). I coded the data inductively in order to be open to emerging areas of relevance and interest, and recorded questions to guide the next set of interviews. I revisited WBL research literature and then re-read the data for affinity or opposition with previous WBL research findings. I returned to the transcriptions and began to code salient data into categories, and began further analysis for comparisons and relationships within and between the categories and emerging dimensions and properties.

When the first interviews were completed and analyzed, I began participant observation. I analyzed participant observation data as I gathered it in order to focus on particular categories and themes that became apparent, and that revealed an alignment with data gathered from the first set of interviews. I asked participants to provide me with their reflective journals on a weekly basis throughout the study. In this way, I could gather and analyze data in order to ascertain both anticipated and unexpected findings. The data from the participant observations and reflective journals, albeit a much smaller source of data than the interviews, were analyzed using the same procedure I used for the first set of interviews. Ongoing analysis of all the data helped me to re-focus and refine my approach and focus for the remaining interviews.

At the mid-point of the study, the third week of August 2000, I arranged appointments with each local learner participant for the second in-depth interviews. The purpose of this was to focus more specifically on collaboration. I also contacted the five foreign-based learners by e-mail and began the second set of e-mail interviews for the same purpose. I conducted the second set of interviews with the three local learner participants in the same manner as for the first set. I began analysis immediately following the interviews by, again, first listening carefully to the tapes, and then transcribing the tape recordings verbatim, and sending them to the learners for verification. In the case of the e-mail interviews, the transcript of the learner responses was contained in their e-mail responses to me. I continued the analysis in the same way as for the first interviews. The second interview assisted me in determining specific categories and their properties for participant observation, and for formulating interview questions. At this point in the study, I looked for any new themes, categories and relationships that arose, as learners become more comfortable or less uncomfortable in the course.

Near the end of the study in mid-September 2000, I made appointments with the local learner participants for the final interview to probe for their thoughts and feelings about collaboration and about learning in the WBL environment. Again, the interviews were transcribed and sent to participants for verification. To elicit the same information from the foreign-based learners, I e-mailed the third and last set of interview questions. The same procedure for analysis used for the first and second interviews was used for the third set of interviews.

At the end of the study, after its official closing date of October 13, 2000 (having been extended for a second time, at the request of some learners), I asked for final reflections from the participants, and continued data analysis in the same manner as with the earlier reflections. I also made appointments with the three local non-learner participants for a final interview to capture their reflective perspectives about the delivery of the course and the use of the bulletin board. These interviews were transcribed and sent to these participants for verification. The last reflections and responses to the interviews were received by the first week of November 2000.

Data Analysis Methods

True to qualitative, and constructivist, methodology, I analyzed data when I began to collect it (Stake, 1995; Bogdan & Biklen, 1998; Merriam, 1998). While I had a sound design for my case study, as a qualitative researcher I was also flexible and open to the unexpected. Issues, case boundaries and arrangements were renegotiated as required to meet the needs of the participants (Stake, 1995). Data collection and analysis was an interactive, simultaneous activity (Merriam, 1998).

Data analysis consisted of data management, reduction, and coding (Savenye & Robinson, 1997; Bogdan & Biklen, 1998). In a case study, raw data requires review for alternative interpretations. Identifying patterns and links between contextual and humanistic elements are activities which contribute to effective interpretation (Stake, 1995). Analysis is an ongoing process from the commencement of the study, so that it is possible to go back and seek data from new angles, or to disconfirm preliminary findings (Stake, 1995). I invoked all of the above activities in the execution of my study.

I decided to use traditional, non-computerized qualitative methods (Bogdan & Biklen, 1998) of data management and analysis in capturing data for this case study. I further pursued and determined categories and their properties and dimensions through reading and re-reading the data, making notations on my thoughts and feelings as I immersed myself in the data. I assigned units of data to these categories and used a numerical system to identify relationships among the data. I extrapolated sub-codes from the major codes in order to break them into smaller categories, using the numerical system to identify themes and relationships. I then paused my analysis for several days, and returned to the data to read and re-read looking for any themes or trends I may have overlooked, and coded them accordingly. I organized the analysed data under the four research questions, and proceeded to write the findings.

Extensive quotations from participants were used both to illustrate and support the findings, and to provide the opportunity for vicariously experiencing the learning process in a Web-based environment (Merriam, 1998). Through the expression of thoughts and emotions of the participants in this case study, we can develop a solid vision and understanding of how and why learners did or did not collaborate as part of their learning process in this WBL environment. Juxtaposed against current WBL research, the findings of this study illuminate and extend the literature on WBL pedagogy.

Validity of the Study

Maxwell (1996) notes that threats to validity stem from "...three main types of understanding--description, interpretation, and theory..." (p.89). In describing or interpreting data, researchers must attempt to ensure that what they have described and

then interpreted rings true for the research participants in their studies. One key method for validation is to conduct member checks with participants to rule out misunderstanding and misinterpretation (Maxwell, 1996). It is also important to revisit theoretical literature to seek out alternative explanations, if they exist, for issues emerging from the data. The research participants reviewed and verified my transcriptions of interviews after each interview was completed. I conducted member checks of the findings stemming from the data I obtained from them by having them review a summary of the findings and provide me with comments if they wished. The trustworthiness of the data was partially fulfilled through its collection from three sources, and through a review and validation of the findings from research participants.

Researcher bias, values and reactivity are threats to validity that are researcher-centric (Maxwell, 1996). To avoid possible contamination of the data, I kept a reflective journal to capture pre-study, during-the-study, and post-study data which may reveal biases and values I may hold. For example, I recorded as a bias, my belief that collaboration is integral to effective learning in both traditional and WBL environments. I asked my participants to keep reflective journals during the study; data from these sources contributed to identification of biases, values or reactivity which influenced the nature of their participation. Intermittent review of these reflections assisted me in identifying potential problems that I corrected in an expeditious manner to ensure the data were value-free.

Linked to this activity was the search for any "silent data" (McMahnon, 1996). Because WBL is conducted mainly through asynchronous, text-based interaction,

participants provided data through their lack of participation as well as through their active participation.

I followed Maxwell's (1996) advice and solicited feedback from other researchers who are familiar with the WBL setting, in the attempt to identify and eliminate potential threats to the validity of my study while I was conducting it.

Strengths and Limitations of Research Orientation in WBL

In every study, the strengths and limitations of the chosen research orientation must be considered. The considerations for the research approach taken for the present study are outlined in this section.

Vicarious Experience

An advantage of taking a case study approach to research in WBL is to afford readers the opportunity to vicariously experience particular phenomena specific to a particular setting or context (Merriam, 1998). In WBL, individuals who may have resisted learning or teaching in Web-based venues may, as a result of reading a case study, be able to view WBL in new and more positive ways. Elements of WBL, which may have caused trepidation, may appear less threatening as they are explicated through a case study. As Merriam (1998) says, "People can learn from a case study, perhaps more willingly than from actual experience" (p. 238), and transferability may be achieved.

Subjectivity

Linked to this is a criticism of qualitative research, in general, and of case study methodology. It is considered too subjective by some, and sometimes subjectivity may lead to misunderstandings of what the data are revealing (Stake, 1995). The fact that case study often creates new questions rather than answering existing ones often frustrates some researchers (Stake, 1995). However, qualitative research and case study methodology is subjective by design. It is often through the subjectivity of the participants, including the researcher, that deeper understandings are possible, and allow the case study's audience a vicarious experience that may lead to naturalistic generalizations (Stake, 1995) and an open-mindedness.

Generalizability

Generalizability is a contentious issue in case study methodology (Bogdan & Biklin, 1998) because a case study focuses on the findings of the particular, which may not be generalized to other settings. Stake (1995) would argue that "particularization" and not "generalization" is the goal of case study research. The findings of this study are to be interpreted by the reader and are not generalized beyond the study. In kind, while I interpret the findings in my discussion and make conclusions about the findings, I do not generalize them beyond the study. I believe, however, that readers of this study may draw inferences from its interpretations, and transfer these inferences to inform their own contexts.

Data Collection in WBL

Certain qualitative data collection methods prove difficult in WBL. Participant observation in an asynchronous Internet environment does not afford data portrayed by body language and the intonations of speech. This is not as much of an issue in a synchronous environment where video is incorporated and allows for, albeit limited by the camera, visual observation. Participant observation has been used in WBL research: however, and, while it is limited by asynchronous textual interaction, it has been found to be an effective method for gathering rich data (Land & Hannafin, 1997). Generally, "...online data collection offers an electronic extension of familiar research techniques, widening the scope of data available to the researcher" (Merriam, 1998, p.128).

On the flip-side of this, adversely affecting data collection online are the potential limits inherent in the software tools employed to do the job (Merriam, 1998). Unfortunately, software programs are often inflexible in terms of being adapted to suit the needs of the participants who may be using them to supply data. If participants are inhibited about using technological tools, or become frustrated by the tool itself, this may adversely affect the data they provide (Merriam, 1998). In this case, difficulties using Website tools was one factor that influenced data collection. It contributed to the sporadic nature of the journal entries, and a lack of bulletin board discussion.

Truthfulness of participants

Another concern and drawback about collecting data online is the notion of truthfulness of participants. There are instances where individuals develop online personalities or alternate personas for their interactions in Internet venues (Merriam,

1998). It could be argued, however, that truthfulness of participants may be a concern of any research venue where qualitative methodology is invoked, and where participants may not be completely truthful. I have no reason to believe that the participants in my study were not truthful. I believe they honestly represented themselves, and were extremely candid as they expressed themselves to me.

Summary

"Finishing a case study is the consummation of a work of art" (Stake, 1995, p. 67). It is timely to approach WBL research with a palette of holistic, constructivist-based, case study methodology in order to paint a picture which reveals the dynamics of the interaction between and among learners and instructors. While the final product is not a painting, I believe I have provided an interesting, descriptive and academically sound study and interpretation, which may be incorporated into a growing WBL pedagogy. WBL is a new frontier for education, and a developing educational institution for this century. This study contributes to its development and viability as a venue where learners, and instructors, may experience the joy of intellectual stimulation and collaboration as they construct knowledge individually and together.

When the research focus is on particular WBL factors, a case study approach reveals those factors in a complete way. Case study allows researchers to view issues in context, and in terms of how they affect and are affected by other elements within that context. It provides for both macro and micro views of the phenomenon or issues under investigation. I believe that this is a necessary and vital direction for research into WBL as an effective and viable educational venue.

The intent of my doctoral study was to contribute to WBL pedagogy by constructing an understanding, based on data from a case study that leads to theoretical refinement, or identifies particular needs for further WBL pedagogy development. In particular, I captured and interpreted data on the factors that affected and, thus, prevented the ability of WBL learners to learn through effective collaboration, where meaningful discussion results in the co-construction of knowledge. I believe this qualitative, constructivist case study facilitated this goal for the reasons outlined in this chapter.

The findings reveal that WBL is not yet an optimum learning environment due to contextual and other factors that prevented collaboration. Chapter Four presents these findings. While some factors that could have facilitated collaboration are revealed, the findings, more profoundly, expose those factors that prevented collaboration in a WBL course.

Chapter 4:

The Findings of the Study

Introduction

In this chapter, it is possible to vicariously experience a WBL course through the descriptions gleaned from the data. Factors that facilitated, and factors that, more poignantly in this study, prevented the learner participants from collaborating with each other are exposed to a degree not previously documented in WBL research. The study is timely in providing an in-depth illumination of the contextual and other factors that prevented collaboration among WBL learners, and in providing recommendations for facilitating collaborative discussion in WBL (Burge, 2000; Carr-Chellman & Duchastel, 2000; Knowlton, 2000; Wilson & Lowry, 2000; Jonassen, et. al., 1996; Lebow, 1993). It is also timely because the level of collaboration achieved in a WBL course, and how that collaborative discussion is facilitated, guided and nurtured by an instructor, is thought to be a determining element in obtaining learning objectives in this medium (Card & Horton, 2000; Knowlton, 2000; Muirhead, 2001). A truly exciting aspect of WBL is that the collaboration achieved among course participants in WBL can extend beyond courses to the creation of virtual communities of expertise and learning. Learners who collaborate in a WBL course may continue beyond the course in collaborative relationships that will enhance not only their future learning, but also their day-to-day professional activities (Trentin, 2001; Hill Duin & Hansen, 1994).

The participants shared their thoughts and views about Web-based learning through a series of in-depth interviews conducted both in-person, and, in the case of the foreign-based learner participants, through e-mail. The e-mail interviews evolved into an ongoing in-depth dialogue between myself and these learner participants. I also read the communications between the participants through the course conferencing site on the Departmental learning Website. I noted my observations and collected the notes posted to the conferencing site by the other participants in the study. As well, I asked all participants to e-mail their reflections about the course to me on a weekly basis, and I noted my reflections on my observations and thoughts on this course and its participants. Lastly, I collected all course guidance and directive materials from the course Website to be included as data for the study.

This single case study focused on the facilitators and barriers to collaboration among participants in a WBL environment, and how these facilitators and barriers affected learning. The research was guided by the following questions:

- What facilitates collaboration in WBL?
- What are the barriers to collaboration in WBL?
- How do the facilitators and barriers affect learners' perceived ability to construct knowledge in WBL?
- What evidence is there that learners are or are not collaborating?

The findings are organized under ten themes:

- Learners had unclear expectations about their participation, and the purpose of the bulletin board.

- There was poor course direction, management, and support for learners.
- Learners experienced a severe lack of time for coursework and activities.
- Learners experienced difficulty using Website tools.
- Learners and non-learners revealed a lack of motivation.
- There was a lack of learner independence.
- Learners demonstrated a lack of self-efficacy in WBL.
- Learners were feeling isolated in WBL.
- Learners and non-learners were experiencing feelings of being in transition to WBL.
- There was silence on the bulletin board as a result of the barriers to collaboration.

Most themes are intertwined and this accentuated their impact on collaboration in WBL in the creation of barriers to collaboration. For example, the degree of learners' independence and self-efficacy in WBL was closely related to their degree of motivation to interact. While there were some findings that revealed learners' perceptions of what could facilitate collaboration in WBL, most of the findings revealed the barriers that actually prevented it in this case.

Essentially, the findings revealed a course doomed to fail in the objective of having learners collaborate with each other to share understandings of course content. Because it failed at this level, a longer term objective of creating a community of learners who would continue to collaborate with each other beyond the course was not achieved. The themes emanating from the findings of this study provide a poignant example of the consequences of a design bereft of pedagogy. This, combined with a lack of continuous

support for learners' needs during the course, created an insurmountable barrier for learners to overcome and achieve collaboration.

Unclear expectations

There were three aspects to this theme. Learners were unclear about: what was expected of them; about their role in the course; and about the purpose of the bulletin board.

Perhaps the most startling and prevalent finding of this study was that learners were unclear about what was expected of them as participants in the course. Beyond the submission of three major assignments, learners were unsure of their roles in other activities such as collaborating with each other on the bulletin board:

> In one way I wasn't sure what to expect....I thought at first we might have an information session.... I didn't really have any idea what they were expecting....I thought they wouldn't want the bulletin board too cluttered. So I thought, well, if they answered a question once, they wouldn't really want another question ....I suppose I didn't know if they wanted to hear much from me or not. (Christine, interview 3)

> I seldom communicate with other learners and I am not sure about their expectation. (Fiona, interview 1)

Lack of clarity of expectations and a lack of guidance influenced learners' perceptions about how to construct knowledge in their course, and minimized their ability to do so. Learners were unsure about what they were expected to do beyond the submission of three major assignments to the instructor, and guidance was restricted to the text appearing on the course Website. While the instructor and course administration were willing to answer questions posed to them by the learners, most learners in the course were either unaware that they could, or too shy to ask questions.

> With respect to the bulletin board....people aren't clear about what they should be doing there. (Researcher, Reflection on emerging data from interviews 1 and 2)

Although there is written direction and guidance provided to learners on the Departmental learning site, there was a need for reinforcement through clear, succinct guidance directly from the instructor about expected learner participation and activities. When asked if they would use the bulletin board to collaborate with other learners in the course if it were a mandatory requirement to pass the course, all eight participants in the study said they would participate. Two of the non-learner participants agreed that it should be mandatory:

> It might be good to have a requirement that they enter the bulletin board....I think it should be mandatory. (Julie, interview 1)
>
> I think if you are going to the expense of putting on a course ...I think there should be some commitment....I also think by making it mandatory, it adds to the seriousness of it.... (Angela, interview 1)

The fact that learners need to know, very clearly, what is expected of them regarding coursework and participation seemed almost too obvious to be considered as a finding; yet, expectations, as a theme, recurred in the data generated throughout the study. I revisited the written course directions and guidance material on the site and asked the non-learner participants for clarification about additional guidance provided to learners.

> I know (course administration) administers it, and provides the instructions...he said it was quite clear what they wanted....maybe I haven't looked at them closely because I just make assumptions, but maybe it is that, and to say this is what's expected. (Angela, interview 1)

> I hate to say it, but I've encouraged them and that's all I can do. (Bill, interview 2)

The ambiguity of what was expected for bulletin board activity was reinforced by learners' perceptions that the bulletin board was only for asking questions of the instructor or course administration. Some learners appeared somewhat fearful of posting messages to the bulletin board as they perceived they might be reprimanded for misusing it: "...they don't want our opinions...." (Michael, interview 1). Others simply didn't know why it was there, but found it interesting to observe the contributions to the bulletin board. It intrigued me, as a participant in the study, that all of the participants wanted a venue for sharing ideas and exchanging information, and perceived that this would benefit their learning of course content, yet almost none of them used the bulletin board

for this purpose. When the learners were specifically asked about why they did not use the bulletin board when they thought it was important to discuss what they were learning with others in the class, they said they did not know what was expected of them in this regard:

> So you don't see it as a place, necessarily to exchange ideas with other learners? (Researcher, interview 1)

> No, because it doesn't seem to have that on there. (Christine, interview 1)

As noted earlier, when asked if participation on the bulletin board was made a mandatory part of the course, all learners said they would participate. When asked if they understood what was meant by "collaborate with each other" in the course instruction, none of the learners recalled reading that specific instruction, and seven of the eight learners were unsure about what collaboration on the bulletin board would mean or why it would be beneficial.

I further explored this theme through probing questions in my later interviews with the learners. Their silence on the bulletin board toward the end of the course spoke volumes to me as a researcher, and I needed to confirm that unclear expectations was indeed a barrier to collaboration among learners. It was confirmed:

> You never know what to expect or what is offered....I didn't know what to expect....I thought that the bulletin board was more designed for somebody to put up a question and get the answer, or if you encountered a

particular problem...I wasn't really having any problems

...I didn't feel I had anything to add. (Christine, interview 2)

I thought [the bulletin board] was for people who are really chatty, and thought they were really intelligent and wanted to tell the world about it. (Michael, interview 3)

In summary, learners' uncertainty about what was expected of them in terms of participation on the bulletin board contributed to their feelings of isolation and to their lack of interaction through the bulletin board. Although they stated that they knew that the bulletin board was there for them to communicate with each other, all learners in the course were unclear about what form of communication was expected. Some learners thought the bulletin board was for posting questions only, which would then be answered by the instructor. Most saw it as a form of chat room where those who wanted to visit with each other could do so. Others saw it as a notice board for information related to the course. The study reveals that clear expectations about collaborative activity must be delineated to all course participants.

Poor course direction, management, and support for learners

Armed with the data that revealed learners in the course did not know what was expected of them on the bulletin board, I went back to the course Website to reflect on and review the instructions and guidelines. An analysis of the course materials located on the Website revealed seven factors emanating from this theme. These factors included: a lack of detail and planning for activities for interaction; learners not following

the direction they were given; a lack of management of workplace interruptions for learners; a lack of management and peer support for WBL learning activities; no formal certification for successful completion of the course; a lack of encouragement for interaction on the bulletin board; and minimal concern for learner honesty in completing course requirements. These factors directly affected collaboration in this course. Because of this, interaction between learners which could lead to collaborative discussion was doomed from the outset of the course.

Lack of detail and planned activities for interaction

While the course site was visually appealing, and, at an initial reading, seemed to be organized in a user-friendly fashion (see Course Map, Appendix D), there was a lack of important detail and planning for interactive activities within the guidance and direction provided on the site.

A glaring absence of detail directly influenced the possibility of collaboration among course participants. In the section entitled, "About This Course", learning objectives for the course are listed (see Appendix D), but no detail was provided about how these objectives will be met or facilitated during the course. One of the objectives is to "experiment with Brainstorming as a technique for getting started on a writing task"; however, learners are not provided with any direction as to how or where this is to take place. This section did not direct learners to the bulletin board as the intended venue in which to engage in brainstorming with other learners, nor did it overtly link learners to the bulletin board for this activity. I checked throughout the Website to see if any specific activities were planned to support the objective of brainstorming, or to support

the objective of having learners interact through discussion on the bulletin board. I located what I would classify as a suggestion in the "Before you Move On" section of the course site. It mentioned the bulletin board as a place to "Stay in touch with your fellow learners and course advisor":

> Please take time throughout the course to check out the bulletin board by clicking the bulletin board in the side bar. Take part in the ongoing writing skills discussion and add your own questions and suggestions there for others to read. (writing skills course, departmental learning Website)

There were no indications of what could be discussed, and no specific discussion activities were presented in this section.

The bulletin board was mentioned in one other section of the course Website entitled "Final Thoughts", which encouraged learners to "Make a connection with your fellow learners":

> Please take the time to check out the bulletin board by clicking the button in the side bar. Take part in the ongoing writing skills discussion. If you have questions, ask them there; or if you can answer a question posed by another course participant, add your opinion. (writing skills course, departmental learning Website)

A further note at the end of this section asks learners to share information through the bulletin board: "If there are any resources you have found to be useful please share them with us and your fellow learners. Just click the bulletin board button, in the side bar, and post to the discussion " (writing skills course, departmental learning Website). Again,

one sees a hint at what learners could do when they entered the bulletin board - ask or answer a question or add an opinion - but there is no planned activity for interaction there. It appeared painfully clear that guidance, beyond the course instruction text on the Website, was required by learners to help them understand the importance of bulletin board exchanges to their learning of course content.

The instructor perceived that more guidance may be required, and that course administration, along with instructors, should look at ways of prompting and reminding learners to use the bulletin board:

> ...I wish I had them all together in a classroom to start the course, at least, or to have a check-in....It would probably be good if we could...the course designer...or I could suggest to the technical people...for another perspective on this, we'll look at the bulletin board....it could be something inserted into the course and say, for answers, look at the bulletin board. (Angela, interview 1)

The instructor envisioned a "pop-up" prompt, located throughout the course materials on the Website, which would reinforce previous guidance and expectations provided on the use of the bulletin board.

The instructor and course administration were in agreement and adamant that collaboration among learners about course content was important, and, perhaps, critical to their ability to take the knowledge and apply it.

> Ideally, I would like people to take certain positions, to, in a course, interject their opinions and experiences with the subject matter....having a debate, with the facilitator being

> a...moderator of the discussion and putting it into focus....because it's another level of activity....sparking new ideas....to understanding, and to understanding their understanding of the material. And I think it's quite important that there is a facilitator there and that it is not just an open forum where anyone can say anything. (Julie, interview 1)

However, when asked if they had explained what they meant by collaboration or discussion to learners in their courses, the answer was that learners were directed to the bulletin board for discussion by way of the course instruction text on the Website, and by an introductory invitation at the outset of the course.

There was no direction or explanation of what they envisioned for collaboration beyond "sharing ideas and helping each other". A lack of attention to detailed objectives, instructions and guidance resulted in a poorly delivered course. Concerns about what was suspected to be preventing learners from interacting never manifested action to address these concerns. For example, the instructor voiced the thought that she should post daily comments to encourage collaboration, but actually did so only twice. This attitude seemed to permeate the handling of other matters that impeded learners in doing their course, and influenced learners' perceptions. This lack of action contributed to the factors that created barriers to collaboration and knowledge construction.

Not following directions/guidance

Closely related to the necessity for clarity of course expectations, and a lack of management and support for learners, is the fact that most learners were not have been

thorough in their review of course directions and guidance provided on a WBL learning site. Despite the written direction provided, in what appeared to be an easily navigated, clear and logical order on the Departmental learning Website, some learners did not read or follow the written guidance provided for them in this venue:

> I don't think people take the time to check. I think what they do is take the course material, I think they even go straight to the exercises. I've got a couple in now and I read them and I think – you haven't read the first part of this course, because you make these simple mistakes. (Angela, interview 2)

The non-learner participants suspected that learners do not read through the course guidance provided to them, and that this results in non-participation in a number of recommended activities, including using the bulletin board as a venue for collaboration.

> I think some of the people just wing the course...they didn't really read the course materials. I don't think they had the time. I think they were overburdened with everything. That's a guess. (Bill, interview 1)

They also speculated on the reasons why learners may not be following the instructions provided on the course site:

> ...[not reading the instructions provided] is the frustration, and I think that some of them don't even look at the course material at all....Just do the exercises....I think because of the WEB now, people's attention spans are fairly limited to begin with; people

> read diagonally, so if they don't see the information they want
> they won't read the bottom line. (Julie, interview 1)

I asked learners about following the directions and guidance provided for them on the course Website. The suspicions of the instructor and course administrators seemed to be true for at least some of the learners. Three admitted to not reading the course guidance material:

> As there is no instructor governing the progress of my
> reading of the materials, I still have not finished reading
> all of them....I can submit the assignment without reading
> the materials. (Lynn, reflection, mid-August)

Michael also provided some insight into why they may not be reading through the material:

> [The site instructions] seems to be a lot of times really wordy, but not
> saying too much at times. (Michael, interview 1)

It is important to compare the reasons cited by the learner participants with the speculations of the non-learner participants for why some learners do not follow the course instructions provided on the learning site. The instructor and administrator both intuited reasons for a lack of attention to directions and materials on the Website, but did nothing to address these concerns.

A notable convergence and juxtaposition in the data here can be observed. On the one hand, learners in the course also gave the same reasons as the non-learners for why they thought it was important to discuss course content with each other. Learners perceived that discussion was important to their learning of a subject, and their ability to

take the knowledge and implement it. On the other hand, in this course, learners made few attempts to enter into discussion on the bulletin board primarily because they did not fully understand the purpose of the bulletin board. Moreover, they were not actively encouraged by the instructor, and the course design did not include specific, planned activities to have learners interact.

Management of workplace interruptions during WBL

Workplace interruption, lack of support from management, and lack of peer support impacted learners' perceived and actual ability to collaborate and to construct knowledge in this course. Michael and Fiona experienced few or no interruptions and their management and peers were aware of their learning activities. In these cases, learners felt free to focus on their learning and to participate in course activities such as the bulletin board. The other learners in the study were constantly interrupted by managers, peers and work duties, and found it almost impossible to find time to do their coursework during working hours. This meant that these learners did the minimum amount required for completion of the coursework, and did not attempt perceived "extra" activities such as interaction on the bulletin board.

In this study, frequent workplace interruptions contributed to learners' frustrations with finding adequate time for doing their coursework and for participating on the bulletin board. As with most work environments, the learners in this study worked in open concept offices consisting of a maze of cubicles. Noise levels did not seem to be an issue, which affected their concentration because they were used to performing their job

duties in this environment. However, constant interruptions by peers, supervisors and workloads created barriers to optimum participation in their WBL course.

> The advantage is I can control when I would like to study, but the problem is I just get too much work and study is always the last thing that I can do. (Oliver, interview 2)

> ...I encountered a lot of interruptions. There were phone calls and colleagues' visits to my office. I was unable to close a door or decline their requests. (Lynn, interview 2)

All learners in the study said they experienced work-related interruptions while they were doing their coursework; however, two learners said that they worked around this by managing their schedules to accommodate both work and course requirements. Only one learner said she preferred to work at home where she was uninterrupted; the other seven noted they were interrupted at home by family and by home and family demands.

One learner perceived that there was no realistic solution to deal with the constant demands and interruptions that interfered with their ability to do their coursework:

> One can perhaps make things easier by being very decisive with colleagues and co-habitants at home, but training is always something that tends to end up far down the urgency ladder and put aside when more urgent things come along. Also, if one is able to set aside time, it often means things pile up and in

a working or home environment, they become obvious and add to the stress factor. (Sean, interview 3)

The work environment interruptions that disrupted learners in this case included those of both a professional and social nature. Only a few of them felt comfortable with deflecting social visits, and all learners in the study left their course activities to attend to spontaneous work-related duties.

Lack of management and peer support for learning activities

Seven of the eight learners felt that there was inadequate support for their learning efforts from managers and peers at work. In some cases this was because their peers were not aware that they were taking a course. Generally, learners and non-learners felt that managers paid "lip service" to the importance of training efforts, and did not support their need for time to do coursework. Two learners perceived that their co-workers felt the burden of extra work when she was doing her coursework:

> Others weren't aware I was taking a course...and I showed [my colleague] the e-mail that I was taking the course and she said, 'well, the work has to get done'....In my particular case...if somebody's not there, everybody just takes [the work] on....Everybody just does more work. (Christine, interview 2)

Learners such as Christine were sensitive to perceived negative reactions from colleagues when she apprised them of the demands on her time due to her learning activities.

> The main reason for my failing...to complete the last course was my job situation. I would probably have

> been in a better position now since I have an assistant working for me. I believe that one needs to obtain a buy-in from one's boss and then communicate the need for "space" to do the course with one's co-workers. (Sean, interview 3)

Sean also felt that he did not have the support from his management or peers at work because he had not negotiated the time to do his coursework.

When learners were probed about what they thought would alleviate this situation, all responded that it would help them if their peers and managers knew what was expected and required in terms of course length, number of assignments, and participation in course activities, such as the bulletin board. They felt that they would be interrupted less if their colleagues and managers were better informed about course demands.

Course administration had anticipated that learners may be interrupted and developed some tools for them to use to deter interruptions while they were doing their WBL course. These tools consisted of a desk sign and a doorknob sign that denote the occupant is at the departmental learning Website, and to "Please do not disturb." (see Appendix E) However, seven out of eight learners reported that these signs did not deter their peers or managers from interrupting them. I suspected that some learners also perceived the signs may be viewed negatively by their colleagues, which may have resulted in consequences for them such as ridicule or ostracism.

Lack of formal certification for successful completion

Although the course was not part of a certified program, consideration was given to coursework when employees applied for promotions or transfers. Eligibility for some jobs and promotions did require that candidates complete certain courses, such as the writing skills courses. For example, Christine and Adrian were voluntarily taking the writing skills courses for possible promotion to the next level in their job ranges. These levels specifically required that candidates successfully complete these courses. Some employees, like Michael, had been required to complete the course as a job requirement in their current positions.

The fact that the course was not part of a certified program of study was demotivating for at least two of the learner participants in the study. There was no tangible document to signify learners' successful completion of the course, and this was of concern to all of the learner participants. When I asked learners about it, they all stated that they would like a formal acknowledgement of their achievement. This was important for potential promotions or job changes in the workplace, as Michael expressed:

> ...if you're putting in a whole lot of effort, and you're not getting recognized for it, I don't know if it makes a whole lot of sense. I would like to be getting a certificate or something like that, so I could go be a bit more saleable. (Michael, interview 2)

In summary, the desire for a tangible acknowledgement was expressed by learners in the course. They also noted that their supervisors at work also wanted to see something to show successful completion for possible promotions. Further to this, one

learner suggested that he would like to see the course as part of a certified program leading to proficiency for particular professional positions. He felt this would motivate many learners to expend more effort participating in course activities.

Lack of encouragement for bulletin board interaction

Directions were provided to learners about where to interact on the course site. By clicking on the bulletin board button, further directions on how to post text to the bulletin board were shown. Despite directions, some participants either did not read the directions, did not follow the directions, or experienced difficulty in attempting to follow the instructions they were given. The instructor and course administration were unsure about how to facilitate interaction, given that learners were generally not following directions and not contributing to the bulletin board:

> The question is, how do you have people interact, how do you prompt them to interact? Why do they want to interact on the Web...we include it in the course material. We say, when you are working on the course and there is an important point, why not put it up on the bulletin board to discuss with your colleagues? But this doesn't seem to be working. (Julie, interview 1)

Julie was puzzled by the lack of interaction on the bulletin board, and felt that learners had been adequately informed as to why it was important for them to discuss the course with each other. Bill was desperate to get discussion going on the bulletin board, and he, too, felt that they had tried different ways to get learners to participate:

> I've encouraged people to use it and offered prizes – a mug...
> And we've put up one or two little messages up in an e-mail

> ...but for some reason they don't use it....It sure has not been taken advantage of by the participants, unfortunately. I don't know...maybe it's more work for them. I think for some reason they might want to use e-mail, but it's the same thing as e-mail, basically, and why not just use it.
>
> (Bill, interview 1)

When Bill revealed they had offered a "mug" to learners as an incentive to use the bulletin board, I intuitively knew something was very wrong with his approach. His effort was well-intentioned, and I sensed that he had learners' best interests at heart in terms of wanting them to derive a meaningful learning experience through collaboration with each other. Offering an incentive to them to do so seemed to me to be lacking insight and pedagogical perspective, and revealed a marketing or commercial attitude toward learning. Not surprisingly, learners were not interested in the mug and offer did nothing to entice their interaction. Bill noted that there was no response to the mug offer at all. In fact, I suspected an offer like this may have insulted them as the factors that prevented them from an activity they viewed as important were serious ones. Bill's intentions were genuine, but offering the mug seemed to me to make the intended function of the bulletin board seem frivolous. I felt it conveyed a rather dismissive, unspoken message to learners: rather than ask them for input as to why they did not use the bulletin board, coax them into using it with a "prize". It seemed to, albeit unintentionally, trivialize the effort needed to engage in exchanging comments through the bulletin board.

It was clear that those delivering the course wanted learners to interact in a way that fostered collaboration, so that learning of subject matter would be enhanced and, perhaps, taken to new levels of knowledge construction. Regrettably, this had not been built into the course objectives or directions, nor was it supported through continuous encouragement by the instructor to interact on the bulletin board. I observed that the instructor and course administrators were mystified and frustrated by the lack of interaction taking place. However, the barriers to interaction created barriers to collaboration, whether they were real or perceived.

> ...more participation, more interchange of information between participants; there doesn't seem to be that. (Angela, interview 1)

This limited learners' abilities to construct knowledge in this WBL environment to the fullest extent possible.

To summarize, learners knew that the bulletin board was there and available to them for "collaboration", but they had little idea of what collaboration meant, or what was expected of them when they used the bulletin board. Further, they were unaware of the benefits collaboration might have had for their learning of the course content.

Management of learner honesty in WBL

A lesser factor that became apparent was learner honesty in WBL. This factor was of more concern to non-learners than learners in the study. Because a few instances of known (to course administration) cheating had taken place on the Departmental learning Website, the course administrator and manager were curious to know whether learners were concerned about honesty in WBL. When I asked learners about this, all of

them said they were not concerned about it because they felt that if people wanted to cheat, they would do it in any learning venue. They did not feel that someone's cheating would cause harm to other learners in a course.

Nonetheless, learner honesty in completing assignments in WBL remained a concern to course administration. They were aware of one instance where a supervisor had coerced an employee to do his WBL course assignments for him. As a result of successfully completing the course, the supervisor was promoted to a higher level. Eventually the employee complained about the situation and the supervisor was demoted as a result. Because of this, and a few other known situations of cheating, course administrators were concerned that their learners may be worried about cheating in WBL to get promotions or transfers.

Lack of time

There were two barriers that derived from learners' feelings of being pressured by a lack of time for their WBL course. One was their sense of not having enough time to do the coursework, let alone interact with other learners, and the other was convenient, individual access to their instructor by e-mail. These factors emerged as barriers despite learners' general impression that WBL was convenient because it was accessible at any time.

When participants were asked about what was better or worse about learning in a Web-based environment, time was raised as both a facilitator and barrier to learning in this WBL course, and prevails as a barrier to collaboration. On the positive side, the

learner participants in the study described the WBL environment as more flexible and convenient than other learning venues:

> I prefer this type of on your own learning because I can work according to my own schedule and at my own pace. (Maria, interview 2)

From the learner's perspective, adequate time may be found for doing coursework and communicating with other course participants because of WBL's inherent flexibility due to anytime, anywhere accessibility.

> There is less restriction than classroom training because it can be done during office hours or even at home after dinner....I still find it a good way of learning because people are busy these days and arranging my own time to learn a course is probably the most efficient and convenient way nowadays.... (Fiona, interview 2)

In this particular case, all learners in the course are also employed in demanding positions. For all of them time is a precious commodity, and one that there is little of when it comes to time for extra-work activities such as learning. In this sense, the flexibility of WBL eases the constraints of time and, as a result, learners are willing to enter into collaboration when time permits:

> Through the Internet, I can ask questions anytime I want and as many as I want....I enjoy the flexibility to proceed at my own speed. My progress will not be affected by interruption from other classmates which happens a lot in the

classroom. The teacher's attention will not be distracted.

(Lynn, interview 2)

Without exception, from the learner's perspective in this study, the nature of the WBL environment provided them with the convenience and flexibility they needed in order to have the time to take a course in the first place. The flexibility to choose the time during the day (or night) to work on their course allowed them to fit it into their busy work schedules, without intruding on their equally busy, in most cases, personal lives. Because they did not have to travel to a particular location at a particular time for a class, these learners had time to take a course.

Once taking the course, all learners in the study stated that beyond finding time in their schedules to do coursework, they also required further adequate time for interaction with other learners and the instructor. While learners in this study viewed interaction with each other as time consuming due to difficulties using Website tools, they also regarded interaction as a completely separate and extra entity to the course itself. They reported that interaction and collaborative discussion was desirable to share their understandings of course content, and to share ideas of how to apply course content to their individual writing challenges.

> It is very important to me to have feedback when using the Website to learn a course, otherwise it will be like reading books by myself without other inputs. (Fiona, interview 3)

Despite this sentiment, the learners viewed interacting on the bulletin board as optional, and, if they perceived that they didn't have time for it, it didn't happen. This meant that desires and good intentions went by the wayside as the course progressed and as learners

perceived they did not have time for any course activities beyond completing assignments.

Lack of time was consistently characterized as a general problem facing the eight learners participating in the study. Through probing questions, it became apparent that lack of time was also a barrier to learners' collaboration in this WBL course. Only two of the eight learner participants, Michael and Fiona, felt that they had adequate time to do their coursework, while the other six learner participants felt they did not. When asked, with the exception of one, all learner participants felt that when and if they had the time, they liked to collaborate with their fellow learners in the course because:

> I find it difficult to establish an active interaction with the instructor and fellow learners due to the heavy workload and the limited time being allocated to the learning. An online conference would be good....(Oliver, interview 1)

> I think the problem with the bulletin board is time, if I had more of it, I may perhaps have used it more.... (Sean, interview 1)

Because learners felt they were struggling to find time to access the Website and do the course assignments, they perceived bulletin board activity as another time-consuming effort in a busy day.

> ...I still have to do my work and try to fit this in. From that perspective, it would be the interaction that I would enjoy.... (Christine, interview 1)

Other factors infringing on course-time, such as being interrupted, caused learners to limit bulletin board activity to simply checking it to see what messages other learners had posted there.

> ...I just like to see people chatter away – see what they come up with, see what they say and that's basically it. (Michael, interview 1)

> I checked the bulletin board every time I went on, and I read some of the questions people had. (Christine, interview 3)

The non-learner participants cited lack-of-time as the reason they thought learners quit WBL courses and do not complete assignments by suggested deadlines, and also as a suspected barrier to collaboration among learners. They suspected that learners did not have time at work or at home to do coursework or to send messages to the bulletin board. This was an assumption on their part, partially based on informal feedback from learners in other WBL courses.

> I'm hopeful that there will be more participation using the bulletin board....but I guess they don't have the time – some of them don't have the time. (Bill, interview 1)

> And the bulletin board – I don't think they have the time to go into it. (Angela, interview 1)

They also felt that learners in the departmental learning Website courses perceive that it takes more time to post a message, because they have to write out their thoughts and send them to the bulletin board, instead of simply talking:

> ...it takes longer to write than to speak. So people are starting to write and think, oh, it's taking too long – never mind, and they'll lose interest and cut off interaction at that point. (Julie, interview 1)

Both learner and non-learner participants cited a lack of time as one barrier to collaboration with each other using the bulletin board. Although there were e-mail communications between learners and instructor, and learners and course administration, there were no e-mail communications between learners in the course. Some learners found it difficult to find even the time to interact with the instructor, and no time to interact on the bulletin board:

> ...due to time constraints, I was unable to interact too much with the instructor except sending her my assignments. I find it difficult to establish an active interaction with the instructor, fellow learners, due to the heavy workload and limited time allocated to learning. (Oliver, interview 1)

Convenience as a barrier to collaboration

As a positive factor, the flexibility of access and time equates to convenience for learners. Although there are due dates for assignments and a course deadline for

completion, there is no pressure on learners to adhere to a rigid schedule of classroom attendance, which might be difficult for learners with work and family responsibilities.

> I am surprised to find out that this way of learning is actually more convenient and flexible than classroom learning....It is hard for adult people to squeeze time to advance their knowledge. We can arrange our own time to learn....(Fiona, interview 2)

In addition to arranging their own time to learn, some learners in the course felt that it was more convenient and expeditious to communicate through the Departmental learning Website as well:

> ...what I like is, usually when you send something, it's how quick it comes back. Not just that, it's handy – it's always there and it's a lot easier doing something on the [departmental learning Website] than going on the phone and calling someone. (Adrian, interview 1)

Moreover, learners also appreciated the convenience of having direct, e-mail access to the instructor who responded quickly to their individual questions and concerns about course material.

> I have to e-mail my instructor to ask for explanations. This is mainly related to assignments and for problems that I came across during the course....I am quite happy that my instructor replied to my questions the next day....(Fiona, interview 1)

In some cases, e-mail access to the instructor was done to the exclusion of participating on the bulletin board:

> I personally seldom post any comments on the bulletin board. I would rather address my questions or concerns to the instructor directly....But I do visit the board regularly.... (Lynn, interview 1)

Convenience can help facilitate collaboration among learners, but it may also serve as a deterrent. Non-learner participants expressed the thought that because it was so convenient to have direct e-mail contact with the instructor, learners were not motivated to attempt communication or collaboration with other learners. "I saw the course more as a relationship between me, the instructor and the course" (Sean, interview 1). This can also be a problem for the instructor who has to reply to individual learners about course content others may also be asking about. The instructor reported that after repeating the same information to a number of learners through e-mail, the learners were directed to check the bulletin board for information:

> And every reply I write to them going into detail about what they could be doing differently. And now when I write to them....I say check the bulletin board. And I go back to check the bulletin board, but there's nothing. (Angela, interview 2)

Learners seemed to prefer the convenience of having individual access to the instructor through e-mail, rather than to use the bulletin board to post questions or concerns that may inspire input from other learners as well as the instructor:

> I have not visited the [departmental learning Website] at all this week. But I had a chat with my instructor via e-mail. (Lynn, reflection, mid-July)

On the one hand, this accessibility enabled learners to construct knowledge either on an individual basis or in a one-to-one collaboration with the instructor. On the other hand, the convenience and benefits of easy access to the subject matter expert, generally through e-mail, posed a barrier to collaboration with other learners on the bulletin board. In fact, most learners in the study, when they did use the bulletin board to communicate, were directing their questions and comments to the instructor or course administrators.

In summary, toward the end of the course, these barriers to collaboration contributed to rendering the bulletin board silent. This was partly due to time concerns because learners found the bulletin board tool difficult and, therefore, time-consuming to use. Technical failure added to learners' anxiety about time. All learners in the course expressed great satisfaction in having personal attention from the instructor at their convenience, and felt it was more expedient to e-mail her directly.

Time and convenience as both facilitators and barriers to learning

Time had positive and negative implications for WBL. Time, as a facilitator, meant that learners in this study perceived unimpeded accessibility to the course and to learning. Time, as a barrier, meant that all participants in the study perceived the lack of consistent time to use all the tools available to them in the construction of their learning, which included collaboration amongst themselves in the Website venue provided for this purpose.

As a facilitator to learning, the flexibility of being able to access the course site regardless of time zone or time of day meant learners did not face the physical restrictions and impositions of an arbitrary time slot for attending a face-to-face class. As

a barrier to collaboration, however, one participant also noted that the delay of up to forty-eight hours in responses to the bulletin board, due to time zone differences, contributed to a decline in interest in participating in bulletin board discussion.

> The time lag poses a barrier...discourages students from generating immediate interaction or discussion....
>
> (Lynn, interview 2)

Closely linked to lack-of-time as a barrier to learning and collaboration on the bulletin board is the convenience of access to a subject matter expert. The convenience of being able to access the instructor directly often resulted in collaboration between instructor and individual learner. Learners perceived that it was less time consuming to communicate through e-mail with the instructor than to interact on the bulletin board, and it created a barrier to collaboration among themselves.

Difficulty with using Website tools

Two barriers emerged from the theme of difficulty using Website tools. There were technical problems that hindered some learners from persevering with certain activities, and others got lost in cyberspace and did not know how to return to the Website.

The departmental learning Website provides clear navigation directions and is designed for ease-of-use by learners. The Website tool created for collaboration among course participants, the bulletin board, was straightforward and easy to use for those with previous experience. Although subject to the occasional technical failure, the bulletin

board was known to the learners in the course as the place they should go to interact with other course participants.

> I would probably use it, but right now I haven't....I think it's good that it's there (Adrian, interview 1).

> I do visit the board regularly although I do not find too much on it. (Maria, interview 1)

Learners in the course perceived that the Website tools, including the bulletin board for interaction, would be easy to use.

> An effective tool could be the bulletin board where one can share thoughts with others. (Lynn, interview 3)

Most of them had used all of the tools during their first WBL course through the Departmental learning Website, but there were varying levels of experience within the group. In reality, when they experienced technical failure, or difficulty using the Website tools, most learners became frustrated and this affected their use of the tools.

At the outset of the study, when asked about using the bulletin board for collaboration, all learner participants said they knew about the bulletin board and felt they would be comfortable using it. Midway through the study it appeared that interaction on the bulletin board was declining, and when asked about the process of posting comments on the bulletin board, five learner participants described it as "awkward" and "...the bulletin board is difficult to use". Most learners felt it was much more convenient to simply send an e-mail to the instructor or course administration than to use the bulletin board to communicate and collaborate with course participants. One of the non-learner

participants also described the bulletin board as "problematic" and "difficult to use". I had noted the problem of disappearing commentary in my reflections about three weeks into the study:

> There is sometimes a problem with disappearing messages-writing due to technical difficulty, which causes frustration. There also seems to be a try it once and then quit forever mentality re Web-based learning tools. (Researcher, mid-July)

One learner described a situation where technical problems with the site had prevented two learners from receiving important guidance about the course. These learners proceeded with the course assignments unaware they were missing vital information. Those learners who were able to access the information were unaware that others could not, and the bulletin board was inaccessible due to the technical failure. None of the learners or the non-learners were notified that the site was experiencing technical difficulties. As a result, the two learners were frustrated in their attempts to do their assignments or to communicate using the bulletin board. They both decided not to take another course through the departmental learning Website.

The technical problem was rectified when one of the learners sent an e-mail to the course administrator and brought it to his attention. Some insight into why such a delay in repairing the site occurred may lie in the view of course administration that once a course is available on the Website, it requires little supervision: "The nice thing is you can just put it up and it runs on its own." (Julie, interview 2)

The bulletin board was not the only tool affected by technical problems. At times, the Website was down and inaccessible to course participants. Other technical failures

prevented learners and non-learners from using the Website "notebooks" for doing and saving assignments, and, on occasion, assignments done on the notebooks were erased during the save action.

> Sometimes, technical problems may hinder the progress and frustrate both the students and the instructor.
>
> (Lynn, interview 1)

Four learners had written notes for the bulletin board only to have them disappear when the appropriate button was clicked to post them on the bulletin board. Because of this, these learners decided not to use the bulletin board again. The course administrator was aware of this problem, and experienced it himself when he used the notebook tool:

> ...in notebook...when you cut and paste the material, you are not able to save all the material...I had trouble doing that – saving it....other issues I know that have arisen have been technical problems with the server. They can have a lot of trouble logging in because the servers go down. (Bill, interview 1)

Experiencing technical difficulties with the bulletin board was enough to cause some learners to decide not to contribute to it again:

> Interaction between students and the instructor is very important, [but] the [bulletin board] in my courses did not work well at all. In the end, I hardly checked what was on and did not contribute.
>
> (Sean, interview 3)

When asked, Bill suggested that these types of problems were usually a matter of getting used to working with the Website tools, or that there was a general breakdown of the infrastructure. He also thought that those who encountered these difficulties were likely not following directions properly. Bill felt that some learners who contacted him to complain about difficulty with the tools were "whiners".

I experienced my own frustrations at the beginning of the study when I could not access the bulletin board area of the Website because of a technical problem. My first reaction was to assume that I was doing something wrong. After repeated attempts, I finally called the learning Website manager and she advised me that they were having technical difficulities with the Website:

> While the course officially started on June 26, the Website was down due to a system-wide problem, so it was not possible to access the site. On June 27, some of the site was functional and other parts were not.
>
> (Researcher, reflection, first week of July)

It took one week before the problem was solved and I could gain access. I found out later that other course participants had also experienced this problem, so that the course could not actually begin until the first week of July. I wondered if this contributed to the discrepancy between those who enrolled in the course and the number of learners who actually took the course. I did ask the question of the course administration; however, I was advised that there is no follow-up with those who enrolled but did not attend.

When Website tools are working properly and without technical failure, learners are able to access course material and successfully do their assignments, thus facilitating

their construction of knowledge. At the beginning of the study, learners perceived the tools available to them on the learning Website as useful and effective in helping them to achieve their learning goals. As the course progressed, as learners used the Website tools, and as they experienced technical difficulties, they were less enthusiastic:

> As for computer courses, the downside is that I'm not used to learning this way. (Michael, interview 1)

> Sometimes it's like you don't know {where you are} – sometimes you go to one Internet link and then back, and you don't know where...so I think I find that reading through a book is easier than hours in front of a screen.... (Christine, interview 2)

Despite the fact that the learner participants in the course had extensive experience using computers and the Web, and two of them were technical experts, they experienced difficulty with the course Website tools as they progressed through the course. The ensuing frustration contributed to their perception that the Web-based course was very time-consuming. Perceived and real difficulty with Website tools resulted in minimum participation from learners.

Course administrators were aware of some learners who were having difficulty with the Website tools; however, others did not contact course administration when they were having trouble. In one instance, two learners used the bulletin board to alert the instructor and course administration to a problem they were having. Other learners commented on this to me in their interviews, and noted that they were experiencing the same problem and that seeing the bulletin board postings was reassuring. When I probed

as to why they did not contact anyone when they had the problem, they said they had assumed that it was their ability with the Website tools and not the tools themselves that was the problem.

The course administrators also noted that the bulletin board as a Website tool was necessary in order to facilitate discussion among participants, and that e-mail may not work for this purpose because it is difficult to control when a number of individuals have access to the parameters:

> ...[discussion]...cannot happen in a Web-based environment unless they are corralled in an area, you need to create a space for them to do it....most of us need this framework if we're on our own. (Julie, interview 1)

She perceived that without a specific area in which to meet for the purpose of discussion, participants may be accidentally missed or accidentally wander off into the WWW.

Learners concurred that an area such as the bulletin board is an important Website tool to discuss course content and share ideas, and perceived this as affecting their ability to learn and retain the course material. "We can then learn by sharing....I think both students and instructor benefit from the interactive exchange of thoughts." (Lynn, interview 2). Yet, there was a disconnect between what they said and did, as evidenced by their lack of participation on the bulletin board.

A further barrier to collaboration in a venue such as the bulletin board, lies in the loss of spontaneity during the act of using the Website tools in order to post text to the board. Because the act of posting comments creates a delay between learners' thoughts

and their subsequent appearance on the bulletin board, spontaneity is often lost in the process:

> In this environment, if you decide to have a side conversation, you have to get there and that's probably the difficulty there- you are adding elements and the spontaneity is gone.
> (Julie, interview 1)

Compounding this is the delay imposed by different time zones which impacts on learners' reading each other's comments. Non-learner participants sensed that this may be one reason for learners' sparse use of the bulletin board. Closely linked to this is learners' perception that it takes extra time to use the Website tools in order to post comments to the bulletin board. Again, a juxtaposition of the data revealing non-learners' perception of barriers against what learners actually said, shows that it is the perception of time that results in minimal participation. For some learners, it is also lack of self-efficacy with Website tools and about their ability to communicate about the subject matter.

Lack of motivation

There were two aspects to this theme. A lack of motivation to interact was a factor in creating a barrier to collaboration among learners. The instructor's lack of pedagogical motivation to inspire collaboration created another barrier factor.

Initially, all of the learner participants described themselves as self-motivated by virtue of their commitment to 'lifelong learning'. All of them were regularly taking courses delivered through traditional classroom and distance learning. However, when it

came to discussing their motivation for this particular course. Michael and Maria described their participation in the course as mandatory:

> ...I think the main issue is that my bosses think that I, and they are extremely poor writers as far as I'm concerned.... They've figured out that I'm a worse writer than them, so they kind of insisted that I take the course.
> (Michael, interview 3)

Michael seemed to view his enrollment in the course as a punishment by his supervisors, rather than as a means to help him improve his writing ability. This seemed to be the case for Maria:

> I would generally be motivated by having interest in a particular subject. However, for this time, I took up the course because I was nominated by my supervisor.
> (Maria, interview 2)

These learners described themselves as less motivated than usual in this course because they were told to take it by their immediate supervisors. While both described themselves as committed to lifelong learning and taking courses, neither intended to collaborate with other learners in the course, and neither had much interaction with the instructor.

> I can't see how it would help me....If I have a question I will ask the instructor. (Michael, interview 2)

> I do not expect any interaction with the other learners, especially if I have to go through the bulletin board. If I want to know something then I will ask the instructor, not other learners. I do not expect to have many questions. (Maria, interview 1)

Later in the study, Michael did attempt to get a discussion going on the bulletin board. When asked why he had decided to do this, he replied that he wanted feedback from other learners to see if there was an alternative perspective for his view of a particular topic related to the course content. When there was no response to the thoughts he posted on the bulletin board, he did not contribute again.

The instructor was aware of at least one of these "mandatory" learners and describes this type of course participant as a "prisoner", and attempted to counter this challenge with extra encouragement in order for them to get as much out of the course as possible:

> There were three kinds of participants: the learners – who are happy learning anything; the vacationers – who don't care what the course is about; and... prisoners who had been sent....but I say, well, since you're here, you might as well get the most out of it. So I find that works. (Angela, interview 2)

Another learner participant, Fiona, who described herself as highly independent and self-motivated to learn, also attempted to collaborate with the other learners on the bulletin board. As noted earlier, she felt it was important to interact, especially in a WBL

course. However, when Fiona did not get any response on the bulletin board, she, like Michael, quit posting messages herself. She was disappointed that there had not been any interaction to her message, and was not motivated to try it again as a result.

The motivation level of the learners in this study contributed to the lack of collaborative interaction on the bulletin board. I began to see this in the data about midway through the study. I also noted a relationship between motivation and the theme of time; a lack of time was often given as a reason for not collaborating on the bulletin board, but I had sensed earlier that a lack of motivation may also be a barrier to collaboration.

Something that two of the eight learner participants said led to my identification of lack of motivation as a theme emerging from the data. All of the learners were in demanding work positions, however, two learners stated that time can be made for learning if they were motivated to do so:

> The learner should manage his own work schedule and choose a day where there is no scheduled meetings....If the course is quite long, I think I will set a particular date and time each week to do it and try to keep the schedule.... (Fiona, interview 3)

> ...I'm busier than you know, but I do try to access it and get the job done....I make time to do the course. (Michael, interview 1)

These two learners also contributed to the bulletin board more often than their peers, and one of them tried to instigate collaborative dialogue with the other learners by

introducing a topic for discussion in which experience with course content could be shared. This prompted the following response, in a reflection sent to me, from another learner in the course:

> It gives me insights on the area that I have never thought of. (Lynn, reflection, mid-August)

When asked to describe the motivation level of learners, the course instructor described the frustrations she felt about their motivation and level of commitment to conducting the course in the way it was intended:

> So, I'm going to prod them to look at the bulletin board and ask them to do something...what they're doing in the course and if they're having problems to share them....I think you get more out of something when you can see or hear somebody asking questions that you may have thought of asking but didn't feel like it. The bulletin board could be more useful, but it hasn't been used. Now, I think I'm a bit guilty of that as well – that's why I'm making an effort in this course to get into [the bulletin board] more. (Angela, interview 1)

However, neither she nor the course administrator posted more than two or three comments on the bulletin board to encourage learners to use it.

Lack of instructor motivation

While the instructor experienced a great deal of frustration because of the lack of interaction, there was limited effort on her part to promote collaboration on the bulletin

board. I found that the motivational level of the learners reflected the motivational level of those delivering the course and contributed to the lack of use of the bulletin board. What became apparent to me as a participant in the study was that there was little encouragement in this regard, and it was not a mandatory course activity. There were several attempts made by the instructor on the bulletin board itself, but there was not really any consistent effort to get learners to collaborate there:

> I'd start out gung-ho, like a lot of these people do, and then life gets in the way. It's so easy to put it off when you don't have time structure in the classroom to do it. (Angela, interview 2)

The fact that participation on the bulletin board was not a mandatory activity for course credit created an intrinsic barrier to collaboration as learners were not self-motivated to use it. When I asked them about it, seven of the eight learners said that they would collaborate with other learners on the bulletin board if it were mandatory for course credit.

This lack of motivation was somewhat evident in the way that both the learners and the instructor participated in my study. I had to gently but consistently remind all participants to send their reflections throughout the study; I felt it was a precarious activity, as I did not want to harass anyone out of the study.

> Very slow to get reflections to come in; at the mercy of the time or motivation of participants – which can be frustrating and worrisome. I can't prod them; I may try to encourage without being pushy. It's a delicate balance. (Researcher, reflection, mid-July)

As the course went on, the motivation level of both learner and non-learner participants seemed to dwindle. Parallel to the lack of motivation for collaboration on the bulletin board was participants' lack of motivation to share their reflections. Both learners and non-learners had to be coaxed to send their reflections. My reflections throughout the study were full of frustration in this regard; however, I did not let it influence my communications with the other participants. In addition to providing data for this study, my reflections provided me with a venue to vent and to note my disappointment (Maxwell, 1996).

Lack of motivation as a barrier

While all participants in the study described themselves as self-motivated, there was evidence of a lack of motivation when some learners perceived that they needed to complete only the three major assignments in order to pass the course. Two learners admitted to being less motivated than usual because they were required to take the course, and, as a result, did the minimum amount of coursework. One of these learners contributed to the bulletin board once, while the other decided not to participate in the bulletin board at all. Despite this, both learners perceived that their lack of motivation did not hinder their ability to learn the course material. It did prevent them from doing extra, recommended reading and exercises, and from interacting on the bulletin board.

There was at least one learner who felt the non-learner participants were not motivated enough in their efforts to guide learners through the course, or to facilitate interaction on the bulletin board:

> I think in a situation like this, where the class is relatively small – you've got twelve people, they can really do something more than they did. (Michael, interview 3)

I had been thinking the same thing from the outset of the course. I had hoped that the instructor would make a concerted effort to get some dialogue going on the bulletin board:

> Perhaps there is a need for more motivation and guidance from the instructor and course administration. Some sort of everyday activity in the bulletin board and a teaser. (Researcher, reflection, mid-August)

I found it intriguing and annoying that everyone said interaction and collaboration on the bulletin board was important to their learning, but that little was done to motivate interaction. A few sentences of encouragement from those charged with the delivery of the course, and the offer of a mug to those who participated in bulletin board discussion seemed to me to be blatantly inadequate:

> There seems to be no commitment to a designated activity to get learners to interact, yet everyone says it's important to them for both personal and learning reasons: better for learning the subject, and for a sense of belonging and possible ongoing relationships. (Researcher, reflection, mid-July)

Learners perceived a lack of effort and motivation on the part of the instructor and course administration, and it contributed to their own lack of motivation to reinforce their learning with what they considered extra efforts: namely, additional reading, exercises

and collaboration with other participants. In this sense, it limited their ability to construct knowledge in this environment.

Lack of learner independence

This theme revealed the significance of learner independence in creating a barrier to interaction with others in WBL. The learners in this course demonstrated varying degrees of independence in the execution of their course activities.

It was a factor that influenced their decisions to post commentary on the bulletin board. Some depended on direct e-mail communication with the instructor for direction or to pose questions about course content, to the exclusion of reading the course materials on the site. Angela was often frustrated with having to guide some of them through the assignments, and she perceived that these learners were too dependent on her.

Five of the learners in the study (Michael, Sean, Oliver, Fiona and Adrian) described themselves as independent and confident about their computer skills and ability to navigate in an Internet environment. These learners were prepared to collaborate with their course peers using the bulletin board:

> I think an ideal Web-based course should be easy to access at anytime....Learners can discuss problems and share ideas that they encounter through the course through a chit-chat board. (Fiona, interview 1)

There was a general perception that the bulletin board was there so learners could help one another. This did not happen very often, as learners tended to e-mail the instructor who felt she had to respond immediately to their inquiries on an individual basis.

> ...if I had questions or if I want to know something, then of course I would use it. (Adrian, interview 1)

> Interaction by means of online communication or through bulletin boards are both helpful. I want to share ideas and opinions with other learners and communicate with instructors to solve my problems. (Fiona, interview 3)

One learner suggested that the instructor should use the bulletin board to respond to individual questions so that all learners in the course could benefit from her answers:

> ...quick responses from the instructor and the instructor providing feedback on each assignment to the whole group, not just to individuals separately, high-lighting common errors and sharing the outstanding work from specific students to the rest of the group. Other learners should actively participate in the sharing of questions and concerns with others. (Lynn, interview 3)

The other four learners in the study stated a preference for face-to-face interaction, such as that found in a traditional classroom, and they felt isolated and unsure in the Internet environment, and reluctant to use the bulletin board for that reason.

Three of the eight learners who were less comfortable and confident in a Web-based environment described themselves as also needing frequent guidance or coaching from an instructor. These learners required prompting to try new ways for acquiring information, such as doing Internet searches, or for communicating with others, such as through the bulletin board. They waited until they received instructions directly from

course administration, to the exclusion of reading course direction and guidance materials themselves.

> I think it is more difficult to learn independently because one looks at online courses much in the same way as one does traditional learning....the problem with self-directed learning is that you are much more prone to time pressures and also your own mind's trickery leading you to perhaps skip parts that you don't feel are necessary. (Sean, interview 2)

Despite the individual attention from the instructor or course administrator, some learners did not follow through with the appropriate activity, such as being directed to the appropriate reading material and practice exercises, much to the frustration of those delivering the course:

> And I do have a feeling...that when they sent me an assignment, which is basically the mid-course assignment...some of the things I looked at – I would ask myself, have you read the material? Have you done the exercises? Because when you're doing that kind of a course, and when you're doing it in a fairly short time, I felt that surely some of it would stick....and that's where a lot of my frustration comes in. (Angela, interview 1)

A lack of learner independence prevented some learners from using the bulletin board to pose questions or discuss course content with all course participants. Their non-response to commentary on the bulletin board also discouraged the more independent learners from trying to use the bulletin board to collaborate with their peers. The

instructor encouraged learner dependence by quickly responding to them individually, and also discouraged bulletin board activity by doing it.

Lack of self-efficacy in WBL

Learners' lack of self-efficacy in WBL revealed itself in three ways, and these were factors in creating barriers to collaboration. Some learners were not efficacious using technology, some feared the unknown and were not self-efficacious in the WBL environment for this reason, and some lacked efficacy in their English writing abilities - despite their protestations to the contrary.

It appeared that there was also a relationship between the degree of dependence on the instructor and course administration and the degree of self-efficacy of the learners. Those who were more self-efficacious with using Website tools and with their writing skills also described themselves as independent learners. Those who were uncertain about using the tools and about their writing skills were likely to contact the instructor or course administrator for guidance.

> They may have had trouble the first time – maybe they didn't use the correct password and they got frustrated with it. I know one participant really got frustrated....she had trouble and she called me about six times....but that's a client that we're dealing with so we have to be patient. (Bill, interview 1)

> ...there's more strategy involved to get things across [in WBL]: explanations, coaxing them, coaching them, mentoring them to get things done.... (Angela, interview 2)

Learners in the course who demonstrated self-efficacy also posted comments on the bulletin board and attempted to collaborate with other learners. They described themselves as comfortable and confident in the Internet environment, and enjoyed taking courses through the Departmental learning Website. These learners also stated that they were confident about their writing skills and did not feel uneasy about putting their thoughts in writing on the bulletin board. They also felt it was important to share ideas about course content.

> ...there's a lot more going on at one time, and we're not all aware at the same time, so if somebody has something – some ideas – throw out some ideas and they can be played with....(Michael, interview 1)

Participants who demonstrated self-efficacy were also willing to collaborate on the bulletin board, but when there was little response to bulletin board postings, their contributions dwindled and then ceased altogether.

Seven of the learners in the study described a desire to interact with other learners about the course, and one learner said it would be useful to share experiences that could help others in the course:

> One thing I find rewarding is the browsing of the bulletin board as participants from different backgrounds gave me insights in writing which was not covered in the materials, and

the responsiveness of the instructor in the feedback.

(Lynn, interview 3)

Four learners who demonstrated self-efficacy, also described themselves as independent learners who preferred taking courses through WBL venues such as the departmental learning Website. They described themselves as confident with using computers and the Internet, and they were not hindered from interacting with others by their perceived lack of ability with the subject matter. They also emphasized the importance of being self-motivated in this kind of learning environment, and were scornful of those who complained about not being able to plan for enough time to do the coursework or to interact with others on the bulletin board:

> I think learning through the Internet also helps build up self-discipline because you have to plan your own time and to complete the course in time. People who are lacking discipline would never be able to complete the courses.
>
> (Fiona, interview 1)

> Even if there is a time difference between me and the instructor, I can still contact other participants in my area to talk about how they feel about the course and exchange ideas and learning experiences....
>
> (Fiona, interview 1)

Learners who were self-confident and independent also felt comfortable scheduling time to facilitate their coursework, and in communicating this to others around them in order to deter interruptions:

> One way to get less interruption is to put up a sign so
> that other people will know you are working on the
> course when you are in the office.
> (Fiona, interview 3)

Fiona, Maria, Sean and, to some extent, Christine demonstrated confidence and independence in the course by completing assignments correctly on their own, were also more likely to contribute to the bulletin board or to attempt to get a discussion going there. The others, who reported feeling less confident in their ability with course content, were also dependent upon the instructor for individual guidance through e-mail. While efficacy and dependence are factors in learners' perceptions of their ability to construct knowledge, they are not exclusively responsible for the lack of interaction in this course, as evidenced by the lack of it.

Michael felt more self-efficacious in WBL than in a traditional classroom because he was adept at using technology, and his learning disability was unknown to the instructor. He perceived that the ability to use tools such as the spelling and grammar tools lessened his inhibitions and fears about participating in the bulletin board, or in communicating with the instructor and other learners through e-mail:

> I'm a lot less self-conscious about it and about the system too.
> I was always reluctant; I always wanted to go back to school
> but my experience with university many years ago made me

very reluctant to go back to another situation like that.

So...a system that is set up this way is good. (Michael, interview 1)

However, Michael gave up after only one attempt to get discussion going on the bulletin board and received no response from either learners or the instructor.

He especially appreciated the ability to have e-mail access to a subject matter expert for individual attention, and felt the responses from the instructor in the course were very helpful. He did believe, however, that the instructor could have done more to encourage interaction on the bulletin board.

The instructor demonstrated self-efficacy in the WBL environment, and was enthusiastic about participating in what she considered to be an innovative educational venue. Through this approach, she was successful in motivating even her "prisoner" learners to at least do the course assignments, if not to participate in any collaborative activity on the bulletin board. In this study, the instructor responded quickly to questions and comments that were posted to the bulletin board, and tried, twice, to encourage collaborative activity there. She experienced frustration when there was technical breakdown. Her frustration was unknown to other participants in the course, as she only expressed them in her reflections to me.

In spite of an apparent desire and willingness to collaborate, most learner participants described their hesitation to use the bulletin board as a result of feeling unsure about their writing abilities, and about the value of their contributions. Contributing to this was fear of the unknown. Their course-mates were unknown entities to them, and a lack of confidence in their knowledge of the subject matter, and writing skills, kept them from venturing onto the bulletin board:

> ...I have no idea how much the others already know...I don't know any of the other people....I didn't have anything to add to anything, or anything extraordinary to share about the course, so I wouldn't really add anything. (Christine, interview 1)

A concern about the value of their contributions for others in the course inhibited them from sharing their thoughts about course content. Michael, although self-efficacious with technology, particularly suffered a lack of self-efficacy in a course that focused on writing skills due to his learning disability:

> I would use [the bulletin board] if I had something valuable to contribute, but so far I haven't given anybody my thoughts.... When it comes to this course, English, I have no valuable opinion. (Michael, interview 1)

Some learners, like Sean, seemed less confident about publicly sharing their thoughts in writing:

> ...writing is such a subjective skill and also guarded with some privacy. (Sean, interview 1)

Adrian revealed the care with which she wrote comments that were going to be posted on the bulletin board:

> ...when you have to write something, you have to make sure your thoughts are correct and that you are putting it down in the correct way. (Adrian, interview 1)

Non-learner participants sensed that learners may have a lack of confidence in their writing abilities and their knowledge, and that this may have inhibited them from

using the bulletin board as a venue for collaboration. Two learners believed that their supervisors thought their skills were lacking because they had been told to take the course. The intuitions of the instructor and course administrator in this regard were correct; however, they did not have a strategy to address this problem.

> It could be a question of confidence of putting something up there. Or, maybe not being comfortable enough with the subject matter to actually ask questions. (Julie, interview 2)

> And I think that's part of it as well – I'll look stupid if I put something up there that I should know the answer to.... (Angela, interview 2)

For some of the foreign-based participants, the instructor and course administrators perceived that a lack of fluency in the English language may have created a barrier to those learners' participation on the bulletin board. They thought that these learners may feel that contributing to the bulletin board would make them vulnerable to criticism or ridicule:

> I also think that for some of them, especially where English is not their first language, some of them are a little insecure. (Angela, interview 1)

Learners may have lacked confidence in their English writing skills more than in their verbal skills, and refrained from posting text to the bulletin board for that reason.

The course in this study was not a language course, but it did strive to teach learners particular applications and nuances of English within a business context. When

the non-native speakers of English were queried about whether they were hesitant to post commentary because of their English language skills, they were adamant that it was not due to anxiety about their ability, or out of fear of having their contributions criticized. On the contrary, they appreciated the opportunity of being able to "see" written commentary on the bulletin board. They felt that it gave them the opportunity to see language used in a less artifical or formal way.

Lack of self-efficacy with subject matter created a barrier to learners' perceived ability or willingness to collaborate on the bulletin board, but it did not necessarily create a barrier to their perception of their ability to construct knowledge on their own. This meant that their construction of knowledge about the subject was limited to the completion of assignments. Learners desired interaction and collaboration with other course participants in order to enhance their learning, but they were reticent to do so because they were unsure of themselves in the presence of others who were unknown to them. This resulted in minimal interaction between participants.

> I am reluctant to contact them during the course because
> I am not sure if they are busy and I may not [get] a response
> Because they don't know me. (Fiona, interview 1)

> ...nobody wants to be the first to do it—again, all stress how
> important this is - but few have attempted it....
> (Researcher, reflection, mid-July)

The self-efficacy of learners in this study is related to their dependence on the instructor. Some learners who wanted to discuss course content with others limited their

interaction to e-mailing the instructor because they were unsure of their abilities with the subject matter:

> I prefer to send e-mail directly to the course instructor as my concerns may not interest the others. The instructor can choose to post my questions on the bulletin board to share with others if, in her perspective, the topic's worth discussion. (Lynn, interview 2)

In this case, the learner depended upon the instructor to determine if her comments would be of collective interest and worthwhile for a public viewing on the bulletin board.

Feeling isolated in WBL

Two barrier factors emerged from learners' sense of isolation in WBL. The first was simply an acute feeling of being alone, and the other was that the act of using the bulletin board seemed to heighten this awareness of isolation.

All of the learner participants described feeling isolated at times, some to a greater degree than others: "It also becomes much more of a solitary experience and it also requires a lot more discipline than actually going to a campus, sitting in a classroom and learning" (Sean, interview 1). Seven of the eight learners also stated that the opportunity to collaborate with others in the course would make them feel like they were part of a group and able to share expertise. Despite the availability of the bulletin board for this purpose, minimal collaboration took place. When probed about reasons for not using the bulletin board, six of the learners said they didn't use it because they "don't know who the other learners in the course are", and some stated that they were hesitant to

"be the first one", and that this made them feel "like I am alone". For others, posting their thoughts on the bulletin board seemed too formal and time-consuming:

> The disadvantage is that I don't have an instructor right in front of me to answer my questions. I also don't have any classmates to whom we can talk and share ideas. Although the bulletin board in this course serves this purpose, participants in this course seldom use the bulletin board and it looks like a more formal way of sharing ideas and course material.... (Fiona, interview 1)

Contributing to the bulletin board seemed to heighten their sense of being alone and isolated from other learners in the course who they hadn't met.

> The problem is that entering the discussion forum requires much more effort than, for instance, just discussing course content on the way to a coffee break. (Sean, interview 1)

I sensed that because they hadn't been formally introduced to each other at the outset of the course, they felt awkward and reticent about posting messages to each other on the bulletin board. The fact that it takes time and effort to post messages on the bulletin board also seems to emphasize the rigidity of communicating online and, hence, contribute to feelings of isolation.

Sense of isolation as a barrier

Learners in the study definitely felt isolated in this learning environment. Not only did they feel isolated from the instructor and other learners in the course, they also

felt isolated from their colleagues in their physical locations. They perceived they were the only ones at their locations taking a course through the departmental learning Website. When asked if an initial, introductory online meeting with all course participants would be of interest, seven out of the eight learners in the study were in favour:

> I think a meeting of the class with the instructor...could be useful. (Oliver, interview 3)

When I probed learners for reasons for wanting at least one online meeting with all course participants, they perceived this kind of meeting as a motivator for sharing knowledge and questions under the guidance of the instructor:

> Without face to face or online contact, it reduces the interest of asking questions. (Fiona, interview 1)

The lack of visual contact made others yearn for a traditional classroom:

> ...there are other times when I want to be in a classroom, and have someone in front, and not just for the questioning part, but more for the response too....you really see what the new thoughts are. (Adrian, interview 1)

Learners' perception that others may not respond because they had never met each other, created a barrier to the kind of interaction which could have enhanced their ability to construct knowledge in this environment.

> I wouldn't e-mail any of the other students because I didn't know any of them. (Christine, interview 2)

In some cases, there were other learners taking the course who were also in the same physical location, but unknown to each other as fellow Website learners. Unfortunately, there was no effort made to effect an introduction of any kind between the course participants.

Feelings of being in transition to WBL

Two factors derived from WBL participants feelings of being in a state of transition. The first was their transition from novice to adept users of technology; some were further along than others. The second was their transition to a new learning and teaching environment.

The non-learner and learner participants generally described the WBL environment as a new way of learning and "something we'll have to get used to". Participation in the bulletin board in order to interact with fellow learners was described as a new concept by all participants in the study, and all of them said they would like to interact with each other within this venue. All participants stated that they thought the bulletin board was "valuable" and "an ideal place to exchange ideas about what we are learning", and that as people got used to the Website environment, they would use tools like the bulletin board more frequently in order to communicate and collaborate with others in the course:

> ...I still think taking course through the Internet is a way
> of learning in the new age....(Fiona, interview 1)

> I only started communicating with my instructor...and posted questions on the bulletin board when I was working on my assignments. I think the reason is...I am not used to asking questions this way. I remember I did not post any questions on the bulletin board during my first course. (Fiona, interview 2)

> The comfort level is getting more when I progressed through the course because I used the bulletin board more often and I found out that there was feedback. (Fiona, interview 3)

From the instructor's perspective, the bulletin board is a new tool for learners and instructors to explore and to use for interaction:

> I guess the bulletin board is one way of doing that. You know when you think about it, because it is such a young area, there are lots of possibilities to try out. (Angela, interview 1)

Most participants in the study described themselves as in transition from one type of classroom to another. As they became more self-efficacious in WBL, participants also became more independent and self-motivated to engage in activities and use the tools available there to help them construct knowledge.

Because the bulletin board was not extensively used for its expressed purpose during this course, I continued to ask probing questions to find out why learners were not using it as much as it was intended, given that they stated, with the exception of one

learner, that interaction among themselves was an important component of the course. The responses usually included the sentiment that they were "getting used to the idea" and that eventually they would use all of the tools available to them to support their learning.

The theme of transition in the data was consistent throughout the study, and was a barrier to collaboration, despite the fact that most participants said they liked this method of learning. Not only did learners have to learn course content, they also had to learn to become adept at using the tools of WBL:

> ...I think it is a good way of learning. It is, however, a different learning experience, and since it is my... second stab at it, it requires both learning a new way of learning and the actual contents of the course itself. (Lynn, interview 1)

Learners keenly felt the difference between asking a question verbally and asking it in writing:

> I think the reason [for not using the bulletin board] is because this is my second time to learn through the Website and I am not used to asking questions this way. (Fiona, interview 1)

However, as learners progressed through the course and also tried the Website tools, some became increasingly self-confident in the environment and accepting of it, and, in that sense, transition facilitated collaboration:

> As the technology advances, I think Website learning will be introduced to more areas and the drawback of not having a face-to-face communication with the instructor, and the other disadvantage of not knowing other learners, will be eliminated. (Fiona, interview 2)

> By the time the second {course} came around, my comfort level was good, so probably I was getting more used to it. (Christine, interview 2)

One participant experienced what I categorized as "reverse transition" when he began to feel restricted by the Website tools. He was comfortable in a Web-based learning environment immediately; however, as he progressed through the course and used the Website tools, he became increasingly frustrated by his experience:

> ...initially I felt very much at ease with the transformation to the virtual classroom – my technological skills are very good...however, as time went by I became more and more aware of the limitations that I felt inherent in the Web-based environment. (Sean, interview 3)

Sean possessed high-level technological skills and perceived the course Website tools to be poorly designed and difficult to use. He felt the tools caused him more time-consuming effort than was necessary to complete and send assignments, or post comments to the bulletin board. This perception was made more acute by his ability to envision a more learner-friendly Website.

When I asked the instructor and course administration participants about the idea of transition, they said that they felt that they were in a transitional stage between teaching in the classroom and through traditional distance learning methods, to teaching in Web-based learning venues:

> ...we're now in transition between computer-based and paper-based....
> The medium works well for some and it doesn't work well for others.
> It's a young area, there are things that can be done to improve it.
> (Bill, interview 2)

> While going through the transition, there are people, me
> included, with one foot in one camp and one in another.
> I'm going through the transition and I'm part of it.
> (Angela, interview 2)

In any case, all participants felt that learning through the Web was inevitable, whether or not it was their preferred venue for taking courses. Most reported that no matter what their personal preference, they felt it was necessary to 'get used' to WBL as a classroom venue:

> I think that personally I prefer the classroom, but this seems
> to be the way things are going. So, I might as well get used
> to it.... (Christine, interview 2)

There was a certain resignation in tone when participants discussed their transition to WBL. While they recognized the benefits, they also felt a sense of loss related to change. Because they felt that change was out of their control, they believed it was necessary to

change their ways of thinking and learning. They continued to actively adapt to change because all learner participants in this study planned to engage in continuous, life-long learning. Despite its difficulties, most learners in this study intended to take more courses through WBL.

Transition as both facilitator and barrier to collaboration

When participants were asked if they could compare the transition to a Web-based learning environment to another transitional experience they had had, all compared it to learning to communicate using e-mail. The transitional aspect of moving from traditional distance learning methods to Web-based venues creates a barrier to learners' perception of their ability to function in this environment. However, as their ability improves and as their self-efficacy increases, and as they become more confident of their abilities in this environment, learners' positive perception of their ability to construct knowledge also increases. This also extended to their perception of using the Website tools at their disposal to learn, for example, the bulletin board:

> This time, as compared to the last two courses I took on the [departmental learning Website], both the instructor and students make more use of the board. (Lynn, interview 2)

From the perspectives of the instructor and course administration, they, like the learners, are in transition between traditional delivery methods and Web-based course delivery.

> ...I quite enjoyed the process....I developed the [course] for distance learning, and then changed that for the virtual

> school. So, it was a process that I was going through....I guess you lose a bit of your control. You almost become the passive—I don't mean passive—you're the receiver as opposed to being the director, and that was the difference for me. (Angela, interview 1)

The instructor was very aware of her transition from classroom teacher to online instructor and summed it up by saying, "...it was my way or the highway, and I've been gradually giving up control along the way" (Angela, interview one). She also perceived that giving up part of that control meant that learners were required to take more responsibility for their learning, and this would influence their ability to construct knowledge. At first, for some learners, it may be a barrier to learning; however, she felt strongly that as learners got used to constructing their own learning, with guidance from an instructor, they improved their learning skills as a result.

Christine echoed the instructor's perception that making the transition to Web-based learning may improve learning skills and also improve retention of knowledge. She perceived that learning in this environment facilitated her confidence and independence in other aspects of her work and life because of the skills she developed in order to construct knowledge. Christine felt she had developed analytical skills from looking at sites linked to the course, and having to discern which sites were useful and appropriate for the learning objectives of the course. She also found that she was taking the initiative in non-course work projects, where she formerly would have waited for direction from a supervisor. Christine found that being responsible for her learning in WBL gave her the confidence to take on more responsibility in her job-related activities.

Additionally, she felt that because she would implement what she learned immediately into her daily work activities, upon logging-out of the course site, her knowledge retention was higher.

The experience of transition for all course participants affected their ability to function and to construct knowledge in WBL. As learners become more experienced with learning through WBL and using the Website tools and venues, they also evolved their transition from traditional and other distance learning venues.

Silence on the bulletin board

The theme of silence was the key to revealing the barriers to collaboration in this course. The lack of written interaction on the bulletin board mirrored learners' perceptions, and was a catalyst for discovering the factors that prevented its being used by the learners in this course.

At first, I was ecstatic to see so much commentary on the bulletin board. A firm believer in the value of collaborative discussion in learning, I had hoped to reveal more factors that facilitated collaboration than prevented it. I was dismayed and somewhat discouraged by the fact that commentary dwindled and ceased midway through the course. I had hoped that there would be lively discussion on the bulletin board. I had expected the instructor would be posting comments there every day in order to encourage discussion among course participants. I had expected to observe learners in collaboration with each other.

Instead, about midway through the course, I faced the visual silence of a blank and inactive bulletin board. My own expectations had been dashed, and I was disappointed to say the least.

> Things are very quiet on the bulletin board. There are no new postings since last week. I know people are working on their assignments, and they are telling me they would like to talk to each other in their reflections. But nobody is doing it - not even the instructor. (Researcher, reflection, third week of August)

After several days of anguish and sleepless nights, I suddenly realized that inherent in the silence of the bulletin board were factors that prevented learners from getting together for collaborative discussion. I recognized that these factors were very important findings for the pedagogical development of WBL, and I was reinspired by the data, "This silence makes absolute sense to me from what I'm seeing in the data!" (Researcher, reflection, first week of September). The journey to that silence is described in this section.

Minimal interaction

Interaction on the learning Website bulletin board for this course looked promising at the beginning of the course, but became sporadic and sparse from mid-course to the end. Much of the interaction consisted of individual learners seeking clarification from the instructor, with responses from the instructor to the questions. I noticed, occasionally, other learners would comment on the questions or answers:

> I'm pleased and excited to see a lot of activity on the bulletin board. It seems to be used mainly as a venue for seeking clarification on course activities, but there was one more provocative message in the sense of someone wanting to get some dialogue going on the bulletin board. (Researcher, reflection, mid-August)

There were few instances of attempted collaboration. At one point, Michael posted both a question and some related, thoughtful commentary: it was an attempt to engage others in a dialogue about a particular application of their learning. It demonstrated criteria found in both the "Soliciting" and "Reacting" categories of pedagogical moves. Some learners were thrilled with his contribution to the bulletin board:

> ...it made me think about this in a new way.
> (Maria, reflection, mid-August)

> A course-mate...has concerns about how to present figures and numbers. Since I do not do any technical writing, I never think of how I should present numbers. After reviewing the instructor's comments, I have a clearer picture....Something that I think is simple and never pay attention to is actually worth discussing. (Lynn, reflection, mid-August)

The fact that the comments and questions posed by learners elicited this type of response from other learners in the course led me to believe that collaboration, as opposed to a simple exchange of information, had taken place.

Toward the end of the study, when I, again, asked learners about the idea of collaborating with other course participants, they said they were enthusiastic about the idea because of the interaction they had seen on the bulletin board. However, much to my frustration, there were few attempts to interact in a collaborative way, and postings to the bulletin board were mainly for information from learners, the instructor and course administration.

Dwindling to silence

Despite the initial flurry of comments posted to the bulletin board, almost all the learner interaction on the bulletin board was about questions and answers that had been posted, and some notes about technical difficulties to which learners responded. On one occasion the instructor attempted to inspire a collaborative discussion about one of the course assignments, but to no avail. Given definitions of collaborative interaction (Bates, 1995; Harasim, et. al., 1995), there was one instance of attempted collaboration by one of the learners, but it elicited only one response on the bulletin board. Instead, learners in this study commented on bulletin board activity in their reflections to me through e-mail. There was evidence in their reflections that the bulletin board comment had inspired the construction of new knowledge as learners thought about the implications of what had been stated by another learner. Unfortunately, their new knowledge was not shared with other course participants through the bulletin board.

The silence that commenced on the bulletin board about midway through the course persevered to the end. This was a great disappointment to the instructor and the course administrator and myself; we had been ecstatic about the initial activity there. I

realized that the silence spoke volumes, and, as I gathered it, I continued to analyse the data to seek out the factors that revealed barriers to collaboration.

By the end of the course, and the study, there was no interaction of any kind on the bulletin board. Some learners did not post any comments to the bulletin board throughout the course, although all learners said they looked at the bulletin board either daily or weekly to see what others had written. Reasons for the silence are found in the barriers to collaboration, and, as discussed in the next chapter, are critical findings for improving WBL.

Summary of the Findings

A dominant and surprising theme arising from the data was that learners were unclear about course expectations, particularly the expectations related to bulletin board activity. All of the learner participants were aware of the bulletin board, but none of them were entirely sure what was expected of them in this venue. Some learners thought it was there for use only as a notice board, or to communicate a technical problem. Because they did not realized that the bulletin board was there for them to interact and collaborate with each other, most did not use it for that purpose.

A lack of detail in course instructions on the Website, and the absence of any planned activities for interactive discussion on the bulletin board were intertwined themes revealing factors that created significant barriers to collaboration among learners in this course.

Insufficient management and peer support impacted the learners' ability to do course activities through workplace interruption. A lack of formal acknowledgement for

successfully completed courses contributed to learners' decreased motivation to do perceived extra course activities.

Another related theme was that most learners in the course were not following the instructions provided on the course Website. The data revealed that most learners did not read through the instructions and, therefore, did not follow the directions and guidance provided there. This affected their assignments and their activity on the bulletin board, much to the frustration of the instructor and course administrators.

While time and convenience were positive forces toward facilitating interaction between course participants, time constraints and convenience as a deterrent were intertwined themes in posing a barrier to collaboration among learners. Closely associated with the major barrier themes were lack of learner self-efficacy in WBL, learner dependence on e-mail access to the instructor, lack of learner and instructor motivation, a sense of isolation, and learner and instructor transition.

A perceived lack of time to do coursework caused some learners in the study to limit their course activities to the submission of assignments. While these learners checked the bulletin board to see what others were posting there, they seldom, if ever, contributed to this activity themselves because they felt constrained by time. Linked with the perception that they did not have time for interaction was the convenience of interacting and collaborating directly with the instructor through e-mail. The ability to have the undivided attention of a subject matter expert was appealing for all learner participants in the course. Some limited their interaction to collaboration with the instructor.

Technical failure, both real and perceived, deterred learners from using the bulletin board. The data revealed that learners' perception of Website tool failure and the

actual failure of these tools discouraged learners from repeated attempts to use them. Time constraints heightened learners' reluctance to persevere in their attempts to collaborate on the bulletin board.

Learner self-efficacy led to varying degrees of dependence on the instructor and course administrators for both subject matter guidance and for using the course Website tools. A lack of self-confidence in these areas prevented some learners in the course from attempting collaboration with their peers.

Lack of motivation was an issue for both learners and non-learners in the course and trancends other factors that prevented collaboration in this course. Data revealed that, in some cases, where time constraints were cited as the reason for non-collaboration on the bulletin board, a lack of motivation to collaborate was the underlying barrier. The instructor perceived that a lack of motivation may have prevented some learners from collaborating because participation on the bulletin board was not a mandatory requirement for successful completion of the course. As well, learners who contributed more to the bulletin board described themselves as motivated to collaborate and to find the time for course activities. Two learners identified themselves as unmotivated because they were required to take the course by their supervisors; however, one of these learners did attempt to collaborate on the bulletin board despite this. The data revealed a lack of learner motivation to collaborate on the bulletin board because it was not a mandatory activity, and it also revealed a lack of non-learner motivation to encourage and facilitate collaboration on the bulletin board.

The themes of isolation and transition emerged from the data as factors that created barriers to collaboration in this course. Data showed that some learners felt

isolated and alone, and that they were getting used to learning in a new kind of environment. Seven learners wanted the kind of interaction with other course participants that would result in collaboration and knowledge building; however, there was minimal effort to interact because they were isolated from other learners and didn't know them. In some cases, using the bulletin board tool made learners feel keenly aware of being alone. All learners in the course, as well as the non-learners, described themselves as changing and getting used to the WBL environment.

Instead of revealing the facilitators to collaboration in WBL, the bulletin board in this course served to mirror the factors that had rendered it silent in this course. The barriers to collaboration in this course were both surprising and significant, and provided great insight into how not to facilitate collaboration among learners in WBL. The discussion in Chapter Five addresses recent research literature that has speculated on or identified some of these barriers; however, they have been further revealed to an unprecedented degree in this case study.

Chapter 5:

A Discussion: Answering the Research Questions

Introduction

In this chapter, the findings of the study are discussed within the context of current WBL literature. The discussion is organized under the research questions that guided the study. Illuminations and new understandings are revealed to show how the study has extended WBL research.

Recommendations for improving WBL are provided at the end of Chapter Five. Proposed WBL components and processes necessary for achieving collaborative discussion among course participants are based on the findings of this case study and the new understandings derived from them.

Overview of the Study

This constructivist, qualitative, single case study provides an in-depth focus and illumination of the factors that prevented or enabled collaboration among participants in a WBL course, and how they affected learning in the course. The case consisted of a WBL course on business writing, and its collective participants, including the learners, the instructor, the course administrators, and myself as researcher. Qualitative methodology for the study included in-depth interviews with each participant, participant reflections and participant observation.

Research question one asked for the identification and description of factors that facilitated collaboration in WBL. The findings constructed in response to this question

illuminated the factors that could have facilitated collaboration in this case, had the factors that created barriers been less formidable than they were. Some findings echoed existing WBL research and provided further in-depth description of phenomena, while other findings provided new insights.

Research question two sought to discover and describe the factors that created barriers to collaboration in WBL. The findings in answer to this question comprised the major contributions of the study. Some replicated the findings of other WBL studies, but provided a more focused description of them. Other findings were new and extended WBL research.

Research question three focussed on descriptions of how the facilitators and barriers affected learners' perceived ability to construct knowledge in WBL. The findings emanating from this question revealed an alignment with existing research, albeit with new dimensions, and some new insights. These were the catalysts for the recommendations and proposed WBL course components and processes to facilitate collaboration, and for implications and conclusions discussed in chapter six.

Research question four aimed at determining the existence of collaboration in the course. The findings in response to it centred on the evidence that learners were not collaborating, and shed light on similar phenomena that have surfaced in recent WBL studies on collaboration. New understandings of these phenomena have also been achieved in this study.

A Discussion of the findings and the literature

The discussion of the findings within the context of current WBL research serves to reveal how this study has illuminated the findings of previous WBL studies, and extended WBL literature. The discussion ensues under the four research questions, and the factors that emerged from the data in answer to them. It is important to acknowledge that there was generally a combination of factors that affected collaboration among learners in this case, and this is discussed where appropriate. As was acutely evident in the findings, there was limited interaction among learners and an instance of attempted collaboration. Hence, the discussion primarily centres on the barriers to collaboration and its implications for learners.

Research Question One:
What facilitates collaboration in Web-based Learning?

The data did reveal factors that attracted learners to the WBL environment, and would be necessary for their participation in WBL learning activities. The factors in answer to research question one, as shown in Figure 2, are time, convenience, easy to use Website tools, and learners' degree of transition from a traditional classroom setting to WBL.

- Uninterrupted time for course assignments and activities and convenience of "anytime" access to WBL site
- Perceived ease-of-use of WBL Website tools
- Degree of transition to WBL environment

Figure 2. Factors that help to facilitate learner collaboration in WBL.

WBL as convenient for learners when they have enough time

Time and convenience were identified by all participants as important for WBL in general, and critical for collaboration to occur in this environment. All twelve participants in the study said that they needed sufficient, uninterrupted time to do their coursework and to interact with others in their course. Participants also stated that in addition to having time, it must be convenient for them to access the bulletin board and to post messages there. WBL provides learners with the convenience and flexibility of taking courses at times that suit their personal schedules (Gabriel, 1999; Garmer & Firestone, 1996; Shimabukuro, 1995; Santoro, 1995; Ellsworth, 1995; Bates, 1995). This is well documented in the literature. Most learners in this study enrolled in a WBL course, in part, for these reasons. They also reported that they planned to continue to pursue courses through WBL because of its flexibility of time and place.

As a facilitator to learning, the learner participants in the course perceived that the convenience of accessibility, regardless of time, made it easier for them to do their coursework because there was no set time when they had to be "in class" or do their assignments. It is clear that learners in the study perceived WBL as a convenient and flexible way to take courses. Even the "prisoner" learners in this course were less annoyed about having to take the course because of its convenient and accessible nature. Learners were able to choose the time convenient for them to access the Website and do the required activities. WBL literature to date shows that most learners perceive this new learning venue as advantageous in terms of time and convenience, and often prefer it to more traditional and distance venues for these reasons (Muirhead, 2001; Janes, 2000; Kearsley, 2000; Daugherty & Funke, 1998).

User-friendly course Website tools facilitate learning and interaction for learners in transition

Closely related to time and convenience is perceived ease-of-use of Website tools. When Website tools were accessed easily and quickly, and were simple to use, participants were willing to use the tools that enabled them to interact with each other. Learners also felt that, as they got used to the WBL environment, they would be more willing to use the Website tools provided in order to collaborate with other course participants.

Most participants, learners and non-learners, described themselves as being in transition between learning in traditional classroom and distance venues, and learning through WBL. Some learners in the study reported becoming more independent and motivated as they gained experience in WBL. This seems understandable as most of us

make what we call successful transitions as we become more confident, and this is also documented in educational theory and research (Kang, 2001; Tapscott, Lowry & Ticoll, 1998; Brown, 1998; Bandura, 1995; Yakimovicz & Murphy, 1995; Logan & Ferraro, 1978). For example, Silberger (1995) found that as learners developed confidence with Web-based environments and tools, they also demonstrated increased confidence in other non-computer based activities. This was true of some learners in this study who described themselves as becoming more confident and independent in other areas of their lives as a result of their increased confidence developed in WBL. Learners in another recent study have also reported an increase in general self-confidence as a result of experience in a WBL course (Gabriel & MacDonald, in press).

Despite what the data revealed about factors that could facilitate collaboration in WBL, there was little interaction among learners on the bulletin board, and only one instance of attempted collaboration. For this reason, the discussion will focus on the barriers to collaboration in WBL, and how those barriers affected learners' perceptions about their ability to construct knowledge in this environment. By explicating the barriers, this study provides insight into what is necessary for facilitating collaboration in WBL, and, in this sense, also provides an answer to research question one.

Research Question 2:

What are the barriers to collaboration in Web-based Learning?

The factors that *could* have facilitated collaboration among learners, were also the harbingers of barriers to collaboration. The major findings of the study were contained in

the data gathered in answer to research question two, and revealed the barriers to collaboration in this case study as shown in Figure 3.

- Ambiguity of course expectations for collaborative activity using bulletin board
- Lack of course organization and support for learners
- Time constraints
- Voluntary learner collaboration
- Lack of learner self efficacy, self-confidence and independence
- Lack of learner and instructor motivation to collaborate
- Perceived sense of isolation and lack of "ice breaker" meeting for course participants
- Convenience of e-mail interaction with instructor
- Perceived or real technical difficulty
- Degree of learner and instructor transition to WBL learning environment
- Ignoring instructions and directions
- Lack of tangible recognition for course completion
- Poor design of Website tools

Figure 3. Factors that created barriers to collaboration in WBL

The importance of clear expectations, detailed instructions and guidance in WBL

Learners who are used to a traditional, face-to-face classroom may feel lost and unsure of themselves without guidance in a new learning environment like WBL. Perkins (1991) noted that in any learning venue it is important to be clear about course

expectations and process, and it is particularly critical in a constructivist model which may be new to the learners involved:

> Learners are asked to compare and contrast an entrenched but barely articulated model with a newly sketched model (by themselves or the teacher) with which they have very little working familiarity. No wonder learners often have a hard time with this path (p. 19).

In this case learners knew they would be constructing their own learning, but there was no discussion about what this process entailed.

In any course, expectations must be made clear. WBL scholars have noted that this is especially important for learners in an environment where they are physically isolated and invisible to each other (Janes, 2000; Benigno & Trentin, 2000; Kearsley, 2000; Harasim, et. al., 1995). This study supports these findings and reveals learners' perceptions of course requirements when they are unsure about what is expected. If participants do not understand what collaborative discussion is or why it is important to their learning of course content, then they may perceive it to be, as they did in this case, simply an extra and time consuming activity. This directly affects their motivation and ability to co-construct knowledge, and limits their ability to construct knowledge on their own.

Knowlton (2000) says clarity of expectations is particularly true of online courses because participants are usually expected to be interdependent in this venue. Clear expectations should be outlined within the delivery of any course regardless of venue, but

it does seem to be sometimes overlooked in WBL. Perhaps it is assumed learners will welcome the opportunity to participate in online discussion, and clarity of expectations for this activity are deemed unnecessary. The reality in this case was that learners were not clear about what they should or could contribute to the bulletin board and this made them uneasy about doing it. Hara and Kling (2000) found that without knowing what is expected of them, or knowing the criteria for meeting expectations, learners experience confusion and anxiety. Benigno and Trentin (2000) further noted that if a portion of learner evaluation in WBL is based on their participation in a discussion forum, it is imperative that expectations be made clear about that participation. Learners in the present study seemed very confused about the purpose of the bulletin board in their course. Unclear expectations, together with the voluntary nature of participation on the bulletin board, created perhaps one of the most serious barriers to collaboration in this course.

Consistent and continuous guidance from an instructor or subject matter expert is also critical to facilitate and support collaborative discussion (Kearsley, 2000; Alexander, 2000; Dereshiwsky & Moan, 2000; Driscoll, 1998; Harasim, et al., 1995). In the absence of persistent instructor presence on venues like the bulletin board, it quickly declines into a notice board for technical problems, or questions and answers. Harasim, et al. (1995) suggest that instructors need to be role models in actively demonstrating participation to learners. Where there is an abundance of interaction among participants, it is equally important that there is consistent and continuous guidance, as discussions can quickly go beyond knowledge co-construction to socializing (Sloffer, et. al., 1999). This did not occur in this study; however, whether there is little or abundant discussion among course

participants, guidance is needed for knowledge construction to evolve from collaborative discussion (Dereshiwsky & Moan, 2000; Janes, 2000). As well, perhaps the bulletin board should have been named differently. The name itself denotes images of notice boards rather than somewhere to go for a discussion. It may be prudent to rename the venue as a discussion room.

Kearsley (2000) says the key to effective learning in WBL, as it is in other educational venues, is to ensure learners are actively engaged. According to this author, learners should be "...designing, planning, problem solving, evaluating, making decisions, or involved in discussions" (Kearsley, 2000, p. 67). He further notes that "...all learning ought to have three major characteristics: collaboration, problem-based, and authenticity" (p.68). The elements necessary to invoke engagement were present in the present study, in the sense that the subject matter and community of learners could have engaged in their learning in these ways. However, specific engagement strategies, such as those suggested by some theorists (Poole, 2000; Driscoll, 1998; Honebein, 1996), were not part of course delivery in this case. Largely because of this there was no collaboration among learners.

Learners in the present study also perceived little workplace support from either peers or managers, despite their supervisors' knowledge of their learning endeavours. Lewe (1997) notes that "Computerization of the workplace has had a massive effect both on how employees learn and how they are to accomplish their job tasks" (p.408). When the workplace is the context for the classroom, most learners have to cope with using a new medium, and with managing their work and professional relationships at the same

time (Breithaupt, et. al., 2002). This can create a barrier to achieving optimum learning, as it did for most learners in the present study.

Most learners in this course were subject to continuous interruption by the demands of their jobs. They were also subject to social or work-related visits from their colleagues. Fuhrer (1993) reminds us that, for many adult learners, "Learning takes place in real-life settings, under real performance requirements on actual individuals, and is vulnerable therefore to social influences that may arise at any time" (p. 179). This was certainly true for learners in this study who accessed their WBL course from their workplace, and experienced little or no support from their peers and managers.

Bierema (1996) states that adult learners need to be encouraged and supported in their efforts in the workplace. He emphasizes that organizations need to acknowledge employees who are lifelong learners as valuable to the workplace. They must be given time and space to engage in coursework without the threat of criticism or interruption. "The ultimate challenge in organizations is to harness adult learners' propensity to be self-directed learners and not create barriers that prevent or discourage it" (Bierema, 1996, p. 25). Although course administrators suspected that management was not overtly supportive of WBL endeavours, they did little to address it. In fact, they may have inadvertently trivialized learners' efforts by offering mugs and "do-not-disturb" signs as support for workplace learning activities.

Convenience of learner - instructor interaction as a negative factor for collaboration

The findings on convenience in this study revealed that easy access to one-on-one collaboration with the instructor also contributed to a lack of interaction via a computer

conferencing tool; in this case, the bulletin board. Implied in this was the instructor's unintentional creation of a barrier to collaboration among learners by her collaboration with them on an individual basis. Those who found it more convenient to communicate directly with the instructor, to the exclusion of communicating through the bulletin board, also saw this ease-of-access to expertise as an advantage over taking a traditionally delivered classroom-based or distance learning course. It seemed more advantageous than attempting to collaborate with all the course participants.

Additional instruction and coaching was provided to learners through personal e-mail interaction with the instructor. The instructor did attempt to redirect them to the bulletin board, but to no avail. The learners who demonstrated dependence were less adept at constructing their own learning and relied on a more traditional instructional approach. Often questions or issues raised in their e-mails were fully covered in the course directions and guidance provided on the Website. It became clear that some of the learners in the course were simply not doing the required reading for the course. All of these factors were a great source of frustration for the instructor. A few recent studies have reported that learners do not necessarily read through direction and guidance provided on WBL sites (Muirhead, 2001; Janes, 2000). The researchers concluded that learners in their studies also preferred direct access to their instructor or subject matter expert to the near exclusion of interaction with each other. Card and Horton (2000) found that learners' perceived ability to construct knowledge in WBL was enhanced by their access to an instructor or subject matter expert. They also found that learners stated a preference for the kind of access they have to the instructor over the access they have in traditionally delivered distance courses. Learners' reasons for that preference have been

further revealed in this study. They align with previous findings, and also show that, in this case, this preference created a barrier to collaboration among WBL learners in a course.

Convenient communication can have negative consequences for instructors as well. Some instructors find that WBL demands more of their time because of frequent e-mail contact by learners (Daeid, 2000; Sloffer, et. al., 1999). Sloffer, et al. found that the instructors in their study were so overwhelmed by answering e-mails from their students that it detracted from their guidance of student discussion on the course's asynchronous conferencing site. The instructor in the present study found that there was more work initially in adapting the course for delivery through WBL; however, Angela found it less time-consuming after that because she was not "teaching", but rather marking assignments and providing comments through e-mail. In fact, she tended to limit her efforts to her e-mail responses to learners, much to the detriment of bulletin board interaction. When Angela found one or two attempts were unsuccessful in provoking discussion on the bulletin board, she quit and focused her efforts on individual e-mail interaction with learners.

WBL studies have documented that learners employ the Website tools that allow them to have convenient and direct communication with an instructor (Sloffer, et. al., 1999; Newman, et. al., 1996). The ease with which learners in this study accessed and, at times, collaborated with the instructor is something they appreciated and utilized. She was able to respond to e-mails she received from learners in a timely fashion. She also found it convenient to be able to discuss the course with learners through e-mail, although she would have preferred they use the bulletin board as requested at the outset

of the course. In the end, the convenience of direct, e-mail access to the instructor deterred interaction among learners on the bulletin board.

WBL researchers are beginning to suspect that planned online collaborative activity may be negatively affected by individual learner-instructor interaction (Muirhead, 2001). This study supports this suspicion and extends the literature by revealing that it was a barrier to collaboration among all course participants. The instructor in the course felt increasingly frustrated and somewhat helpless when, despite her continuous effort to redirect e-mailing learners to the bulletin board for questions and comments, learners seemed to ignore her direction and continued to send e-mails to her. Further research into the convenience of e-mail access to an instructor and the extent to which it is a barrier to collaboration could comprise a study in its own right.

Ignoring instructions and directions on the course site

Even if learners have read instructions provided on a course Website, they may not follow the directions given (Muirhead, 2001; Land & Hannafin, 1997). Whether this is contrary to the assumption that assumes learners are independent, responsible and self-motivated because they choose to learn in WBL is yet to be determined. This study reveals that not all WBL participants portray those qualities when it comes to their learning activities - at least, not yet (Johnson, 2001). This may mean all are less independent, self-motivated and responsible, and actually require more structure within the WBL environment.

This study also reveals ways in which learners' who neglected to follow directions experienced difficulty or failure when they attempted to post comments to the bulletin

board. When learners' perceived a difficulty or an inability to use the bulletin board for this purpose, they gave up and, in most cases, did not try again. This created a tangible barrier to collaborative knowledge construction. Despite individual attention, some learners in the present study did not follow through with the appropriate activity. A similar learner response was documented in Land and Hannafin's study where learners who had in-person instruction and coaching on how to navigate a Website and its links to the Internet, went off into unknown Website links when they encountered a difficulty (Land & Hannafin, 1997). As a result, they usually got lost and had difficulty completing assignments.

Some learners in this study did not follow directions regarding course content or matters of WBL navigation, and this was evident in the nature of difficulties they encountered. Researchers have discovered that learners' decisions not to follow directions can influence their level of success in a WBL course (Land & Hannafin, 1997). Some learners in the present study had to redo assignments, and required much more individual help from the instructor with assignments. Based on the kind of assistance and correction they required, the instructor was convinced that they had not followed directions provided on the course site. This seemed to annoy the instructor, especially when there was little interaction among learners.

On the other side of this challenge, instructors and course administrators need to pay close attention to matters of length and wordiness in their provisions of course-related materials on a WBL site. Some learners in this course found the instructions too lengthy and unclear, and simply quit reading. It was particularly daunting for one learner who was dyslexic, and described the course directions as too wordy. Instructions need to

be detailed, yet simple and clear, and available to learners for reference through a simple "point and click". Instructors must also provide learners with direction and guidance throughout an online course (Muirhead, 2001; Janes, 2000). Recent WBL studies suggest instructors and designers need to consult learners about the appropriateness and usability of the course venues and their contents (Nielsen & Tahir, 2000). In general, the findings of this study showcase the reasons why these elements are important to WBL, and to ensure learners use Website venues provided in the way they were intended.

Lack of course certification as a de-motivator for collaboration

Learners in this case were indeed proud of their accomplishments, yet their pride seemed undermined by the fact that their learning efforts did not result in formal recognition. Most learners wanted a certificate or some kind of formal acknowledgment of their learning achievement. The lack of this affected learners' motivation to engage in non-mandatory course activities, as has been noted in other studies (Bauer & Anderson, 2000).

Certification by a qualified instructor or accredited educational institution is important to adult learners for reasons of self-esteem (Bostock, 1998; Gooler, 1990; Tough, 1990). In a perfect workplace learning world, all efforts of self-directed learners would be recognized by themselves and their organizations as "...remarkably capable, powerful, and successful at achieving serious learning objectives on their own" (Tough, 1990, p.294). Learners in this study wanted to be able to display certificates to show completion of courses. In addition to an acknowledgement of their achievments and

efforts to improve themselves, certificates may also help to encourage support from peers and management for learning in the workplace.

The time factor

Like the learners in other studies (Fabos & Young, 1999), learners in this study reported that interaction and collaborative discussion was a desirable and important activity, and that it would help them to better understand course content. Despite this, they viewed it as an "add-on" and, if they perceived that they didn't have time for it, it wouldn't happen. Canada (2000) notes a similar finding in a study where most learners completed only the mandatory assignments. In the present study, it meant that desires and good intentions went by the wayside as the course progressed and as learners perceived they did not have time for any course activities beyond completing assignments. WBL researchers have revealed that time is of primary consideration for learners (Mann, 2000; Gabriel, 1999; Fabos & Young, 1999; Ahola-Sidaway, et al., 1990).

Time as a concern for both instructors and learners in WBL was a major theme drawn from the findings of this study. Learners and instructors in other studies have either perceived or experienced that WBL takes more of their time than traditionally delivered classroom or distance courses (Gabriel & MacDonald, in press; Kang, 2001; Blanchfield, Patrick & Simpson, 2000; Mann, 2000). Becoming adept at using computers, the Internet and Website tools all contribute, to varying degrees, to the length of time it takes learners, and some instructors, to do course-related assignments and other

requirements. The findings of this study supports previous research that reveals time as a barrier to learning in WBL (Mann, 2000).

As a barrier to collaboration, time as a factor is beginning to be documented in the literature (Schrum & Benson, 2000). Recent research suggests that WBL designers and instructors are perceiving that time may be a barrier to collaborative discussion. In its revelation that engaging in bulletin board interaction is perceived by learners as taking too much time, the present study also illuminates reasons for learners "lurking" within the bulletin board, rather than participating in a discussion. Because some learners perceived they did not have time to interact, they would simply log on to the bulletin board and watch for a short time. Others would log on, check the comments, and leave immediately to do coursework. Some learners felt it took longer to write out their thoughts and contribute them to the bulletin board than it would if they were able to speak to other participants. This perception, which, in some cases became reality when they did contribute, prevented them from engaging in many interactions. Related to this, when awkward Website tools caused a barrier to interaction, learners eventually gave-up and stopped trying to log on to the site because they felt it was taking too much of their time. Learners may initially feel they do have time for interaction, and are willing to enter into collaborative discussion, and then either diminish their participation or give up altogether.

Poorly designed Website tools and technical failure as barriers to collaboration

The finding that awkward Website tools and technical failure become barriers to collaboration in this study supports WBL literature that revealed Website technology can

be a barrier to learning in this environment (Nielsen & Tahir, 2000; Hannigan & Browne, 2000; Harmon & Jones, 1999; Forman, 1994). Learners in this study were experienced in the use of computers, the Internet and using the departmental learning Website, albeit at varying levels of ability (Johnson, 2001; Ross, 1998). Despite this, some found the tools of their departmental learning Website course awkward and inefficient. The frustrations emanating from their bad experiences with the tools, and from intermittent technical failure, served to diminish and then completely squelch their participation in bulletin board activity. This may be explained by learners' descriptions of how their contributions, painstakingly written, disappeared in the attempt to post them on the bulletin board. They said it made them feel like they had wasted time, wasted effort, and had lost some really good thoughts. It also made them feel helpless and hopeless about using the Website tool. Exacerbating this circumstance was the fact that it seemed to take forever for the course administrators to fix the problem. Seal and Cann (2000) found evidence in their own and other studies that technical ability influenced contributions to WBL discussion forums. In a study that incorporated online learning, they found that when learners' technical ability was limited, combined with actual technical breakdown, as in this study, hesitation to use Website tools such as the bulletin board was increased. They further noted the importance of instructor guidance and attention to technical difficulties that learners may be having.

In reality, when learners in the study experienced technical failure, or difficulty using the Website tools, most became frustrated and this affected their use of the tools. This finding supports previous research where participants' perceptions of the efficacy of the tools directly affected their willingness and persistence in actually using them (Ross,

1998; Harmon & Jones, 1999; Hill, 1997; Anderson & Joerg, 1996; Land & Hannafin, 1997). Most learners in this study were initially willing to use the bulletin board for interaction with each other, in part because they perceived it would be easy and not take too much time. The learner participants also felt that they would persevere through perceived and real difficulties with the technology if computer conferencing had been mandatory for passing the course. In this case, contributing to the bulletin board was not a mandatory requirement for passing the course, and learners ceased trying when they experienced difficulties.

The latter finding notwithstanding, some recent WBL research shows that learners will persist through experiences of tool and technical failure if the learning activity is compulsory (Oliver & Omari, 2001; Blanchfield, et. al., 2000). Linked to this is a need for additional time for a collaboration activity. This is beginning to be documented in the literature, and often is directly related to the "slowness" of using the Website tools provided for interaction (Blanchfield, et. al., 2000; Mann, 2000). The findings of this study provide the further insight that if interaction on the bulletin board were a mandatory course requirement for completion and credit, learners would also find the time to contribute to collaborative discussion on the bulletin board.

The course administrator and the Website manager often did not know that most learners viewed the Website tools as difficult to use, and this created another barrier to collaboration. The administrator was aware of one or two instances, but generally dismissed these learners as whiners. They were also often unaware of technical failure, outside of server failure, until one or two weeks had passed. They seemed to rely on the learners to notify them of problems and, generally, learners did not do this immediately.

WBL researchers recommend that WBL sites be consistently monitored for these types of problems and that there be a resource available to learners if they run into either perceived or real difficulty with using Website tools (Oliver & Omari, 2001; Harmon & Jones, 1999). Morrison & Guenther (2000) emphasize the importance of well-designed Website pages and tools, particularly if learner interaction and dialogue is desired. This study reveals learners' thoughts and actions when they encountered problems related to the tools, or when there was technical failure (Land & Hannafin, 1997; Hill Duin & Hansen, 1994). More importantly, it shows the extent to which lack of administrative attention to these problems serves as a barrier to collaborative activity within WBL.

The influence of learner and instructor self-efficacy in WBL on collaboration

Learner self-efficacy is also directly linked to perceptions of whether or not WBL tools are easy or difficult to use, and in turn influences learners' decisions to persevere or give up (Land & Hannafin, 1997). These perceptions are often grounded in the level of past experience using computers and Internet technology. As in other studies, learners in this study had varying degrees of experience using technology (Johnson, 2001). All of them used computers in the performance of their jobs, and all of them had taken at least one previous WBL course through the departmental learning Website.

Some studies have revealed that self-efficacious learners usually participate more in computer conferencing than learners who demonstrate little self-efficacy (Gabriel, 1999; Hill & Hannafin, 1997). Contrarily, Johnson (2001) proposes that learners who lack self-efficacy may be more willing to contribute to an online discussion than one that takes place in a traditional classroom. In line with the Gabriel and Hill and Hannafin

findings, two of the less self-efficacious learners in the present study said they were less willing to contribute to a discussion through the bulletin board than they would be in a traditional classroom. There was also a contradiction between learners' stated willingness to participate on the bulletin board and their reasons for not doing it. Aside from other factors that created barriers to collaboration in this case, five learners in the course also demonstrated a lack of self-efficacy. Firstly, they were uncomfortable at the thought of communicating with people they did not know. Secondly, some of them felt they had nothing "valuable" to contribute, and were either shy or unsure about their abilities with the course content. Thirdly, a few were not efficacious about their ability to write in English, which was their second language, although they also said that this was not a factor in their reluctance to participate.

Recent research is also revealing that the level of demonstrated instructor self-efficacy and encouragement in WBL also influences learner participation in collaborative activities through the Website (Saye, 1997). In studies where WBL has comprised a portion of course delivery, researchers found it was valuable to have an initial meeting where learners are introduced (Card & Horton, 2000; Gabriel, 1999). They found it increased learners' comfort with communication in the WBL environment. In a course delivered solely through WBL, it is even more critical to have, at least, this initial meeting. This can be accomplished asynchronously through the bulletin board. Participants may introduce themselves with a very brief autobiography of themselves, and highlight their interests and goals related to the course. If time zones and schedules permit, participants may also meet online in a synchronous venue and do the same in a sort of "round-table" fashion. Learners in the present study agreed that they would feel

much more comfortable communicating through the bulletin board with each other if they had participated in this type of initial activity.

WBL literature documents the value of initial "icebreaker" meetings for course participants (Kearsley, 2000; Card & Horton, 2000; Gabriel, 1999). The findings of this study further reveal learners' reasons for lacking comfort and self-efficacy in this environment. WBL learners, who do not have any other type of contact with others in the course, see an initial online meeting as integral to their self-efficacy in this environment, and, therefore, their willingness to participate in a venue such as the bulletin board. An important outcome of this meeting can be the evolution of course participants into a community of learners. Kearsley (2000) notes that initial meetings may be particularly important when learners are from different countries, as in this study. Cultural differences in social customs can impact interaction, and Kearsley suggests that this be discussed openly with learners at the beginning of a course.

Lee (1999) argues that asynchronous conferencing venues provide a "...safer mode than in a face-to-face mode....a great implication for language learning in terms of giving learners an opportunity to internalize all linguistic inputs through the written discourse, which could not be all retained in a face-to-face classroom setting" (p.7). Trentin (1998) concurs with this and notes that:

> Interacting on a par with fellow participants produces a number of benefits for the learning process, especially when conducted in writing. Formulating and expressing one's own ideas, together with thinking about and reacting to those of others, are extremely important cognitive

abilities. (Trentin, 1998, p.37)

The learners who were taking the course from other countries appreciated being able to see commentary on the bulletin board, limited though it was, as they felt it helped them to learn to write English in the same way as their English-speaking colleagues. When asked, they also reported that they did not feel shy or inhibited about contributing to the bulletin board because English was their second language. However, despite this, they did not contribute much or often, and seemed to prefer direct e-mail communication with the instructor.

One learner in the study reported that he was dyslexic, and that this disability had marred previous learning experiences. He felt more comfortable and efficacious in WBL because he could access tools to check his spelling and grammar. To date there is an absence of research dealing specifically with WBL and its effectiveness as an environment for those with a learning disability such as dyslexia. This would be an interesting subject for investigation in its own right; however, it may be a challenge to elicit volunteers who would be willing to disclose their learning disabilities.

Learner dependence and lack of motivation as a result of negative perceptions

Levels of confidence and independence in learners directly affects their perceived ability to construct knowledge, and certainly affects their ability and willingness to interact with others online. This is consistent with other studies where less efficacious and independent learners required frequent help from an instructor or course administrator (Hill & Hannafin, 1997; Land & Hannafin, 1997).

It would seem likely that all WBL participants must possess a high degree of independence because they knowingly participate in physical isolation from their coursemates. Approximately half of the participants in this study described themselves as independent. WBL learners cannot be assumed to be independent, responsible and self-motivated learners in this environment, even when they describe themselves as having those attributes. This study reveals learners' reasons for not reading through and following directions, guidelines and instructional course materials on the Website. Moreover, those who felt they were independent learners were also the ones most willing to participate in a collaborative discussion with their course mates. Canada (2000) suggests that online learners "...require such independence and initiative simply to acquire the knowledge they are supposed to gain in a course" (p.37). Kearsley (2000) adds that WBL learners must assume responsibility for their participation and learning in this environment. All the participants in this study demonstrated some degree of independence and responsibility, with the four who described themselves as independent leading the way in being prepared to collaborate on the bulletin board.

The findings of this study suggest that WBL learners need to be self-motivated, independent and organized to keep up with the assignments and to acquire the knowledge they seek to learn. This concurs with current WBL research (Kearsley, 2000; Canada, 2000; Muirhead, 2000; Schrum, 1998). Online interaction through a conferencing tool also seems to require extra effort and extra self-motivation from learners. This finding is also reminiscent of other studies (Canada, 2000; Estes & Clark, 1999).

Perceived or real lack of time is, indeed, a barrier to engaging in activities that are viewed by learners as "extra's" (Canada, 2000; Janes, 2000). However, two learners in

the course confirmed that lack of motivation contributes to this barrier because, in their opinions, time can be found or made to fulfill all course requirements and activities. In addition, the fact that collaboration on the bulletin board was not a compulsory requirement rendered participants less motivated to find the time to do it. Seven learners said that if it were compulsory, they would participate. Harasim, et. al. (1995) note that "if participation in learning networks is offered as a completely voluntary, add-on, ungraded activity, pragmatic students will not participate at all" (p.185). The lack of motivation demonstrated in this study calls into question the notion that learners who voluntarily engage in WBL must also be self-motivated. The findings of the present study concur with previous research. In several studies learners performed activities if they were compulsory or there were assigned grades for the activity (Benson Soong, et. al., 2001; Blanchfield, et. al., 2000; Downing & Rath, 1997; Huang, 1997).

The impact of feelings of isolation on collaboration

Learners in this study felt isolated from other course participants and this keenly affected their perceived ability to co-construct knowledge. Previous studies found that WBL learners who have been introduced to each other have more success in collaborative online activities (Card & Horton, 2000; Gabriel, 1999). Incorporating suggestions for how the sense of isolation might be overcome, by learners in this study, may help to lessen learners' sense of isolation in future courses.

Often, when learners have not been formally introduced, they are reluctant to post messages to each other on a bulletin board (Kearsley, 2000; Trentin, 1998). Most learners in the study missed the interaction usually found in a traditional classroom. This

finding is typical of almost all WBL studies to date (Schrum & Benson; 2000). Researchers have noted that asynchronous conferencing can frustrate participants when there is no immediate feedback and the spontaneity typical of face-to-face discussions is lost (Lee, 1999). Knowlton (2000) also notes that interaction among learners in WBL is not only necessary for construction of knowledge, it humanizes an environment that is decidedly unhuman. The absence of visual and audio clues of socialization create a cognitive dissonance that limits knowledge co-construction (Knowlton, 2000).

A further insight from this study is that learners' feelings of isolation were heightened by the physical act of writing and posting their comments on the bulletin board. They reported that the awkwardness and slowness of using the Website tools to do this made them keenly aware of being alone. It also made having a Web-based "conversation" seem very rigid and formal when contrasted with the kind of spontaneous banter that can erupt in a traditional classroom. With limited ability to experience the back and forth nature of commentary that generally evolves into collaboration, learners in this study discontinued their efforts to interact on the bulletin board. There is some similarity between this finding and Kitchen and McDougall's (1999) finding that learners perceived commentary used in an online forum was of an "overly formal, artificial nature" (p.252). As a result, learners' contributions were sparse and terse, and more "cooperative...than truly collaborative" (Kitchen & McDougall, 1999, p.254).

When learners were afforded the opportunity to meet each other at least once, it seemed to increase their participation in Web-based conferencing (Schrum & Benson, 2000). Learners in some studies wanted to get to know each other so that when they entered into discussion they would have a sense of their peers (Schrum & Benson, 2000;

Gabriel, 1999). Trentin (1998) suggested that this may be particularly important because learners are communicating with each other in writing. Studies about the nature of collaboration in WBL have only recently been undertaken, and most of them have included other venues for the learners to interact such as a classroom or teleconference (Schrum & Benson, 2000; Sloffer, et. al., 1999). In this study, learners were reticent to interact with people they had not met or interacted with previously. Seven of the eight learners would have liked an initial meeting with all course participants, in whatever online venue was most convenient for all. Without it, these learners said they would not likely take the first step into a Web-based discussion forum, thus further isolating themselves and creating a barrier to collaborative discussion.

Degree of transition as a catalyst for interaction and collaboration

The findings of this study portray the participants' perspectives on their transition from traditional learning venues to WBL, and how it affected their ability and motivation to learn and collaborate. The experience of transition from one environment to another, was both a facilitator and a barrier to collaboration among course participants. In this case, as they continued to make the transition to WBL by taking more courses through the Departmental learning Website, learners also became more willing to engage in collaboration with others within this environment.

Logan (2000) says that transition is a natural and integral part of evolving educational practice. As learners and instructors move into a new educational setting, they apply methods and ways of communicating inherent in traditional settings. As they become more and more confident in the new environment, processes and methodology

are gradually evolved until there is little essence, if any, of the old left (Logan, 2000). WBL is no exception in following this pattern of evolution, nor are its participants in their adaptation to it.

As learners progressed through this course, most demonstrated increasing confidence in their use of Website tools, and in their ability to construct knowledge. Some learners also described a boost in self-confidence and independence in other facets of their lives as a result of their WBL experiences (Gabriel & MacDonald, in press). Research shows that learner self-efficacy increases with continuous successful experiences in a new learning venture (Dalgarno, 2001; Bandura, 1995, Yakamovicz & Murphy, 1995). In this study, transition was also a factor in learners' ability and desire to collaborate. As they became more comfortable and confident, they also expressed their willingness to collaborate on the bulletin board. Unfortunately, they didn't make a transition to the point where there was much effort to actually do it.

The transitional experiences of the WBL participants in this study are historically consistent. Transition has always been experienced by learners and instructors as educational structures have evolved over time, resulting from educational and industrial innovation and advances in technology (Logan, 2000). Kearsley (2000) points out that as online instructors gain experience in WBL, they acquire and improve the skills necessary for achieving collaboration among course participants. This study reveals transition as a factor that affects the ability of learners to construct knowledge through collaborative discussion in an online venue. It also underscores the effect of transition on the instructor's role in employing methodology to "...capitalize on the collaborative potential..." of WBL (Kearsley, 2000, p.86-87). Part of that methodology may be to

include learners by making them aware of what constructing their own knowledge entails, and how collaboration with others contributes to the process of knowledge construction. This may help learners in their transition to WBL.

Research Question 3:

How do the facilitators and barriers affect learners' perceived ability to construct knowledge in Web-based Learning?

Learners' perception of their ability to construct knowledge in WBL was predominantly negative because of the factors that created barriers to their collaboration in this environment. The factors that prevented collaboration also extended to other activities learners performed in order to construct knowledge. As a result, learning was diminished. The factors that created barriers to collaboration, shown in Table 1, far outweighed the factors that could have facilitated it.

The perceptions that disabled collaboration in WBL

Time, convenience and Website tools either promote or impede learning in the WBL environment. When learners perceived that they had adequate time and found the Website simple and convenient to use, they planned to go beyond the minimum requirement of completing assignments to activities like collaborating on the bulletin board. In this study, when learners found they were under time constraints, experienced technical difficulty, or found Website tools awkward to use, they did only what was required to complete the course. This was done to the exclusion of activities, such as collaboration with other learners. The convenience of taking a course through WBL

motivates learners to enroll in them; however, the convenience of e-mail access to an instructor, minimizes learners' motivation to interact and collaborate with their peers.

Table 1: Learners' perception of ability to construct knowledge affected positively and/or negatively by factors

Factors	Positive Perception	Negative Perception
Time	•	•
Convenience of WBL	•	
Clarity of course expectations		•
Course guidance, instructions & support		•
Website tools & technical difficulty	•	•
E-mail access to instructor	•	
Lack of self-confidence & independence		•
Learner motivation	•	•
Instructor motivation		•
Isolation		•
Transition	•	•

Perceived course expectations, and the degree of learner self-efficacy, independence, motivation, transition and isolation all contribute or detract from learners' ability to construct knowledge in WBL. Ambiguous course expectations and a lack of detail or planned activities posed the most serious barrier to collaboration among learners in this WBL course, and to the higher-level thinking and knowledge construction that

collaborative activity could have produced. Learners in this study were unsure about the expectations of them related to bulletin board activity and, as a result, there was minimal participation in this venue. Because it was not a mandatory requirement, learners were less motivated to contribute to collaborative activity.

The degree of confidence learners had with respect to both subject matter and their ability to use the course Website tools affected the amount of interaction they had with other course participants on the bulletin board. The less confident learners preferred one-to-one contact with the instructor, and were more dependent on the instructor and course administration. Confident learners were more independent, willing and motivated to interact on the bulletin board.

Most learners in the course felt isolated due to a lack of interaction with others in the course, yet there was minimal effort to use the bulletin board. All participants in the course perceived WBL as the predominant course delivery venue of the future, and all described their current ability within this venue as "in transition". Most, learners and non-learners, described becoming more comfortable in WBL and with Website tools as they progressed through the course, and perceived that their ability to learn, and instruct, in this environment improved with experience.

The adverse effect of negative perceptions about ability with technology

In this study, learners' initial perception of their ability to construct knowledge using the tools and venues provided on the Website were very positive. All were experienced computer and Internet users, and they viewed WBL as a convenient way to take a course. When they encountered technical difficulties, and perceived that their

ability may be lacking, learners in this study elected to do only what was necessary to complete the course. This meant that they persevered through technical difficulties in order to complete compulsory requirements. Some researchers recommend making WBL activities compulsory to ensure learner participation (Blanchfield, et. al., 2000). If collaboration among learners in this study had been compulsory, they may indeed have persevered to overcome perceived difficulties.

As a caveat to recommending that bulletin board participation be compulsory, daily monitoring of a WBL site for technical problems learners may be having is also recommended (Oliver & Omari, 2001). Other studies have shown that it is critical for WBL learners to have immediate access to someone who can guide them through problems they are having with Website tools and venues (Oliver & Omari, 2001; Carswell, Thomas, Petre, Price & Richards, 2000). This study further reveals learners' perceptions about requesting help when they encounter problems. When some learners perceived technical problems they also perceived it was their own level of competence with using the Website tools and venues that was to blame. They were hesitant to ask for help for fear of being perceived as less intelligent. This finding echoes recent studies where learners refrained from using a WBL discussion forum because of perceived lack of technical ability (Seale & Cann, 2000).

The study extends the literature by describing the effect of these perceptions on activities such as collaborative discussion. Recent research has revealed suspicions that learners' unfamiliarity "...with the tools and the training strategies employed might have determined the unsatisfactory participation" (Ferraris, Manca, Persico, & Sarti, 2000, p. 86). When learners in this study perceived they had little ability to use the Website tools

and venues provided, they did only what was necessary, to the exclusion of collaboration with other participants. This limited their construction of knowledge in WBL to the minimum required for course credit.

The findings of this study concur with previous research. Recent studies revealed that learners' perceptions, positive or negative, of their abilities to use technology had a direct impact on intention to use and actual use of distance learning technologies (Christensen, Anakwe & Kessler, 2001; Ross, 1998; Card & Horton, 2000; Harmon & Jones, 1999; Hill, 1997; Anderson & Joerg, 1996; Land & Hannafin, 1997). The present study extends WBL research by revealing that the inherent nature of WBL as a social-constructivist learning environment can also serve to prevent learners from constructing knowledge together when they perceive their ability is limited or non-existent. The same tools and processes that enable learners to construct knowledge can disable them when it comes to activities like collaborative discussion. This dichotomy, based on learners' positive or negative perceptions, permeates the findings of this study, and is unique from previous WBL research in this way. There is literature to support the idea that invoking familiar learning techniques within a new context is a natural occurrence as learners transition to a new and evolving educational structure (Logan, 2000). Gradually, as learners get used to the new environment, initial negative perceptions become positive as they have successful experiences. This occurred, albeit to a limited degree, in this study over the duration of the course.

Perception became reality for learners in this study when they became anxious about having enough time to access the course and do assignments. Other factors impacted on their perception that the coursework took longer to accomplish due to

technical failure and difficulty using Website tools. This anxiety about time caused most learners to abstain from contributing to collaborative discussion on the bulletin board, as it was perceived as taking extra time and effort. This finding supports recent studies where learners were not using the conferencing venue provided for their interaction (Blanchfield, et. al., 2000). A difference between this study and other studies lies in the fact that the learners in the other studies had other venues for face-to-face access to each other, and used these for collaboration, rather than their computer conferencing venue.

Research Question 4:

What evidence is there that learners are or are not collaborating?

The evidence that learners were not collaborating was clearly portrayed by the silence on the bulletin board. While interaction on the bulletin board was evident at the beginning of the course, it ended in silence about midway through the course. There were few instances of interaction that revealed collaborative activity, and most interaction consisted of the transmission of information. The facilitators and barriers to collaboration describe the reasons for learners' interaction and non-interaction on the bulletin board. Learners' perceptions of their ability to construct knowledge in WBL were affected negatively by the barriers to collaboration. Collaboration was acutely affected by the lack of support or encouragement for it from the instructor and course administrator. There were no built-in activities to promote the use of the bulletin board in this course, such as an introductory meeting of learners, or the sharing of learners' applications of course elements to work situations. Learners were unclear about bulletin

board use and the nature of their expected contribution to it. They were also less motivated to interact on the bulletin board, because they perceived it was not a mandatory requirement for successful completion of the course.

Lack of learner interaction and collaboration

There was minimal interaction between learners in this course, and one instance of collaboration where learners interacted through responding, and constructed new knowledge by reacting. This occurrence was a direct result of commentary posted on the bulletin board. Yakimovicz and Murphy (1995) found that as learners experienced success in communicating with each other, they also realize the value of collaboration in WBL. Some learners in the present study voiced this sentiment as well; however, it did not seem to motivate them to actually act on their feelings.

Seale and Cann (2000) found that while learners in a case study did not contribute to a WBL discussion forum, they did "...engage in 'off-line' discussion with others " (p.319). Learners in the Seale and Cann study were able to do this face-to-face because only part of their course was conducted through WBL. However, the similarity between this finding and its manifestation in the present study needs to be acknowledged. While the learners in the Departmental learning Website course did not engage in off-line discussion with each other, they did discuss their thoughts and reactions to bulletin board commentary in their off-line reflections to me.

As well, off-line interaction with the instructor through e-mail was done to the near exclusion of interaction or collaborative discussion on the bulletin board. It reveals that there may be a need for parameters around e-mail access to the instructor to limit e-

mail exchanges that tend toward collaborative discussion about course content (Huang, 997). If collaboration among course participants is desired, e-mail access to the instructor may need to be limited to personal and informational matters.

Another recent WBL study found that learners' participation in collaborative activities "...was scarce or irregular....We had a hard job fostering and sometimes pressing for participation both in the discussion and the group work...." (Ferraris, et. al., 2000). The study involved both WBL and face-to-face group work. The researchers also noted the difference between 'presence' and 'active participation' when learners would post questions or comments that were not part of a discussion (Ferrais et al., 2000). The present study revealed a similar tendency to simply post questions or comments that did not engender collaborative discussion.

A deafening silence

Learners' silence on the bulletin board embodied much of the truth in the study (McMahnon, 1996). Recent studies have suggested that a lack of activity in online communication venues is largely due to learners' motivation (Blanchfield, et. al., 2000). The learners in this study were prepared to collaborate, but it didn't happen. A lack of a collaborative dimension in the design and delivery of the course, and support for learners created barriers to its manifestation on the bulletin board. The silence on the bulletin board mirrored the factors that caused the absence of learner interaction there. This study has revealed some important reasons behind learners' lack of motivation to interact, and names the barriers to collaboration that rendered a WBL conferencing venue silent.

Summary

WBL theorists have noted that course expectations must be made clear in any learning situation, but especially to learners in an environment where they are physically isolated and invisible to each other (Janes, 2000; Kearsley, 2000; Harasim, et. al., 1995). As demonstrated in this study, lack of clear expectations directly affects learners' ability and motivation to co-construct knowledge, and limits their ability to do so on their own as well.

Linked to this is the finding that poor course organization, support and detailed instructions severely limit learners' abilities to collaborate. A lack of understanding of what collaboration meant within the context of the course resulted in learners' sense of confusion about their bulletin board activity. A lack of detailed explanation in the course instructions on the Website contributed to this confusion, and the instructor did not explain the importance of collaboration to the learning of course content.

On the positive side, the learner participants in the course perceived that the convenience of accessibility regardless of time makes it easier for them to do their coursework, because there is no set time they have to be "in class" or do their assignments (Kearsley, 2000). WBL literature to date suggests that most learners perceive this new learning venue as advantageous in terms of time and convenience, and often prefer it to more traditional and distance venues for these reasons (Muirhead, 2001; Janes, 2000).

The findings of this study concur with previous research which revealed that learners' perceptions of the abilities to use technology, positive or negative, has a direct impact on both learner intention to use and actual use of distance learning technologies

(Christensen, et. al., 2001; Ross, 1998; Card & Horton, 2000; Harmon & Jones, 1999; Hill, 1997; Anderson & Joerg, 1996; Land & Hannafin, 1997). The study also extends WBL research by revealing that the inherent nature of WBL as a social-constructivist learning environment can also serve to prevent learners from constructing knowledge together when they perceive their ability is limited or non-existent. The same tools and processes that enable learners to construct knowledge can disable them when it comes to activities like collaborative discussion. This contradiction, based on learners' positive or negative perceptions, permeates the findings of this study, and is unique from previous WBL research in this way. There is literature to support the idea that invoking familiar learning techniques within a new context is a natural occurrence as learners make the transition to a new and evolving educational structure (Logan, 2000). Gradually, as learners get used to a new environment, initial negative perceptions become positive as they have successful experiences. This occurred, albeit to a limited degree, in this study over the duration of the course.

When learners in this study encountered technical difficulties, they elected to do what was necessary to complete the course. This meant that they persisted through technical difficulties to complete compulsory assignments only. Some researchers recommend making WBL activities compulsory to ensure learner participation (Blanchfield, et. al., 2000).

In this study, levels of confidence and independence in learners directly affected their perceived ability to construct knowledge, and certainly affects their ability and willingness to interact with others online. This is consistent with other studies where less

efficacious and independent learners required frequent help from an instructor or course administrator (Hill & Hannafin, 1997; Land & Hannafin, 1997).

Some learners in the course were motivated to do only the compulsory requirements of the course because they perceived their ability to construct knowledge in WBL was limited by other factors such as time, unclear expectations, and a lack of confidence. Studies are beginning to show that desired online participation must become required online participation in order to motivate learners to persevere (Blanchfield, et. al., 2000).

Learners in this study felt isolated from other course participants and this keenly affected their perceived ability to co-construct knowledge. Previous studies suggest that WBL learners who have been introduced to each other have more success in collaborative online activities (Card & Horton, 2000; Gabriel, 1999).

The transitional experiences of the WBL participants in this study are consistent with the transition experienced by learners and instructors as educational structures have evolved over time as a direct result of educational and industrial innovation and advances in technology (Logan, 2000).

Recommendations based on the themes that emerged from the findings of this study will assist WBL instructors in encouraging their learners to engage in interaction that will lead to collaboration, and further their ability to make a full and successful transition to the WBL environment. The following recommended WBL components and processes address the barriers experienced by the learners in this study, in order to improve the experiences of future WBL learners and instructors.

Recommendations for Facilitating Collaboration in WBL

A framework for collaborative discussion in WBL will assist online instructors in facilitating and guiding learners in their co-construction of knowledge (Northrup, 2001; Stathakos & Davie, 2000; Card & Harmon, 2000; Muirhead, 2001; Mann, 2000; Ruokamo & Pohjolainen, 2000; Kent & McNergney, 1999). Naming the components and processes required to facilitate collaboration in WBL is timely. It may also inspire other researchers to improve upon them, and further WBL pedagogy in the process. It is important that WBL researchers move their focus more to what takes place between participants within the WBL learning environment, than on the technology that supports it (McConnell, 2002; Witherspoon & Johnstone, 2001; Simonson, 2000; Jung, 2000; Carr & Carr, 2000; Burge, 2000; Lewis, 1999; Mayer, 1997).

Because the findings are based on a qualitative, single case study, the achievement of deep understandings and revelations can serve as an example to help guide the development of WBL pedagogy. Gained through an intense focus on the particular, these findings both support existing theory and contribute to theory-building. The following recommendations, based on the findings of the study and within the context of current WBL research, are proposed for facilitating collaboration among WBL course participants:

- An instructional approach, informed by existing WBL pedagogy, to course design and delivery must be taken, and should include input from instructors and learners who have participated in WBL courses. Detailed objectives, instruction and explanations for activities, such as collaboration, need to be easily available to learners. These objectives also need to be supported by planned and facilitated

activities. Clear guidance and expectations should be easily available on the WBL Website for learners to reference at anytime throughout the course through a simple "point and click". In addition to Website tools, course content and relevant links, learners need to be able to refer to clear, succinct direction, and to contact persons for further clarification if required. This recommendation supports existing WBL literature in this regard, but it is further recommended that the course instructor reinforce guidance and expectations at an initial online meeting.

- If collaborative discussion is believed to be a necessary activity to support learning objectives in a WBL course, then the participation needs to be perceived by learners as compulsory. Sometimes it is necessary to invoke "should's" in order to facilitate "could's". Based on the findings of the study, within the context of WBL literature, it seems clear that participation in collaborative discussion should be viewed as compulsory so that learners can co-construct knowledge through reflection, discussion and the development of new understandings. It is also important to help them to come together as a community of learners in the course, and, ideally, extend the learning community beyond the course. However, as Henderson (1996) says, "Creating a community of learners does not occur by imposing rules on a group of strangers" (p.139). The establishment of a 'Classroom Covenant' (Henderson, 1996) for interaction between course participants could serve the purpose of strongly encouraging learner compliance with course interaction requirements. In addition, the allotment of course marks to defined collaborative activity will strengthen learners' commitment.

- Linked with making collaboration a perceived compulsory activity is the recommendation for at least an initial online meeting of all course participants. To ensure participation in the meeting, it is recommended that this meeting be mandatory. The findings of this study point to the inclusion of an initial meeting that will serve to raise learners' comfort with both the WBL context and the activity of online conferencing. It will reduce their sense of isolation and reinforce that their contributions are important and necessary to constructing knowledge. Facilitated by the course instructor, the meeting will establish clear expectations for participating and contributing to course activities, with particular emphasis on collaborative discussion in the venue provided. This will also be an opportunity for the instructor to explicate the activity of collaboration and to ensure that learners understand what is required of them, and why collaboration is so important to the process of learning course content.

- WBL learners need to know they have access to immediate technical assistance on a 24/7 basis throughout a course. This recommendation will help facilitate collaboration and knowledge construction in WBL. Learners will feel more confident and comfortable, and less isolated, knowing that technical support is available to them when they run into difficulty.

- Once learners are participating in a WBL collaboration venue, such as the bulletin board in this study, it is important that an instructor demonstrate a consistent and continuous presence there. The role of the instructor within this activity is to inspire

and guide discussion, and to keep it relevant to learning objectives for the course. The "should's" of course content to be learned can be easily accomplished en route to pursuing what "could" be learned. The presence and guidance provided by an instructor is critical to the achievement of collaborative discussion. It is recommended that WBL instructors be "visible" on a daily basis to learners in their role as guides and facilitators. A side benefit of this may be a decreased number of individual e-mails from learners to instructor.

- Learners also need to be encouraged to take ownership of the collaborative environment, so that learning is not seen as residing in the instructor alone but in the interactions and contributions of all participants. In each discussion, assigning team contributions might foster involvement of all learners.

- A final recommendation is that there must be parameters around e-mail access to an instructor in WBL. Learners in this study communicated directly with the instructor to the exclusion of collaboration on the bulletin board. All of them enjoyed the access to the instructor, and some admitted they did not collaborate with other learners because of it. In order to ensure that collaborative discussion among course participants takes place on the Website venue provided for that purpose, e-mail access to an instructor should be limited to administrative and personal information.

The recommendations outlined here and as shown in Figure 4 have been derived from the findings of the study. They involve the implementation of components and

processes to ensure learners achieve an optimum level of learning in WBL through collaborative discussion.

- Use input from potential learners for WBL course design.
- Provision of clear expectations of learners regarding course activities and assignments, and detailed instructions and objectives supported by planned activities.
- Perceived compulsory "attendance" of course participants in initial online conference for introductions and explanation of course context, objectives and requirements.
- Perceived compulsory learner participation in online conferencing venue for purpose of collaboration through learner-devised covenant, and mark allocation.
- 24/7 technical assistance available to course participants.
- Consistent and daily visible presence of instructor in online conferencing venue.
- Clear parameters around learner e-mail access to instructor.

Figure 4. Recommendations for facilitating collaboration in WBL

Summary

In an ideal WBL course, participants begin as individuals, with their individual goals and objectives for the course, and leave as members of a learning community. In a process that includes clear and detailed guidance and direction on the Website and reinforced by the instructor, learners construct knowledge individually and together in an

ongoing generative process of learning. In addition to guidance and instructions about the course, the instructor plays a pivotal, continuous role in facilitating discussion among learners in the course. E-mail communication between the instructor and individual learners is strictly limited to personal or administrative concerns.

Once learners meet, first as a collection of individuals, they become a community of learners as they co-construct knowledge and develop new understandings. At the conclusion of the course, they move into a new realm of understanding and knowledge and may continue their collaboration beyond the course as a community of expertise.

The learning process is supported technologically by a Website and tool design that, firstly, meets the pedagogical objectives of the course, and, secondly, provides immediate access to technical support at any time. Feedback is elicited from course participants so improvements may be made to the design elements. This image of a WBL experience is captured in Figure 5.

Given the findings of the present study, together with our knowledge of past work in this domain, it will be a challenge to move the WBL experience closer to that ideal and apply the recommended components and processes shown in Figure 5 to every course. If, however, collaboration among learners is a desired activity, they will provide sound course organization and support to nurture and facilitate the process.

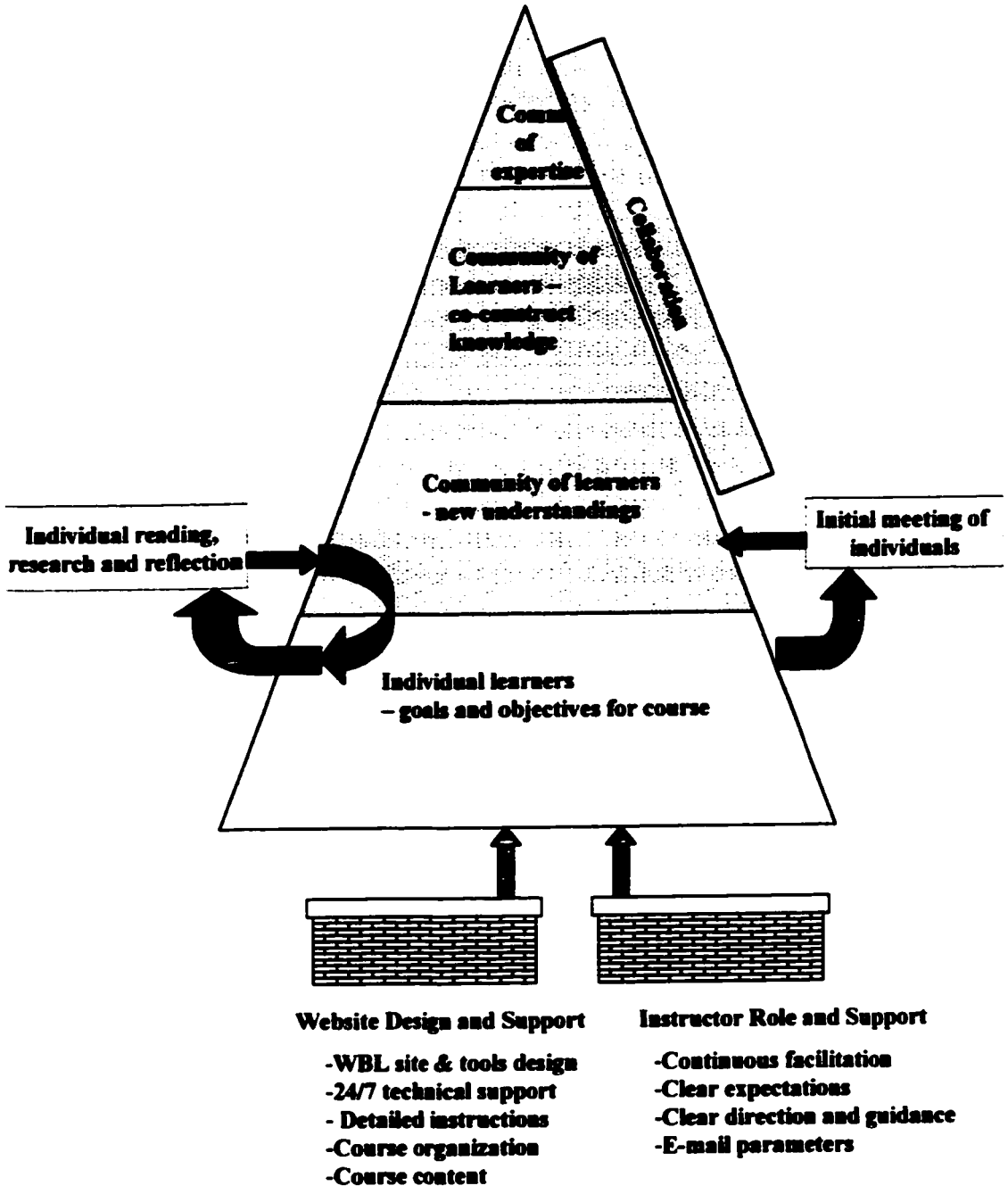


Figure 5. Facilitating collaboration for optimum learning in WBL.

Based on the findings of the study, and subsequent recommendations, the proposed WBL components and processes shown in Figure 5 illustrate the facilitation of collaboration among course participants:

1) Expectations regarding collaboration are simply and clearly outlined by the instructor and on the Website, as are detailed course objectives, instructions to learners, and built-in activities to meet objectives;

2) Guidance about what constitutes collaborative discussion, including a definition of collaboration, and an example of collaborative discussion are provided by the instructor and on the Website;

3) Where collaboration among learners is desired, participation in online conferencing is a compulsory course requirement, albeit through a covenant crafted and agreed to by the participants. Marks are assigned for genuine participation, and individual and team collaborative assignments or contributions. Course may also be part of a certified program of study.

4) Clear parameters are provided about e-mail access to the instructor by the instructor and on the Website;

5) An initial, compulsory meeting, either asynchronous or synchronous, is held when the course commences;

6) Course participants move through a cycle of collaborative discussion about course content combined with individual research and reflection, which is continuously instructor-facilitated. As learners construct knowledge they progress from a community of learners to a community of experts who may continue to collaborate beyond the course.

7) There is consistent, daily instructor presence, and instructor guidance throughout each discussion.

8) There is immediate technical assistance available to participants on a 24/7 basis for the duration of the course, and a feedback loop for improvement.

9) While the previous points apply to all WBL courses that desire collaboration among learners, there needs to be management and peer support for learners who are engaging in WBL from their workplace. This includes tangible recognition of successful WBL endeavours.

If the recommendations are implemented to support the course components and processes, the barriers to collaboration among course participants should be lessened or eliminated altogether.

As an educator, my interest in WBL as a "classroom" for the 21st century arose out of my concern that WBL provide, as best it can, an environment where learners co-construct knowledge through collaboration under the guidance of instructors. In order to attain this goal, educators and educational researchers need to take ownership of the

implementation of Internet technology into the construction of WBL. WBL must be designed to support learning objectives that result in knowledge construction (Schoenfeld, 1999). An integral part of the design process is to ensure all aspects of the design support the ability of learners to collaborate with each other. This is inherent in the recommendations based on the findings of the study, and illustrated in Figure 5.

Chapter 6: Implications of the Study, Conclusions and Recommendations for Further Research

Introduction

Classroom discussion where collaboration among learners about the subject being learned is often the objective of many instructors. "Teachers from Socrates to Slavin have advocated the use of instructional techniques that encourage learners to learn from one another" (Kitchen & McDougall, 1999). The earliest philosopher teachers, such as Plato and Aristotle, used active discussion, albeit in different ways, as a means to achieve understanding and learning (Logan, 2000). They planted the seeds of discourse by laying out their reflections and interpretations of particular subjects, and then encouraged and guided their "learners" or "apprentices" in debate and discussion. Often these discussions would become collaborations in the making of meaning. This "method" of teaching has continued and evolved through centuries of teaching and learning. One of the educational gurus of the twentieth century, John Dewey, propelled this tradition of reflection and collaboration forward within his theories of purposeful inquiry and problem resolution in pedagogy (Grimmett & Erickson, 1988).

Collaboration among scholars, throughout centuries, including the present one, has produced many books and other media to assist in the dissemination and making of knowledge. It should be duly noted that the advent of the printed page and other media for learning did not eliminate the need for teachers; on the contrary, it increased the need for them (Logan, 2000; Bates, 1995). Likewise, the evolution of communication modes

have continuously influenced and changed educational structure, and this is true of the Internet and the Web (Logan, 2000; Cox, 2000). A constant in changing educational environments is "...the goal of obtaining more efficient and effective learning" (Ely, 1999; Cox, 2000).

Collaboration among people, in general, who come together for a specific purpose, have sometimes produced the tools and conveniences the world enjoys today, including the Internet. New understandings and inventions begin with an idea, which is reflected upon by the inventor, made tangible, and then, perhaps, improved as a result of collaboration with peers and users of inventions. Collaboration in learning and other situations takes place when individuals externalize their own constructions of knowledge, and contribute to and imbibe the knowledge and experience of others through discussion (Kearsley, 2000). In a learning situation, it makes sense to encourage the externalization of differing and similar viewpoints as a focus for discussion (Moyse & Elsom-Cook, 1992). Ideally, this results in refinement and understanding, and, ultimately, in learning (Garmer & Firestone, 1996).

WBL is rapidly becoming a popular venue for learning and it is changing educational structure as educational researchers study the learning context this environment provides, and strive to develop pedagogy to ensure its efficacy for learners and instructors. Cox (2000) emphasizes that:

> We do not yet fully understand how to provide effective education online or on a large scale, but there are enough promising signs to believe that it can be done with quality and integrity....as a new institution we can focus with fresh

> attention on the core challenge of all educational institutions: trying to promote effective learning using the best available talent and tools. (Cox, 2000, p.18)

Recently, WBL researchers have begun to look at the benefits for learning when there is collaboration among course participants (McConnell, 2002; Muirhead, 2001; Northrup, 2001; Stathakos & Davie, 2000). It is important at this stage of WBL theoretical development to home in on the factors that enable or inhibit collaboration in WBL.

Some of the findings of this case study are consistent with general WBL research literature about factors that affect instructors and learners. Over the past few years, WBL researchers have begun to focus on collaboration in this environment. The findings of this study contribute to a growing body of WBL literature about collaboration among learners in a WBL course.

The factors that facilitated and created barriers to collaboration in WBL permeated the data derived from this qualitative case study of a WBL course and its participants. Within the barriers that prevented learners from collaborating, and the perceptions that these learners had of their ability to construct knowledge in this environment, lie the implications of the study and recommendations for future WBL course delivery.

Recommendations derived from the study contribute to the development of WBL pedagogy and, in some ways, suggest a pragmatic approach as the means to create an intellectually stimulating environment for learning. The pragmatic and the creative are not necessarily mutually exclusive, and have often served to balance each other in the development of new educational structures.

Suggestions for further research on collaboration in WBL focus on testing the processes proposed in the model for facilitating collaborative discussion. Other findings of interest that surfaced from the data in the study provide some new and interesting directions for the study and improvement of WBL as an educational venue that can be accessed by all.

Limitations of the Study

The limitations of the study may reside in: the researcher's bias for collaboration as an integral component of effective WBL; the amount of detail provided about the participants in a case study; procedural difficulties, such as whether conducting interviews through e-mail is as effective as in-person interviews; and transferability of the study. Each of these is addressed as limitations to both acknowledge their presence as issues, and to show that they do not jeopardize the integrity of the study.

Researcher bias

It is important to note my bias for collaboration as essential for effective learning in WBL as a possible limitation of the study. As an instructor and learner, I firmly believe that collaboration among course participants leads to deeper understandings of course content. When learners collaborate, they reconcile their knowledge and experiences with those of others and emerge with new perspectives. Ultimately, this can result in refinement of understanding and the development of new knowledge. It is my belief in the importance of critical thinking skills for dealing with all of life's endeavours,

including learning, that underlies my commitment to the incorporation of collaboration as an integral part of course delivery.

Profiles of Participants

Profiles of the participants were limited to a brief summary of their experience with WBL within the primary context of their workplaces. In some cases it was possible to get more of a glimpse into the context of their lives outside the office, in other cases it was not possible because participants were not forthcoming with that kind of information. It is always interesting to have a rich description of participants in a case study, and it helps to create deeper understandings within the context of their experiences. This particular WBL course on business writing comprised this case study, and the participants in the course collectively and individually provided the data. The descriptions provided of the course and of the participants create a sufficient, if not ideal, understanding of the full personal context from which they participated in WBL.

Procedural difficulties

As the researcher, I experienced several procedural difficulties including: technological breakdown, the unwillingness of learners from other countries to participate in telephone interviews, and the lack of interaction among course participants from which data could be obtained. However, as revealed in the findings of the study, and as argued in the discussion, it was precisely because of these procedural difficulties that I was able to illuminate so vividly the barriers to collaboration among learners in a WBL environment. Mainly through in-depth interviews, and participants' reflections, I

was able to garner rich data. I also experienced, firsthand, some of the factors that created barriers to interaction, such as the frustration of technological breakdown and feelings of isolation. So, while procedural difficulties may have prevented me from conducting my research as originally planned, I invoked my Constructivist researcher stance and was able to change my methodology to overcome the challenges presented. In doings so I believe that I protected the efficacy of my study, and of my ability as a researcher.

Online Data Collection

Whether or not in-depth e-mail interviewing is less or more effective for data collection has yet to be determined. It may be argued that what is lost due to spontaneous response is gained through reflective response (Mann & Stewart, 2000; Merriam, 1998). At the outset of the study, in-depth interviews were planned with all of the course participants. This was to be achieved through in-person interviews with local participants, and through telephone interviews with foreign-based participants. Methodology had to be adjusted when the foreign-based participants expressed their preference for the interviews to be conducted through e-mail (Stake, 1995). Their reasons for this were twofold. Firstly, despite my availability at any time, time zone differences did not allow for a convenient time, for them, to spend the time required on the telephone outside of their office setting. Secondly, within their office setting, they feared they would be constantly interrupted during an interview. Without exception and unknown to each other, the foreign-based participants expressed a preference for e-mail interviews. The responses I received to my interview questions were deeply reflective at

times, and I think this is evident in the quotations used to support the findings provided in this chapter.

Transferability

Case study focuses on the findings of the particular, and by definition may not be generalized to other settings. However, it can be argued that the goal of case study is the particular and not the general so that in-depth understandings may be achieved (Stake, 1995). Construction of knowledge about the particular case may also contribute to theory-building (Yin, 1984). Readers of case studies may choose to view other similar situations or settings with a new perspective or new understandings and perhaps achieve improvement or new understanding within the other setting as a result of a transfer of what they have learned from a case study (Merriam, 1998).

Implications of the Study

The implications of the study are derived from the experiences of the learners, and how these experiences influenced their perceptions of their ability to perform course activities and to interact with each other. A clear picture of WBL from the learners' perspective is important because:

> The larger lesson is that any pedagogy - but especially constructivism, given its commitments - does well to include a vision of how students experience it. They, after all, are the ones who have to try to walk in the shoes we theorists, teachers, and designers cobble

together for them. (Perkins, 1991, p. 21)

This study suggests that learners' perceptions of their ability to construct knowledge in WBL are directly and dramatically affected by the factors that also created barriers to collaboration. The factors that have been determined to prevent or enable collaboration also extend to other course-related activities they perform. Learning is either diminished or enhanced as a result. Because barriers were perceived as insurmountable, learners had minimal interaction on the bulletin board and there was limited collaboration. The barriers influenced the perceptions of both confident and non-confident learners, and eroded confidence levels of both.

Facilitators and barriers to collaboration

WBL researchers have consistently recommended that course and conduct expectations need to be clearly laid out, more than in WBL in traditional settings. While this seems strikingly obvious, it is not always done. This study confirms that clear expectations are required for collaborative discussion, perhaps supported by examples of acceptable participation and outcomes. The implication for research is to reinforce WBL pedagogy with respect to making course requirements and expectations clear, generally, and, specifically, to include clarity of expectations for activities such as collaboration. Further studies need to be conducted to determine if this aids in its facilitation.

WBL researchers have suggested that at least one meeting between course participants helps to facilitate the online collaboration component of a course (Witherspoon & Johnstone, 2001; Alexander, 2000; Lewis, Whitaker & Julian; 1995; Gabriel, 1999). The recommendations of the study support these findings. Learner

participation in this initial gathering may also have to be perceived by learners as mandatory to ensure their participation. The implications here lie in a strengthening of WBL pedagogy. Future studies could focus on this, and determine the degree to which an initial meeting contributes to collaboration among learners in a course where participants interact solely online.

Flexibility of time and convenience of access were positive forces in creating a willingness to collaborate. Conversely, perceived and real time constraints, and the convenience of access to the instructor for individual attention created barriers to collaboration taking place. As discussed within the context of current WBL literature, researchers have recently found that when WBL activities are compulsory, learners will persevere through perceived difficulties in order to complete them. The recommendations for facilitating collaboration in WBL illustrate that if collaborative discussion among learners is an objective, then it should be perceived as a compulsory activity. The implication of this for WBL research into collaboration is to conduct studies where this is implemented.

This study confirms the suspicion that a lack of collaboration on conferencing venues is due to e-mail access to an instructor. Another recommendation of this study is to create clear parameters around instructor-learner e-mail communication. Studies need to be done where e-mail access to instructors is strictly limited to administrative topics. This will aid in determining the effect on learner collaboration in the conferencing venue.

WBL studies have consistently shown technical breakdown and Website tools as a primary factor in either facilitating or preventing learners' WBL activities. The

necessity for immediate technical assistance for learners throughout a WBL course, on an "anytime" basis, is abundantly clear.

Linked to this is the need for strengthening Website and tool design. To this end, a feedback loop is suggested as a means to include learners and instructors in designing WBL that actually facilitates learning objectives. The implications for research are in reinforcing the critical importance of learner-centred WBL design for sites and tools, and the absolute necessity for 24/7 technical support to learners in this environment. Future studies will confirm whether this dramatically improves participation in WBL course activities, including collaboration.

Contributing to WBL Theory

This study has contributed to WBL theory-building by constructing an in-depth understanding of the factors that affected collaboration among WBL learners and how these factors affected learners' perceived ability to construct knowledge in this environment. Because learners in this case did not participate in other non-WBL venues, the study is unique in its qualitative explication of the factors affecting collaboration in WBL. WBL pedagogical development is furthered through an intense examination of new and previously identified barriers to WBL collaboration.

Insights for Practice

If instructors approach WBL with a view to what "could" be learned, as opposed to what "should" be learned (de Caprariis, 2000), collaborative discussion would be named as the integral component for that vision to become reality. The "should's" can be

accomplished without too much difficulty; the "could's" can be largely accomplished through elimination of barriers to collaboration in WBL, and by implementing tools and strategies that make it easy for participants to "talk" to each other.

In situations where WBL is undertaken from the workplace, management, course administrators and instructors need to go beyond lip service for professional development, and value and support workplace learning in concrete ways.

Creating Constructivist learning environments

For WBL to truly function as a social constructivist learning environment, course participants must work together to construct knowledge (Burge, 2000; Wilson & Lowry, 2000; Carr-Chellman & Duchastel, 2000; Oliver, 2000; Burge, 1994). For this to happen successfully, all stakeholders need to be a part of the course planning process, including Website design (Sullivan, 1994). Ideally, once ensconced in a course, the participants, including the instructor, work together to negotiate and construct the outline of the course, topics to be covered, assignments to be completed, research required to meet the course objectives, and the means for all of this to occur (de Caprariis, 2000). Inherent in this is that they enter into planned and guided collaborative discussion which propels them to new understandings and insights derived from a multiplicity of perspectives (Muirhead, 2001; Oliver, 2000; Allegra, 1997).

Facilitating collaboration

Instructors and learners need to understand what it means to enter into collaboration. They need to be aware that by moving from a discussion of unique and

individual points-of-view, to a dialogue where participants are fully engaged, listening for understandings, seeking clarification, and reaching agreement, they will have achieved their objective.

Facilitating collaboration also requires an explanation of what is expected of learners in a course when they collaborate. They may require tangible and attainable objectives to follow, with the instructor as facilitator. Some suggested principles include making learners aware of the following expectations for collaboration:

- Full participation and presence by minimizing distractions;
- A sharing of responsibility for taking interaction from discussion to dialogue;
- Listening/watching for meaningful contributions and mutual understanding;
- Respecting timeframes for achieving objectives.

In order to facilitate WBL collaboration among learners, WBL courses may require more than one instructor. Depending on course size, WBL "classrooms" may require a team of subject matter experts to teach and to facilitate collaborative discussion among learners. Universities may need to prepare for an increased demand for instructors who are fluent in both traditional and WBL pedagogy (Ellis & Phelps, 2000; Archer, 1999). These instructors will not only be needed within educational institutions, they will also be sought after by public and private sector organizations for professional development initiatives. Nurturing the skills of collaboration within WBL to achieve learning objectives will also carry over into the workplace as professionals collaborate in Web-based work environments. Faculties of Education may become both a focus and

catalyst for modeling WBL integrity and success as a learning environment for other disciplines and professions. This is a challenging responsibility and an opportunity for university educators and educational researchers.

Managing technology

> Once a new technology rolls over you, if you're
> not part of the steamroller, you're part of the road.
> (Brand, 1987, p.9)

Despite this kind of sentiment and, admittedly, the speed-of-light advances in technology, educators must take care not to be "steam-rolled" by advances in technology, but they also must take the driver's seat and use technology to support new educational structures. In kind, we must not push learners into technology-driven environments for the sake of "progress". Learners' adaptation to new learning environments, and their success within them must be nurtured and guided.

It is important to keep advances in technology and their implications for education in perspective. The push to get onto the technology "steamroller" in the late 1980's has, throughout the 1990's, gradually been replaced with a more careful approach to its implementation. The perspective for the twenty-first century seems to be that technological development and use be driven by the requirements of its users. We must take this a step further by highlighting the importance of sound WBL pedagogy as an essential building block for successful WBL (Simonson, 2000; Breithaupt, et. al. 2002). The real future of WBL is not in technology: its future and success lies in the creation of WBL pedagogy to support instructors and learners in the WBL classroom.

Transition to online discussion

Electronic discussion groups, facilitated by WBL tools such as the bulletin board in this case, require the invocation of the recommended components and processes described in this thesis to achieve collaboration among participants. Transposing the best practices of face-to-face communication and collaboration to asynchronous conferencing venues necessitates a different approach than that taken in the traditional classroom. In kind, eliminating negative interaction and communication from these venues also requires an altered pedagogical approach (Davis, 1997). It seems clear, from this study, that achieving collaborative discussion that results in knowledge building requires much structure and guidance in WBL. Whether this is an oxymoron for an inherently constructivist learning environment is yet to be determined, and could be an interesting and valuable topic for another thesis.

Despite their perceived limited ability or inability to construct knowledge, learners were, in some cases grudgingly, positive about their future WBL efforts. They realized that they were making a transition to a new educational environment and, mainly for reasons of convenience and accessibility, they remain committed to WBL as a preferred learning venue. If WBL is to succeed as a constructivist learning environment, it will continue to be important for WBL research to capture learners' perspectives on their experiences in WBL courses (Witherspoon & Johnstone, 2001).

Conclusions

Through the thoughts and emotions described so eloquently and unabashedly by the participants in the study, a solid understanding has been achieved of why learners did

not collaborate in a WBL course. New and deeper insights have contributed to the recommendation of WBL components and processes that will facilitate collaborative discussion in WBL. This also contributes to the development of WBL pedagogy toward the goal of creating an educational structure that becomes an effective and positive constructivist learning environment for learners.

This study has highlighted the fact that WBL as an educational environment is under development, and that its participants are in the process of making a transition from the traditional classroom and distance learning venues. While they are in transition, they are holding on to former learning styles as they find their way within a new educational structure. As they adapt to the new environment and new ways of learning, they perceive new abilities as they construct knowledge. Recent literature puts the transition to WBL into perspective by comparing its development to the evolution of educational structures, from the time of Plato and Aristotle to the present (Logan, 2000). The implications for research are in understanding and accepting that WBL is an educational structure in transition, and that it will be that way for some time. Continued studies of this environment and its participants, such as the present one, will strengthen existing WBL pedagogy and further develop it.

The study extends WBL literature in its descriptions of the factors that created barriers to collaboration, and the impact these factors have on learners' perceived ability to construct knowledge in WBL. Rich descriptions emanating from the data help us to vicariously experience a WBL learning environment by providing a vision of how learners experience WBL (Perkins, 1992). Major barriers to collaboration in WBL are a lack of course direction, management and support for learners, clarity of expectations,

and lack of time. Intertwined with these barriers are other factors such as accessibility to the instructor, difficulty using Website tools, technical failure, lack of learner self-efficacy and motivation, and feelings of isolation, and level of transition. Collectively, these factors formed formidable learner perceptions that prevented them from engaging in collaborative discussion of course content.

I believe new understandings have been achieved as a result of this study. These understandings supplement existing WBL literature by revealing factors that particularly inhibit collaborative discussion in a WBL. The price WBL participants pay for these barriers to collaboration is great. It prevents the co-construction of knowledge in what could be an ideal social-constructivist learning environment (Wilson & Lowry, 2000). It lessens the quality of learning achieved in an environment where high levels of intellectual exchange and growth could easily occur. Regrettably, these barriers prevent participants from establishing intellectual and professional relationships that extended beyond WBL coursework (Trentin, 2001).

The intent of this study was to contribute to WBL pedagogy by constructing an understanding that leads to theoretical refinement and identifying particular needs for further development. It has achieved this goal, and may be incorporated into a growing WBL pedagogy. Ultimately, readers of this study will vicariously experience WBL to some degree, and, hopefully, the experience will be both stimulating and useful.

Recommendations for Further Research

The act of research to find answers to important questions about a phenomenon often creates more questions to be answered. Developing pedagogy for WBL requires much further research for a full understanding of its environment and participants.

The focus on collaboration in WBL is intensifying as studies begin to reveal its significance in the construction of knowledge, and in the creation of learning communities. Further research into how collaborative discussion can be facilitated will be an important contribution to WBL pedagogy. The following recommendations will help to build learner-centred theory. Most will involve research that will test the processes illustrated in this study to determine if the ensuing recommendations actually facilitate collaborative discussion in WBL.

- Given that collaboration is a desired component of a course, further research is required to establish whether learners' perceptions of participation as compulsory facilitates collaborative discussion in the venue provided. The distinction between participating by being present and actually engaging in interactive discussion will be an important consideration.

- Research is also required into the degree to which an initial online meeting of all course participants serves to raise learners' comfort level and reduce their sense of isolation.

- The role of an instructor in facilitating collaborative discussion requires in-depth study. Research into the influence of clarity of expectations and context, as provided by an instructor, also could be a focus within the study.

- Linked to investigating the role of WBL instructors is the need for studying the role played by e-mail and other access to an instructor in creating a barrier to collaboration.

- Studying the best practices of constructivist learning venues outside of WBL may provide insight about how this philosophy could be fostered within WBL.

- Access to technical support in WBL seems to be an ongoing focus of WBL research. A specific focus on the role it plays in facilitating or preventing collaborative discussion would further an important aspect of WBL pedagogy.

- More research into WBL in the workplace would be timely as many public and private enterprises are establishing their own WBL networks, or linking to those provided by colleges and universities. They are doing this because of the demand for continued education by their workforce. It is recommended that areas for research include a focus on: the effect of workplace interruptions on WBL; the influence of management and peer support for learners taking courses through WBL; and on professional certification and the role WBL plays within it.

- Another focus for WBL research is to study ways in which WBL facilitates learning for those with learning disabilities. In this study, a learner who described himself as learning disabled also described himself as more self-efficacious in the WBL environment. Further research into WBL as a venue for learning for those with diagnosed learning disabilities would contribute to the development of an important area of WBL pedagogy.

Parting Reflections and Thoughts for the Future of WBL

When I began this venture into the world of WBL, my goal was to make a contribution to the development of WBL pedagogy. I was excited about the possibilities of this new educational venue and its potential as both a convenient and an effective learning environment. At the same time, I was increasingly concerned about the learners and instructors who were bravely adopting WBL as their classroom and struggling with its many challenges. Some of these challenges were a direct result of design that focused too much on technology and business objectives. Professionally and intuitively, I knew that the design of WBL sites, software, courses and infrastructure had to be approached from a pedagogical perspective for it to be successful.

During the last two years, and, I believe, largely due to WBL researchers, improvements have been made to the WBL environment because the focus is shifting from the mesmerizing advances in technology, to the learners and instructors who populate WBL courses. The continuing affirmation of WBL as a constructivist learning environment has influenced both WBL pedagogy and course design. Researchers, instructors and learners are also discovering the potential for achieving high levels of

learning through an unprecedented opportunity for collaboration in a setting where time and location do not impede participation. In order to achieve this potential, and to create WBL venues that facilitate collaboration, further research and pedagogical development are required.

I have achieved my current objectives in contributing to this effort through this study. I have answered some important questions, and provided findings and recommendations that will further WBL pedagogy and improve WBL as an educational structure. In having done so, however, and despite the inevitable rollercoaster of joy and frustration of the research process, I find I am anxious to delve into further studies to seek answers to questions that have emanated from this one.

WBL is maturing from infancy to toddlerhood. It is still very young and struggling with its first steps, but the promise of its potential integrity and viability as an educational environment is apparent. There are many gaps yet to fill in the research literature, and more studies are required that are conducted in courses that are exclusively online. Much of the research to date has been in courses where WBL activity was only one part. As well, research methodology will continue to evolve to meet the needs of researchers and participants in WBL studies. The prospects for WBL research are numerous and exciting, and will contribute to establishing WBL as a sound educational institution in its own right.

REFERENCES

Ahola-Sidaway, J., MacLean, M., & Treuhaft, J. (1990). Computer-mediated communication and school administrators: A case study of a university in-service course. *Canadian Journal of Educational Communication, 19*, (1), 53-73.

Albright, M., & Graf, D. (1992). *Teaching in the information age: The role of educational technology.* San Francisco: Jossey-Bas Inc.

Alexander, J. O. (1999). Collaborative design, constructivist learning, information technology immersion & electronic communities: A case study. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century*, 7 (1-2), 1-30. Retrieved October 27, 2000, from http://www.jan.ucc.nau.edu/~ipct-j/1999/n1-2/alexander.html

Allegra, M., Chifari, A., Fulantelli, G., & Ottaviano, S. (1999). An online cooperative learning environment. *Canadian Journal of Educational Communications, 26* (2), 125-131.

Anderson, T., & Joerg, W. (1996). WWW to support classroom teaching. *Canadian Journal of Educational Communications, 25*(1), 19-35.

Archer, W., Garrison, R., & Anderson, T. (1999). Adopting disruptive technologies in traditional universities: continuing education as an incubator for innovation [Electronic version]. *The Canadian Journal of University Continuing Education, 25*(1), 1-9.

Bagi, J., & Crooks, S. M. (2001). Synchronous WWW-based course-support system: online constructivist learning [Electronic version]. *Education at a Distance, 15*(4), 1-8.

Bandura, A. (1995). *Self-efficacy in changing societies.* Cambridge: Cambridge University Press.

Barone, C. A., & Luker, M. A. (2000). The role of advanced networks in the education of the future. In Luker, M. A. (Ed.), *Preparing your campus for a networked future.* San Francisco: Jossey-Bass, Inc.

Bates, A. W. (1995). *Technology, open learning and distance education.* London: Routledge.

Bauer, J. F., & Anderson, R. S. (2000). Evaluating students' written performance in the online classroom. In Weiss, R. E., Knowlton, D. S., & Speck, B. W. (Eds.), *Principles of Effective Teaching in the Online Classroom: New Directions for Adult and Continuing Education,* (84), 23-28. San Francisco: Jossey-Bass.

Benigno, V., & Trentin, G. (2000). The evaluation of online courses. *Journal of Computer Assisted Learning, 16,* 259-270.

Benson Soong, M. H., Chan, H.C., Chua, B.C., & Loh, K.F. (2001). Critical success factors for online course resources. *Computers & Education, 36,* 101-120.

Berge, Z. L. (2000). Components of the online classroom. In Weiss, R. E., Knowlton, D. S., & Speck, B. W. (Eds.), *Principles of Effective Teaching in the Online Classroom: New Directions for Adult and Continuing Education,* (84), 23-28. San Francisco: Jossey-Bass.

Bierema, L. L. (1996). Development of the individual leads to more productive workplaces. In Rowden, R. W. *Workplace learning: Debating five critical questions of theory and practice.* San Francisco: Jossey-Bass Inc.

Blanchfield, L., Patrick, I., & Simpson, O. (2000). Computer conferencing for guidance and support in the OU. *British Journal of Educational Technology, 31*(4), 295-306.

Blanton, W., Moorman, G., & Trathen, W. (1997). Telecommunications and teacher education: a social constructivist review. *Review of Research in Education, 23,* 235 - 275.

Bogdan, R., & Biklen, S. (1998). *Qualitative research in education.* Needham Heights, MA: Allyn & Bacon.

Bostock, S. J. (1998). Constructivism in mass higher education: a case study. *British Journal of Educational Technology, 29*(3), 225-240.

Brand, S. (1987). *The media lab: Inventing the future at MIT.* New York: Viking, 1987.

Breithaupt, K., MacDonald, C. J., Stodel, E. J., & Farres, L. G. (in press). Quality standards for Web-based Learning: The Demand Driven Learning Model. *Training and Development Journal.*

Brookfield, S. D. (1986). *Understanding and facilitating adult learning.* San Francisco: Jossey-Bass Inc.

Brown, B. M. (1998). Digital classrooms: Some myths about developing new educational programs using the Internet. *T.H.E. Journal, December,* 1-5. Retrieved February 2, 1999, from http://www.thejournal.com/magazine/comment/feat02.html

Brown, J. S. (2000). Growing up digital. *Change, March/April,* 11-20.

Burge, E. J. (1994). Learning in computer conferenced contexts: The learners' perspective. *Journal of Distance Education, 9*(1), 19-43.

Burge, E. J. (1999). Using learning technologies: Ideas for keeping one's balance. *Educational Technology, 39*(6), 45-49.

Burge, E. J. (2000). Synthesis: Learners and learning are the issues. In Burge. E. (Ed.), *The Strategic Use of Learning Technologies: New Directions for Adult and Continuing Education,* (88), 79-88. San Francisco: Jossey-Bass.

Cahoon, B. (1998). Adult learning and the Internet: Themes and things to come. In Cahoon, B. (Ed.), *Adult Learning and the Internet: New Directions for Adult and Continuing Education,* (78), 71-76. San Francisco: Jossey-Bass.

Canada, M. (2000). Students as seekers in online courses. In Weiss, R. E., Knowlton, D. S., & Speck, B. W. (Eds.), *Principles of Effective Teaching in the Online Classroom: New Directions for Adult andCcontinuing Education*, (84), 35-40. San Francisco: Jossey-Bass.

Card, K. A., & Horton, L. (2000). Providing access to graduate education using computer-mediated communication. *International Journal of Instructional Media, 27*(3), 235-243.

Carr, C. S., & Carr, A. M. (2000). Instructional design in distance education (IDDE): A Web-based performance support system for educators and designers. *The Quarterly Review of Distance Education, 1*(4), 317-325.

Carr-Chellman, A., & Duchastel, P. (2000). The ideal online course. *British Journal of Educational Technology, 31*(3), 229-241

Carstens, R. W., & Worsfold, V. L. (2000). Epilogue: A cautionary note about online classrooms. In Weiss, R. E., Knowlton, D. S., & Speck, B. W. (Eds.), *Principles of Effective Teaching in the Online Classroom: New Directions For Adult And Continuing Education,* (84), 83-87. San Francisco: Jossey-Bass.

Carswell, L., Thomas, P., Petre, M., Price, B., & Richards, M. (2000). Distance education via the Internet: the student experience. *British Journal of Educational Technology, 31*(1), 29-46.

Chaffee, E. E. (2000). Finding the will and the way. In Luker, M. A. (Ed.), *Preparing your campus for a networked future.* San Francisco: Jossey-Bass, Inc.

Christensen, E. W., Anakwe, U. P., & Kessler, E. H. (2001). Receptivity to distance learning: the effect of technology, reputation, constraints, and learning preferences. *Journal of Research on Computing in Education, 33*(3), 263-277.

Clift, R. T., Houston, W. R., & Pugach, M. C. (1990). *Encouraging reflective practice in education.* New York: Teachers College Press.

Cohen, N. H. (1995). *Mentoring adult learners: A guide for educators and trainers.* Malabar, FL: Krieger Publishing Company.

Cox, G. M. (2000). Why I left a university Internet education company. *Change, November/December,* 12-27.

Cramer, S. F. (1994). Assessing effectiveness in the collaborative classroom. In Bosworth, K., & Hamilton, S. J. (Eds.), *Collaborative learning: Underlying processes and effective techniques.* San Francisco: Jossey-Bass Inc.

Creswell, J. (1998). *Qualitative inquiry and research design: Choosing among five traditions.* Thousand Oaks, CA: Sage Publications, Inc.

Cutler, R. H. (1995). Distributed presence and community in cyberspace. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 3 (2),* 12 -32. Retrieved January 5, 1999, from http://www.helsinki.fi/science/optek/1995/n2/cutler.txt

Daeid, N. N. (2001). The development of interactive World Wide Web based teaching materials in Forensic Science. *British Journal of Educational Technology, 32*(1), 105-108.

Dalgarno, B. (2001). Interpretations of constructivism and consequences for computer assisted learning. *British Educational Communications and Technology Agency, 32*(1), 1-11.

Daugherty, M., & Funke, B. L. (1998). University faculty and student perceptions of Web-based Instruction. *Journal of Distance Education, 13*(1), 21-39.

Davis, M. (1997). Fragmented by technologies [1]: A community in cyberspace. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 5(1-2),* 7-18. Retrieved October 27, 2000, from http://www.helsinki.fi/science/optek/1997/n1/davis.txt

De Caprariis, P. (2000). Constructivism in online learning: a view from the science faculty. *Educational Technology, XL*(6), 41-45.

Dede, C. (1995). The evolution of constructivist learning environments: immersion in distributed, virtual worlds. *Educational Technology, 35*(5), 46-53.

Dereshiwsky, M. I., & Moan, E. R. (2000). Good connections: Strategies to maximize student engagement [Electronic version]. *Education at a Distance, 14*(11), 1-54.

Dowling, D. (1997). Teaching literature on the World Wide Web. In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Downing, C., & Rath, G. (1999). The Internet as intranet: Moving toward the electronic classroom. *Journal of Educational Technology Systems, 25*(3), 273-291.

Driscoll, M. (1998). *Web-based training: Using technology to design adult learning experiences.* San Francisco: Jossey-Bass/Pfeiffer.

Duchastel, P. (1997). A Web-based model for university instruction. *Journal of Educational Technology Systems, 25*(3), 221-228.

Duffy, T. M., & Jonassen, D. H. (1992). *Constructivism and the technology of instruction: A conversation.* Hillsdale, NJ: Lawrence Erlbaum Associates, Inc.

Dunlap, J., & Grabinger, S. (1996). Rich environments for active learning in the higher education environment. In Wilson, B. (Ed.), *Constructivist learning environments: Case studies in instructional design.* Englewood Cliffs, NJ: Educational Technology Publications.

Eastmond, D. V., & Rohfeld, R. W. (1993). A report of Syracuse university's computer-facilitated learning program in adult education. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 1*(3), 1-9. Retrieved October 27, 2000, from http://www.helsinki.fi/science/optek/1993/n3/easmond.txt

Ebersole, S. (1997). Cognitive issues in the design and deployment of interactive hypermedia: implications for authoring WWW sites. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 5*(1-2), 1-14. Retrieved October 27, 2000, from http://www.helsinki.fi/science/optek/1997/ebersole.txt

Edelson, D., Pea, R., & Gomez, L. (1996). Constructivism in the collaboratory. In Wilson, B. (Ed.), *Constructivist learning environments: Case studies in instructional design.* Englewood Cliffs, NJ: Educational Technology Publications.

Eisner, E. W. (1991). *The enlightened eye.* New York: Macmillian Publishing Company.

Ellis, A., & Phelps, R. (2000). Managing staff development for Web-based teaching: A four-stage model and its application. In Mann, B. (Ed.), *Perspectives in Web course management.* Toronto, ON: Canadian Scholars' Press, Inc.

Ellsworth, J. H. (1995). Using computer-mediated communication in teaching university courses. In Berge, Z. L., & Collins, M. P. (Eds.), *Computer mediated communication and the online classroom.* Cresskill, NJ: Hampton Press, Inc.

El-Tigi, M., & Branch, R. (1997). Designing for interaction, learner control, and feedback during Web-based Instruction. *Educational Technology, 37*(3), 23-29.

Ely, D. (1999). Toward a philosophy of instructional technology: Thirty years on. *British Journal of Educational Technology, 30*(4), 305-310.

Erskine, L., Carter-Tod, D., & Burton, J. (1997). Dialogical techniques for the design of Web sites. *International Journal of Human-Computer Studies, 47*, 169-195.

Estes, F., & Clark, R. E. (1999). Authentic educational technology: The lynchpin between theory and practice. *Educational Technology, 39*(6), 5-13.

Fabos, B., & Young, M. D. (1999). Telecommunications in the classroom: Rhetoric versus reality. *Review of Educational Research, 69*(3), 217-259.

Ferraris, M., Manca, S., Persico, D., & Sarti, L. (2000). Managing the change from face-to-face to distance training for SMEs. *Computers & Education, 34*, 77-91.

Flannery, J. L. (1994). Teacher as co-conspirator: Knowledge and authority in collaborative learning. In Bosworth, K., & Hamilton, S. J. (Eds.), *Collaborative learning: Underlying processes and effective techniques.* San Francisco: Jossey-Bass Inc.

Forman, J. (1994). Literacy, collaboration, and technology: New connections and challenges. In Selfe, C. L., & Hilligoss, S. (Eds.), *Literacy and computers.* New York: The Modern Language Association of America.

Freitag, E., & Sullivan, H. (1995). Matching learner preference to amount of instruction: An alternative form of learner control. *Educational Technology Research and Development, 43*(2), 5 - 14.

Frost, N., & Taylor, R. (2001). Patterns of change in the university: The impact of 'lifelong learning' and the 'world of work'. *Studies in the Education of Adults, 33*(1), 58.

Fuhrer, U. (1993). Behaviour setting analysis of situated learning: The case of newcomers. In Chaiklin, S. & Lave, J. (Eds.), *Understanding practice: Perspectives on activity and context.* Victoria, Australia: Cambridge University Press.

Furnell, S., Evans, M., & Bailey, P. (2000). The promise of online distance learning: Addressing academic and institutional concerns. *The Quarterly Review of Distance Education, 1*(4), 281-291.

Gabriel, M. A. (1999). Communication and learning: How distance learners construct meaning in the computer conferencing environment. Unpublished doctoral dissertation, University of Ottawa, ON.

Gabriel, M. A. & MacDonald, C. J. (in press). Pursuing an online MBA: Student perspectives. *Canadian Journal of Educational Communications.*

Garmer, A. K., & Firestone, C. M. (1996). *Creating a learning society: Initiatives for education and technology.* Washington, DC: The Aspen Institute.

Gerlach, J. M. (1994). Is this collaboration? In Bosworth, K., & Hamilton, S. J. (Eds.), *Collaborative learning: Underlying processes and effective techniques.* San Francisco: Jossey-Bass Inc.

Gilbert, L., & Moore, D. R. (1998). Building interactivity into Web courses: Tools for social and instructional interaction. *Educational Technology, 38*(3), 29-35.

Glassman, M. (2000). Creating a nexus between tele-teaching and tele-learning. In Mann, B. (Ed.), *Perspectives in Web Course Management.* Toronto: Canadian Scholars' Press, Inc.

Gooler, D. D. (1990). Changing the way we live and learn in the information age. In Smith, R. M. (Ed.), *Learning to learn across the life span.* San Francisco: Jossey-Bass Inc.

Gray, S. (1997). Training teachers, faculty members, and staff. In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Greller, L., & Barnes, S. (1993). Groupware and interpersonal text: The computer as a medium of communication. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 1*(2), 1 - 7. Retrieved May 1, 1999, from http://www.helsinki.fi/science/optek/1993/n2/greller.txt

Grimmett, P. P., & Erikson, G. L. (1988). *Reflection in teacher education.* Vancouver, BC: Pacific Educational Press.

Gruender, D. (1996). Constructivism and learning: A philosophical appraisal. *Educational Technology, 36*(3), 21-28.

Guba, G., & Lincoln, Y. (1994). Competing paradigms in qualitative research. In Denzin, N., & Lincoln, Y. (Eds.), *Handbook of qualitative research.* Thousand Oaks, CA: Sage Publications, Inc.

Hacker, D. J., & Niederhauser, D. S. (2000). Promoting deep and durable learning in the online classroom. In Weiss, R. E., Knowlton, D. S., & Speck, B. W. (Eds.), *Principles of Effective Teaching in the Online Classroom: New Directions For Adult And Continuing Education,* (84), 53-63. San Francisco: Jossey-Bass.

Hamilton, S. J. (1994). Freedom transformed: Toward a developmental model for the construction of collaborative learning environments. In Bosworth, K., & Hamilton, S. J. (Eds), *Collaborative learning: Underlying processes and effective techniques.* San Francisco: Jossey-Bass Inc.

Hammond, M. (2000). Communication within online forums: The opportunities. the constraints and the value of a communicative approach. *Computers & Education, 35.* 251-262.

Hannigan, C., & Browne, M. (2000). Project management: Going the distance. *International Journal of Instructional Media, 27*(4), 343-356.

Hansen, L., & Frick, T. (1997). Evaluation guidelines for Web-based course authoring systems. In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Hara, N., & Kling, R. (2000). Students' distress with a Web-based distance education course. Retrieved October 27, 2000, from Indiana University Website from http://www.slis.indiana.edu/CSI/wp00-01.html

Harasim, L. (1990). *Online education: Perspectives on a new environment.* New York: Praeger Publishers.

Harasim, L., Hiltz, S., Teles, L., & Turoff, M. (1995). *Learning networks: A field guide to teaching and learning online.* Cambridge, MA: The MIT Press.

Harmon, S. W., & Jones, M. G. (1999). The five levels of Web use in education: Factors to consider in planning online courses. *Educational Technology, 39*(6). 28-32.

Haughey, M., & Anderson, T. (1998). *Networked learning: The pedagogy of the Internet.* Montreal, PQ: McGraw-Hill.

Henderson, J.G. (1996). *Reflective teaching: The study of your constructivist practices.* Englewood Cliffs, NJ: Prentice-Hall, Inc.

Hezel, R. T., & Dominguez, P. S. (2001). Strategic planning in e-learning collaborations: A recipe for optimizing success [Electronic version]. *Education at a Distance, 15*(4), 1-2.

Hickey, D. T. (1997). Motivation and contemporary socio-constructivist instructional perspectives. *Educational Psychologist, 32*(3). 175 - 193.

Hidi, S., & Harackiewicz, J. M. (2000). Motivating the academically unmotivated: A critical issue for the 21st century. *Review of Educational Research, 70* (2). 151-179.

Hill, J. (1997). Distance learning environments via the World Wide Web. In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Hill, J., & Hannafin, M. (1997). Cognitive strategies and learning from the World Wide Web. *Educational Technology Research & Development, 45*(4), 37 – 64.

Hill Duin, A., & Hansen, C. (1994). Reading and writing on computer networks as social construction and social interaction. In Selfe, C. L., & Hilligoss, S. (Eds.), *Literacy and Computers.* New York: The Modern Language Association of America.

Hiltz, S.R. (1994). *The virtual classroom: Learning without limits via computer networks.* Norwood, N.J.: Ablex Publishing Corporation.

Holt, M. E. (1998). Ethical considerations in Internet-based adult education. In Cahoon, B. (Ed.), *Adult learning and the Internet.* San Francisco: Jossey-Bass Inc.

Honebein, P. (1996). Seven goals for the design of constructivist learning environments. In Wilson, B. (Ed.), *Constructivist learning environments: Case studies in instructional design.* Englewood Cliffs, NJ: Educational Technology Publications.

Huang, A. (1997). Challenges and opportunities of online education. *Journal of Educational Technology Systems, 25*(3), 229-247.

Hung, D., & Nichani, M. (2001). Constructivism and e-learning: Balancing between the individual and social levels of cognition. *Educational Technology, 41*(2), 40-44.

Ingram, A., L., Hathorn, L. G., & Evans, A. (2000). Beyond chat on the Internet. *Computers & Education, 35,* 21-35.

Janes, D. (2000). International collaborative group interaction: An online experience. In Mann, B. (Ed.), *Perspectives in Web Course Management.* Toronto, ON: Canadian Scholars' Press, Inc.

Jenlink, P., & Carr, A. A. (1996). Conversation as a medium for change in education. *Educational Technology, 36*(1), 31-39.

Johnson, S. M. (2001). Teaching introductory international relations in an entirely Web-based environment [Electronic version]. *Education at a Distance, 15*(1), 1-13.

Johnson-Eilola, J. (1994). Reading and writing in hypertext: Vertigo and euphoria. In Selfe, C. L., & Hilligoss, S. (Eds.), *Literacy and computers.* New York: The Modern Language Association of America.

John-Steiner, V. P., & Meehan, T. M. (2000). Creativity and collaboration in knowledge construction. In Lee, C. D., & Smagorinsky, P. (Eds.), *Vygotskian perspectives on literacy research: Constructing meaning through collaborative inquiry.* Cambridge, U.K.: Cambridge University Press.

Jonassen, D. (1991). Objectivism versus constructivism: Do we need a new philosophical paradigm? *Educational Technology Research and Development, 39*(2), 5 – 14.

Jonassen, D. H., Peck, K. L., & Wilson, B. G. (1999). *Learning with technology: A constructivist perspective.* In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Jonassen, D., Dyer, D., Peters, K., Robinson, T., Harvey, D., King, M., & Loughner, P. (1997). Cognitive flexibility hypertexts on the Web: Engaging learners in meaning making. In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Jonassen, D., Myers, J. M., & McKillop, A. (1996). From construtivism to constructionism: Learning *with* hypermedia/multimedia rather than from it. In Wilson, B. (Ed.), *Constructivist learning environments: Case studies in instructional design.* Englewood Cliffs, NJ: Educational Technology Publications.

Jung, I. (2000). Technology innovations and the development of distance education: Korean experience. *Open Learning, 15*(3), 217-231.

Kang, S. (2001). Toward a collaborative model for the design of Web-based courses. *Educational Technology, 41*(2), 22-30.

Kearsley, G. (2000). *Online education: Learning and teaching in cyberspace.* Canada: Wadsworth, a division of Thomson Learning, Inc.

Kent, T. W., & McNergney, R. F. (1999). *Will technology really change education?* Thousand Oaks, CA: Corwin Press, Inc.

King, S. (1994). Analysis of electronic support groups for recovering addicts. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 2*(3), 47 - 56. Retrieved May 1, 1999, from http://www.helsinki.fi/science/optec/1994/n3/king.txt

Kirsh, D. (1997). Interactivity and multimedia interfaces. *Instructional Science, 25*(2), 79-96.

Kitchen, D., & McDougall, D. (1999). Collaborative learning on the Internet. *Journal of Educational Technology Systems, 27*(3), 245-257.

Knowlton, D. S. (2000). A Theoretical framework for the online classroom: A defense and delineation of a student-centred pedagogy. In Weiss, R. E., Knowlton, D. S., & Speck, B. W. (Eds.), *Principles of Effective Teaching in the Online Classroom: New Directions For Adult And Continuing Education,* (84), 5-14. San Francisco: Jossey-Bass.

Kook, J. (1997). Computers and communication networks in educational settings in the twenty-first century: Preparation for educators' new roles. *Educational Technology, 37*(2), 56-61.

Land, S., & Hannafin, M. (1997). Patterns of understanding with open-ended learning environments: a qualitative study. *Educational Technology Research & Development, 45*(2), 47 – 73.

Langer, E. (1997). *The power of mindful learning.* Reading, MA: Addison-Wesley Longman, Inc.

Lauzon, A. C. (1999). Situating cognition and crossing borders: Resisting the hegemony of mediated education. *British Journal of Educational Technology, 30*(3), 261-276.

Lave, J., & Wenger, E. (1991). *Situated learning: Legitimate peripheral participation.* Cambridge: Cambridge University Press.

Lawless, K., & Brown, S. (1997). Multimedia learning environments: Issues of learner control and navigation. *Instructional Science, 25*(2), 117-131.

Lebow, D. (1993). Constructivist values for instructional systems design: Five principles toward a new mindset. *Educational Technology Research and Development, 41*(3), 4 – 16.

Lee, C. (1999). An exploration of pedagogical implications of using networked-based computer mediated communication in the communicative language classroom. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 7*(2), 1-17.

Lewe, G. (1997). Reflections on workplace education and learning. In Taylor, M. C. (Ed.), *Workplace education: The changing landscape.* Toronto, ON: Culture Concepts Inc.

Lewis, J., Whitaker, J., & Julian, J. (1995). Distance education for the 21st century: The future of national and international telecomputing networks in distance education. In Berge Z. L., & Collins, M. P. (Eds.), *Computer Mediated Communication & the Online Classroom (Vol. 3 - Distance Learning).* Creshill, NJ: Hampton Press Inc.

Lewis, R. (1999). The role of technology in learning: Managing to achieve a vision. *British Journal of Educational Technology 30*(2), 141-150.

Logan, F. A., & Ferraro, D. P. (1978). *Systematic analyses of learning and motivation.* New York: John Wiley & Sons, Inc.

Logan, R. K. (2000). *The sixth language.* Toronto, ON: Stoddart Publishing Co. Limited.

Lohr, L., Ross, S., & Morrison, G. (1995). Using a hypertext environment for teaching process writing: An evaluation study of three student groups. *Educational Technology Research and Development, 43*(2), 5 - 51.

Lougher, N. (1980). The technology of teaching: Art or science? In Winterburn, R., & Evans, L. *Educational Technology to the Year 2000.* London: Kogan Page Limited.

Luker, M. A. (2000). What campus leaders can do today. In Luker, M. A. (Ed.), *Preparing your campus for a networked future.* San Francisco: Jossey-Bass, Inc.

MacDonald, C.J., Breithaupt, K., Stodel, E., Farres, L., & Gabriel, M. (2001). Evaluation of Web-based educational programs: A pilot study of the Demand-Driven Learning Model. *The Internet and Higher Education: A Quarterly Review of Innovations in Post-Secondary Education, 4*(1), 9 - 30.

MacDonald, C. J, & Gabriel, M. A. (1999). Toward a partnership model for Web-based Learning. *The Internet and Higher Education: A Quarterly Review of Innovations in Post-Secondary Education, 1*(3), 203 - 216.

Mann, C., & Stewart, F. (2000). *Internet communication and qualitative research.* London: Sage Publications Inc.

Marchese, T. (2000). Learning and e-learning. *Change, September/October, 4.*

Marcinkiewicz, H. R. (1993-94). Computers and teachers: factors influencing computer use in the classroom. *Journal of Research on Computing in Education, 26* (2), 220 - 237.

Marina, S. T. (2001). Facing the challenges, getting the right way with distance learning [Electronic version]. *Education at a Distance, 15*(3), 1-10.

Marjanovic, O. (1999). Learning and teaching in a synchronous collaborative environment. *Journal of Computer Assisted Learning,* (15), 129-138.

Marshall, C., & Rossman, G. (1996). *Designing qualitative research.* Thousand Oaks, CA: Sage Publications, Inc.

Martin, R. (1997). Key issues in transitioning from distance education to distributed learning. *Online Chronicle of Distance Education & Communication, 12*(1), 1 - 5. Retrieved May 1, 1999, from http://www.fcae.nova.edu/disted/sprin/98/martin.html

Maule, R. W. (1993). The network classroom. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 1*(1), 1 -12. Retrieved May 1, 1999, from http://www.helsinki.fi/science/optek/1993/n1/maule.txt

Maxwell, J. (1996). *Qualitative research design.* Thousand Oaks, CA: Sage Publications, Inc.

Mayer, R. E. (1997). Multimedia learning: Are we asking the right questions? *Educational Psychologist, 31*(1), 1 - 19.

McConnell, D. (2000). *Implementing Computer Supported Cooperative Learning.* London: Kogan Page.

McConnell, D. (2002). The experience of collaborative assessment in e-learning. *Studies in Continuing Education, 24*(1), 73-92.

McCormack, C., & Jones, D. (1998). *Building a Web-based education system.* New York: John Wiley & Sons, Inc.

McIssac, M., & Gunawardena, C. (1996). Distance education. In Jonassen, D. (Ed.), *Handbook of research for educational communications and technology.* New York: Simon & Schuster MacMillan.

McMahnon, M. (1996). Significant absences. *Qualitative Inuiry, 2*(3), 320 – 336.

Merriam, S. (1988). *Case study research in education.* San Francisco: Jossey-Bass Inc.

Merriam, S. (1998). *Qualitative research and case study applications in education.* San Francisco: Jossey-Bass Inc.

Mitchell, C., Kerr, J., & DiPetta, T. (1998). *The frontier of Web-based Instruction or how several faculties of education and individual faculty members came to understand and love (or hate) Web-based course delivery in late 20th century Ontario.* Unpublished paper presented at the meeting of the Congress of the Social Sciences and Humanities.

Moller, L. A., Harvey, D., Downs, M., Godshalk, V. (2000). Identifying factors that effect learning community development and performance in asynchronous distance education. *The Quarterly Review of Distance Education, 1*(4), 293-305.

Morrison, D., & Collins, A. (1996). Epistemic fluency and constructivist learning environments. In Wilson, B. (Ed.), *Constructivist learning environments: Case studies in instructional design.* Englewood Cliffs, NJ: Educational Technology Publications.

Morrison, G. R. (2001). Theory, research and practice [Electronic version]. *Education at a Distance, 15*(4), 1-3.

Morrison, G. R., & Guenther, P. F. (2000). Designing instruction for learning in electronic classrooms. In Weiss, R. E., Knowlton, D. S., & Speck, B. W. (Eds.), *Principles of Effective Teaching in the Online Classroom. New Directions For Adult And Continuing Education, (84),* 15-22. San Francisco: Jossey-Bass.

Moyse, R., & Elsom-Cook, M. (1992). *Knowledge negotiation.* London: Academic Press Inc.

Muire, C., Nazarian, M. J., & Gilmer, P. J. (1999). Web-based technology in a constructivist community of learners. *British Journal of Educational Technology 30*(1), 65-68.

Muirhead, B. (2001). Enhancing social interaction in computer-mediated distance education [Electronic version]. *Education at a Distance, 15*(4), 1-22.

Nelson, C. E. (1994). Critical thinking and collaborative learning. In Bosworth, K., & Hamilton, S. J. (Eds.), *Collaborative learning: Underlying processes and effective techniques.* San Francisco: Jossey-Bass Inc.

Newman, D., Johnson, R., Cochrane, C., & Webb, B. (1996). An experiment in group learning technology: Evaluating critical thinking in face-to-face and computer-supported seminars. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 4*(1), 57 -74. Retrieved May 1, 1999, from http://www.helsinki.fi/science/optek/1996/n1/newman.txt

Newman, D., Webb, B., & Cochrane, C. (1995). A content analysis method to measure critical thinking in face-to-face and computer supported group learning. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 3* (2), 56 -77. Retrieved May 1, 1999, from http://www.helsinki.fi/science/optek/1996/n1/newman.txt

Nielsen, J., & Tahir, M. (2000). Keep your users in mind [Electronic version]. *Internet World Magazine, December,* 1-4.

Northrup, P. (2001). A framework for designing interactivity into Web-based instruction. *Educational Technology, 41*(2), 31-39.

Oliver, K. M. (2000). Methods for developing constructivist learning on the Web. *Educational Technology, XL*(6), 5-15.

Oliver, R., & Omari, A. (2001). Student responses to collaborating and learning in a Web-based environment. *Journal of Computer Assisted Learning, 17*, 34-47.

Page, R. N. (2000). Future Directions in Qualitative Research. *Harvard Educational Review, 70*(1), 100-108.

Passerini, K., & Granger, M. J. (2000). A developmental model for distance learning using the Internet. *Computers & Education, 34*, 1-15.

Perkins, D. N. (1992). What constructivism demands of the learner. In Duffy, T. M. & Jonassen, D. H. (Eds.), *Constructivism and the technology of instruction: A conversation.* Hillsdale, NJ: Lawrence Erlbaum Associates, Inc.

Perkins, D. N. (1991). What constructivism demands of the learner. *Educational Technology, September*, 19-21.

Piantanida, M., & Garman, N. B. (1999). *The qualitative dissertation: A guide for students and faculty.* Thousand Oaks, CA: Corwin Press.

Poole, D. M. (2000). Student participation in a discussion-oriented online course: A case study. *Journal of Research on Computing in Education, 33*(2), 162-177.

Reeves, T., & Okey, J. (1996). Alternative assessment for constructivist learning environments. In Wilson, B. (Ed.), *Constructivist learning environments: Case studies in instructional design.* Englewood Cliffs, NJ: Educational Technology Publications.

Reigeluth, C. M., & Squire, K. (1998). Emerging work on the new paradigm of instructional theories. *Educational Technology, 38*(4), 41- 47.

Relan, A., & Gillani, B. (1997). Web-based Instruction and the traditional classroom: Similarities and differences. In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Rodrigues, S. (2000). The Interpretive zone between software designers and a science educator: Grounding instructional multimedia design in learning theory. *Journal of Research on Computing in Education, 33*(1), 1-15.

Rogoff, B. (1997). Observing sociocultural activity on three planes: Participatory appropriation, guided participation, and apprenticeship. In Wertsch, J., Del Rio, P., & Alvarez, A. (Eds.), *Sociocultural studies of mind.* Cambridge: Cambridge University Press.

Ross, J. A. (1998). Differential participation of males and females in a computer-mediated communication course [Electronic version]. *The Canadian Journal of Continuing Education, 24* (1), 1-9.

Rowden, R. W. (1996). Current realities and future challenges. In Rowden, R. W. (Ed.), *Workplace learning: Debating five critical questions of theory and practice.* San Francisco: Jossey-Bass Inc.

Ruokamo, H., & Pohjolainen, S. (2000). Distance learning in a multimedia networks project: Main results. *British Journal of Educational Technology, 31*(2), 117-125.

Santoro, G. M. (1995). What is computer-mediated communication. In Berge, Z. L., & Collins, M. P. (Eds.), *Computer mediated communication and the online classroom.* NJ: Hampton Press, Inc.

Savenye, W. C., & Robinson, R. S. (1997). Qualitative research issues and methods: An introduction for educational technologists. In Savenye, W. C., & Robinson, R. S. (Eds.), *Research Methodologies in Educational Communications and Technology.* NJ: Educational Technology Publications, Inc.

Saye, J. (1997). Technology and educational empowerment: Students' perspectives. *Educational Technology Research & Development, 45*(2), 5 – 25.

Schoenfeld, A. H. (1999). Looking toward the 21st century: Challenges of educational theory and practice. *Educational Researcher, 28*, (7), 4-14.

Schon, D. A. (1987). *Educating the reflective practitioner.* San Francisco, CA: Jossey-Bass Inc.

Schrum, L. (1998). Online education: A study of emerging pedagogy. In Cahoon, B. (Ed.), *Adult Learning and the Internet: New Directions For Adult And Continuing Education*, (78), 53-61. San Francisco: Jossey-Bass.

Schrum, L., & Benson, A. (2000). Lessons to consider: Online learning from student and faculty perspectives. In Mann, B. (Ed.), *Perspectives in Web Course Management.* Toronto, ON: Canadian Scholars' Press, Inc.

Schwandt, T. (1994). Constructivist, interpretivist approaches to human inquiry. In Denzin, N., & Lincoln, Y. (Eds.), *Handbook of qualitative research.* Thousand Oaks, CA: Sage Publications, Inc.

Seale, J., & Cann, A. J. (2000). Reflection online or off-line: The role of learning technologies in encouraging students to reflect. *Computers & Education, 34*, 309-320.

Sexton, T. L. (1997). Constructivist thinking within the history of ideas: The challenge of a new paradigm. In Sexton, T. L., & Griffin, B. L. (Eds.), *Constructivist thinking in counseling practice, research, and training.* New York: Teachers College Press.

Shimabukuro, J. N. (1995). CMC and writing instruction: A future scenario. In Berge, Z. L., & Collins, M. P. (Eds.), *Computer mediated communication and the online classroom.* NJ: Hampton Press, Inc.

Shotsberger, P. G. (1997). Emerging roles for instructors and learners in the Web-based Instruction classroom. In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Silberger, K. (1995). The higher education electronic infrastructure: The impact on libraries and computer centres. In Berge, Z. L., & Collins, M. P. (Eds.), *Computer mediated communication and the online classroom.* NJ: Hampton Press, Inc.

Silva, M., & Breuleux, A. (1994). The use of participatory design in the implementation of Internet-based collaborative learning activities in K-12 classrooms. *Interpersonal Computing and Technology: An Electronic Journal for the 21st Century, 2* (3), 99 -128. Retrieved May 1, 1999, from http://www.helsinki.fi/science/optek/1994/n3/silva.txt

Simonson, M. (2000). Making decisions: The use of electronic technology in online classrooms. In Weiss, R. E., Knowlton, D. S., & Speck, B. W. (Eds.), *Principles of Effective Teaching in the Online Classroom: New Directions For Adult And Continuing Education, (84),* 29-34. San Francisco: Jossey-Bass.

Sloffer, S., Dueber, B., & Duffy, T. (1999). *Critical thinking in an asynchronous conferencing system: An examination of three university courses.* Unpublished paper presented at the meeting of the American Educational Research Association, Montreal, PQ.

Smith, W. A. S., & Stroud, M. A. (1982). Distance education and new communications technologies. In Knapper, C. K. (Ed.), *Expanding Learning Through New Communications Technologies: New Directions For Teaching And Learning, March*(9), 6-20.

Spiro, R., Feltovich, P., Jacobson, M., & Coulson, R. (1991). Cognitive flexibility, constructivism, and hypertext: Random access instruction for advanced knowledge acquisition in ill-structured domains. *Educational Technology, 31*(5), 24-33.

Stake, R. E. (1995). *The art of case study research.* Thousand Oaks, CA: Sage Publications, Inc.

Stathakos, J., & Davie, L. (2000). *Learning partnerships in the online classroom: A collaborative design model.* Unpublished paper presented at the TCC 2000 Conference.

Sullivan, P. (1994). Computer technology and collaborative learning. In Bosworth, K., & Hamilton, S. J. (Eds.), *Collaborative learning: Underlying processes and effective techniques.* San Francisco: Jossey-Bass Inc.

Tapscott, D., Lowy, A., & Ticoll, D. (1998). *Blueprint to the digital economy.* New York: McGraw-Hill.

Tough, A. (1990). Encouraging self-planned learning. In Smith, R. M. (Ed.), *Learning to learn across the life span.* San Francisco: Jossey-Bass Inc.

Trentin, G. (1998). Computer conferencing systems as seen by a designer of online courses. *Educational Technology, 38*(3), 36-43.

Trentin, G. (1999). Network-based collaborative education. *International Journal of Instructional Media, 26,* (2), 145-157.

Trentin, G. (2001). From formal training to communities of practice via network-based learning. *Educational Technology, 41*(2), 5-14.

Turoff, M. (1997). Alternative futures for distance learning: The force and the darkside. Paper presented at the UNESCO/OPEN UNIVERSITY International Colloquium, Paris, France. April 27-29. Retrieved April 2, 2001, from http://www.westqa.edu/~distance/turoff11.html

Valde, R., Bower, R., & Thomas, R. (1996). Developing preservice teacher's computer competencies. *Journal of Technology and Teacher Education, 4* (2), 83 - 90.

Van den Berg, R. (1999). The permanent importance of the subjective reality of teachers during educational innovation: A concerns-based approach. *American Educational Research Journal, 36,* (4), 879-906.

Van Manen, M. (1990). *Researching lived experience: Human science for an action sensitive pedagogy.* University of Western Ontario, London, ON: The Althouse Press.

Weiss, R. E. (2000). Humanizing the online classroom. In Weiss, R. E., Knowlton, D. S., & Speck, B. W. (Eds.), *Principles of Effective Teaching in the Online Classroom: New Directions For Adult And Continuing Education, (84),* 47-51. San Francisco: Jossey-Bass.

Westera, W., & Sloep, P. (1998). The virtual company; toward a self-directed. competence-based learning environment in distance education. *Educational Technology. 38(1),* 32-36.

White, C. (2000). Collaborative online course development: converting correspondence courses to the Web. *Educational Technology, XL*(6), 58-60.

Willis, B. & Dickinson, J. (1997). Distance education and the World WideWeb. In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Wilson, B. (1996). *Constructivist learning environments: Case studies in instructional design.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Wilson, B., & Lowry, M. (2000). Constructivist learning on the Web. In Burge. E. (Ed.), *The Strategic Use of Learning Technologies: New Directions For Adult And Continuing Education, (88),* 79-88. San Francisco: Jossey-Bass.

Witherspoon, J. P., & Johnstone, S. M. (2001). Quality in online education: Results from a revolution [Electronic version]. *Education at a Distance, 15*(3), 1-12.

Yakimovicz, A. D., & Murphy, K. L. (1995). Constructivism and collaboration on the Internet: Case study of a graduate class experience. *Computers Education, 24*(3), 203-209.

Yin, R. K. (1984). *Case study research: Design and methods.* Beverly Hills, CA: Sage Publications, Inc.

Zellner, R. (1997). Management of instructional materials and student products in Web-based Instruction. In Khan, Badrul H. (Ed.), *Web-based Instruction.* Englewood Cliffs, NJ: Educational Technology Publications, Inc.

Appendix A – Message of Introduction

June XX, 2000

To: Course Participants – Writing Skills 2
From: Deborah Tiwari
Re: Participation in Doctoral Research Study

The [departmental learning Website] Manager has informed me that you have expressed interest in participating in my doctoral research study about "Issues Affecting Collaboration Among Learners in a Web-based Learning Environment". I am thrilled that you are able to participate.

The study will take place, approximately, over an _8 - 10_ week timeframe, commencing June 26, and ending August 31, 2000 (approximately). During this time, I will be occasionally observing interaction among participants as it happens in the course venue provided for this activity via the Website. I will also interview you about your thoughts and feelings about learning in a Web-based environment. I will also provide you with an electronic template for a weekly journal in which to document your reflective thoughts and feelings about learning in WBI.

Before I may begin the study, I require your signature on the attached consent form which outlines the purpose of the study and the extent of your participation in it. If you have any questions. feel free to either call me or e-mail me at the number and e-mail address on the form.

I will be contacting you by e-mail soon to arrange an interview, and to provide you with some guidance and the electronic template for your personal reflections regarding the course.

I look forward to meeting you, and I am very appreciative and excited about your participation in my doctoral research study.

Deborah E. Tiwari
dtiwari@cyberus.ca

Background and Experience of Researcher-Participant

Background

Deborah Tiwari holds a B.A. (English honours program), a B.Ed. (English, reading strategies, and communications arts), and a Master's degree in Education (thesis on Reader Response and English Curricula). Deborah is presently a senior advisor and consultant to private and public sector clients. She has a family, and is a volunteer at her son's school, whenever time permits, to help children with reading difficulties.

Experience

Deborah was a co-researcher in a qualitative study about children's activities during the Ottawa ice storm in January 1998. The study was conducted in partial fulfillment of the requirements of a doctoral qualitative research course. In-depth interviews, participant observation and reflective journals were used for data collection.

During ten years spent working in the telecommunications industry, Deborah managed market development and research. As part of this role, she selected appropriate research methodology for market research, supervised data collection and performed data analysis and interpretation.

Deborah has taught English literature at the secondary level, English as a second language at the university level, and English for business at the college level in regular and distance education programs.

Appendix B – Informed Consent

Informed Consent

Participant Consent - Students

Principal Investigator: Deborah E. Tiwari
Affiliation: Doctoral Student, University of Ottawa
Telephone number: (613) 841-7099; E-Mail: dtiwari@cyberus.ca

Whenever a research project is undertaken with human participants, the written consent of the participants must be obtained. This does not imply that the project in question necessarily involves a risk. In view of the respect owed the participants, the University of Ottawa and the research funding agencies have made this type of agreement mandatory.

The purpose of the study is to capture and interpret data on the issues that affect the ability of Web-based Instruction (WBI) learners to collaborate amongst themselves during a course, and to understand the nature of collaboration among WBI learners in terms of how it contributes to the process of constructing learning in WBI. The research will be conducted by Deborah Tiwari, Ph.D. student in the Faculty of Education, University of Ottawa, and supervised by Dr. C.J. MacDonald of the Faculty of Education, University of Ottawa.

If I agree to participate, my participation will consist of the following:

1) To keep a reflective journal for the period of the study (from the beginning of the course through to course conclusion), in which I will note my thoughts and feelings about my experiences during the WBI course.

2) To participate in three, twenty-five (25) minute (approximately) interviews with the researcher (at the beginning, near the mid-point, and near the end of the course), and to review the transcript of each interview to verify the content.

3) To allow the researcher to observe me when I am engaged online either in computer conferencing or on the course bulletin board with other course participants, at any time during the course.

I am free to withdraw from the project at anytime, before or during an interview, I may refuse to participate, and refuse to answer questions, without consequences.

I have received assurance from the researcher that the information I will share will remain strictly confidential. I, in turn, assure other participants that I will treat in the same confidential manner any information I may obtain in the context of this project. I understand that pseudonyms will be used for participants in the study. I understand that information obtained by the researcher will be stored in a secure manner in a locked cabinet for a period of not less than seven (7) years.

Any information, requests or complaints about the ethical conduct of the project may be addressed to the Research Ethics Board (613-562-5800, ext. 4057). If I have any questions, I may contact Professor Colla MacDonald, Tel. (613)562-5800 (ext.4110). There are two copies of the consent form, one of which I may keep.

_____ _____

Participant's signature Date

_____ _____

Researcher's signature Date

_____ _____

Research Supervisor's signature Date

I,_____, am interested in participating in the study Issues Affecting Collaboration Among Learners in a Web-based Learning Environment conducted by Ph.D. student Deborah E. Tiwari and supervised by Dr. C.J. MacDonald of the Faculty of Education of the University of Ottawa.

Optional: I wish to receive a summary of the findings of this study which will be available by December, 2000(approximate date), at the following address:

_____.

Informed Consent

Participant Consent – Non-learners

Principal Investigator: Deborah E. Tiwari
Affiliation: Doctoral Student, University of Ottawa
Telephone number: (613) 841-7099; E-Mail: dtiwari@cyberus.ca

Whenever a research project is undertaken with human participants, the written consent of the participants must be obtained. This does not imply that the project in question necessarily involves a risk. In view of the respect owed the participants, the University of Ottawa and the research funding agencies have made this type of agreement mandatory.

The purpose of the study is to capture and interpret data on the issues that affect the ability of Web-based Instruction (WBI) learners to collaborate amongst themselves during a course, and to understand the nature of collaboration among WBI learners in terms of how it contributes to the process of constructing learning in WBI. The research will be conducted by Deborah Tiwari, Ph.D. student in the Faculty of Education, University of Ottawa, and supervised by Dr. C.J. MacDonald of the Faculty of Education, University of Ottawa.

If I agree to participate, my participation will consist of the following:

1) To keep a reflective journal for the period of the study (from the beginning of the course through to course conclusion), in which I will note my thoughts and feelings about my experiences during the WBI course.

2) To participate in one sixty (60) minute interview with the researcher and to review the transcript of the interview to verify the content.

I am free to withdraw from the project at anytime, before or during an interview, I may refuse to participate, and refuse to answer questions, without consequences.

I have received assurance from the researcher that the information I will share will remain strictly confidential. I, in turn, assure other participants that I will treat in the same confidential manner any information I may obtain in the context of this project. I understand that pseudonyms will be used for participants in the study. I understand that information obtained by the researcher will be stored in a secure manner in a locked cabinet for a period of not less than seven (7) years.

Any information, requests or complaints about the ethical conduct of the project may be addressed to the Research Ethics Board (613-562-5800, ext. 4057). If I have any questions, I may contact Professor Colla MacDonald, Tel. (613)562-5800 (ext.4110). There are two copies of the consent form, one of which I may keep.

_____ _____

Participant's signature Date

_____ _____

Researcher's signature Date

_____ _____

Research Supervisor's signature Date

I,_____, am interested in participating in the study Issues Affecting Collaboration Among Learners in a Web-based Learning Environment conducted by Ph.D. student Deborah E. Tiwari, and supervised by Dr. C.J. MacDonald of the Faculty of Education of the University of Ottawa.

Optional: I wish to receive a summary of the findings of this study which will be available by December, 2000 (approximate date), at the following address:

_____.

Appendix C – Message 2 to Participants

Hi X:

Thank you for agreeing to participate in my research study.

I would like to arrange a time next week for our first interview. Would (time) on (date) be convenient? If not, please suggest a time that is good for you. I want this to be convenient for your schedule, so please feel free to suggest a time that works best for you.

Also, for your weekly reflection, I've written a bit of a guideline for participants; I don't want this to be a time-consuming chore, so I hope this will be helpful for you. I am trying to capture all perspectives of all participants involved in any way with the course. Some guidance as follows:

Please write down your thoughts and feelings about your learning experiences with the Web-based course through the [departmental learning Website]. This may be as long or as short as you wish. If possible, please think about your experience immediately after your interaction with the Website, the instructor, and with learners in the course. In particular, please write about your thoughts and feelings about your interactions through e-mail and the Website bulletin board. Please be assured that what you write is strictly confidential. At the end of each week, beginning this week and ending on August 31, 2000, please send your thoughts to me at: dtiwari@cyberus.ca

Each time you note your thoughts and feelings, please include the information below:

Date:
Time:
Web-based Activity:
Purpose of Activity:
Duration of Activity:

What I thought and felt while doing the above activities: write about your thoughts and feelings - as much as you like.

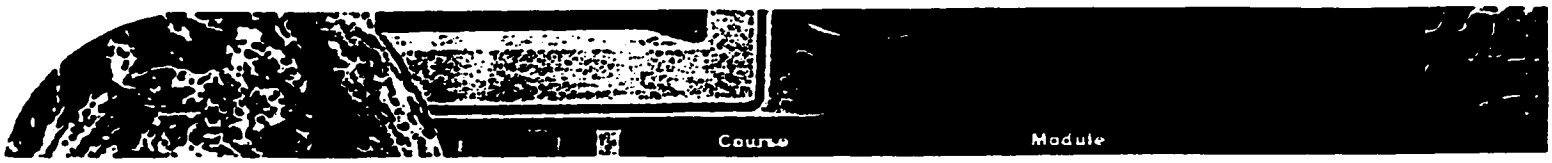
Thanks, X. I hope to hear from you soon. Or, if you prefer, please call me at (613) 841-7099.

Thanks again,

Deborah Tiwari

Appendix D - Course Map/Outline and Course Objectives

Course Map/Outline



Resource Centre | **Writing Skills II** | **Course Map**

On-Line Documents

Books, Videos, CDs

My Notepad

Utilities / Tools

Bulletin Board

Help

Course Evaluation

Navigation

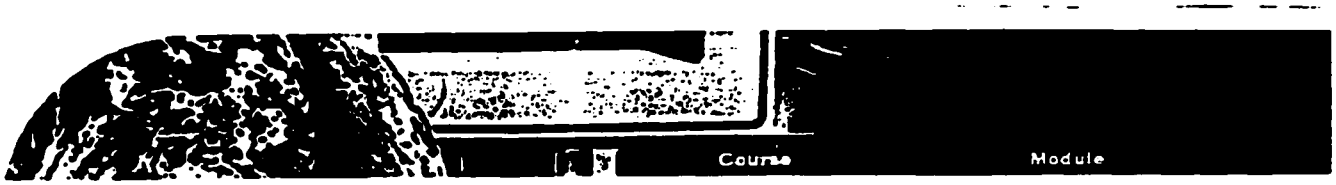
Course Map

Course Menu

Back To Campus

Course Map

Module 1 - Opening	Module 2 - Organizing Yourself to Write	Module 3 - The Active Voice	Module 4 - Review and Revise Your Writing	Module 5 - Business Writing	Course Post Quiz
1.3 Sharpening the Saw	2.3 Two Writing Tasks	3.3 The Passive Minutes	4.3 One Step at a Time	5.4 Keep it Simple	6.0 Course Post Quiz
1.4 Self-Assessment	2.4 A Writing Checklist	3.4 Active VS Passive	4.4 Editing / Proofreading	5.5 Open / Closings	
1.5 Just Checking	2.5 Prepare a Document	3.5 Active / Passive Voice	4.5 Write First; Edit Afterwards	5.6 Improve Openings	
1.8 Part 2 Course Highlights	2.6 Overcoming Writer's Block	3.6 Identifying the Passive Voice	4.6 Editing Exercise	5.7 Improving Closings	
1.9 Part 3 Active Voice	2.7 Why Brainstorming Works	3.7 Active / Passive Voice	4.7 Spell Checker	5.8 Practice Openings Lines	
	2.8 Brainstorming	3.8 Write in the Active Voice	4.8 Proofreading Exercise	5.9 Tone in Business Writing	
	2.9 Brainstorming Instructions	3.9 How Active is Your Voice	4.9 Fog Index?	5.10 Checklist for Business Letters & Memos	
	2.10 How to Structure Your Writing	3.10 A Strong Writing Style	4.10 Calculate the Fog Index	5.11 Check Your Files	
	2.11 Finders Keepers	3.11 Concrete Language	4.11 Calculating the Fog Index	5.12 Messages for Electronic Mail	
	2.12 Finders Keepers	3.12 Wordiness	4.12 Writing Less Foggy	5.13 Do's & Don'ts of Email	
	2.13 Choosing a Structure	3.13 Wordiness & Tone	4.13 Checking Your Fogginess	5.14 More Do's and Don'ts	
	2.14 Choose Your Structure	3.14 Challenge Activity	4.14 Challenge Activity	5.15 Learning Activity: More Do's & Don'ts	
	2.15 Challenge Activity	3.15 Test Your Learning - Part 3	4.15 Wasted Words	5.16 Report Writing	
	2.16 Test Your Learning - Part 2			5.17 Structuring Your Report	
				5.18 Linking Ideas	



On-Line Documents
Books, Videos, CDs
My Notepad

Utilities / Tools

Bulletin Board
Help
Course Evaluation

Navigation

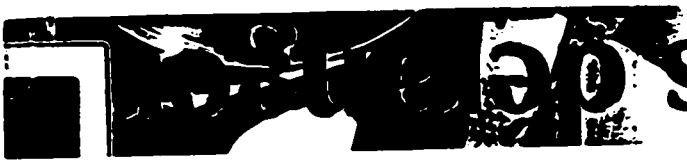
Course Map
Course Menu
Back To Campus

About This Course

Learning Objectives

- assess your own level of knowledge about writing
- experiment with Brainstorming as a technique for getting started on a writing task
- become familiar with the most commonly-used writing structures
- explore techniques for improving writing style
- ensure written work meets the highest standards
- practice techniques for editing and proofreading
- review practices of clear and simple business writing
- examine structure for writing reports

Desk notice



Door notice

Please
DO NOT
DISTURB

Appendix F – Instruments

1. Interview Guide (General Questions)

Interview Guide for Interview 1 with Learners

1) Can you tell me about your various experiences with using computers and taking courses through web-based instruction – both positive and negative?
2) Can you describe X problem in more detail, and what you do when X happens?
3) Can you describe what is better or worse about learning through WBI compared to other learning venues?
4) Can you tell me about your expectations for this course?
5) Can you describe the kind of interaction you have had with other WBI learners?
6) Can you describe how interaction with other learners helps or hinders learning in WBI?
7) Can you describe how interacation has helped you in this course?
8) Can you describe ways in which you have used text or symbols to express tone or feeling through your written text when you are interacting with other learner(s)?

Interview Guide for Interviews 2 & 3 with Learners

1) Can you describe how the communication you are having with other learners in this course is better/worse than in other WBI courses you have taken?
2) Can you describe how the communication you are having with other learners in this course is better/worse than in other learning environments?
3) How would you characterize the interaction you are having with the other learners in this course?
4) Can you describe how interaction in this course has helped you learn. (Examples)
5) Can you describe ways in which you use text or symbols to convey tone or feeling in your written text when you are communicating with other learners in this course. (Examples)
6) Can you describe how has the instructor has communicated and interacted with learners in this course?
7) Based on your experience in this course, how would you compare the interaction and communication to what you have experienced in other WBI courses? (Examples)
8) Based on your experience in this course, how would you compare your ability to learn in WBI to other learning environments?
9) Can you describe how your expectations about this course are or are not being met?
10) Can you tell me about the kinds of improvements you would make for learning in WBI?

Interview Guide for Interview with:

Course Instructor, Technical Support Administrator, and Virtual Campus Manager

1) Can you describe your role in course delivery through Web-Based Instruction?
2) Can you describe your role in facilitating communication among learners in WBI?
3) Can you describe the issues that you think impact learners' ability to collaborate among themselves in WBI, in general, and for the learners in this course?
4) Can you describe how interaction among learners in WBI, both asynchronous and synchronous, contributes to their learning?
5) Can you describe your vision of the ideal WBI course?

2. Template for Reflective Journals

Personal Reflective Journal

.....

Guide: Please write about your thoughts and feelings about your learning experiences in this web-based course through the Virtual Campus. Your reflection may be as lengthy or as brief as you wish. If possible, please reflect upon your experience immediately after your interaction with the website, the instructor, and with other learners in the course. In particular, please document your thoughts and feelings about your interactions through e-mail, the website bulletin board and the website chatroom. Please be assured that your reflection is strictly confidential. At the end of each week, beginning this week and for the duration of the course, please send your reflective journal to me at:
dtiwari@cyberus.ca

.....

For each reflection, please include the information below:

Date:
Time:
Web-based Activity:
Purpose of Activity:
Duration of Activity:

Reflection:

Université d'Ottawa • University of Ottawa

PERMISSION DE REPRODUIRE ET DE DISTRIBUER LA THÈSE

PERMISSION TO REPRODUCE AND DISTRIBUTE THE THESIS

NOM DE L'AUTEUR / NAME OF AUTHOR	Bernard G. Van Den Hoven
ADRESSE POSTALE / MAILING ADDRESS:	23880 Thompson Gate Richmond BC V6V 1C5
GRADE / DEGREE:	**ANNÉE D'OBTENTION / YEAR GRANTED**
Ph.D. (Chemistry)	2002
TITRE DE LA THÈSE / TITLE OF THESIS:	
New Innovations in Rhodium Catalyzed Transformation of *a*-Functionalized Alkynes Utilizing Carbon Monoxide and Hydrogen	

L'auteur permet, par la présente, la consultation et le prêt de cette thèse en conformité avec les règlements établis par le bibliothécaire en chef de l'Université d'Ottawa. L'auteur autorise aussi l'Université d'Ottawa, ses successeurs et cessionnaires, à reproduire cet exemplaire par photograhie ou photocopie pour fins de prêt ou de vente au prix coûtant aux bibliothèques ou aux chercheurs qui en feront la demande.

Les droits de publication par tout autre moyen et pour vente au public demeureront la propriété de l'auteur de la thèse sous réserve des règlements de l'Université d'Ottawa en matière de publication de thèses.

The author hereby permits the consultation and the lending of this thesis pursuant to the regulations established by the Chief Librarian of the University of Ottawa. The author also authorizes the University of Ottawa, its successors and assignees, to make reproductions of this copy by photographic means or by photocopying and to lend or sell such reproductions at cost to libraries and to scholars requesting them.

The right to publish the thesis by other means and to sell it to the public is reserved to the author, subject to the regulations of the University of Ottawa governing the publication of theses.

N.B. LE MASCULIN COMPREND ÉGALEMENT LE FÉMININ

October 23, 2002 — Bernard G. Van Den Hoven

DATE — (AUTEUR) SIGNATURE (AUTHOR)

Université d'Ottawa · University of Ottawa

Université d'Ottawa • University of Ottawa

FACULTÉ DES ÉTUDES SUPÉRIEURES ET POSTDOCTORALES

FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

VAN DEN HOVEN, Bernard G.

AUTEUR DE LA THÈSE - AUTHOR OF THESIS

Ph.D. (Chemistry)

GRADE - DEGREE

Chemistry

FACULTÉ, ÉCOLE, DÉPARTEMENT - FACULTY, SCHOOL, DEPARTMENT

TITRE DE LA THÈSE - TITLE OF THE THESIS

New Innovations in Rhodium Catalyzed Transformation of α-Functionalized Alkynes Utilizing Carbon Monoxide and Hydrogen

Howard Alper

DIRECTEUR DE LA THÈSE - THESIS SUPERVISOR

EXAMINATEURS DE LA THÈSE - THESIS EXAMINERS

M. Doyle

A. Fallis

W. Ogilvie

D. Richeson

J.-M. De Koninck, Ph.D.

LE DOYEN DE LA FACULTÉ DES ÉTUDES SUPÉRIEURES ET POSTDOCTORALES

SIGNATURE

DEAN OF THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

New Innovations in Rhodium Catalyzed Transformation of α-Functionalized Alkynes Utilizing Carbon Monoxide and Hydrogen

by

BERNARD G. VAN DEN HOVEN

A Thesis Submitted to the Faculty of Graduate and Postdoctoral Studies
In Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

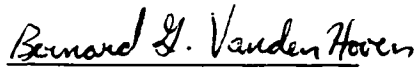
Ottawa-Carleton Chemistry Institute

&

Centre for Catalysis Research and Innovation

Department of Chemistry
University of Ottawa
Ottawa, Ontario
Canada

Ph.D. Candidate



Bernard G. Van den Hoven

Supervisor

Professor Howard Alper

THE UNIVERSITY OF OTTAWA
October 2002

To My Wife

Table of Contents

Acknowledgements

I would like to express my gratitude to my supervisor, Professor Howard Alper, for his kindness, generosity, and encouragement to try my own ideas even though they did not always work well. Without his support the work presented in this thesis would not have been possible. He is a great teacher, friend and mentor, and I will cherish the time I have spent in Ottawa.

Next I would like to thank my wife, Jie Zhan, whose friendship, support and understanding during these past 2 years of my graduate studies has been my motivation. Mostly I want to thank her for her love and support, which was continuous and unconditional. Her presence in my life has meant more to me than she could possibly know.

My family has also been a great support for me, and I would like to thank my mother and father, as well as my brothers and sisters for their love and encouragement to study, and always do my best even during difficult times.

I would also like to thank my friends and colleagues that I have met here in Ottawa. Special thanks go to Drs. Wen-Jing Xiao, Shlomo Antebi, Eun-Joo Jang, Soumen Sensarma, Shui-Ming Lu, Yong-Shou Lin as well as Christine Bourque, and Jan Reynhardt for their help and friendship throughout the years.

Finally, last but by no means least, I would like to extend my deepest thanks to the support staff within the Department of Chemistry and Faculty of Science at the University of Ottawa for their help, support and whose presence has made this thesis possible.

Abstract

Identifying the important roles that functional groups play when substituted alkynes are placed under hydroformylation conditions (reactions incorporating carbon monoxide and hydrogen gas with catalytic amounts of a rhodium complex) is a valuable tool for organic synthesis. Novel and unexpected chemistry have resulted from establishing the primary and secondary roles of certain functional groups. The primary role is the ability to direct a rhodium complex to add to a triple bond, and the secondary role involves directing the type of chemistry that will take place after the addition. The following examples demonstrate this dual relationship resulting in the preparation of α,β-unsaturated aldehydes, N-heterocyclic enols, and important ring systems with potential biological activity. The selected 5-membered heterocycles generated are important materials in treating inflammatory diseases, cancer and heart disease, as well as allowing for the inhibition of HIV protease (see page xvi).

The reaction of aliphatic 1-en-3-ynes (**2.2**) with synthesis gas (12 atm) in the presence of the zwitterionic rhodium complex, (η^6-$C_6H_5BPh_3$)$^-$Rh$^+$(1,5-COD) (**1.1**) (4 mol %), and triphenyl phosphite (16 mol %) at 60 °C affords formyl-dienes (**2.3**) in high regioselectivity. This catalytic system provides a useful method for the hydroformylation of both non-functionalized and functionalized conjugated enynes under mild conditions, affording formyl-dienes in 50 to 70 % isolated yields.

The hydroformylation of 2-acetylenic thiophenes (**3.4**) is readily accomplished by using the zwitterionic rhodium catalyst **1.1** (2 to 4 mol %) and triphenyl phosphite (8 to 16 mol %) in the presence of CO and H_2 (18 atm, 2:1) at 60 °C. This catalytic system

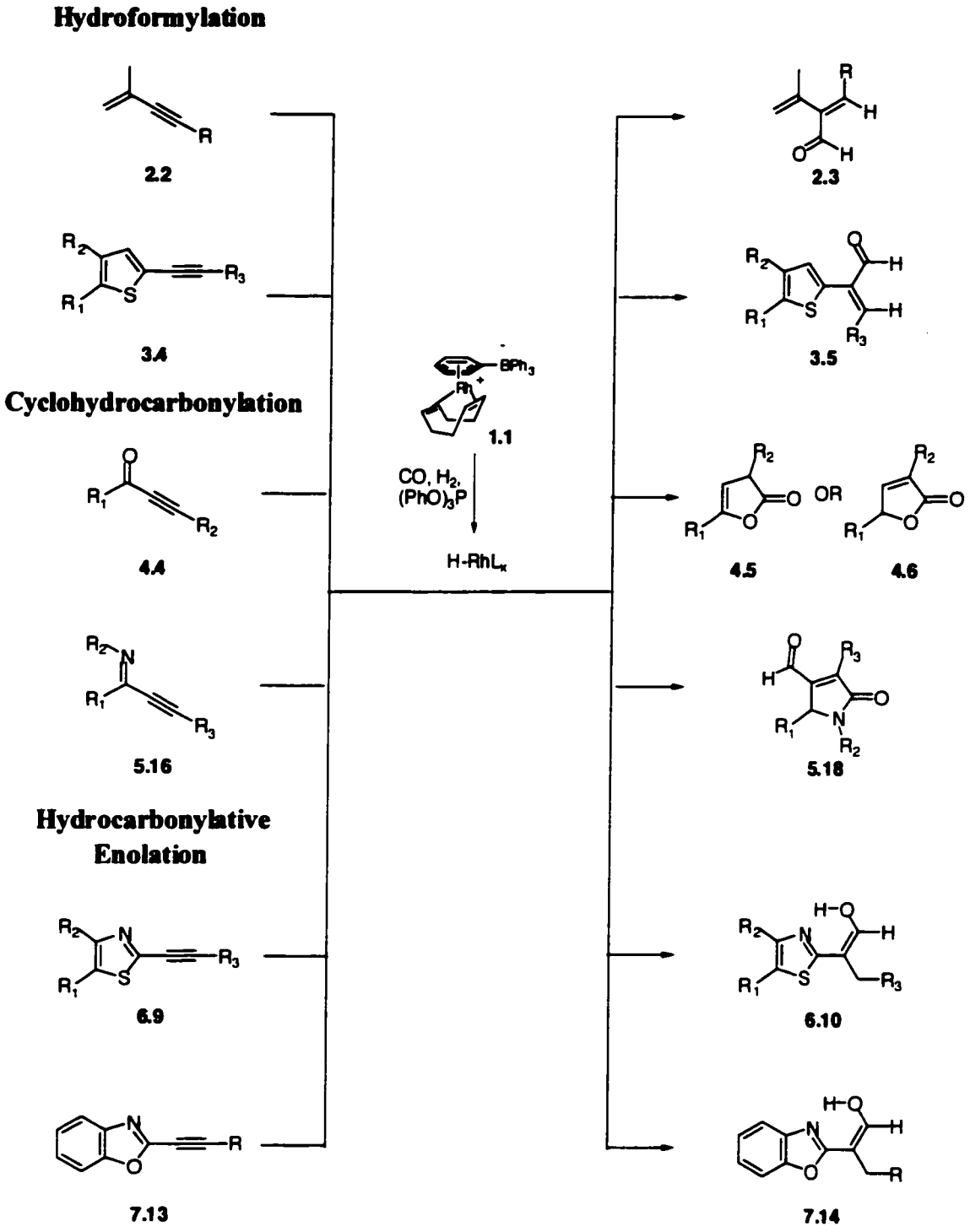
affords, as the major product, the α,β-unsaturated aldehyde with the aldehyde and thiophene attached to the same olefin carbon atom (**3.5**). Assistance of sulfur from the heterocycle provides excellent regioselectivities of 64 to 100 % and additive yields of 65 to 97 % when the acetylenic unit is a propargyl ether or ester, phenylacetylene, or an enyne.

α-Keto alkynes (**4.4**) react with CO and H_2 (21 atm using a 5:1 ratio or 42 atm for a 1:1 ratio) in the presence of catalytic quantities of the zwitterionic rhodium complex **1.1** (2 mol %) and triphenyl phosphite (8 to 32 mol %) at 70 to 120 °C to form either the 2-, 2(3*H*)- (**4.5**) or 2(5*H*)-furanones (**4.6**) in 61 – 93 % yields. The cyclohydrocarbonylation reaction is readily accomplished using substrates containing alkyl, aryl, vinyl, and alkoxyl groups at the acetylenic terminal, as well as a variety of primary, secondary and tertiary alkyl, aryl, and hetero-aryl groups connected to the ketone functionality. Structural and electronic properties present in the starting materials mediate the chemo- and regioselectivity of the reaction.

The tandem cyclohydrocarbonylative/CO insertion of α-imino alkynes (**5.16**) employs CO, H_2 (21 atm, 5: 1 or 42 atm, 11:1), and catalytic quantities of the zwitterionic rhodium complex **1.1** (2 mol %) and triphenyl phosphite (8 mol %) at 75 to 100 °C affording aldehyde substituted pyrrolinones (**5.18**) in 67 to 82 % yields. This unique transformation is readily applied to α-imino alkynes containing alkyl, alkoxy, vinyl, and aryl substituents. The ability to prepare highly functionalized pyrrolinones makes this an attractive route to important and versatile pharmaceuticals such as piracetam, oxiracetam, and dimiracetam.

Hydrocarbonylative enolation of 2-acetylenic thiazoles (**6.9**) in the presence of CO, H_2 (21 atm, 1:1), and catalytic quantities of the zwitterionic rhodium complex **1.1** (2 mol %) and triphenyl phosphite (8 mol %) at 70 to 110 °C affords (*Z*)-2-thiazol-2-ylalk-1-en-1-ols (**6.10**) in 61 to 90 % yields. This novel transformation of a 5- heterocycle is readily applied to 2-acetylenic thiazoles containing hydro, alkyl, alkyl halide, vinyl, and benzo substituents in positions 4 and 5 of the thiazole ring in addition to alkyl, ether, ester, vinyl, and aryl substituted alkynes at position 2.

Hydrocarbonylative enolation of 2-acetylenic benzoxazoles (**7.13**) in the presence of CO, H_2 (21 atm, 1:1), and catalytic quantities of the zwitterionic rhodium complex **1.1** (2 mol %) and triphenyl phosphite (8 mol %) at 90 - 110 °C affords (*Z*)-2-benzoxazol-2-ylalk-1-en-1-ols (**7.14**) in 37 to 87 % yields. This transformation of a benzo-heterocycle is readily applied to 2-acetylenic benzoxazoles with alkyl, chloroalkyl, and aryl substituted alkynes at position 2.


Hydroformylation
2.2
2.3
3.4
3.5
Cyclohydrocarbonylation
1.1
CO, H2,
(PhO)3P
H-RhLx
4.4
4.5
OR
4.6
5.16
5.18
Hydrocarbonylative
Enolation
6.9
6.10
7.13
7.14

List of Schemes

List of Tables

Alkynyl Units

List of Figures

List of Abbreviations

Ac	Acetyl
acac	Acetylacetonate
Ar	Aryl
atm	Atmosphere
br	Broad
Bu	Butyl
Bz	Benzyl
CN	Cyano or Nitrile
CO	Carbon Monoxide
COD	1,5-Cycooctadiene
COSY	Correlated Spectroscopy
Cp	Cyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Cy	Cyclohexyl
CTAB	Cetyltrimethylammonium Bromide
d	Doublet
dd	Doublet of Doublets
dba	Dibenzylidene acetone
DME	Dimethoxyethane
DMF	N,N-Dimethyl formamide
Dppb	1,4-Bis(diphenylphosphino)butane

EA	Elemental Analysis
EI	Electron Ionization
Et	Ethyl
FAB	Fast Atom Bombardment
GC	Gas Chromatography
h	Hour
HPLC	High Performance Liquid Chromatography
HRMS	High Resolution Mass Spectroscopy
Hz	Hertz
IR	Infrared Spectroscopy
L	Ligand
Me	Methyl
m/e or m/z	Charge to Mass Ratio
M_n	Number Average Molecular Weight
Mp	Melting Point
MS	Molecular Spectroscopy
M_w	Weight Average Molecular weight
NMR	Nuclear Magnetic Resonance
NOE	Nuclear Overhauser Effect
NOESY	Nuclear Overhauser and Exchange Spectroscopy
PDI	Polydispersity Index (M_w/M_n)
Ph	Phenyl
PhH	Benzene

ppm	Parts per Million (δ scale)
psi	Pounds per Square Inch
q	Quartet
R	Substituent
RI	Refractive Index
R_L	Large Substituent
R_S	Small Substituent
RT or r.t.	Room Temperature
s	Singlet
t	Triplet
tBDMS	tert-Butyldimethylsilyl
THF	Tetrahydrofuran
THP	Tetrahydropyranyl
TMS	Trimethylsilyl
UV	Ultraviolet

CHAPTER 1

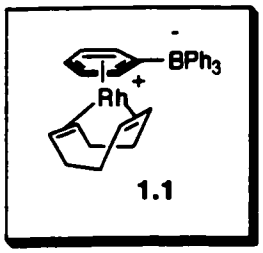
GENERAL INTRODUCTION

This thesis will describe our research on the zwitterionic rhodium catalyzed hydroformylation of α-functionalized alkynes and related reactions.

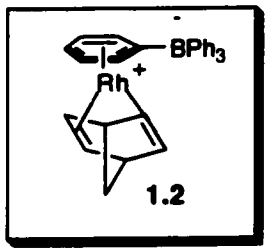
In the general introduction to follow, we will focus on the chemistry performed by zwitterionic rhodium complexes including hydroformylation, carbonylation and non-carbonylative based chemistry. The vast carbonylation chemistry of alkynes will also be discussed in Chapter 1 due to the importance of alkynes in this thesis. Hydroformylation reactions of conjugated enynes and 2-acetylenic thiophenes will be described in Chapters 2 and 3. Specifically, we will describe an important catalyst system for the controlled hydroformylation of internal alkynes to α,β-unsaturated aldehydes, and investigate how functionalities influence the ratios of isomeric unsaturated aldehydes, as well as organize th categorization of functional groups toward strong and weak stereochemical control. In Chapters 4 and 5 our efforts toward the cyclohydrocarbonylation of α-keto- and α-iminoalkynes to afford their corresponding 5–membered unsaturated lactone and lactam ring systems will be discussed utilizing hydroformylation type conditions. The novel hydrocarbonylative enolation of 2-acetylenic thiazoles and oxazoles to their pharmacologically important thiazolylenol and oxazolylenol ring systems will be explored in Chapters 6 and 7.

1.1 Introduction to the Chemistry of the Zwitterionic Rhodium Complexes (η^6-$C_6H_5BPh_3$)$^-$Rh$^+$(1,5-COD) and (η^6-$C_6H_5BPh_3$)$^-$Rh$^+$(Norbornadiene)

In 1970, Schrock and Osborn discovered an anomalous behavior when tetraphenylborate was utilized as an anion towards cationic rhodium complexes in place of perchlorate or hexafluorophosphate.[1] The tetraphenylborate group was capable of readily coordinating to transition metals via a π-bonded interaction of one of the phenyl rings. Such transition metal complexes were readily isolated by further complexation with diolefins. Two diolefinic complexes are shown below, in particular the (η^6-$C_6H_5BPh_3$)$^-$Rh$^+$(1,5-cyclooctadiene) **1.1** and (η^6-$C_6H_5BPh_3$)$^-$Rh$^+$(norbornadiene) **1.2**.



1.1



1.2

The initial hope for these complexes with zwitterionic characteristics was to function as homogeneous hydrogenation catalysts for the reduction of olefins,[2] ketones,[3] acetylenes,[4] and diolefins.[5]

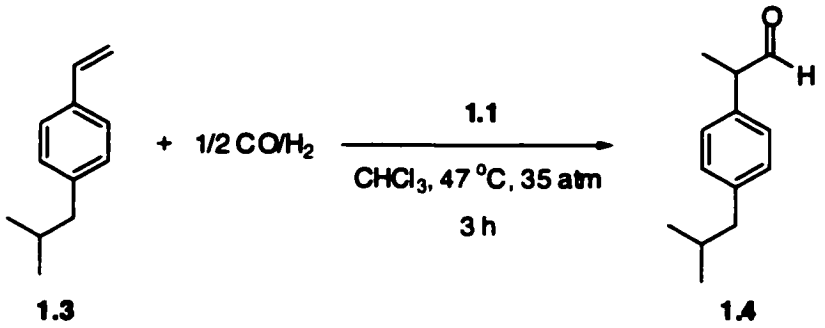
In 1990, new interest in these complexes arose for the hydroformylation of olefins.[6] The dual behavior of cationic rhodium and anionic boron was anticipated to result in a unique catalytic environment directing the regiochemistry of the hydroformylation process. The resulting cationic rhodium hydride created from a CO/H_2

atmosphere and subsequent alkyl intermediates may be more susceptible to olefin coordination (and metal hydride addition) and then carbonyl insertion, respectively. In addition, the anionic triphenylboron substituent attached to the arene ring may exert steric and/or electronic effects subject to the stereochemistry of the intermediate which also has the olefin bound to the rhodium. The ability of the zwitterionic rhodium to regioselectively hydroformylate olefins has since been extended to olefins that are simple and functionalized, as well as the tandem hydroformylative hydroamination of alkenes, and the silylhydroformylation, silylformylation, and germylformylation of alkynes. The following section will cover the innovative nature of the zwitterionic rhodium complexes toward reactive substrates showing both its regio- and chemoselectivity, and its potential for new chemistry.

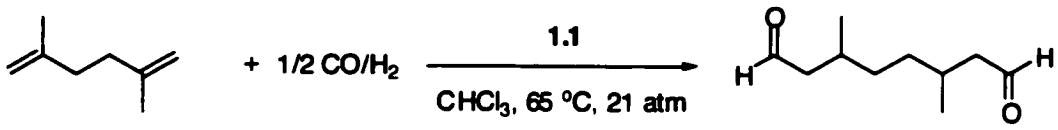
1.1.1 Reactions with Alkenes

1.1.1.1 Hydroformylation

In 1990, Amer and Alper[6] reported the first use of the zwitterionic complex (**1.1**) to catalyze the hydroformylation of olefins. A wide range of olefins were reacted under exceptionally mild conditions (14 - 35 atm CO/H_2 (1/2), 47 - 80 °C and 1 mol % **1.1**), and the process was highly regioselective for certain classes of alkenes, including aryl olefins, vinyl ethers, and 1,1-disubstituted olefins.

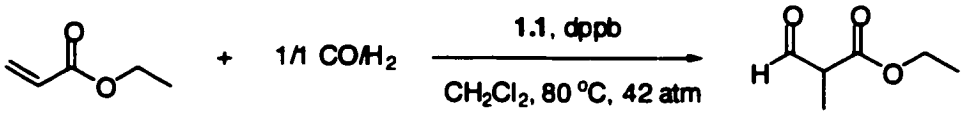


1.3 1.4 (1-1)



1.5 1.6 (1-2)

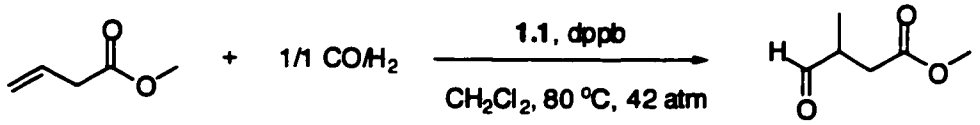
The hydroformylation of isobutylstyrene (**1.3**) to 2-(4-isobutylphenyl)propanal (**1.4**) was achieved in quantitative conversion and isolated yield (Eq 1-1). This is significant since subsequent oxidation of the aldehyde affords ibuprofen, a leading nonsteroidal anti-inflammatory agent. In addition, both aromatic and aliphatic 1,1-disubstituted olefins undergo hydroformylation affording the linear aldehyde as the only product (Eq 1-2). For example, 2,5-dimethyl-1,6-hexadiene (**1.5**) is cleanly converted to 3,6-dimethyloctane-1,8-dial (**1.6**) in 90 % yield.



1.7 1.8 (1-3)

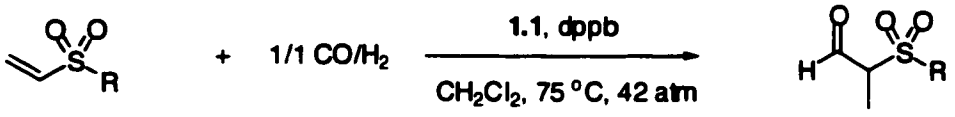
Further studies by Alper and Zhou took advantage of the beneficial influence of 1,4-bis(diphenylphosphino)butane (dppb) in conjunction with the zwitterionic rhodium

complex **1.1** on functionalized alkenes. The hydroformylation of α,β-unsaturated esters was achieved in excellent regioselectivities for the branched chain aldehydic ester.[7] Treatment of ethyl acrylate (**1.7**) with synthesis gas (42 atm), 1 mol % **1.1**, and 2 mol % dppb, at 80 °C afforded the branched chain aldehyde **1.8** in 98 % selectivity and 79 % isolated yield (Eq 1-3). The regiochemistry of the zwitterionic complex-dppb catalytic system is consistently superior to other rhodium complexes affording branched aldehydic esters in yields of 56 to 79 %.[8]



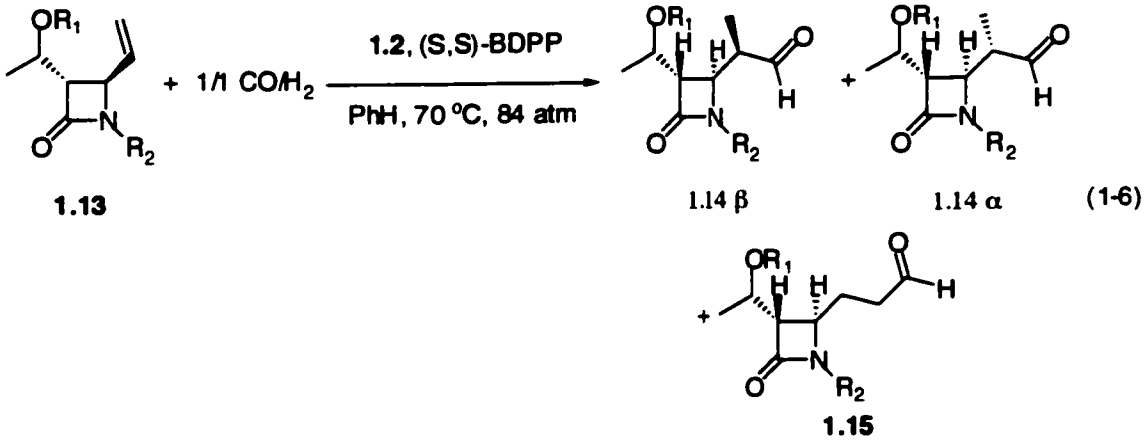
1.9 **1.10** (1-4)

The same conditions were also applied to allyl acetate (**1.9**) and related compounds, to form branched aldehydes (**1.10**) in high selectivity and yields (Eq 1-4).[9] Branched to linear ratios ranging from 70:30 to 97:3 were found depending on the substituents. The zwitterionic rhodium complex and dppb system did not catalyze the hydroformylation of allyl acetates having a disubstituted double bond (both 1,1- and 1,2-disubstituted allyl acetates).



1.11 **1.12** (1-5)

A series of vinyl sulfones (**1.11**) were subjected to hydroformylation by Alper and Totland in the presence of **1.1** to give only branched-chain aldehydes (**1.12**) in 83 – 98 % yields (Eq 1-5).[13] In all cases, the hydroformylation of vinyl sulfones in the presence of 2 equivalents of dppb relative to **1.1** at 42 atm of CO/H_2 (1/1) and 75 °C, resulted in complete conversion of the starting material. Although the hydroformylation of phenyl vinyl sulfoxide[13] was not as facile as the vinyl sulfones, the corresponding aldehyde was obtained in as much as 50 % yield. Applying the hydroformylation reaction to organic sulfur compounds, particularly sulfones and sulfoxides, is important from a synthetic standpoint.[10] Molecules containing a sulfone moiety are useful for chain extension reactions due to the good leaving group ability of the RSO_2 unit.[11] Sulfoxides are often used in aldol-type condensations to make chain extensions en route to the synthesis of natural products.[12]



1.13 **1.14 β** **1.14 α** (1-6)

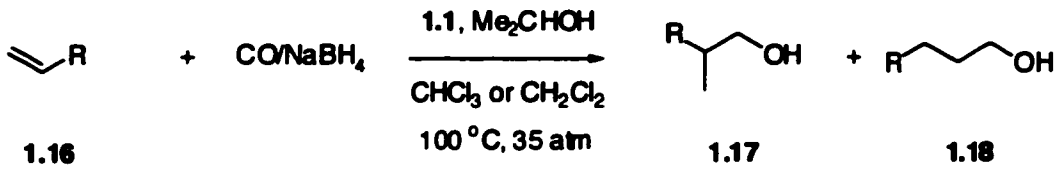
1.15

The hydroformylation of a variety of 4-vinyl β-lactams (**1.13**) was explored by Alper and Park utilizing the zwitterionic rhodium complex **1.2** in the presence of chiral ligands, ultimately generating an important aldehyde precursor to the unnatural

antibiotics of 1-methylcarbapenems.[14] Steric and electronic effects of substrates at several positions of the β-lactam were investigated leading to the determination of the optimal R_1 and R_2 substituents (Me, TBS, BOC). The zwitterionic rhodium complex **1.2** and (*S*,*S*)-2,4-bis(diphenylphosphino)pentane catalyzed the hydroformylation of 4-vinyl β-lactams to the **1.14β** aldehyde in regioselctivities of 60 – 99 % and diastereoselectivities of 80 to > 99 % **de** (Eq 1-6).

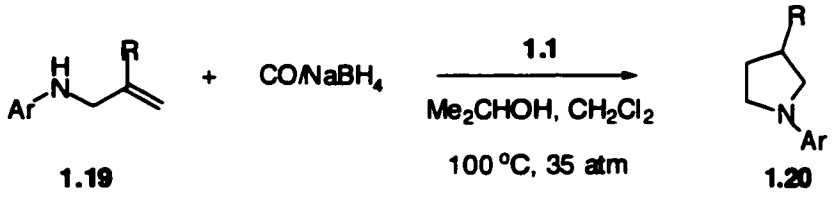
1.1.1.2 Reductive Carbonylation

Another important process introduced by Alper and Zhou is the conversion of alkenes to alcohols by reductive carbonylation. The use of **1.1** for achieving the regioselective synthesis of branched or linear alcohols is subject to the nature of the alkene reactant.[15] These constitute the first examples of a borohydride based hydroformylation reaction, as well as the first regioselective route to branched chain alcohols from styrene derivatives. Treatment of **1.16** with 1 equivalent of sodium borohydride, 1 mol % of **1.1**, and 35 atm of carbon monoxide at 100 °C afforded branched alcohols (**1.17**) in 75 to 95 % regioselectivities for aryl substituted alkenes, and linear alcohols (**1.18**) in 90 to 100 % regioselectivities when aliphatic olefins are subject to the same conditions respectively (Eq 1-7). The additive yields of both the branched and linear alcohols total 70 to 90 %.



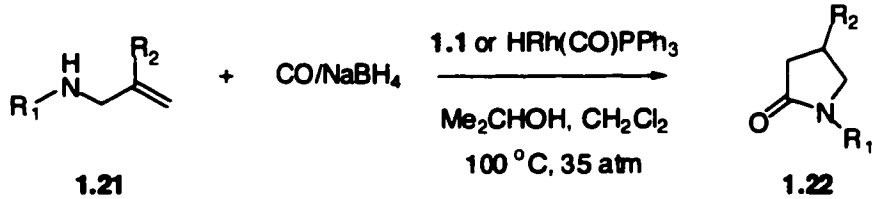
1.16 1.17 1.18 (1-7)

The carbonylation of allylic amines utilizing relatively mild conditions by **1.1** in the presence of sodium borohydride, selectively provides pyrrolidines (**1.20**) or pyrrolidinones (**1.22**) in good yields.[16]



1.19 1.20 (1-8)

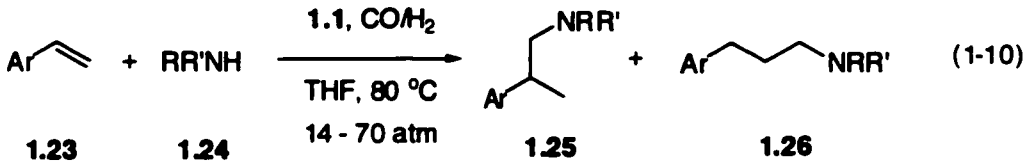
Substituted N-allylanilines (**1.19**) afforded 1-arylpyrrolidines (**1.20**) in 30 to 84 % isolated yields (Eq 1-8). Pyrrolidinones (**1.22**) were isolated as the only product when aliphatic N-allyl or N-(methylallyl) amines (**1.21**) were reacted with an excess of $NaBH_4$, 1 mol % **1.1**, and 35 atm of CO at 100 °C in 20 – 90 % yields (Eq 1-9).



1.21 1.22 (1-9)

1.1.1.3 Hydroaminomethylation

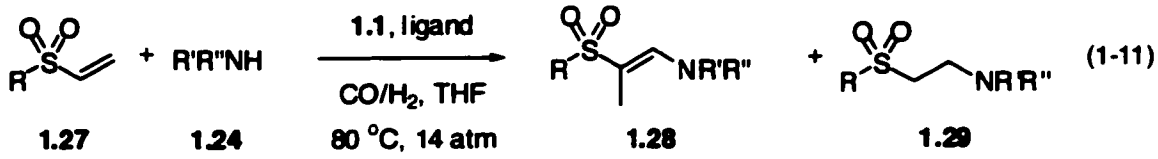
The hydroaminomethylation of various aryl olefins (**1.23**) carried out by Alper and coworkers utilized the zwitterionic rhodium complex **1.1** as the catalyst, under relatively mild conditions. The corresponding branched methylated amines (**1.25**) were obtained in high regioselectivites and isolated yields of 60 to 85 % (Eq 1-10).[17] Substituted aromatic rings (**1.23**) in conjunction with primary and secondary amines (**1.24**) react with 0.5 % **1.1**, 14 to 70 atm of synthesis gas at 80 °C to readily form the hydroaminomethylated products in 24 hours.



1.1.1.4 Hydroaminovinylation

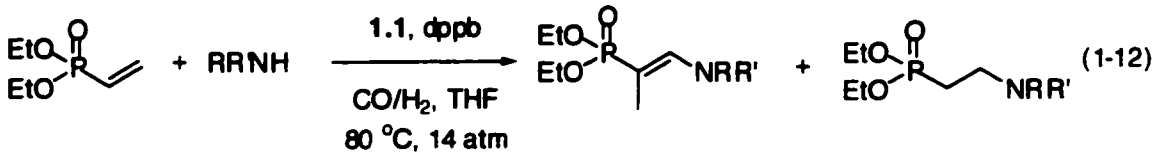
Functionalized vinyl sulfones and phosphonates have wide applications in organic synthesis.[18] Organonitrogen-based vinyl sulfones and vinyl phosphonates are important intermediates involved in biochemical syntheses.[19,20] As an extension to hydroaminomethylation just described, Alper and coworkers reacted vinyl sulfones and a vinyl phosphonate under hydroaminomethylation conditions. Methyl, ethyl, and phenyl substituted vinyl sulfones (**1.27**) react with a variety of amines (both primary and secondary) to give the branched hydroaminovinylation products **1.28** (Eq 1-11).[21]

Utilizing 1 mol % **1.1**, excess amine, the bidentate ligands ±BINAP or dppb, and 14 atm of synthesis gas at 80 °C affords **1.28** in 43 to 89 % isolated yields.



1.27 **1.24** **1.28** **1.29**

The hydroaminovinylation of diethyl vinyl phosphonate (**1.30**), using the above catalytic system of **1.1**/dppb, and in the presence of primary or secondary amines, afforded **1.31** in 66 to 89 % isolated yields (Eq 1-12).



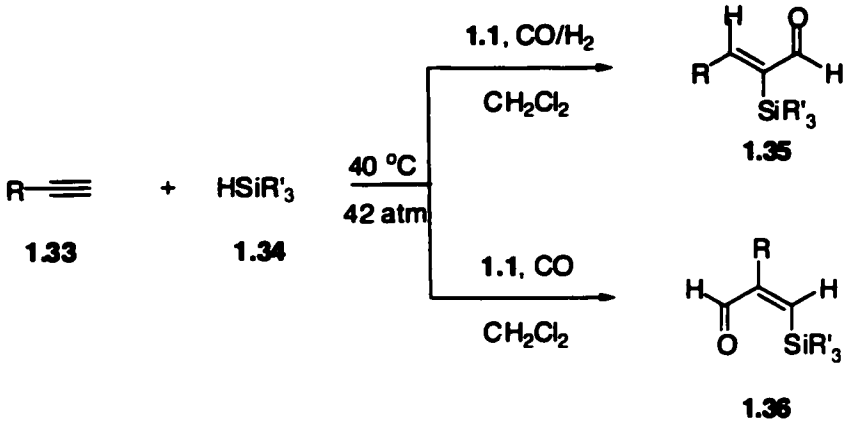
1.30 **1.24** **1.31** **1.32**

1.1.2 Reactions with Alkynes

1.1.2.1 Silylhydroformylation

The first use of a mixture of $HSiR_3/CO/H_2$ in reaction with alkynes was introduced by Alper and Zhou[22] resulting in a unique silylhydroformylation product when catalytic amounts of **1.1** is used with 42 atm of CO/H_2 (1/1) at 40 °C. When non-functionalized terminal alkynes (**1.33**) and silanes (**1.34**) are used concurrently the

silylformylation affords the (*E*)-isomer **1.35**, and a functionalized terminal alkyne gives as the net silylhydroformylation product, the (*Z*)-isomer **1.36** (Eq 1-13). The (*Z*)-isomer is the exclusive product when other Rh catalysts are used in silylformylation.[23]



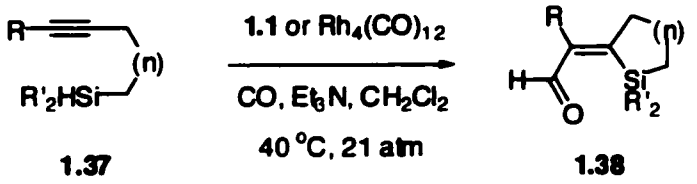
(1-13)

1.1.2.2 Silylformylation

Treatment of terminal alkynes with a hydrosilane and carbon monoxide usually results in formylation at the internal *sp* carbon, affording (*Z*)-3-silyl-2-alkenals **1.36** in high yields and a high degree of regio- and stereochemical control.[24] Although several examples of silylcarbocyclization reactions have been reported,[25] genuine intramolecular silylformylation with acetylenic and hydrosilane groups belonging to the same molecule has not been reported prior to 1995.

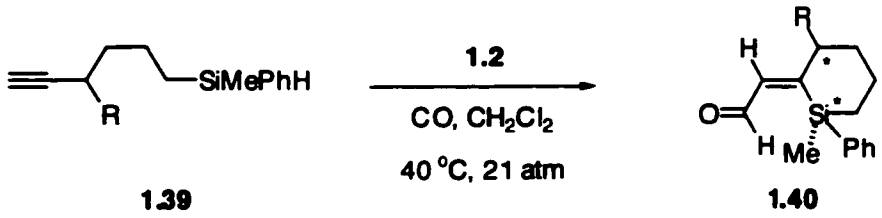
The reaction of 1-alkynyl hydrosilanes (**1.37**) with CO (21 atm) and a catalytic amount of either the zwitterionic rhodium complex **1.1** or $Rh_4(CO)_{12}$ and triethylamine (one equivalent with respect to **1.37**) gave the corresponding aldehyde **1.38** in 37 to 83 % yields (Eq 1-14).[26] The yield of the aldehyde is affected by the substituents attached to

the silicon atom. Higher product yields were obtained when starting from alkynyl methylphenylsilanes rather than alkynyldiphenylsilanes.



1.37 1.38 (1-14)

In contrast to the intermolecular reaction, it is not the internal *sp* carbon which is selectively formylated but the terminal one in the case of alkynylsilanes. This was the first example of reverse regioselectivity in the silylformylation of terminal alkynes These results demonstrate that the silylformylation process can distinguish between the two *sp* carbons of the acetylenic bond. The reaction is totally regio- and stereospecific and leads to the formation of the previously unknown (*Z*)-2-(formylmethylidene)-silacycloalkanes **1.38**.



1.39 1.40 (1-15)

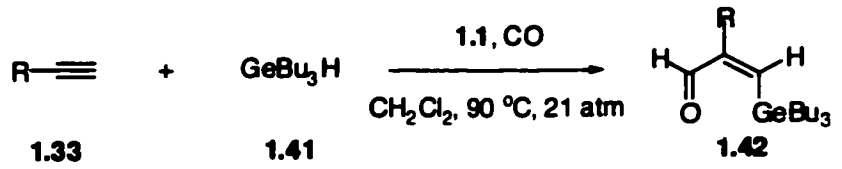
Salvadori and coworkers employed 3-alkyl-6-(methylphenylsilyl)-1-hexyne (**1.39**) where R = tert-butyl with 1 mol % of the zwitterionic rhodium complex **1.2**, and 21 atm of carbon monoxide at 40 °C affording the regio- and diastereoselective product **1.40** exclusively as the cis-isomer in 70 % isolated yield (Eq 1-15).[27] Surprisingly, when 3-

methyl-6-(methylphenylsilyl)-1-hexyne (R = Me) was silylformylated, no diastereoselectivity was observed, both isomers (***cis*** and ***trans***) being formed in a 50:50 mixture, in a combined yield of 73 %.

Both linear and branched silylacetylenes undergo the intramolecular silylformylation reaction in the presence of carbon monoxide and a zwitterionic rhodium complex. These compounds, **1.38** and **1.40**, can be easily transformed into allenes,[28] dienes,[29] dienones,[30] and α,β-unsaturated ketones,[31] and are important precursors for the synthesis of more complicated molecules via Peterson olefination,[32] Nazarov type cyclopentanone annulation,[33] or Trost-type cyclopentane annulation.[34]

1.1.2.3 Germylformylation

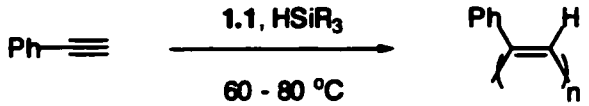
Germylformylation, reported by Alper and Monteil in 1995,[35] constituted the first examples of the addition of both carbon monoxide and hydrogermane (**1.41**) to an unsaturated substrate (Eq 1-16). The rhodium-catalyzed germylformylation of alkynes is a novel and selective route to the corresponding (***Z***)-3-germylalk-2-enals **1.42**. Introducing a terminal alkyne with 1 equivalent of $GeBu_3H$ and a catalytic amount (1 mol %) of the zwitterionic rhodium complex **1.1** under CO (21 atm) at 90 °C affords the (***Z***)-3-tri-***n***-butylgermylalkenals in 31 – 82 % isolated yields. These first examples of germylformylation occur with high levels of regio- and stereoselectivity. The (***Z***)-3-germylalkenals are potentially useful building blocks in organic synthesis as their silicon[28-34] and tin counterparts.[36]



1.33 1.41 1.42 (1-16)

1.1.2.4 Polymerization

Alper and Goldberg observed a unique extension to hydrosilylation resulting from a mixture of phenylacetylene (**1.43**), hydrosilane, and catalyst **1.1** at 60 – 80 °C. Stereoregular poly(phenylacetylene) (PPA) having a cis-transoidal structure (**1.44**) was obtained (Eq 1-17) with almost no hydrosilylation.[37] GPC analysis of the material produced a polymer with M_w 2600 - 34700 (M_w/M_n 1.7 – 5.0) in 43 to 85 % yields depending on the temperature and silane used. The polymerization of phenylacetylene is known to be catalyzed mostly by group 5 and 6 transition metal catalysts[38] and Zieglar-Natta catalysts,[39] as well as palladium and nickel complexes.[41] Some rhodium(I) complexes such as $[Rh(COD)Cl]_2$ and $[Rh(COD)(L\text{-}L)]^+X^-$ (L-L = bidentate ligand) also polymerize **1.43** to give stereoregular cis-PPA.[42] The majority of neutral and cationic rhodium complexes are well-known to be very active hydrosilylation catalysts and no polymerization occurs using them in conjunction with phenylacetylene and $HSiR_3$.[43] The zwitterionic rhodium complex **1.1**, unlike its neutral and cationic counterparts, does not readily induce hydrosilylation of **1.43**, but does catalyze its polymerization giving rise to the stereoregular PPA.

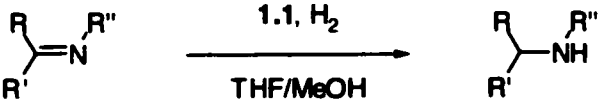


1.43 1.44 (1-17)

1.1.3 Other Reactions

1.1.3.1 Hydrogenation of Imines

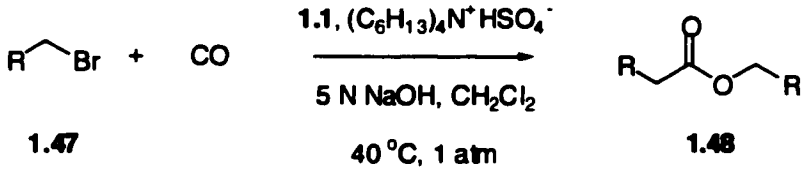
The catalytic hydrogenation of imines to amines is of considerable interest,[44] especially in the asymmetric hydrogenation of prochiral imines. Both early (Ti)[45] and late (Ir, Rh, Ru)[46-48] transition metal complexes have been applied as the catalyst precursors, with neutral and cationic rhodium(I) complexes being the most numerous. Alper and coworkers carried out the reaction of imines (**1.45**) utilizing **1.1** and added dppb in a 9/1 THF/methanol mixture to catalyze the hydrogenation of both electronic and sterically sensitive aldimines and ketimines. At 40 °C with a total hydrogen pressure of 14 - 42 atm provides **1.46** as the only product in 47 – 99 % conversions (Eq 1-18).[49]



1.45 1.46 (1-18)

1.1.3.2 Carbonylation of Benzylic and Allylic Bromides

The catalytic activity of **1.1** under phase transfer conditions was first examined by Alper and Amaratunga in 1995. There are no prior reports of rhodium complexes being used as the metal catalyst in phase transfer catalyzed carbonylations. Benzylic and allylic halides (**1.47**) when treated with carbon monoxide (1 atm) and **1.1** in methylene chloride, 5 N sodium hydroxide, and tetra-*n*-hexylammonium hydrogen sulfate as the phase transfer agent, affords ester **1.48** in 40 – 76 % isolated yields with minor amounts of the corresponding acid and/or ketone as byproducts (Eq 1-19).[50] When $Pd(PPh_3)_4$ is used as the catalyst for the carbonylation of halides, esters and acids are formed in low yields.[51] As well, the zwitterionic rhodium complex brings about alkoxycarbonylation, while cationic and neutral rhodium complexes catalyze symmetrical ketone formation and the corresponding acid of **1.48**.[50]



1.47 **1.48** (1-19)

1.2 Introduction to the Chemistry of Alkynes and Carbon Monoxide by Transition Metal Catalysis

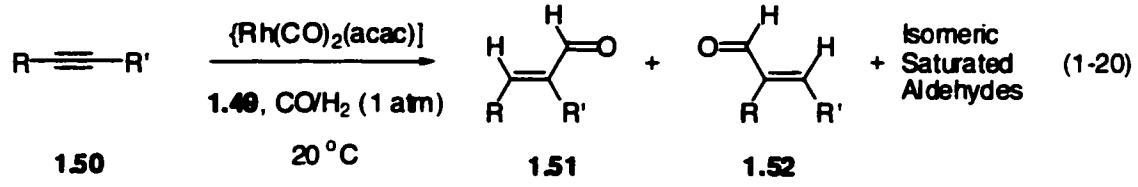
In industry, alkynes are used as carbon building blocks for the synthesis of fine chemicals. The presence of CO pressure, heat, and a suitable catalyst enables alkynes to readily take part in a large number of reactions which transforms the triple bond. In the past only some syntheses with acetylene were practical for industrial use with homogeneous catalysts, and initially complexes of the late transition metals Fe, Co, Ni, Cu, Zn, Cd, Hg, and Pb were employed as catalysts. In recent years the use of complexes of Rh, Ru, Pd, and Pt has opened up a multiplicity of new reactions possibilities for alkynes. These methods have quickly found their way into the arsenal of the synthetic organic chemist.

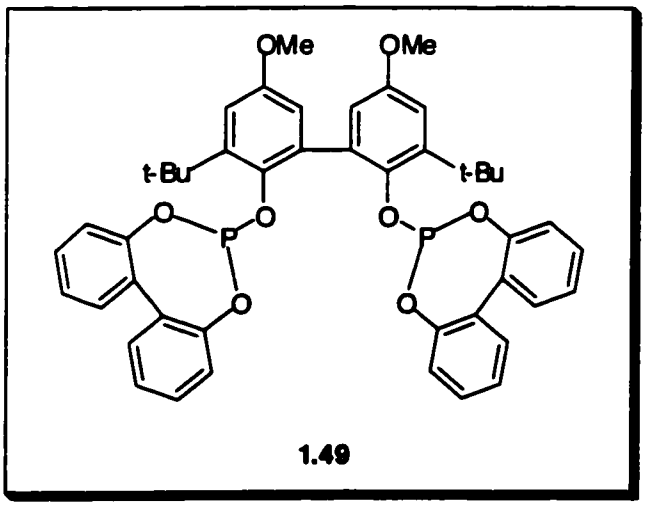
1.2.1 Hydroformylation

There are few examples of the selective hydroformylation of alkynes to yield unsaturated aldehydes. Attempts to generalize the reaction have had minimal success. A catalyst capable of the stereoselective hydroformylation of alkynes to provide the conjugated aldehyde, without producing significant amounts of either the corresponding saturated aldehyde or non-carbonylated alkene, would be useful as a method for the stereoselective synthesis of trisubstituted olefins.

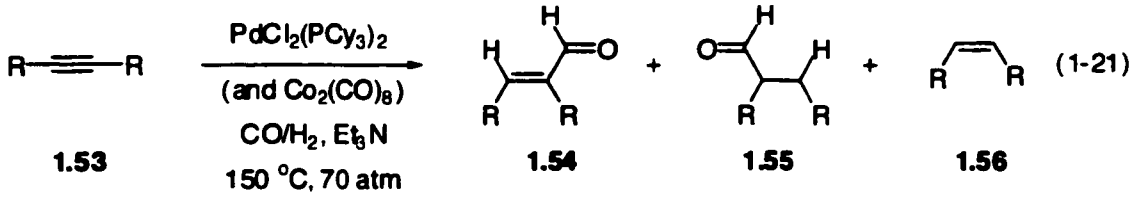
In 1995 Buchwald and coworkers,[52] reported the first useful hydroformylation catalytic system consisting of $Rh(CO)_2acac$ (acac = acetylacetonate), and the

bisphosphite ligand **1.49**, for the selective hydroformylation of alkynes to α,β-unsaturated aldehydes under mild reaction conditions (Eq 1-20).[53] In the presence of 2 mol % of $Rh(CO)_2acac$, 2.1 mol % of **1.49** and 1 atm synthesis gas (1:1 CO/H_2), symmetric and unsymmetrical internal alkynes (**1.50**) were converted at room temperature into α,β-unsaturated aldehydes without significant formation of the saturated aldehydes. The aldehyde products were obtained in good yields (56 – 90 %) and in 67 – 97 % selectivities starting from symmetrical alkynes, and in 51 – 64 % isolated yields, and 65 – 74 % selectivities for the major regioisomer from unsymmetrical aromatic alkynes.





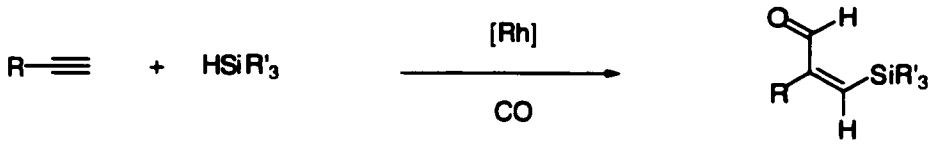
As an extension to the study by Hidai and coworkers on the hydroformylation of olefins catalyzed by mixed-metal systems,[54] various combinations of transition metal complexes were surveyed in the hydroformylation of acetylenes.[55] Two catalytic systems were reported, the use of $PdCl_2(PCy_3)_2$ (Cy = cyclohexyl) to catalyze the selective hydroformylation of symmetrical internal alkynes to give the corresponding α,β-unsaturated aldehydes, and the use of the $PdCl_2(PCy_3)_2$-$Co_2(CO)_8$ bimetallic catalyst system which significantly (six-fold) improved the catalytic activity (Eq 1-21). Examination of the hydroformylation of internal alkynes (**1.53**) with the $PdCl_2(PCy_3)_2$ catalyst exhibited very high selectivity to **1.54** with the formation of the saturated aldehyde **1.55** and the hydrogenation product **1.56** in very low conversion. The reaction proceeds at a relatively high temperature (150 °C) and pressure (35 atm CO, 35 atm H_2), and the use of the Pd or Pd-Co bimetallic catalyst (Pd/Co atomic ratio 1/1) systems result in selectivities of 77 to 95 % and 47 to 89 % isolated yields of **1.54** depending on the alkyl or aryl R group.



1.53 **1.54** **1.55** **1.56**

1.2.2 Silylformylation

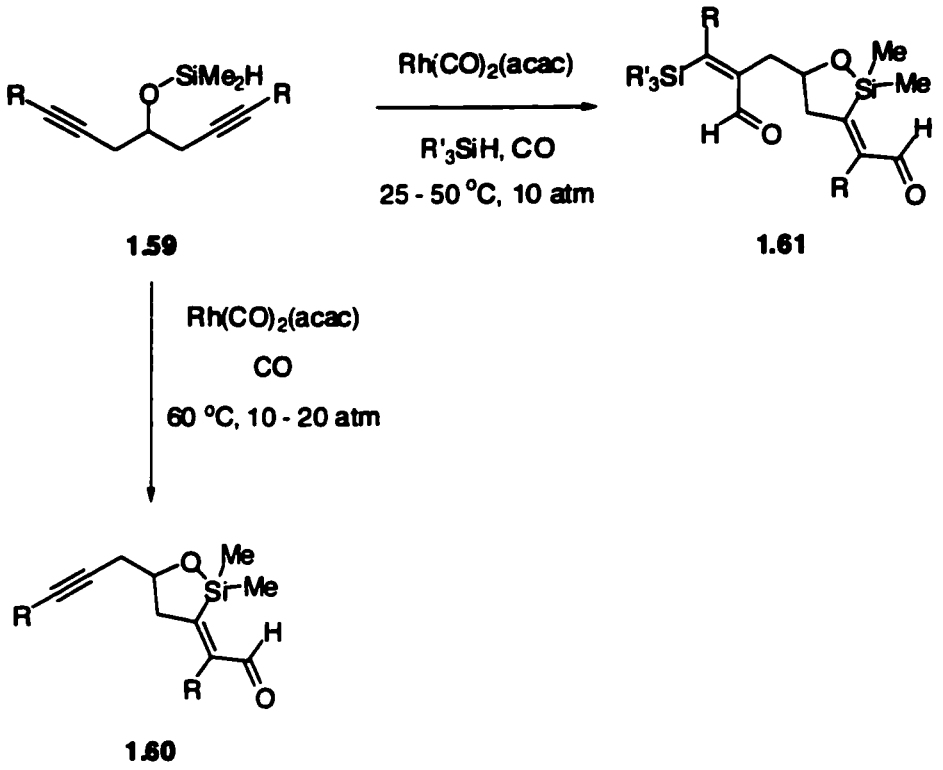
The silylformylation of alkynes as a method for the regio- and stereoselective synthesis of (*Z*)-3-silyl-2-alkenals in high yields was independently reported by Ojima and Matsudo and coworkers (Eq 1-22).[23] Some advances include the applications to the synthesis of 4-silyated 1-aza-1,3-butadienes,[56] β-substituted (*E*)-crotysilanes,[57] and pyrrolizidine alkaloids,[58] as well as the extension of the reaction to silylcarbocyclization and silylcarbotricyclization of triynes.[59] While the catalysts usually employed are $Rh_4(CO)_{12}$, or $Rh_2Co_2(CO)_{12}$, the best results were obtained with $[Rh_2(pfb)_4]$ (pfb = perfluorobutyrate),[59] while rhodium acetate is much less efficient.[60] In addition, rhodium complexes with a P,N-donor ligand have been evaluated by Espinet and coworkers enabling the silylformylation of alkynes to proceed with high regio- and chemoselectivity at 1 atm CO and room temperature.[61]



(1-22)

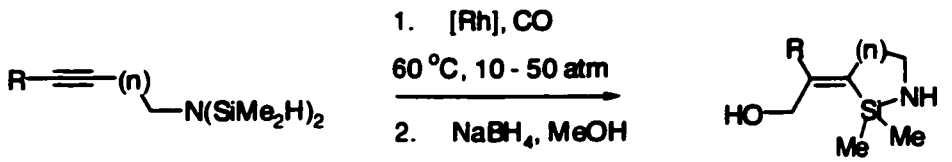
1.33 **1.57** **1.58**

Desymmetrization of dimethylsiloxyalkadiynes, investigated by Ojima and Bonalouv, resulted in the intramolecular silylformylation of 4-dimethylsiloxy-1,6-heptadiyne **1.59** (R = H). The transformation proceeded smoothly using $Rh(CO)_2acac$ to give 5-exo(formylmethylene)-oxasilacyclopentane **1.60** (R = H) in 98 % yield (Eq 1-23).[62]



(1-23)

In a similar manner, the reaction of 5-dimethyl-2,7-nonadiyne **1.59** (R = CH_3) at 60 °C and 20 atm CO cleanly gave the corresponding intramolecular silylformylation product **1.60** (R = CH_3) in 82 % yield. As well, desymmetrization of **1.59** (R = H) via sequential double silylformylation takes place using $Rh(CO)_2acac$ in the presence of $HSiMe_2Ph$ or $HSiEt_3$ at 25 °C and 10 atm CO to give **1.61** (R = H) in quantitative yield. The reaction using the bulky and less reactive hydrosilane, $HSiMe_2tBu$, required 50 °C for 24 h to completely afford the double silylation product in 98 % yield.

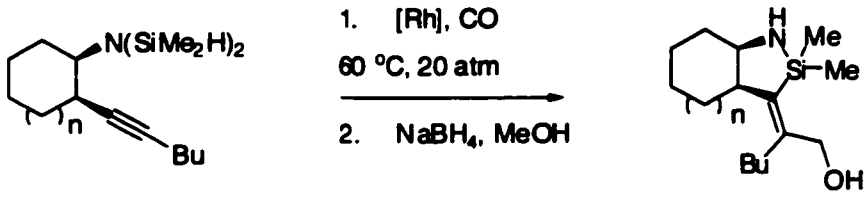


(1-24)

1.62 **1.63**

Ojima and Vidal[63] placed bis(dimethylsilylamino)-3-octyne **1.62** (R = Bu, n = 1) in the presence of $(tBuNC)_4RhCo(CO)_4$, $Rh_2Co(Co)_{12}$, or $Rh(CO)_2acac$ in toluene at 60 °C to give 2-silyl-5-exo-(-formylpentyl-1-ene)-2-aza-1-silacyclopentane as the only product. (Eq 1-24). To obtain a stable derivative, the aldehyde underwent $NaBH_4$ reduction to the corresponding alcohol **1.63** in 52 % yield starting from $Rh(CO)_2acac$, 80 % yield using $(tBuNC)_4RhCo(CO)_4$, and in 75 % yield using $Rh_2Co_2(CO)_{12}$. The same protocol was used for 1-bis(dimethylamino)-4-alkynes (**1.62**) with R = butyl or phenyl (n = 2) at 60 °C and 50 atm immediately followed by $NaBH_4$ reduction to afford 6-exo-(1-hydroxymethylalkyl-1-ene)-2-azasilacyclohexanes in 71 – 90 % isolated yields depending on the rhodium catalyst used.

An example involving the generation of bicyclic ring systems, is the conversion of **1.64** to **1.65** (Eq. 1-25). Using the above conditions, **1.64** (n = 0 or 1) leads to **1.65** in 61 to 84 % isolated yields.

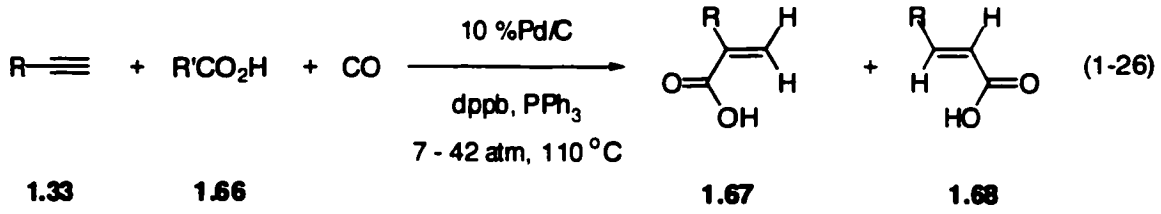


(1-25)

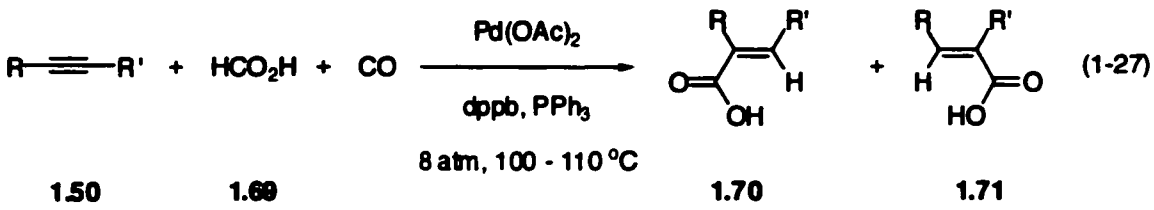
1.64 **1.65**

1.2.3 Hydrocarboxylation

Heterogeneous catalysts like Pd/C readily affect the hydrocarboxylation of olefins.[64] Alper and coworkers obtained carboxylic acids in a regioselective manner using a heterogeneous catalyst (10 % or 5% Pd/C) in the presence of formic acid or oxalic acid and phosphine ligands. Alkynes (**1.33**) react with formic or oxalic acid (**1.65**) in the presence of a catalytic amount of 10 % Pd/C, PPh_3, and dppb at 110 °C and 7 atm of CO to form the corresponding unsaturated carboxylic acids **1.67** and **1.68** (Eq. 1-26).[65] The results of these reactions contrast to the alkene hydrocarboxylation where PPh_3 has no beneficial effect. The activity of the alkyne system increases with the addition of PPh_3 and the best yields were found using Pd/PPh_3/dppb ratio 1:4:2.



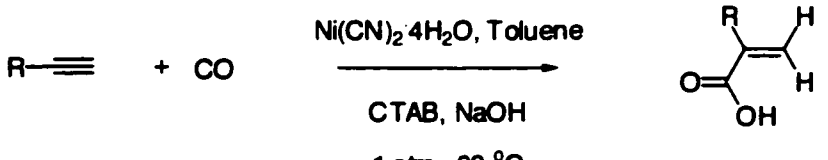
The heterogeneous catalyst has activity resembling that of a homogeneous catalyst[66] with yields of 55 to 80 % using formic acid, and yields of 55 to 82 % in the case of oxalic acid. For alkynes, the unsaturated acid **1.67** is the principal regioisomer. This heterogeneous system (Pd/C-HCO_2H or Pd/C-oxalic acid) was also compatible with other functional groups, such as cyano, chloro, vinyl, formyl, and carboxyl. The hydrocarboxylation reaction requires higher CO pressure (42 atm) when oxalic acid is used in place of formic acid.



(1-27)

1.50 **1.69** **1.70** **1.71**

Alper and Zargarian determined that both terminal and internal alkynes can be hydrocarboxylated with formic acid in the presence of catalytic amounts of $Pd(OAc)_2$ and phosphine ligands.[66] This reaction requires a temperature of 100 – 110 °C at 8 atm of CO pressure. Terminal alkynes give combined yields of 63 – 96 % for the two regioisomers **167** and **168**, and in **167/168** ratios of 87/13 to 94/6 for sterically unencumbered R groups, and in ratios of 0/100 and 21/79 for tert-butyl and trimethylsilyl R groups. Internal alkynes (**1.50**) also undergo catalytic hydrocarboxylation to the two regioisomers **1.70** and **1.71** having **1.70/1.71** ratios, where R is larger in size than R', of 20/80 for iPr/Me versus 69/36 for Ph/Et in 58 to 96 % combined yields (Eq 1-27).



(1-28)

1.33 **1.67**

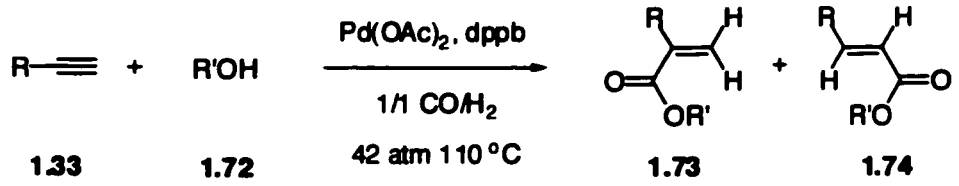
In 1990, Alper and Amer examined the reaction of alkynes under phase transfer conditions. Terminal alkynes react in toluene with 1 atm carbon monoxide, 5 N sodium hydroxide and catalytic amounts of hydrated nickel cyanide and cetyltrimethylammonium bromide (CTAB) as the phase transfer agent at 90 °C to give

the acid **1.67** as the only product in 62 to 95 % isolated yields, where R is an alkyl or aryl group (Eq 1-28).[67] No carboxylic acids were formed when internal alkynes were used as reactants. Phase transfer catalysis enables one to obtain regiospecific hydrocarboxylation of terminal alkynes to methylene acids under mild conditions. This was the first true hydrocarboxylation phase transfer catalyst system where an acyl metal carbonyl complex[68] was not required to facilitate the reaction.

1.2.4 Hydroesterification

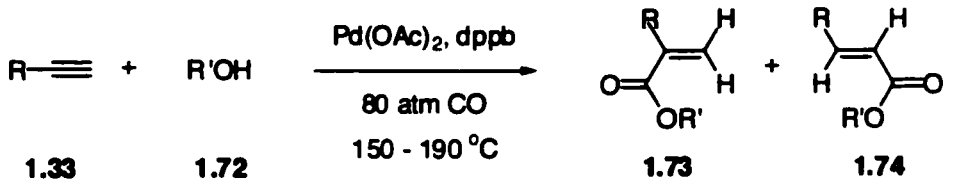
The catalytic hydroesterification and hydrocarboxylation of alkynes and other π-bonded compounds are reactions with important industrial potential.[69] The hydroesterification of alkynes usually leads to excellent selectivity for the branched α,β-unsaturated ester **1.73** or a mixture of esters **1.73** and **1.74** (Eq. 1-29).[70] A new catalytic system developed by El Ali and coworkers for the regioselective hydroesterification of terminal acetylenes catalyzed by Pd(II) and a diphosphine ligand afforded linear α,β-unsaturated ester **1.74** as the major product under mild conditions. Esters were obtained in 67 – 98 % yields in the presence of catalytic amounts of $Pd(OAc)_2$ and dppb under 42 atm of CO/H_2 (1/1) and 110 °C. The preference for the linear ester was 58 to 100 %, when incorporating primary alcohols and aliphatic alkynes, and 57 - 75 % selectivity for tertiary and secondary alcohols with aliphatic alkynes.[71] Poor selectivity resulted from phenylacetylene and 1-butanol, making the branched ester **1.73** the major component.

This method occurs under milder reaction conditions, providing significant improvement over the present systems described in the literature for α,β-unsaturated linear esters.[72]



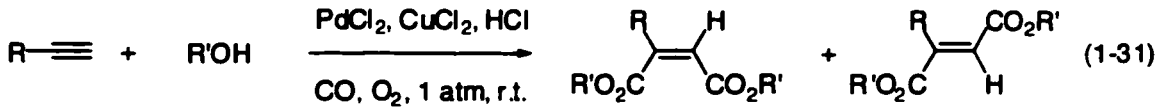
1.33 **1.72** **1.73** **1.74** (1-29)

The palladium-catalyzed hydroesterification of alkynes in the presence of dppb affords unsaturated esters in a highly regioselective manner. The first example of the preparation of primary, secondary, and tertiary esters by the hydroesterification of alkynes was reported by Alper and El Ali in 1991 (Eq 1-30).[70b] Treatment of a terminal alkyne with an equimolar quantity of alcohol, catalytic amounts of $Pd(dba)_2$ and dppb, and carbon monoxide at 80 atm and 150 - 190 °C gave branched esters (**1.73**) in 25 - 65 % yields. In most cases negligible amounts of linear esters were detected. The alkyne was stable towards the incorporation of alkoxy, chloro, and cyano functional groups.



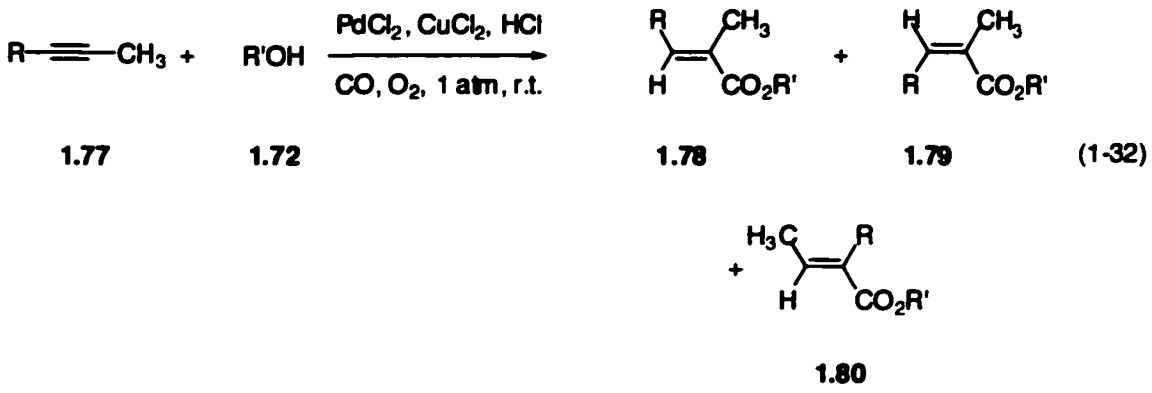
1.33 **1.72** **1.73** **1.74** (1-30)

Alkynes react in a CO/O_2 atmosphere in a regioselective manner to give monoesters or diesters. Alper and coworkers treated carbon monoxide, oxygen, methanol, hydrochloric acid, catalytic amounts of palladium and copper chloride, at room temperature and atmospheric pressure with a series of mono-substituted alkynes to give the cis-diester as the principal product with the trans-isomer as a byproduct (Eq 1-31).[73] In no cases were α,β-unsaturated monoesters detected when methanol, ethanol and propanol were employed. The cis-isomer was obtained in 74 - 89 % yields for alkyl and aryl substituted alkynes.



1.33 **1.72** **1.75** **1.76** (1-31)

Interestingly, 2-alkynes (**1.77**) also react regioselectively, but to give monoesters (**1.78**) and not diesters (Eq 1-32). Furthermore, the monoester formed is of cis-stereochemistry, and was isolated in 65 - 76 % isolated yields. This methodology has several attractive features, including the absence of polymeric materials,[74] and only diesters are obtained from terminal alkynes.



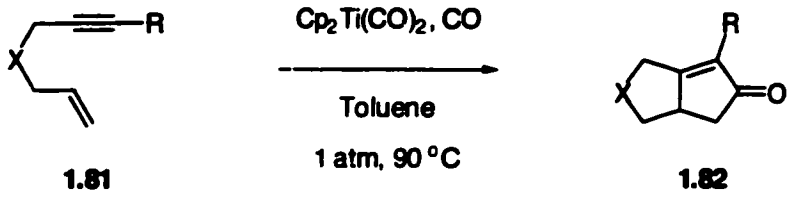
1.77 **1.72** **1.78** **1.79** (1-32)

1.80

1.2.5 Cyclocarbonylation

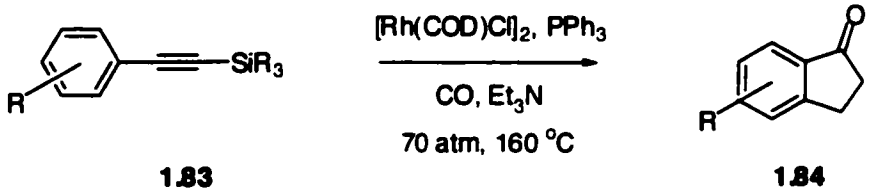
Tandem reactions incorporating cyclocarbonylation procedures generate several bonds in one step, and provides a simple and efficient route to complex organic molecules. Such transformations, utilizing transition metal catalyzed syntheses, include the preparation of cyclopentenones,[75] cyclopentadienones,[76] furanones,[77] and pyrrolinones.[78]

The Pauson-Khand conversion of enynes (**1.81**) to bicyclic cyclopentenones (**1.82**), employing 5 – 20 mol % of titanocene dicarbonyl with 1.25 atm of CO at 90 °C, was recently reported by Buchwald and coworkers (Eq. 1-33).[79] The methodology shows excellent functional group tolerance leading to **1.82** in 58 to 96 % yields when "X" consists of O, NR' or CR'_2 functionalities (R and R' may be H, alkyl, aryl or ester groups). In addition, the titanocene catalyst cyclizes a variety of 1,6- and 1,7-enynes and 1,1- and 1,2-disubstituted olefin-containing enynes under high chemoselective control.



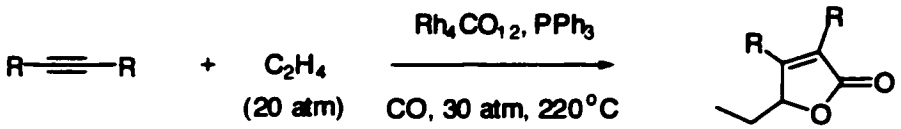
1.81 **1.82** (1-33)

Another potentially useful cyclocarbonylation procedure by Takeuchi and Yasue leads to indenones.[80] The rhodium-catalyzed desilylation/carbonylation occurs under water-gas shift reaction conditions, where CO (70 atm) and aryltrimethylsilylacetylenes (**1.83**) react at 160 °C to form 2,3-dihydro-1*H*-inden-1-ones (**1.84**) in 67 - 90 % yields (Eq 1-34).



1.83 **1.84** (1-34)

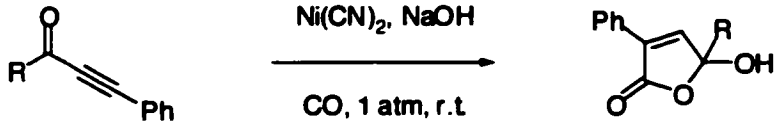
The Rh-catalyzed synthesis of 2(5*H*)-furanones from alkynes under water-gas shift reaction conditions readily occurs with high chemoselectivity. Both internal and terminal alkynes could be employed as substrates. The 5-ethyl-2(5*H*)-furanones were prepared by $Rh_4(CO)_{12}$-catalyzed carbonylation of an alkyne, ethylene (20 atm), and CO (30 atm) in the presence of alcohols as the hydrogen source at 220 °C to afford **1.85** in 27 – 69 % yields.(Eq 1-35).[81]



(1-35)

1.53 **1.85**

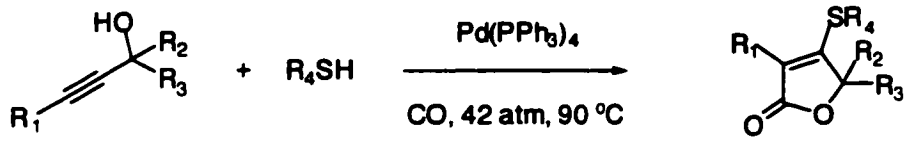
In 1995, Arzoumanian and coworkers treated 4-phenyl-3-alkyn-2-ones with carbon monoxide (1 atm) and catalytic amounts of $Ni(CN)_2$ under phase transfer conditions (toluene, 5 N NaOH, and tetra-***n***-butyl ammonium bromide – TBAB) to afford the hydroxylactone **1.87**. When R = methyl, **1.87** was formed in 78 % yield, and in contrast **1.87** is obtained in 35 % yield when R = ***tert***-butyl (Eq 1-36).[82] The latter is produced in a mixture with the ring opened keto acid. The structure of the final product is dependent on the nature of the substituent used for the alkynyl group. Phenylacetylene based alkynones give mixtures of 5-hydroxyfuranones and keto acids, while hexyne based alkynones afford only keto acids.



(1-36)

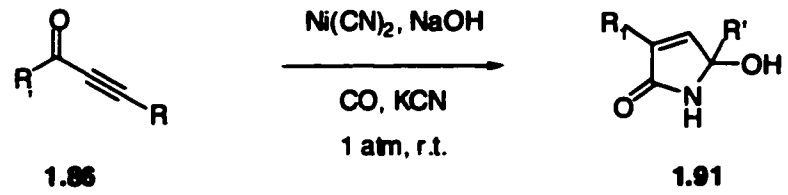
1.86 **1.87**

Arenethiols and alkanethiols (**1.89**) were employed successfully by Alper and Xiao in a reaction together with primary, secondary, and tertiary acyclic propargyl alcohols (**1.88**) containing a terminal acetylene (Eq 1-37).[83] In particular, the use of 3 mol % $Pd(PPh_3)_4$ in DME with 42 atm of CO at 90 °C afforded the sulfur substituted furanones (**1.90**) in 67 – 88 % yield. Non-sulfur containing furanones were also formed by direct carbonylation of propargylic alcohols with the aid of bis(dibenzylidene acetone)palladium(0) and dppb.[84]



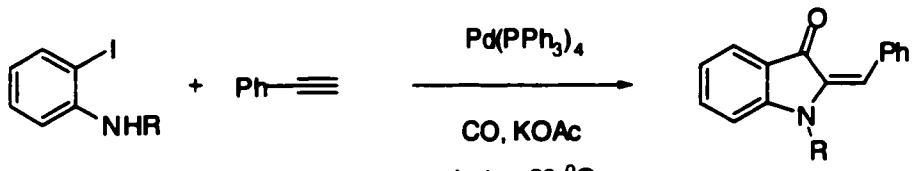
1.88 **1.89** **1.90** (1-37)

Arzoumanian and coworkers took their carbonylation reaction one step further in 1997, and treated conjugated alkynones (**1.86**) in the presence of excess potassium cyanide. Treating **1.86** with KCN, 5 N sodium hydroxide, 25 mol % $Ni(CN)_2 \cdot 4H_2O$ and 1 atm of carbon monoxide, at 25 to 60 °C gave the unsaturated hydroxylactam **1.91**, in 56 to 83 % yields (Eq 1-38).[85] Mechanistic studies have shown that the versatile hydrocyanation mediator, $[Ni(CN)_4]_4^{2-}$, is the active Ni catalyst (prepared in situ from $Ni(CN)_2$).



1.86 1.91 (1-38)

Tandem reactions with three components: an aromatic halide, CO, and an unsaturated reactive unit were adopted for the synthesis of flavone,[86] thiochromanone,[87] indolone,[88] furanone,[89] benzopyranone,[90] benzoxazinone,[91] and pyrido[3,2-e]1,3-oxazinone derivatives.[92] The synthetic potential of this methodology is illustrated by the variety of products which can be prepared by minor changes of the reactants. This is clearly demonstrated by the reaction of 2-haloanilines with CO (1 atm) and alkynes at 80 °C to give indoxyl derivatives (Eq 1-39).[88] Interestingly, the resulting arylpalladium(II) complex reacts preferentially with CO and not the alkyne, which is contrary to previous examples.



1.92 1.43 1.93 (1-39)

1.3 Aims of Research

Although a large number of catalytic systems have been developed for the carbonylation of alkynes, this area of chemistry has still not reached its full potential. The search for improvement in carbonylation technology continues, with the goal of increasing the diversity and complexity of potential substrates and reaction products. A review of the literature on the carbonylation of unsaturated organic compounds shows that these reactions provide convenient, efficient one-step methods for the preparation of a variety of unsaturated functionalized materials.[93] However, there are few reports in the literature on transition metal-catalyzed carbonylation reactions employing functional groups to influence and initiate new chemistry in the presence of CO and H_2.

The project undertaken involves an examination of the effects of α-functionalized alkynes in the presence of a zwitterionic rhodium complex under hydroformylation conditions. The purpose of this investigation is to gain insight into the roles functional groups play toward the addition of rhodium to a triple bond, and what role they play in determining the resulting carbonylation chemistry. Understanding how to use these characteristics of functional group involvement will enable us to develop novel transformations with high chemo-, regio- and stereoselectivities, as well as economical and efficient methodologies for organic intermediates with pharmacogolical potential.

CHAPTER 2

REGIOSELECTIVE HYDROFORMYLATION OF ENYNES CATALYZED BY A ZWITTERIONIC RHODIUM COMPLEX AND TRIPHENYL PHOSPHITE

2.1 Introduction

The hydroformylation of alkenes is an important industrial process which has been extensively investigated for many years.[94] In contrast, the hydroformylation of alkynes to give α,β-unsaturated aldehydes has attracted less attention until recently, since past research resulted in poor product yields and selectivities.[95]

In 1995, Buchwald and co-workers[53] reported an effective hydroformylation catalyst composed of $Rh(CO)_2acac$ (acac = acetylacetonate) and a sophisticated bisphosphite ligand. This catalyst system enabled the hydroformylation of internal alkynes to occur under mild conditions and with good selectivities.

Recently, Hidai and co-workers,[55] reported a bimetallic catalyst to hydroformylate internal acetylenes. The conditions used by Hidai and co-workers were not as mild as those of Buchwald, although the conversion and selectivity were good. The Hidai group described the hydroformylation of the conjugated enyne (*Z*)-1,4-diphenyl-1-buten-3-yne to form (2*E*,4*Z*)-2,5-diphenyl-2,4-pentadienal as the exclusive hydroformylation product in 80 % conversion and 39 % isolated yield. Doyama and others[96-98] noted that when an alkyne is conjugated to an alkene, the triple bond is more

reactive towards hydroformylation. Conjugated enynes undergo hydroformylation giving formyl-dienes in either a linear or branched fashion.

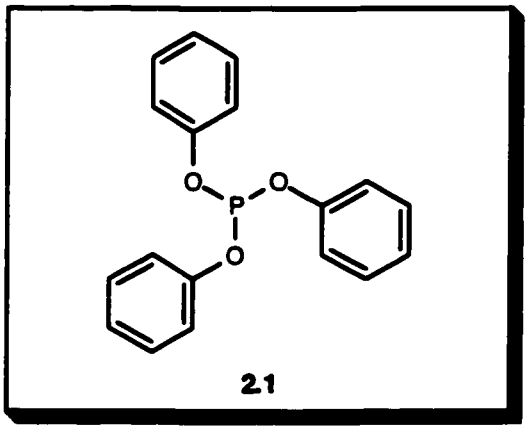
2.2 Aim of Research

Enynes find practical use in the preparations of polymers,[99] substituted benzenes,[100] and in enediyne antibiotics.[101] The catalytic hydroformylation of conjugated enynes is an attractive synthetic route for the preparation of formyl-dienes; an interesting subgroup of substituted dienes used in the preparation of cyclized materials and as chain extensions.[102] Enynes may be prepared through a variety of methods including the reaction of an alkyne with various organometallic species affording acetylenes bearing alkyl, vinyl, aryl or heteroaryl groups α to the triple bond.[103] More recent methods have been developed using palladium and tris(2,6-dimethoxyphenyl)phosphine to self-couple terminal alkynes, or cross-couple terminal alkynes to functionalized internal alkynes.[104]

The following sections describe the use of catalytic quantities of the zwitterionic rhodium complex **1.1**, in the presence of triphenyl phosphite, to attain the hydroformylation of both simple and functionalized enynes in good conversions and selectivities, and moderate yields.

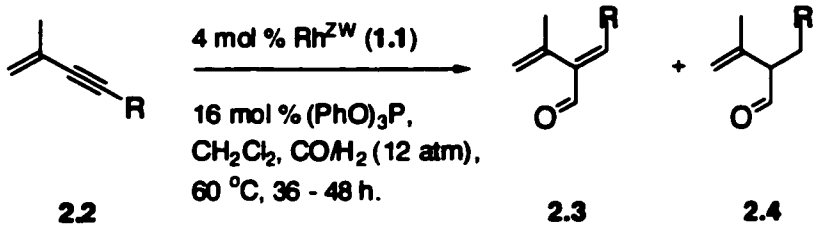
2.3 Results and Discussion

The phosphite skeleton of the ligand used by Buchwald and coworkers (**1.49**),[53] when applied in conjunction with a rhodium catalyst, enables the hydroformylation of internal alkynes to be carried out under very mild conditions (see Chapter 1).



2.1

It was envisaged that this catalytic system could also be used to carry out the hydroformylation of enynes under mild conditions as well. We reasoned that a much simpler phosphite such as triphenyl phosphite (**2.1**) could be used for the hydroformylation of enynes. Indeed, the catalytic system of **1.1** with triphenyl phosphite gives preferential hydroformylation of the triple bond in conjugated enynes affording unsaturated aldehydes in high selectivity (Eq. 2-1).



2.2 2.3 2.4 (2-1)

Treatment of enynes (**2.2**) (3 - 6 mmol) with 4 mol % **1.1**, 16 mol % triphenyl phosphite, and 12 atm of CO/H_2 (total pressure) in CH_2Cl_2 affords one formyl-diene in all cases. The branched formyl diene (**2.3**) is the major product, with the non-conjugated unsaturated aldehyde (**2.4**) as a by product in all reactions. Unidentified polymeric material was also formed, in accord with similar behavior for 2,2-disubstituted olefins.[105]

2.3.1 Reaction Optimization.

The optimization of this process was effected using 2,7-dimethyl-1-octen-3-yne (**2.2a**) as the model substrate. The hydroformylation process is temperature, solvent, ligand, and catalyst dependent (Table 2-1). The highest isolated yield of **2.3a** resulted using the conditions described in the previous paragraph (Table 2-1, entry 1). Decreasing the temperature by 10 °C (60 to 50 °C) leads to only 50 % conversion of the enyne (**2.2a**) after 48 hours (Table 2-1, entry 2). Increasing the temperature by 10 °C (60 to 70 °C) leads to completion of the reaction in 24 hours. An undesirable consequence of the increased reactivity is the substantial increase in the formation of **2.4a** (Table 2-1, entry

3). Use of benzene, THF or ether as the solvent results in lower yields of **2.3a** (Table 2-1, entries 4 - 6). Mono (Ph_3P) and bidentate (dppb) phosphine ligands give inferior results when compared with $(PhO)_3P$ (Table 2-1, entries 7 and 8). Ligand **1.49** affords comparable results to $(PhO)_3P$ (Table 2-1, entry 9). The substituents present on **1.49** have a significant influence on the rate of the reaction, resulting in a six fold rate increase. $Rh(CO)_2acac$ and $CO(Ph_3P)_2RhCl$ are inferior to **1.1** when placed in combination with $(PhO)_3P$ (Table 2-1, entries 10 and 11).

Table 2-1. Hydroformylation of 2,7-Dimethyl-1-octen-3-yne (2.2a) Using Different Catalyst Systems and Solvents[a]

Entry	[Rh]	Ligand	Solvent	t (h)	Conv. (%)[b]	Product Ratio (2.3/2.4) [c]	Isolated Yield 2.3a (%)[d]
1	Rh^{ZW} (1.1)	$(PhO)_3P$	CH_2Cl_2	48	>95	10:1	52
2		$(PhO)_3P$[e]	CH_2Cl_2	48	50	10:1	26
3		$(PhO)_3P$[f]	CH_2Cl_2	24[g]	100	3:1	37
4		$(PhO)_3P$	Et_2O	48	<10	2.3a	-
5		$(PhO)_3P$	Benzene	48	100	4:1	42
6		$(PhO)_3P$	THF	48	60	20:1	39
7		Ph_3P	CH_2Cl_2	48	50	2 (:1)[h]	16
8		dppb[i]	CH_2Cl_2	48	<10[j]	-	-
9		1.49[k]	CH_2Cl_2	8[g]	80	10:1	51
10	$Rh(CO)_2acac$	$(PhO)_3P$	CH_2Cl_2	48	67	5:1	33
11	$CO(PPh_3)_2RhCl$	$(PhO)_3P$	CH_2Cl_2	48	< 5	2.3a	-

[a] Reaction conditions: enyne (2.2a), 3 mmol; rhodium catalyst, 0.12 mmol; triphenyl phosphite, 0.48 mmol; CH_2Cl_2, 10 mL; CO, 6 atm; H_2, 6 atm; 60 °C. [b] The percent conversion was determined by ^1H NMR. [c] The ratio of 2.3/2.4 was determined by ^1H NMR. [d] The product was isolated by Kugelrohr distillation followed by column chromatography using pentane:ether (90:10) as eluant. [e] 50 °C. [f] 70 °C. [g] A pressure drop of 6 atm was observed, and the reaction was stopped; this was consistent with a complete reaction. [h] A cyclopentenone was identified by ^1H NMR in a ratio of 1:2 to

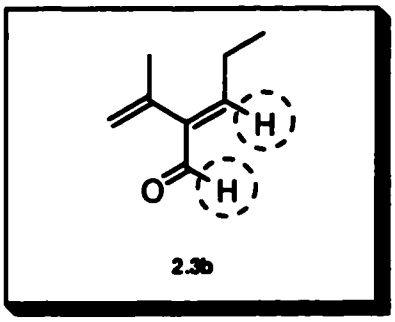
2.3a. [i] A 2:1 ratio of dppb:**1.1** was used. [j] The reaction gave multiple products. [k] A 1.5:1 ratio of **1.49/1.1** was used.

2.3.2 NMR Determination of Regiochemistry

In nuclear magnetic resonance spectroscopy (NMR), when irradiation of a proton results in the enhancement of ^{13}C signals to which the proton is directly bonded, or enhancement of signals to nonbonded protons over short distances, the result gives rise to the Nuclear Overhauser Effect (NOE).[106] This NOE occurs due to nuclear relaxation through-space by dipolar interactions. The ^{1}H ^{1}H through space interaction increases the usual observable signal up to 20 %. An NOE difference spectrum is calculated by obtaining two spectra: a specified proton irradiated ^{1}H spectrum, and the other is a conventional ^{1}H spectrum; the latter is subtracted from the former leaving only the enhancement. A measurable effect can be expected between ^{1}H atoms over a distance of up to 4 Å (0.4 nm). An example of this distance relates to the distance between 1,3-diaxial protons in a cyclohexane ring.

Distinguishing between a trisubstituted (*E*)-double bond and the corresponding (*Z*)-double bond is not a trivial assignment. The NOE difference spectrum is indeed a

powerful tool for this purpose, and was utilized to determine the regiochemistry of the formyl-dienes obtained from the hydroformylation of enynes. Using product **2.3b** as an example (Fig. 2-1), irradiation of the aldehydic ^{1}H at δ 9.29 (s, 1H), led to a strong enhancement of the olefinic ^{1}H at δ 6.40 (t, 1H, J = 7.6 Hz). As well, irradiation of the olefinic ^{1}H (δ 6.40) gives rise to a strong enhancement of the aldehydic ^{1}H (δ 9.29). These results indicate the CHO and CH are on the same side of the 2,3-double bond, therefore indication of an (***E***) configuration as drawn below.



2.3b

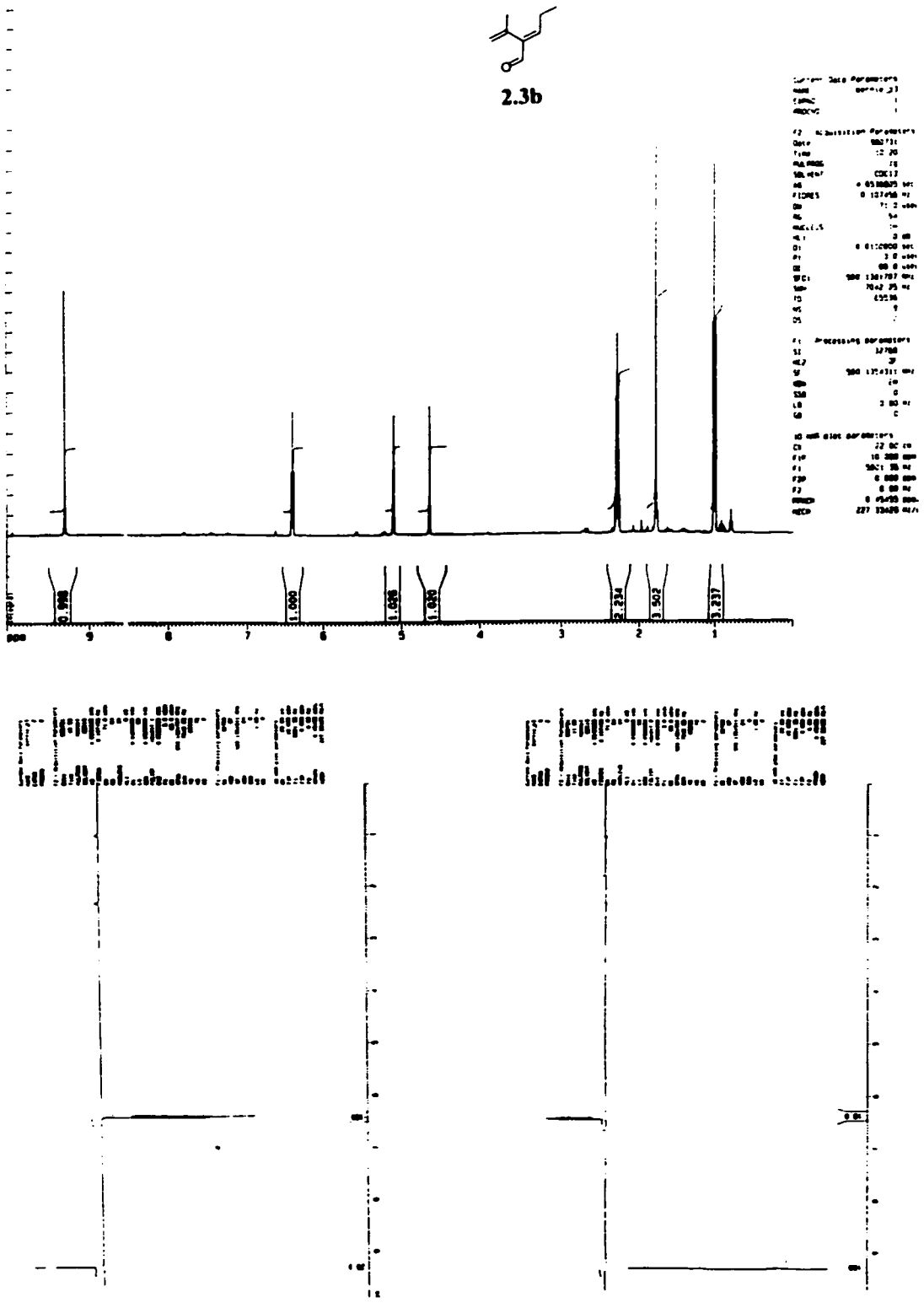
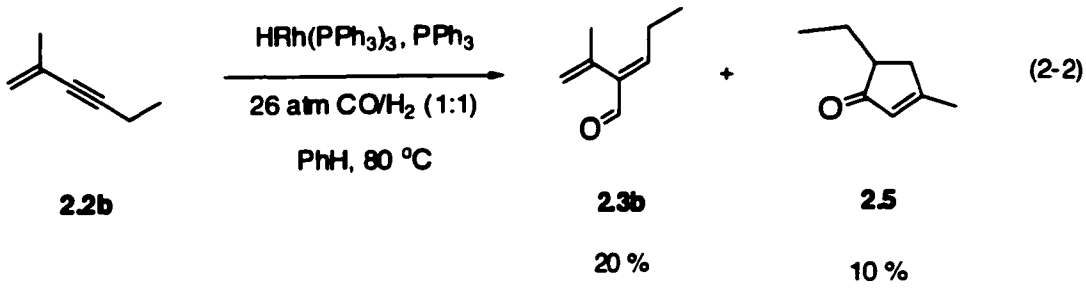


Figure 2-1. NOE Difference Experiment on 2.3b

2.3.3 Reactions of Enynes

The hydroformylation of **2.2b** (Table 2-2) was reported previously by Campi and Jackson[98] using carbonylhydridotris(triphenylphosphine)rhodium(I) and excess triphenylphosphine as the catalytic system at 80 °C, and 26 atm of synthesis gas in benzene. The formyl diene **2.3b** and the cyclopentenone **2.5** were formed in 20 % and 10 % yields, respectively (Eq. 2-2).

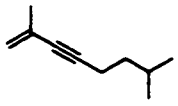
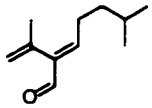
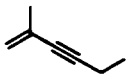
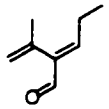
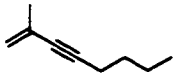
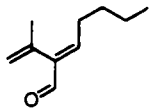
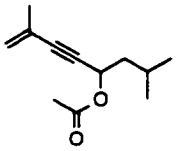
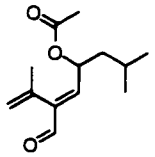
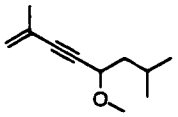
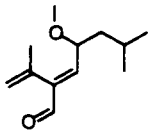
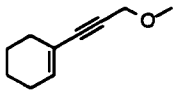
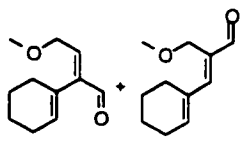


2.2b **2.3b** 20 % + **2.5** 10 % (2-2)

Under the conditions described herein the formyl-dienes (**2.3**) were obtained in 50 - 70 % isolated yields (Table 2-2).

In our investigation we examined three types of conjugated enynes: internal acetylenes, terminal acetylenes, and functionalized internal acetylenes at the β-position to the triple bond. In the first case (Table 2-2) only one unsaturated aldehyde was obtained in 50 - 55 % yield (**2.3a**, **2.3b** and **2.3c**). In the second group, terminal acetylenes, a multiple number of products were observed from 1-ethynylcyclohexene after 12 hours. In this situation there was no selectivity, possibly due to the lack of any steric interaction with the "R" substituent, as in the internal acetylene case.

Table 2-2. Hydroformylation of Enynes (2.2) with CO/H_2 Using Zwitterionic Rhodium (1.1) and $(PhO)_3P$[a]

Substrate	t (h)	Conv. (%)[b]	Product Ratio[c] (2.3/2.4)	Product	Isolated Yield (%)[d]
 **2.2a**	48	>95	9.7/1	 **2.3a**	55
 **2.2b**	36	100	8.2/1	 **2.3b**	50
 **2.2c**	48	>95	8.6/1	 **2.3c**	55
 **2.2d**	48	100	7.5/1	 **2.3d**	51
 **2.2e**	48	100	8.8/1	 **2.3e**	50
 **2.2f**	24	100	14.3/1	 **2.3f:2.3f', 2:1**	70

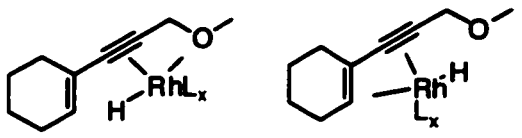
[a] Reaction conditions: enyne (**2.2**), 6 mmol; **1.1**, 0.24 mmol; triphenylphosphite, 0.96 mmol; CH_2Cl_2, 10 mL; CO, 6 atm; H_2, 6 atm; 60 °C; 36 - 48 hours. [b] The percent conversion was determined by ^1H NMR. [c] The ratio of **2.3/2.4** was determined by ^1H NMR. [d] The product was isolated by Kugelrohr distillation followed by column chromatography using pentane:ether (90:10) as eluant.

The third group of enynes used indicated the formation of a second formyl-diene. When a methyl ether is placed in the position β to the triple bond, i.e. **2.2f**, a second isomer of the formyl-diene (**2.3f'**) is produced in a ratio of 1:2 relative to the usual product **2.3f** (Table 2-2, entry 6). In contrast, only one product (**2.3e**) was formed when 2,7-dimethyl-5-methoxy-1-octen-3-yne (**2.2e**) was the substrate (Table 2-2, entry 5). As well, only one formyl-diene, in 51 % isolated yield (**2.3d**), resulted from the hydroformylation of an ester substituted enyne **2.2d** (Table 2-2, entry 4). The major difference between **2.2e** and **2.2f** is the substitution at the α carbon to the acetylene unit. Substrate **2.2e** contains a secondary ether unit, and **2.2f** consists of a primary ether unit. Substitution effects appear to play a key role in generating one or two isomeric formyl-dienes.

2.3.4 Mechanistic Aspects

The appearance of the minor product **2.3f'** from **2.2f** may be explained by prior coordination of the rhodium catalyst with the oxygen atom of the methyl ether and the triple bond (**2.6**) followed by subsequent hydroformylation (see Fig. 2-2). This same double coordination is possible between the alkene and the alkyne in the conjugated enyne prior to hydroformylation (**2.7**). When a functional group is placed at the opposite side of the enyne creating a steric effect, only one product is possible. Depending on the coordinating ability of the group at the β-position to the alkyne, different ratios of products are conceivable.

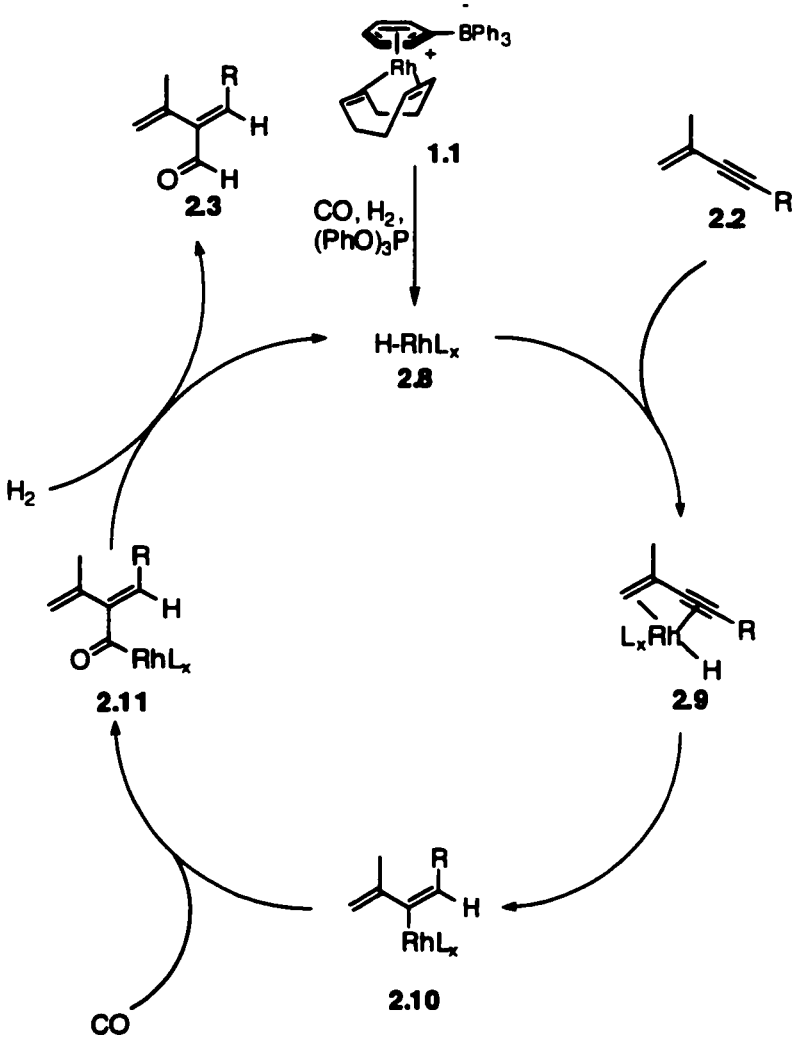
A possible mechanism for the hydroformylation of enynes is outlined in Scheme 2-1. The active rhodium catalyst (**2.8**) was generated from the reaction of **1.1** in the presence of CO, H_2 and $(PhO)_3P$. The second step may involve coordination of the rhodium with the enyne via the double and triple bonds (**2.9**), followed by the intramolecular addition of the rhodium hydride to the triple bond of the enyne affording the *(E)*-isomer (**2.10**). In the case of the ether substituent of **2.2f**, the initial coordination is between the rhodium catalyst, the triple bond and the ether oxygen. This initial complexation governs the selectivity of the resulting unsaturated product. Carbonyl insertion (**2.11**), and regeneration of the active rhodium catalyst by hydrogen (**2.8**), affords the formyl-diene (**2.3**).



2.6 2.7

Figure 2-2. Rhodium Coordination Prior to Hydroformylation

Scheme 2-1. Proposed Mechanism



2.4 Conclusion

In conclusion, the catalyst system of the zwitterionic rhodium conplex (**1.1**) and triphenyl phosphite is of value for the hydroformylation of conjugated enynes. The use of a readily available phosphite ligand under mild conditions makes this process of considerable commercial promise. Hydroformylation in the presence of an ether or an ester linkage allows ready access to products with the potential for further interesting chemistry.

CHAPTER 3

THE FIRST REGIOSELECTIVE HYDROFORMYLATION OF 2-ACETYLENIC THIOPHENES CATALYZED BY A ZWITTERIONIC RHODIUM COMPLEX AND TRIPHENYL PHOSPHITE

3.1 Introduction

The coordinating ability of sulfur containing compounds to reactive sites of metal complexes has long been a limiting factor towards the catalysis of sulfur containing materials.[107] Catalysis in the presence of sulfur has been of considerable interest for many years due to applications in organic chemistry,[108] the pharmaceutical[109] and polymer industries.[110]

In past years, we have shown how catalysis may be used for the selective aerobic oxidation of sulfides,[111] carbonylation of thiazolidines,[112] and thiocarbonylation of propargylic alcohols,[83] allenes,[113] allylic alcohols[114] and enynes[115] with thiols and carbon monoxide affording unsaturated thioesters and dithioesters. To our knowledge, the hydroformylation of a triple bond to form an α,β-unsaturated aldehyde in the presence of sulfur has not been accomplished.

3.2 Aim of Research

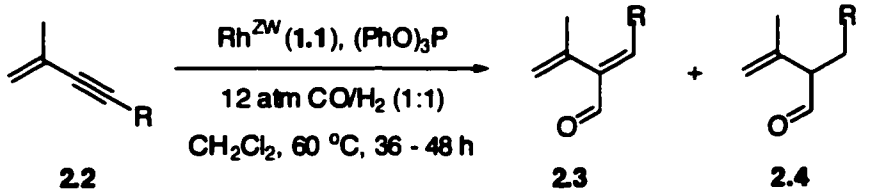
Acetylenic thiophenes and other acetylenic sulfur containing heterocycles occur naturally in plants,[116] and may be readily prepared by the Pd/CuI coupling of haloheterocycles with terminal alkynes.[117] Over the past few years, increased attention has been given to sulfur containing heterocycles which contain substituted unsaturated groups.[118] Hydroformylation of an acetylenic unit in these heterocycles would result in the formation of either a branched or linear α,β-unsaturated aldehyde with a thiophene conjugating unit. These novel materials would have the potential to be further modified to new functionalities, or transformed by cyclization[119] or addition reactions;[120] ultimately assisting in the preparation of drugs[121] and pesticides.[122]

The following sections describe the use of catalytic quantities of **1.1**, in the presence of triphenyl phosphite, CO and H_2 to attain the hydroformylation of both simple and functionalized acetylenic thiophenes in good to excellent conversions, selectivities, and yields.

3.3 Results and Discussion

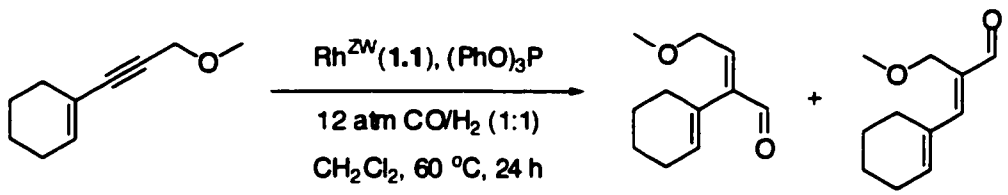
The hydroformylation of conjugated enynes was performed using the zwitterionic rhodium complex (**1.1**) and triphenyl phosphite, 3 to 6 mmols of enyne, and 12 atm of

synthesis gas at 60 °C for 36 to 48 hours (Eq. 3-1). Under these conditions branched formyl-dienes were obtained in 50 - 70 % yields (see Chapter 2).



2.2 **2.3** **2.4** (3-1)

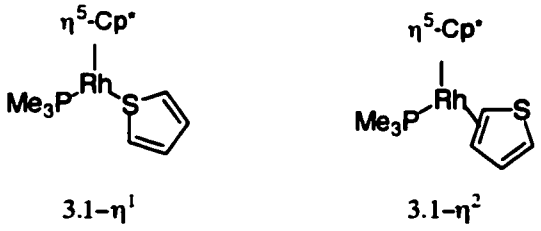
During this investigation an interesting substrate was examined to gain insight into the mechanism of the reaction. The hydroformylation of 1-(3-methoxyprop-1-ynyl)cyclohexene (**2.2f**) resulted in two formyl dienes with a branched to linear ratio of 2:1 (Eq. 3-2). These results prompted us to investigate the effects of additional functionalities, and to gain a better understanding of their role in the hydroformylation process.



2.2f 2 : 1 **2.3f** (3-2)

In 1997, a theoretical study on the binding of thiophenes to transition metals noted two possible modes of complexation to rhodium (Fig. 3-1).[123] The **3.1**-η^1 complex (15 kcal/mol) was appreciably lower in binding energy than the **3.1**-η^2 complex (30

kcal/mol). This study suggested to us the possibility of a sulfur assisted hydroformylation of acetylenic thiophenes. In many studies,[96-98] including our own work on the hydroformylation of enynes, it was observed when there is both a double and triple bond present within a molecule, the triple bond is more reactive. This is consistent with the binding energy for the rhodium - triple bond coordination being lower than the binding energy for the metal coordinating to a double bond. One could also infer that the **3.1-η^1** binding energy to the thiophene sulfur would be similar to that for a triple bond to rhodium. Having both of these functionalities adjacent to each other would result in a beneficial arrangement for the rhodium catalyzed hydroformylation of the triple bond.



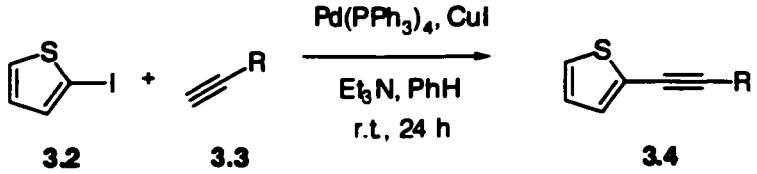
3.1-η^1 3.1-η^2

Figure 3-1. Thiophene Coordination to a Rhodium Complex

It was observed during our study on the hydroformylation of enynes, that triphenyl phosphite is less active as a ligand than the functionalized bisphosphite ligand used by Buchwald and co-workers.[53] By controlling the substitution within the aromatic phosphite structure the kinetics of the reaction can be readily controlled. As well it may be desirable in some cases to use a less active catalytic system to attain a product when the substrate is more active.

3.3.1 Preparation of Acetylenic Thiophenes

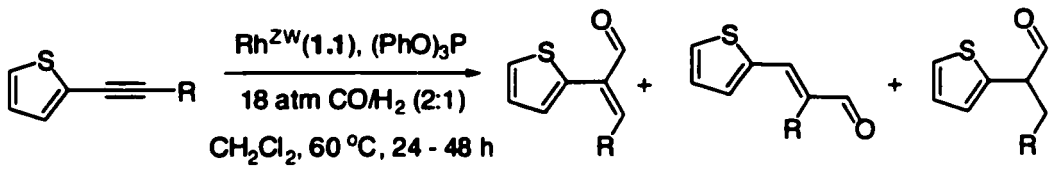
Acetylenic thiophenes may be readily prepared by the direct coupling of halo substituted thiophenes (-Br and -I) with terminal alkynes in the presence of tetrakis(triphenylphoshine)palladium, CuI, and base (Eq. 3-3).[117] The acetylenic unit may have functionalities including alkyl, propargyl ether, alcohol or ester, phenylacetylene, and enyne. Yields ranging from 65 to 90 % were obtained in these reactions (Table 3-1).



3.2 3.3 3.4 (3-3)

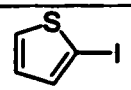
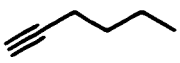
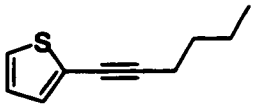
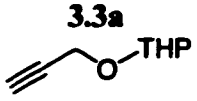
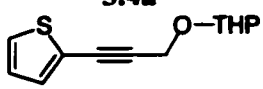
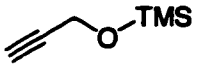
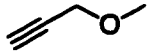
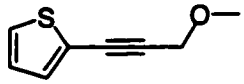
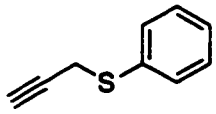
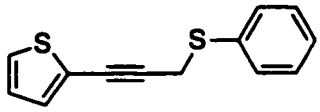
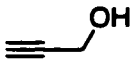
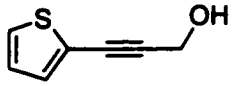
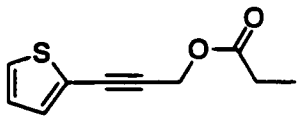
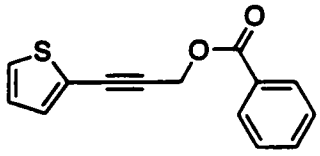
3.3.2 Reaction Optimization

In principle, the hydroformylation of 2-acetylenic thiophenes could afford the isomeric unsaturated aldehydes **3.5** and **3.6** (Eq. 3-4).

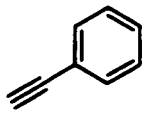
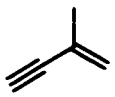
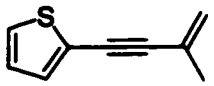
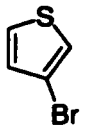
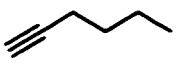
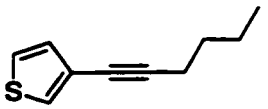
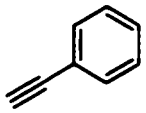
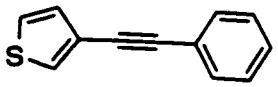
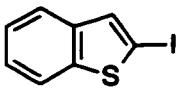
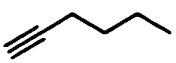
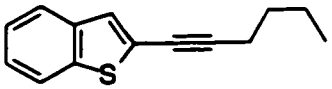
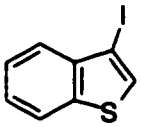
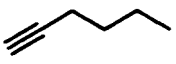
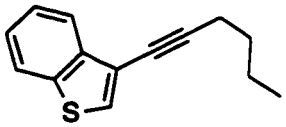


3.4 3.5 3.6 3.7 (3-4)

Table 3-1. Preparation of 2-Acetylenic Thiophenes [a]

Entry	3.2	3.3	3.4	Isolated Yield of 3.4 (%)[b]
1	 **3.2a**	 **3.3a**	 **3.4a**	86
2		 **3.3b**	 **3.4b**	83
3		 **3.3c**	 **3.4c**	82
4		 **3.3d**	 **3.4d**	86
5		 **3.3e**	 **3.4e**	74
6		 **3.3f**	 **3.4f**	65
7			 **3.4g[c]**	89
8			 **3.4h[c]**	90

(Table 3-1. Continued)

Entry	3.2	3.3	3.4	Isolated Yield of 3.4 (%)[b]
9		 **3.3g**	 **3.4i**	78
10		 **3.3h**	 **3.4j**	81
11	 **3.2b**[d]	 **3.3a**	 **3.4k**	79
12		 **3.3g**	 **3.4l**	75
13	 **3.2c**	 **3.3a**	 **3.4m**[e,f]	86
14	 **3.2d**	 **3.3a**	 **3.4n**[e,f]	85

[a] Reaction conditions: heterocycle (**3.2**), 20 mmol; alkyne (**3.3**), 25 - 30 mmol; $Pd(PPh_3)_4$, 0.2 mmol; CuI, 0.5 mmol; PhH, 50 mL; Et_3N, 15 mL; room temperature, 24 h. [b] The product was isolated by Kugelrohr distilation. [c] The ester was prepared by esterification of **3.4f**, and isolated by silica gel column chromatography using pentane:ether (90:10). [d] CH_2Cl_2 instead of PhH, reflux, 5 days. [e] Reflux. [f] The product was isolated via preparative HPLC size exclusion chromatography using $CHCl_3$ as the eluant.

Our initial investigation of thiophenynes utilized the same conditions employed for the hydroformylation of enynes. Using 3 mmol of 2-(hex-1-ynyl)thiophene (**3.4a**), 4 mol % **1.1**, 16 mol % $(PhO)_3P$, 10 mL CH_2Cl_2, 6 atm CO, and 6 atm H_2 at 60 °C for 48 hours resulted in only 70 % conversion of **3.5a** accompanied by a dark red discoloration of the reaction mixture. Increasing the solvent volume to 20 mL of CH_2Cl_2 resulted in the reaction proceeding to completion. The reaction mixture was yellow, and a substantial amount of **3.7a**, R = n-C_4H_9 was formed here. The amount of the latter was reduced to <10 % of the total yield by increasing the CO to H_2 ratio to 2:1. By increasing the total pressure to 18 atm, the reaction was complete after 48 hours resulting in a 93 % isolated yield of **3.5a**. When functionalized 2-alkynylthiophenes were used as reactants less catalyst and shorter reaction times were required to obtain complete conversion. Acetylenic thiophenes containing propargyl ether or ester functionalities required 1.5 mol % of **1.1**, 6 mol % of $(PhO)_3P$, and a reaction time of 24 hours. Substrates having a double bond or a phenyl group were best hydroformylated with 2 mol % of **1.1**, 8 mol % of $(PhO)_3P$, and a reaction time of 24 hours.

3.3.3 Reactions of 2-Acetylenic Thiophenes Where R = n-Butyl

The hydroformylation of 2- and 3-substituted acetylenic alkyl thiophenynes is completely regioselective affording **3.5** as the only product. For example, **3.5a** and **3.5k**

were obtained from **3.4a** and **3.4k**, respectively, with < 10 % of **3.7** as a by-product (Table 3-2, entries 1 and 2). Interestingly, the process becomes less selective using the corresponding benzothiophene reactants, **3.4m** and **3.4n**. Hydroformylation of 2-(hex-1-ynyl)benzothiophene (**3.4m**) affords two aldehydes in 88 % isolated yield with the ratio of **3.5m/3.6m** being 5:1 (Table 3-2, entry 3). The hydroformylation of the isomeric 3-(hex-1-ynyl)benzothiophene (**3.4n**) also favored the branched aldehyde **3.5n**, but in a 64/21 ratio of **3.5n/3.6n** (Table 3-2, entry 4). The influence of the fused benzene ring may be explained by visualizing the approach of **1.1** toward the alkynylbenzothiophene (Fig 3-2). The freedom of rotation of the tetraphenylborate group bound to the rhodium complex (via π-complexation to one arene ring) is limited when **1.1** is in close proximity to the 2-alkynylbenzothiophene. The freedom of rotation becomes even more constrained when **3.4n** was used as the substrate, thus affording **3.5n/3.6n** in a lower ratio than **3.5m/3.6m**.

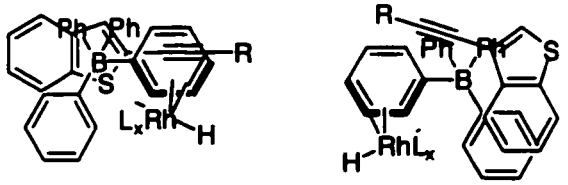
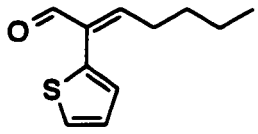
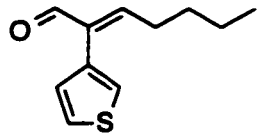
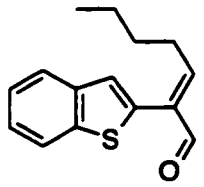
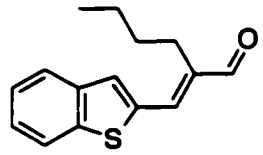
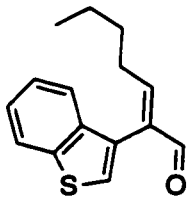
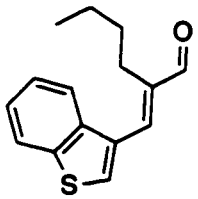


Figure 3-2. Approach of 1.1 to an alkynylbenzothiophene

Table 3-2. Hydroformylation of Derivatives Containing Alkyl Acetylenic Units [a]

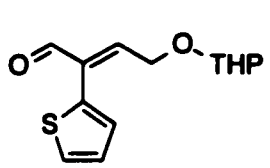
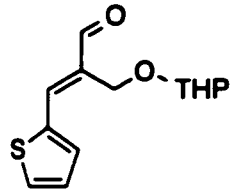
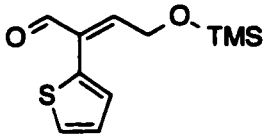
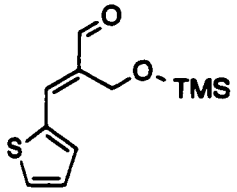
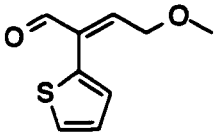
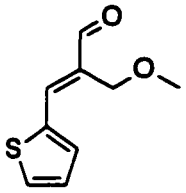
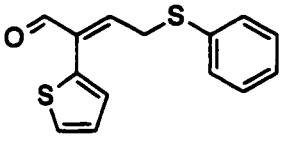
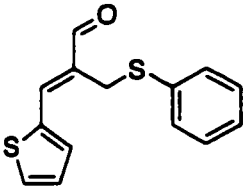
Entry	3.4	Time (h)	Conv. (%)[b]	Product (Isolated Yield)[c,d]
1	**3.4a**	48	100	 (93)[e] **3.5a**
2	**3.4k**	48	100	 (90)[f] **3.5k**
3	**3.4m**	24	100	 (73) **3.5m**  (15) **3.6m**
4[g]	**3.4n**	48	100	 (64) **3.5n**  (21) **3.6n**

[a] Reaction conditions: **3.4**, 3 mmol; **1.1**, 0.12 mmol (4 %), $(PhO)_3P$, 0.48 mmol (16 %); CH_2Cl_2, 20 mL; CO, 12 atm; H_2, 6 atm; 60 °C. [b] The percent conversion was determined by ^1H NMR. [c] The ratio of **3.5**/**3.6** was determined by the ratio of their aldehyde ^1H NMR signals. [d] The products were isolated by silica gel column chromatography using a pentane ether gradient ranging from 90:10 to 75:25 as eluant. [e] ~ 7 % of **3.7a**, R = C_4H_9 was also formed. [f] ~ 9 % of the saturated aldehyde (**3.7k**)was formed as well. [g] The products were isolated by silica gel column chromatography using a pentane ether gradient ranging from 95:5 to 85:15 as eluant.

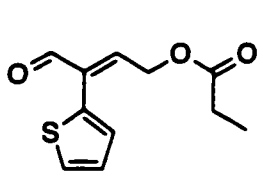
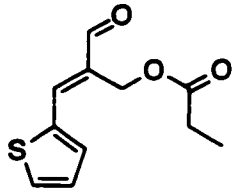
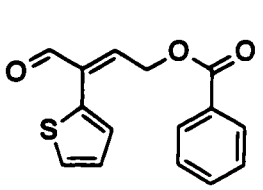
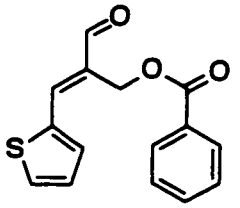
3.3.4 Reactions of 2-Acetylenic Thiophenes Containing Propargyl Ether and Ester Units

Hydroformylation of propargyl ether or ester derivatives of 2-acetylenic thiophenes affords two α,β-unsaturated aldehydes, the major product being **3.5** in all cases (Table 3-3). The ratio of **3.5/3.6** ranged from 2.5 - 3.3/1 in accumulative yields of 94 – 97 % (Table 3-3, entries 1 to 4), while 2-acetylenic thiophenes containing propargyl ester units were obtained in a 1.8 - 2.3/1 ratio using **3.4g** and **3.4h** as substrates in 88 – 93 % additive yields (Table 3-3, entries 5 and 6). The size of the substituent connected to the propargyloxy chain in these examples influences the regioselectivity slightly. A tertiary or aromatic substituent at the oxygen atom increases the preference for **3.5** to **3.6** by 4 to 6 % relative to the use of primary or secondary groups.

Table 3-3. Hydroformylation of Thiophenynes Containing Propargyl Ether and Ester Units [a]

Entry	3.4	Conv. (%)[b]	Product (Isolated Yield)[c,d]	
1	**3.4b**	100	 (69) **3.5b**	 (25) **3.6b**
2	**3.4c**	100	 (73) **3.5c**	 (22) **3.6c**
3	**3.4d**	100	 (70) **3.5d**	 (27) **3.6d**
4[e]	**3.4e**	100	 (73) **3.5e**	 (23) **3.6e**

[Table 3-3. Continued)

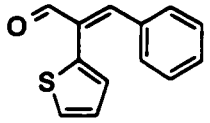
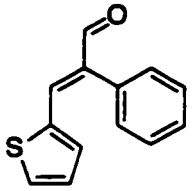
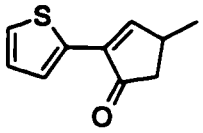
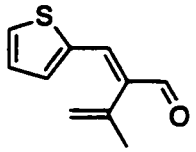
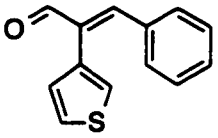
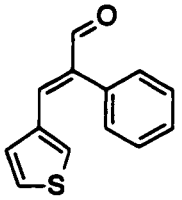
Entry	3.4	Conv. (%)[b]	Product (Isolated Yield)[c,d]	
5[f]	**3.4g**	100	 (57) **3.5g**	 (31) **3.6g**
6[f]	**3.4h**	100	 (63) **53.h**	 (30) **3.6h**

[a] Reaction conditions: **3.4**, 3 mmol; **1.1**, 0.045 mmol (1.5 %), $(PhO)_3P$, 0.18 mmol (6 %); CH_2Cl_2, 20 mL; CO, 12 atm; H_2, 6 atm; 60 °C, 24 h. [b] The percent conversion was determined by ^1H NMR. [c] The ratio of **3.5/3.6** was determined by the ratio of the aldehyde signals in the proton NMR. [d] The products were isolated by silica gel column chromatography using a pentane ether gradient ranging from 90:10 to 75:25 as eluant. [e] **1.1**, 0.06 mmol; $(PhO)_3P$, 0.24 mmol. [f] The products were isolated by silica gel column chromatography using a pentane ether gradient ranging from 90:10 to 50:50 as eluant.

3.3.5 Reactions of 2-Acetylenic Thiophenes Where R= Phenyl or Vinyl

Good regioselectivity was also observed when the acetylenic unit has an aryl or vinyl group. The results for the hydroformylation of 2-(1-phenylethynyl)thiophene (**3.4i**) compared to 3-(1-phenylethynyl)thiophene (**3.4l**) (Table 3-4, entries 1 and 3) follow the same trend as that observed for 2- versus 3-alkynylbenzothiophenes (**3.4m** and **3.4n**). The preference for **3.5** is greater for both substrates with ratios of **3.5i/3.6i** of 83/15 compared to **3.5l/3.6l** of 58/30. This is consistent with the proposed influence of the heterocyclic sulfur relative to the position of the triple bond. The further the sulfur atom is from the alkyne unit, the less its influence on the regioselectivity of the hydroformylation reaction. The 1-en-3-yne derivative (**3.4j**) affords a cyclopentenone (**3.8**) as the major product in 48 % isolated yield (Table 3-4, entry 2) possibly by intramolecular cyclization of the aldehyde (**3.5j**). The minor product in 17 % isolated yield is the formyl-diene (**3.6j**) which is in accord with our previous investigation of enynes (see Chapter 2).

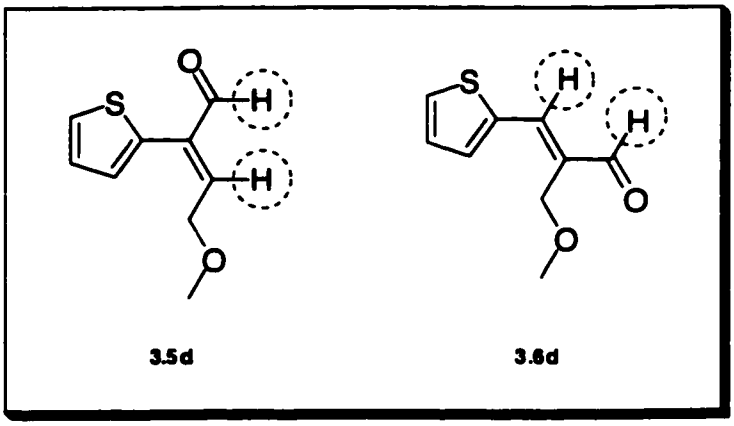
Table 3-4. Hydroformylation of Acetylenic Thiophenes Containing Phenyl or Vinyl Groups [a]

\Entry	3.4	Conv. (%)[b]	Product (Isolated Yield)[c,d]	
1	**3.4i**	100		
			(83) **3.5i**	(15) **3.6i**
2	**3.4j**	100		
			(48) **3.8**	(17) **3.6j**
3	**3.4l**	100		
			(58) **3.5l**	(30) **3.6l**

[a] Reaction conditions: **3.4**, 3 mmol; **1.1**, 0.06 mmol (2 %), $(PhO)_3P$, 0.24 mmol (8 %); CH_2Cl_2, 20 mL; CO, 12 atm; H_2, 6 atm; 60 °C, 24 h. [b] The percent conversion was determined by ^1H NMR. [c] The ratio of **3.5/3.6** was determined by the ratio of the aldehyde ^1H NMR signals. [d] The products were isolated by silica gel column chromatography using a pentane ether gradient ranging from 90:10 to 75:25 as eluant.

3.3.6 NMR Determination of Regiochemistry

Distinguishing between the trisubstituted (*E*)-double bond and the corresponding (*Z*)-double bond from the isomeric products resulting from the hydroformylation of thiophenynes was determined by NOE difference experiments. Product **3.5d** (Fig. 3-3) and **3.6d** (Fig. 3-4) were used as examples of the two isomers. In the case of **3.5d**, irradiation of the aldehydic ^{1}H at δ 9.56 (s, 1H) led to a strong enhancement of the olefinic ^{1}H at δ 6.71 (t, 1H, . J = 5.4 Hz). As well, irradiation of the olefinic ^{1}H (δ 6.71) gives rise to a strong enhancement of the aldehydic 1H (δ 9.56). Therefore **3.5d** has the (*E*) configuration as drawn below. Similarly when the aldehyde ^{1}H of **3.6d** at δ 9.54 (s, 1H) was irradiated a strong enhancement of the olefinic ^{1}H at δ 7.56 (s, 1H) was observed. In addition, irradiation of the olefinic ^{1}H (δ 7.56) gives rise to a strong enhancement of the aldehydic ^{1}H (δ 9.54). These results show that for both isomers of the α,β-unsaturated aldehydes have the CHO and CH on the same side of the 2,3-double bond, both isomers are (*E*)-isomers.



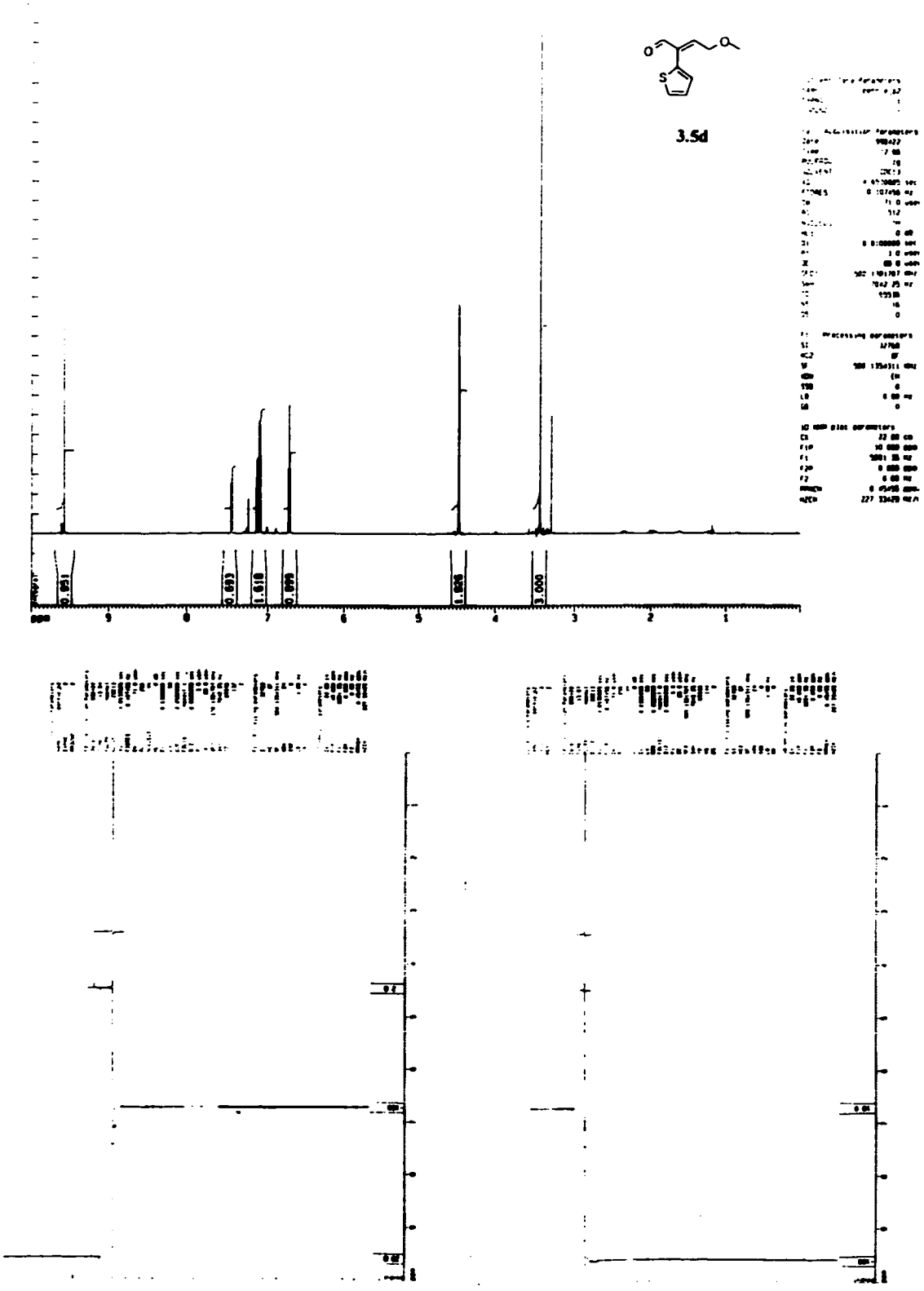


Figure 3-3. NOE Difference Experiment on 3.5d

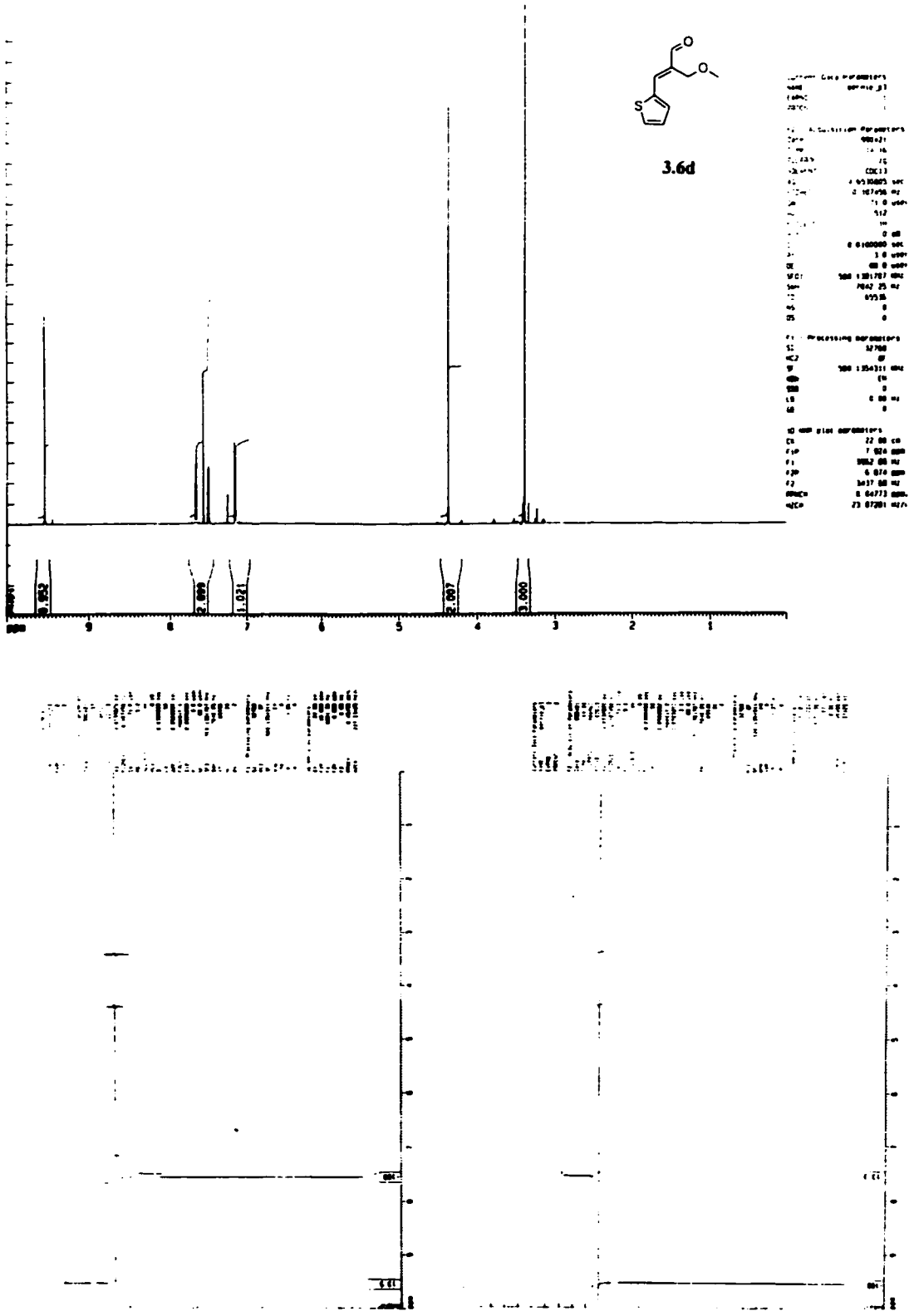
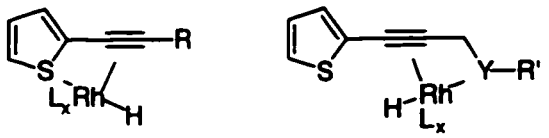


Figure 3-4. NOE Difference Experiment on 3.6d

3.3.7 Mechanistic Aspects

The above data demonstrates the influence of the heterocyclic sulfur atom on the hydroformylation process. Co-complexation between the thiophene sulfur and the alkyne unit (**3.9**) may be generated for acetylenic thiophenes containing other functionalized groups (Fig. 3-5). For reactants which contain ether and ester groups, a competing binding for rhodium is that of the alkyne and the functional unit **3.10** (Fig. 3-5). The preference for **3.5** relative to **3.6** may be due to a lower binding energy for **3.9** than for **3.10**. The coupled interaction with the lowest binding energy will become the major product, and the higher binding energy interaction will result in attaining the minor product.

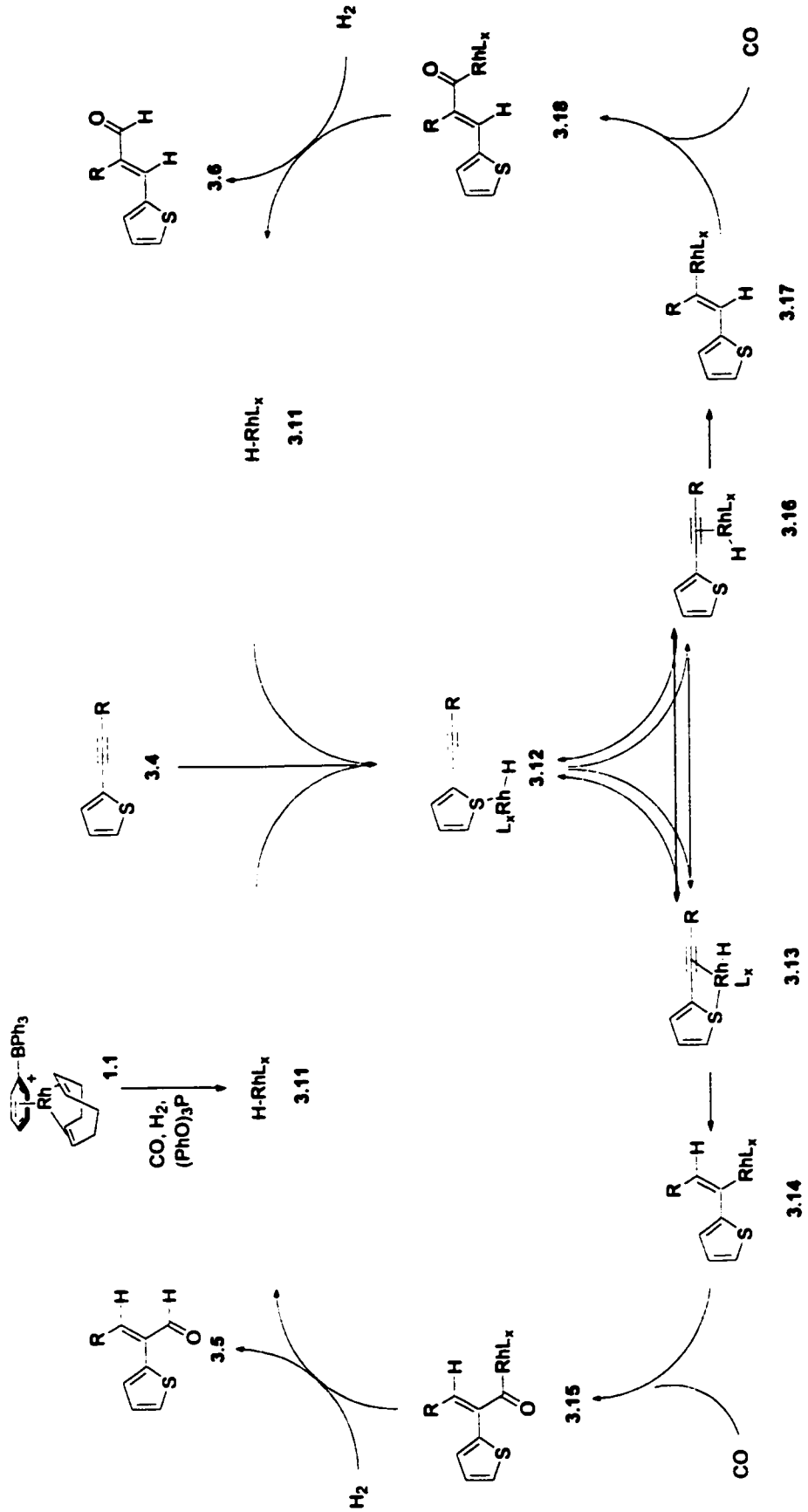


3.9 **3.10**

Figure 3-5. Rhodium coordination prior to hydroformylation

A possible mechanism for the heterocyclic sulfur directed hydroformylation of 2-alkynylthiophenes, shown in Scheme 3-1, consists of the following steps. The rhodium hydride (**3.11**) binds to the heterocycle forming an η^1-sulfur-donor ligand complex **3.12.**

Scheme 3-1. Proposed Mechanism



The triple bond then coordinates to the metal to give one of two Rh/alkynylthiophene intermediates (**3.13** or **3.16**). Intramolecular addition of the rhodium hydride to the preferred triple bond – rhodium intermediate **3.13** affords the (*E*)-isomer **3.14**. Subsequent CO insertion into **3.14** would give the acyl rhodium carbonyl species (**3.15**). The reaction of the rhodium complex with hydrogen gives the thiophene branched α,β-unsaturated aldehyde **3.5**, and regenerates the rhodium hydride **3.11**. Subsequently, intramolecular addition of the rhodium hydride to the triple bond of the alkynylthiophene/rhodium intermediate **3.16** affords the opposite (*E*)-isomer **3.17**,. which, on CO insertion, could form the acyl rhodium carbonyl intermediate **3.18**. The reaction of the rhodium complex with hydrogen provides the α,β-unsaturated aldehyde **3.6**, and regenerates the hydride **3.11**.

3.4 Conclusion

In conclusion, this study has demonstrated the significant influence of a thiophene sulfur on the regioselectivity of the hydroformylation of alkynes. Good - complete regioselectivity was observed in these reactions. This research has led to a greater understanding of the factors that influence the hydroformylation process. Some of the aldehydes formed are novel and have potential in both pharmaceutical and agrochemical businesses.

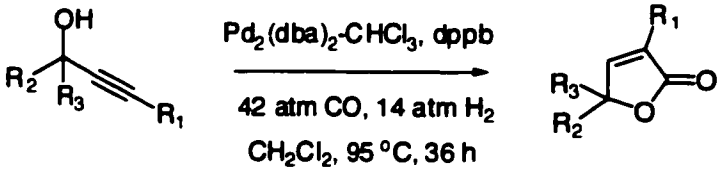
CHAPTER 4

CHEMO- AND REGIOSELECTIVE CYCLOHYDROCARBONYLATION OF α-KETO ALKYNES CATALYZED BY A ZWITTERIONIC RHODIUM COMPLEX AND TRIPHENYL PHOSPHITE

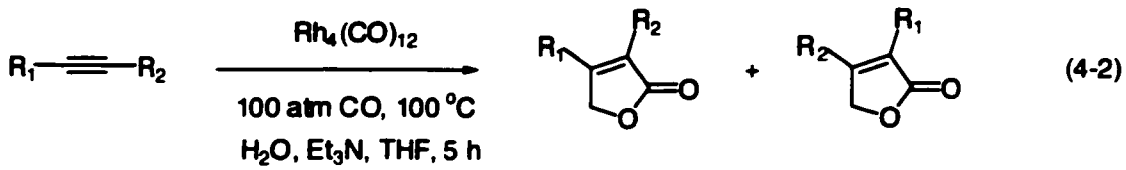
4.1 Introduction

Furanones have been of interest for many years due to their biological activity.[124] A variety of transition metal catalyzed methods have been utilized for the preparation of γ-lactones including the transition metal catalyzed cyclocarbonylation of alkenols,[125] alkynols,[126] alkynes[127] and alkynoic acids.[128] Several of these reactions are of value for the synthesis of multifunctionalized lactones.

The cyclocarbonylation of acetylene containing substrates requires high temperatures and pressures for both palladium[84] (Eq. 4-1) and rhodium[127a] catalyzed reactions (Eq. 4-2). Obstacles have been encountered in attaining good yields of these highly substituted furanones under milder temperatures and pressures.[127d,127k] The ability to use milder conditions may be of importance for the preparation of chiral furanones from achiral substrates, as found for the asymmetric hydroformylation of alkenes.[129]



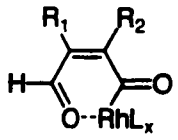
(4-1)



(4-2)

4.2 Aim of Research

Previous work with $Rh_4(CO)_{12}$ utilizing internal alkynes[127a,127c] postulated a dicarbonyl-metal complex as a reaction intermediate (**4.1**). Here, R_1 and R_2 were alkyl or aromatic groups. A similar intermediate may result from the hydroformylation of an α-keto alkyne if the carbonylation step occurred at the triple bond carbon closest to R_2.



4.1

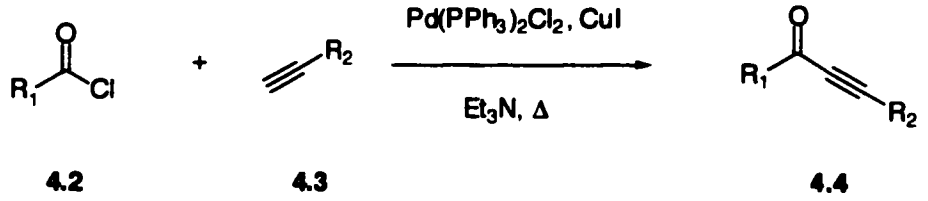
The use of an achiral substrate, an alkynone, would create a new chiral center in the preparation of furanones. In addition, in 1996, tetra-substituted 3(2*H*)-furanones were readily prepared in moderate yields from 4-hydroxyalk-2-ynones and alkyl halides using tandem CO_2 addition-elimination conditions.[130]

This chapter reports the use of catalytic quantities of **1.1**, in the presence of triphenyl phosphite, CO, and H_2 for the cyclohydrocarbonylation of multi-functionalized α-keto alkynes to give 2-, 2(3*H*)- and 2(5*H*)-furanones in good to excellent chemo- and regioselectivities, conversions, and yields.

4.3 Results and Discussion

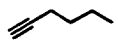
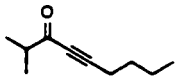
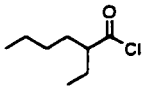
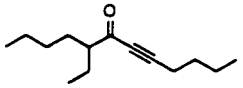
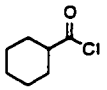
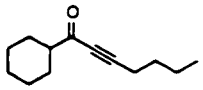
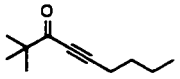
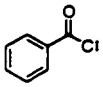
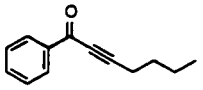
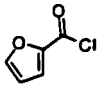
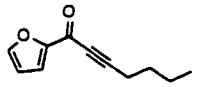
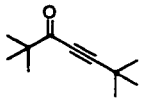
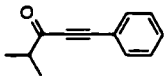
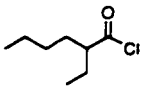
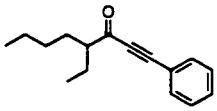
4.3.1 Preparation of Starting Materials

There are a number of procedures to prepare alkynones.[131-134] A facile approach is the coupling of terminal alkynes and acyl chlorides described by Hagihara and coworkers using catalytic quantities of $Pd(PPh_3)_2Cl_2$ and CuI in the presence of Et_3N (Eq. 4-3).[131] This procedure was applied to the coupling of secondary and tertiary alkyl, and aryl R_1 groups with alkyl, alkoxy, vinyl, and aryl terminal alkynes in 56 to 87 % yields (Table 4-1).

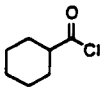
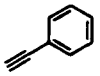
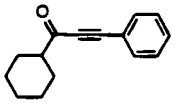
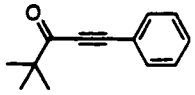
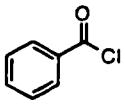
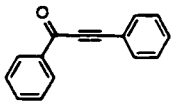
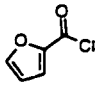
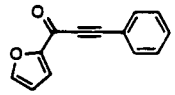
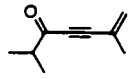
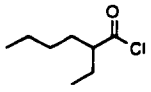
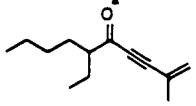
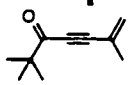
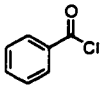
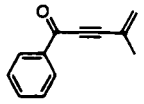
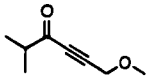


4.2 **4.3** **4.4** (4-3)

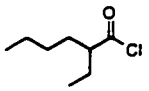
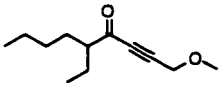
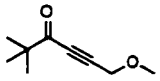
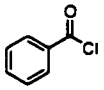
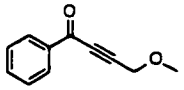
Table 4-1. Preparation of α-Keto Alkynes [a]

Entry	4.2	4.3	T (°C)	4.4	Isolated Yield[b] (%)
1	 **4.2a**	 **4.3a**	50	 **4.4b**	56
2	 **4.2b**		50	 **4.4c**	87
3	 **4.2c**		50	 **4.4d**	83
4	 **4.2d**		50	 **4.4e**	75
5	 **4.2e**		RT	 **4.4f**	70
6	 **4.2f**		RT	 **4.4g**	85
7	 **2a**	 **4.3b**	50	 **4.4h**	56
8	 **4.2a**	 **4.3c**	50	 **4.4j**	81
9	 **4.2b**		50	 **4.4k**	85

(Table 4-1. Continued)

Entry	4.2	4.3	T (°C)	4.4	Isolated Yield[b] (%)
10	 **4.2c**	 **4.3c**	50	 **4.4l**	78
11	 **4.2d**		50	 **4.4m**	84
12	 **4.2e**		RT	 **4.4n**[c]	78
13	 **4.2f**		RT	 **4.4o**[c]	81
14	 **4.2a**	 **4.3d**	50	 **4.4p**	59
15	 **4.2b**		50	 **4.4q**	77
16	 **4.2d**		50	 **4.4r**	67
17	 **4.2e**		RT	 **4.4s**	72
18	 **4.2a**	 **4.3e**	50	 **4.4t**	57

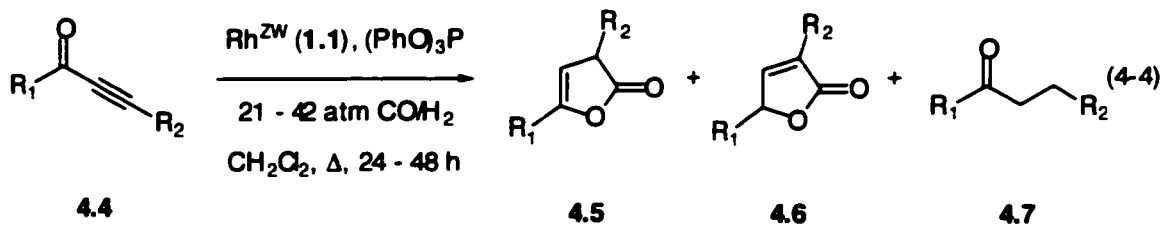
(Table 4-1. Continued)

Entry	4.2	4.3	T (°C)	4.4	Isolated Yield[b] (%)
19	 **4.2b**	 **4.3e**	50	 **4.4u**	65
20	 **4.2d**		50	 **4.4v**	68
21	 **4.2e**		RT	 **4.4w**	62

[a] Reaction conditions: acyl chloride (**4.2**), 20 mmol; alkyne (**4.3**), 25 - 30 mmol; $Pd(PPh_3)_2Cl_2$, 0.05 mmol (0.25 %); CuI, 0.25 mmol (1.25 %); Et_3N, 40 mL, 24 h. [b] The products were isolated by Kugelrohr distillation. [c] Products **4.4n** and **4.4o** were isolated by flash silica gel chromatography using pentane:ether (90:10) as eluant followed by crystallization.

4.3.2 Reaction Optimization

α-Keto alkynes are cyclohydrocarbonylated by using the zwitterionic rhodium complex (**1.1**) and $(PhO)_3P$ under conditions similar to those utilized for the hydroformylation of conjugated enynes and thiophenynes. Using 2 mol % **1.1**, 8 - 32 mol % $(PhO)_3P$, 1.5 mmol **4.4**, 17.5 - 38.5 atm CO, and 3.5 atm H_2 at 70 - 120 °C for 24 to 48 hours afforded either the 2(3*H*)-furanone (**4.5**) or 2(5*H*)-furanone (**4.6**), and the hydrogenated alkynone **4.7** (Eq. 4-4).



The conditions for the cyclohydrocarbonylation of α-keto alkynes were optimized using 2,2-dimethylnon-4-yn-3-one (**4.4e**) as a model substrate. Treating the alkynone with 2 mol % **1.1**, 8 mol % $(PhO)_3P$, 10 mL of CH_2Cl_2, 14 atm CO, 7 atm H_2 at 60 °C for 20 hours resulted in no reaction (Table 4-2, entry 1). Increasing the temperature from 100 to 120 °C after 20 hours favored the production of ketone **4.7e** (Table 4-2, entries 2 and 3). Increasing the CO/H_2 ratio to 5:1 at 21 atm CO/H_2, gave low to moderate selectivity (Table 4-2, entries 4 and 5). However, increasing the pressure to 42 atm, with a CO/H_2 ratio of 11:1, results in a moderate preference for **4.5e** to **4.7e**

(Table 4-2 entries 6 and 7). The amount of $(PhO)_3P$ influenced the ratio of **4.5** to **4.7**. Increasing the amount of $(PhO)_3P$ from 8 to 32 % raised the preference for **4.5e** from 1.4:1 to 1.9:1 at 80 °C with lower conversion (Table 4-2, entries 8 and 9). At 90 °C, full conversion of the reaction occurred with a **4.5/4.7** product ratio of 1.8:1 (Table 4-2, entry 11). Applying the conditions of Table 4-2, entry 7 (42 atm, CO/H_2 of 11:1, 80 °C, and 20 hours) to $(EtO)_3P$, and phosphine ligands Ph_3P and dppb resulted in the predominant production of **4.7e** (Table 4-3, entries 2 to 4).

Table 4-2. Reaction Optimization Using 4.4e [a]

Entry	$(PhO)_3P$ (mol %)	Pressure (atm)	$CO:H_2$	T (°C)	t (h)	Conv. [b] (%)	**4.5**:**4.7** [c]
1	8	21	2:1	60	20	N.R.	-
2	8	21	2:1	120	20	100	1:1.8
3	8	21	2:1	100	20	100	1:1.6
4	8	21	5:1	100	20	100	1.1:1
5	8	21	5:1	90	20	75	1.7:1
6	8	42	11:1	90	20	100	1:1
7	8	42	11:1	80	20	93	1.4:1
8	16	42	11:1	80	20	85	1.7:1
9	32	42	11:1	80	20	73	1.9:1
10	32	42	11:1	90	20	100	1.8:1

[a] Reaction conditions: **4.4**, 1.5 mmol; **1.1**, 0.03 mmol (2 %); $(PhO)_3P$, 0.12 - 0.48 mmol (8 - 32 %); CH_2Cl_2, 10 mL; CO, 14 - 38.5 atm; H_2, 3.5 - 7 atm; 60 - 120 °C, 20 h. [b] The percent conversion was determined by ^1H NMR. [c] The ratio of **4.5**:**4.7** was determined by ^1H NMR. Trace amounts of **4.6** were detected in these reactions

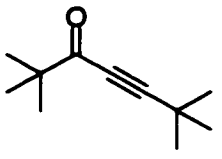
Table 4-3. Catalyst and Ligand Optimization Using 4.4e [a]

Entry	Ligand	Conv. [b] (%)	**4.5**:**4.6**:**4.7** [c]
1	$(PhO)_3P$	93	1.4:t:1
2	$(EtO)_3P$	23	t:t:1
3	Ph_3P	100	t:t:1
4	dppb [d]	100	t:t:1

[a] Reaction conditions: **4.4**, 1.5 mmol; **1.1**, 0.03 mmol (2 %); ligand, 0.12 mmol (8 %); CH_2Cl_2, 10 mL; CO, 38.5 atm; H_2, 3.5 atm; 80 °C, 20 h. [b] The percent conversion was determined by ^1H NMR. [c] The ratio of **4.5**:**4.6**:**4.7** was determined by ^1H NMR. [d] dppb, 0.06 mmol (4 %),

4.3.3 Reactions of α-Keto Alkynes where R_2 is an Alkyl Chain

The cyclohydrocarbonylation reaction of conjugated ynones may be readily applied to a variety of substrates using 2 mol % **1.1**, 32 mol % $(PhO)_3P$, 1.5 mmol **4.4**, 38.5 atm CO, 3.5 atm H_2 at 90 °C for 24 hours. The structure of the functional group in the R_1 position significantly affects the ratio of **4.5** to **4.7**. Increasing the size of R_1 group from primary to secondary lowers the preference for **4.5** from 91 to 83 % yields (Table 4-4, entries 1 to 3). Using a cyclohexyl, phenyl or furanyl group results in a decreased preference of **4.5** ranging from 61 to 68 % (Table 4-4, entries 4 to 8). The use of a furanyl substituent favors **4.5g** after 18 h, and **4.6g** after 24 h. Attempts to isolate **4.5g** by silica gel chromatography results in its isomerization to **4.6g**. In addition, the complete isomerization of **4.5f** to **4.6f** was observed utilizing a reaction time of 36 hours (Table 4-4, entry 7). Replacing the n-butyl group of **4.4e** with *tert*-butyl - i.e. 2,2,6,6-tetramethylhept-4-yn-3-one (**4.4h**) - results in no cyclohydrocarbonylation products. The substrate **4.4h** did not react at 90 °C, and only gave a 50 % conversion to **4.7h** at 120 °C (Eq. 4-5).



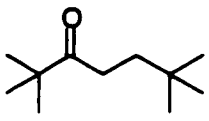
4.4h

Rh^{ZW} (**1.1**), $(PhO)_3P$

42 atm CO/H_2 (11:1)

CH_2Cl_2, 120 °C, 24 h

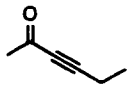
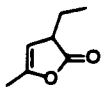
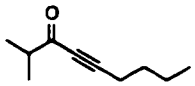
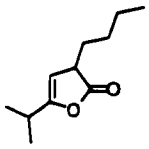
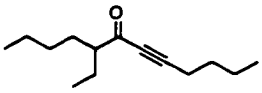
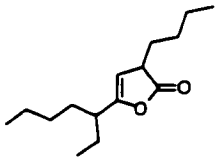
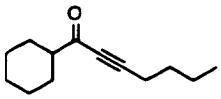
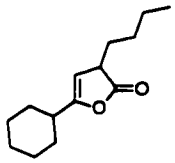
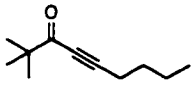
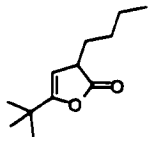
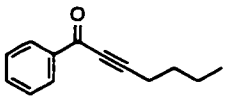
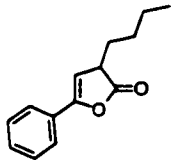
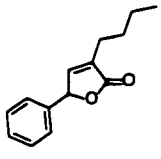
50 % Conversion



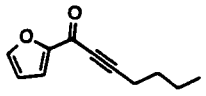
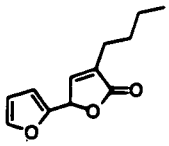
4.7h

(4-5)

Table 4-4. Cyclohydrocarbonylation where R_2 is an Alkyl Chain [a]

Entry	4.4	Conv. [b] (%)	Heterocycle	Isolated Yield [c] (%)
1	 **4.4a**	100	 **4.5a**	91
2	 **4.4b**	100	 **4.5b**	88
3	 **4.4c**	100	 **4.5c**	83
4 [d]	 **4.4d**	90	 **4.5d**	63
5	 **4.4e**	100	 **4.5e**	64
6	 **4.4f**	100	 **4.5f [e]**	63
7 [e]		100	 **4.6f [e]**	61

(Table 4-4. Continued)

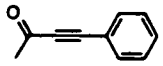
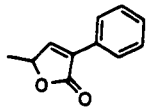
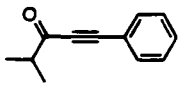
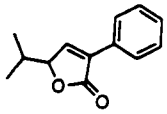
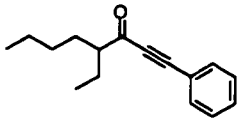
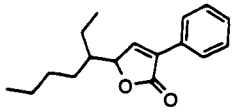
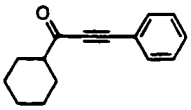
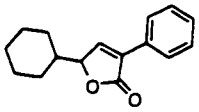
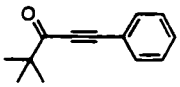
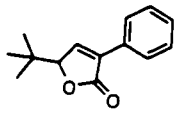
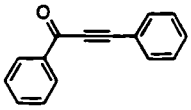
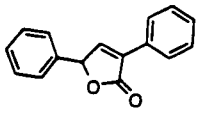
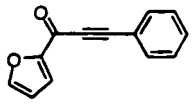
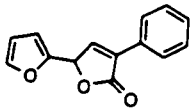
Entry	4.4	Conv. [b] (%)	Heterocycle	Isolated Yield [c] (%)
8	 **4.4g**	100	 **4.6g** [e]	68

[a] Reaction conditions: **4.4**, 1.5 mmol; **1.1**, 0.03 mmol (2 %); $(PhO)_3P$, 0.48 mmol (32 %); CH_2Cl_2, 10 mL; CO, 38.5 atm; H_2, 3.5 atm; 90 °C, 24 h. [b] The percent conversion was determined by ^1H NMR. [c] The products were isolated by Kugelrohr distillation followed by flash silica gel chromatography using pentane:ether (99:1) as eluant. [d] 36 h. [e] The products were isolated by flash silica gel chromatography using pentane:ether (85:15) as eluant.

4.3.4 Reactions of α-Keto Alkynes where R_2 is a Phenyl Group

High selectivity for the 2(5*H*)-furanone (**4.6**) was attained when the R_2 unit of **4.4** is a phenyl group. The temperature was increased from 90 °C to 120 °C to enable furanone production to be complete in 24 - 48 hours due to decreased reactivity for reactions **4.4i – 4.4o** compared with **4.4a – 4.4g** (Table 4-5). The reaction was complete in 24 hours when R_1 was a primary alkyl, or aryl group. Secondary and tertiary alkyl substituted substrates required 36 to 48 hours for completion. The preference for furanone production was far superior when R_2 is a phenyl group rather than an alkyl chain, resulting in yields of **4.6** ranging from 84 to 93 % when R_1 is an alkyl group (Table 4-5, entries 1 to 5), and 63 to 68 % when R_1 is aryl group (Table 4-5, entries 6 and 7). Having an aromatic ring bound to the triple bond appears to favor the formation of the unsaturated γ-lactone.

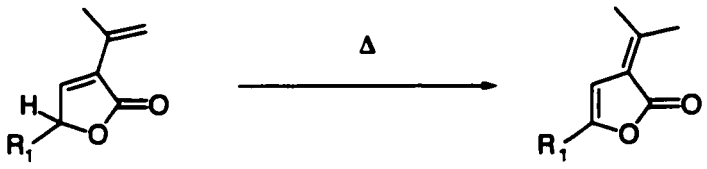
Table 4-5. Cyclohydrocarbonylation Reactions where R_2 is a Phenyl Group [a]

Entry	4.4	t (h)	Conv. [b] (%)	Heterocycle	Isolated Yield [c] (%)
1	 **4.4i**	24	100	 **4.6i**	93
2	 **4.4j**	36	100	 **4.6j**	88
3	 **4.4k**	36	100	 **4.6k**	87
4	 **4.4l**	48	100	 **4.6l**	84
5	 **4.4m**	48	100	 **4.6m**	85
6	 **4.4n**	24	100	 **4.6n**	61
7	 **4.4o**	24	100	 **4.6o**	67

[a] Reaction conditions: **4.4**, 1.5 mmol; **1.1**, 0.03 mmol (2 %); $(PhO)_3P$, 0.48 mmol (32 %); CH_2Cl_2, 10 mL; CO, 38.5 atm; H_2, 3.5 atm; 120 °C. [b] The percent conversion was determined by ^1H NMR. [c] The products were isolated by flash silica gel chromatography using pentane:ether (90:10) as eluant followed by crystallization.

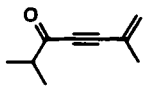
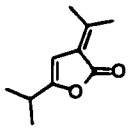
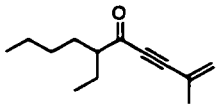
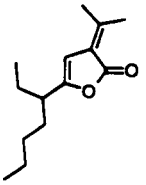
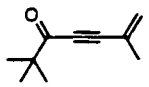
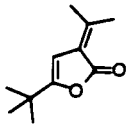
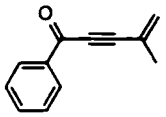
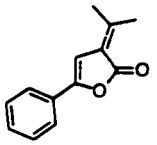
4.3.5 Reactions of α-Keto Alkynes where R_2 is a Vinyl Group

The hydroformylation reaction of α-keto alkynes, with functionalized R_2 groups such as vinyl (Table 4-6), and methoxymethyl (Table 4-7), resulted in a lower yield of **4.7**. The cyclohydrocarbonylation of α-keto alkynes with smaller functional groups at the acetylenic terminal may be readily accomplished under milder pressure (21 atm, CO/H_2 being 5/1) and lower temperature (70 °C). Interestingly, 2-furanones (**4.8**) were obtained from enynones, and may result from a 1 - 5 proton shift of **4.6** (Eq. 4-6). The 2-furanone (**4.8**) was obtained in 69 - 76 % yields with some oligomeric materials (Table 4-6, entries 1 to 4). An increased preference for furanone production was observed when R_1 was either a secondary or tertiary alkyl or aryl group. The addition of an R_2 group capable of coordinating with the rhodium prior to addition to the triple bond readily promoted the carbonylation of the triple bond at the carbon nearest R_2 as observed previously in our studies on the hydroformylation of enynes and thiophenynes (see Chapters 2 and 3).



4.6 **4.8** (4-6)

Table 4-6. Cyclohydrocarbonylation Reactions where R_2 is a Vinyl Group [a]

Entry	4.4	t (h)	Conv. [b] (%)	Heterocycle	Isolated Yield [c] (%)
1	 **4.4p**	24	100	 **4.8p**	71
2	 **4.4q**	24	100	 **4.8q**	76
3	 **4.4r**	36	100	 **4.8r**	69
4	 **4.4s**	24	100	 **4.8s [d]**	75

[a] Reaction conditions: **4.4**, 1.5 mmol; **1.1**, 0.03 mmol (2 %); $(PhO)_3P$, 0.12 mmol (8 %); CH_2Cl_2, 10 mL; CO, 17.5 atm; H_2, 3.5 atm; 70 °C. [b] The percent conversion was determined by ^1H NMR. [c] The products were isolated by Kugelrohr distillation followed by flash silica gel chromatography using pentane:ether (97.5:2.5) as eluant. [d] Flash silica gel chromatography using pentane:ether (90:10) as eluant.

4.3.6 Reactions of α-Keto Alkynes where R_2 is a Methoxymethyl Group

The cyclohydrocarbonylation of methoxymethyl substituted acetylenes resulted in the production of the 2(3*H*)-furanones **4.5** in 89 to 93 % yields (Table 4-7, entries 1 to 3). Demethoxylation occurs in the reaction, possibly in the final stages of the catalytic cycle transforming the methoxymethyl to a methyl group (Scheme 4-1). It is conceivable that prior to the final hydrogen addition step to form **4.5**, the rhodium-furanone complex is in an orientation that allows the metal to coordinate with the oxygen from the methoxymethyl group. Hydrogen abstraction and rhodium migration leads to formaldehyde production, and the methyl substituted furanone. Interestingly, the phenyl substituted alkynone (**4.4w**) affords the methyl substituted 2(5*H*)-furanone **4.6w** (Table 4-7, entry 4). The 2(3*H*)-furanone appears to be the kinetic product, and the 2(5*H*)-furanone is the thermodynamic product. The placement of an electron withdrawing group in position 5 promotes the isomerization of **4.5** to **4.6** when there is a weakly donating alkyl substituent in position 3.

Scheme 4-1. Possible route to demethoxylation.

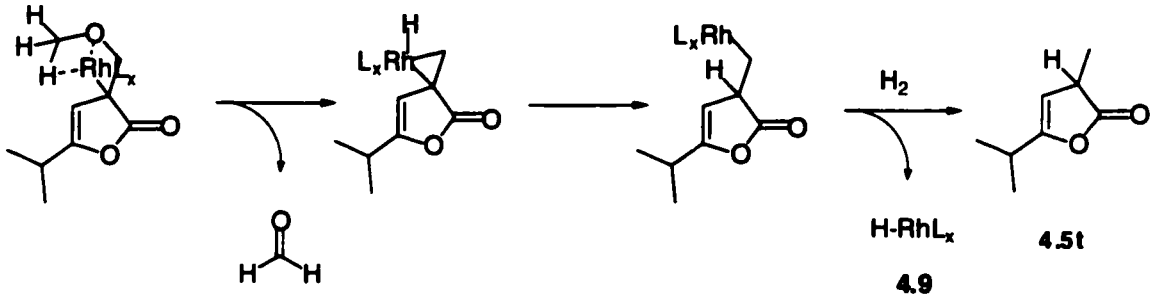
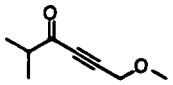
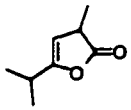
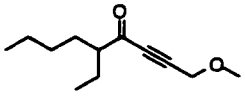
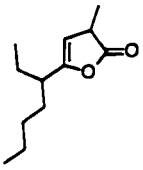
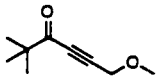
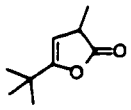
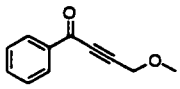
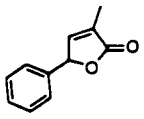


Table 4-7. Cyclohydrocarbonylation Reactions where R_2 is a Methoxymethyl Group [a]

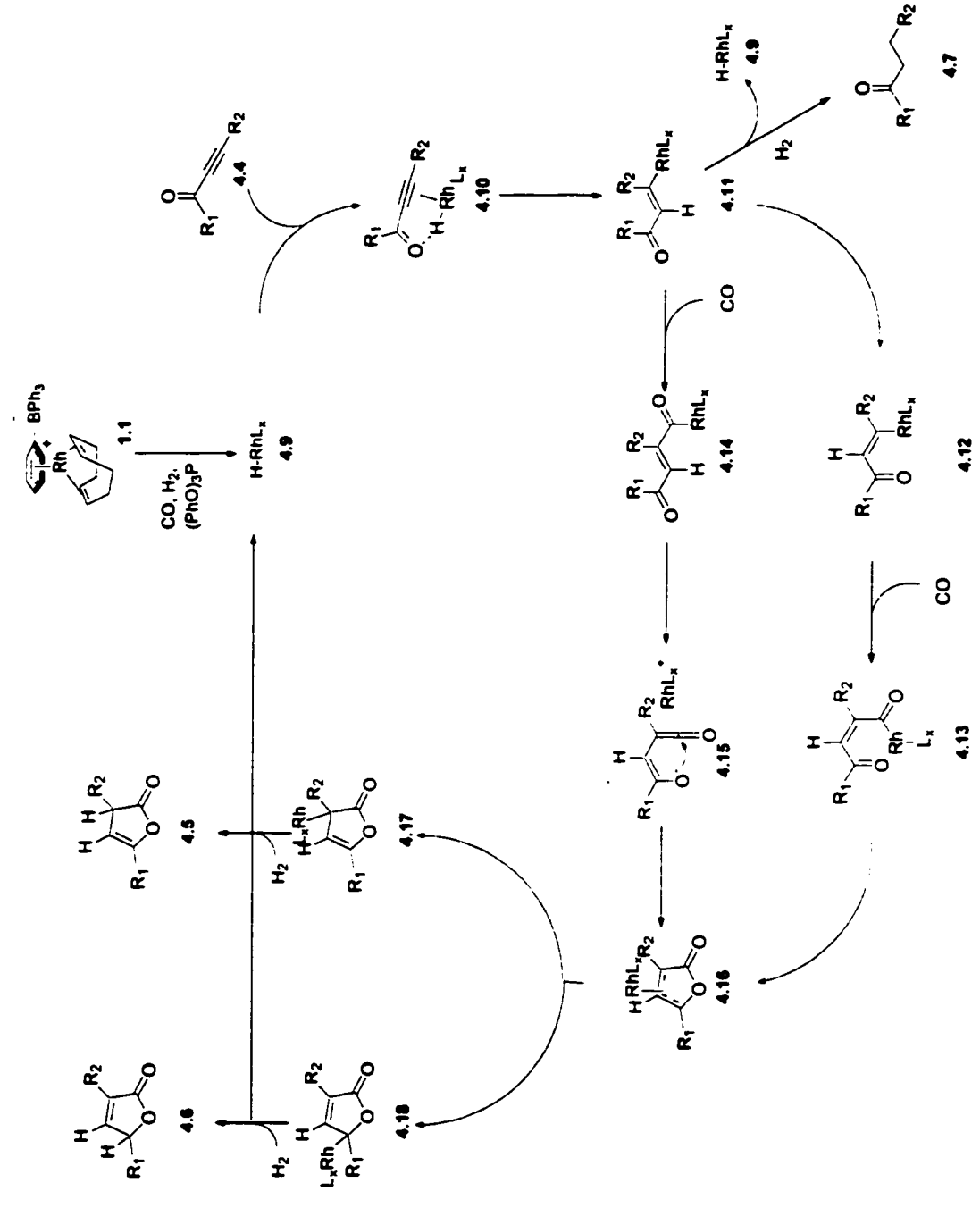
Entry	4.4	t (h)	Conv. [b] (%)	Heterocycle	Isolated Yield [c] (%)
1	 **4.4t**	24	100	 **4.5t**	92
2	 **4.4u**	24	100	 **4.5u**	91
3	 **4.4v**	36	100	 **4.5v**	89
4	 **4.4w**	24	100	 **4.6w [d]**	93

[a] Reaction conditions: **4.4**, 1.5 mmol; **1.1**, 0.03 mmol (2 %); $(PhO)_3P$, 0.12 mmol (8 %); CH_2Cl_2, 10 mL; CO, 17.5 atm; H_2, 3.5 atm; 70 °C. [b] The percent conversion was determined by ^1H NMR. [c] The products were isolated by Kugelrohr distillation followed by flash silica gel chromatography using pentane:ether (95:5) as eluant. [d] Flash silica gel chromatography using pentane:ether (85:15) as eluant.

4.3.7 Mechanistic Aspects

It was indicated that a number of factors influenced the preparation of the unsaturated γ-lactones from α-keto alkynes. Only a five-membered ring was formed indicating that the acyl-rhodium intermediate always originates at the triple bond carbon closest to R_2. The nature of R_1 and R_2 substantially influences both the formation of the unsaturated lactone and the hydrogenation product **4.7**. Given this information one can envisage a mechanism (Scheme 4-2) for the preparation of furanones from α-keto alkynes which involve the following steps. The Rh-H (**4.9**) binds to the triple bond of the alkynone with possible weak H-bonding interaction to the ketone functionality (**4.10**). Intramolecular addition of the rhodium hydride to the triple bond of the α-keto alkyne can afford the ***E***-isomer **4.11**. Depending upon the extent of the interaction between R_1 and R_2 one of two possible paths may occur. Appreciable steric interaction between R_1 and R_2 would destabilize **4.11** resulting in further hydrogenation of the alkenyl intermediate to the ketone **4.7** and regeneration of **4.9**. If **4.11** is stable, carbonylation (**4.14**) and rearrangement to the zwitterionic ketene (**4.15**), or isomerization (**4.12**) and carbonylation (**4.13**) would generate **4.16** via intramolecular cyclization. Either the rhodium-furanone complex **4.17** or **4.18** will form depending on the R_1 and R_2 substituent. The reaction of either rhodium complex with H_2 affords the 2(3*H*)-furanone **4.5** or the 2(5*H*)-furanone **4.6**, and regeneration of the rhodium hydride **4.9**.

Scheme 4-2. Proposed Mechanism



4.4 Conclusion

In conclusion, the cyclohydrocarbonylation of α-keto alkynes was readily accomplished by the zwitterionic rhodium complex **1.1** and triphenyl phosphite in the presence of CO and H_2. The temperatures and pressures required were sometimes milder than those previously reported for other reactions (especially when functionalized α-keto alkynes were used). Good chemo- and regioselectivity were observed for a variety of multifunctionalized alkynones to produce 2-, 2(3*H*)- or 2(5*H*)-furanone as the dominant product. This research has the potential to be used in the synthesis of chiral furanones from achiral substrates.

CHAPTER 5

INNOVATIVE SYNTHESIS OF 4-CARBALDEHYDEPYRROLIN-2-ONES BY ZWITTERIONIC RHODIUM COMPLEX CATALYZED CHEMO- AND REGIOSELECTIVE TANDEM CYCLOHYDROCARBONYLATION/CO INSERTION OF α-IMINO ALKYNES

5.1 Introduction

It has been our goal to discover and develop rhodium catalyzed transformations of functionalized alkynes utilizing the zwitterionic rhodium complex $(\eta^6\text{-}C_6H_5BPh_3)^-Rh^+$(1,5-COD) (**1.1**) in the presence of CO and H_2. A fascinating aspect to this research concerns the chemo- and regioselectivity effects directed by functional groups adjacent to a triple bond. We have demonstrated the regioselective hydroformylation of both enynes (see Chapter 2) and acetylenic thiophenes (see Chapter 3) to their α,β-unsaturated aldehydes, and the chemo- and regioselective cyclohydrocarbonylation of α-keto alkynes to furanones (see Chapter 4).

Pyrrolinones, especially in enantiomerically pure forms, are pharmacologically active materials that are important synthons in the preparation of γ-amino acids[135], various alkaloids,[136] and natural products.[137] These five-membered rings express antitumor properties,[138] as well as inhibition of COX-2[139] and HIV-1 protease.[140] The versatility of pyrrolinones is extended upon hydrogenation to their pyrrolidinone analogs. Additional biological activities have been described ranging from HIV protease inhibition,[141] cognitive performance enhancement,[142] selective estrogen receptor

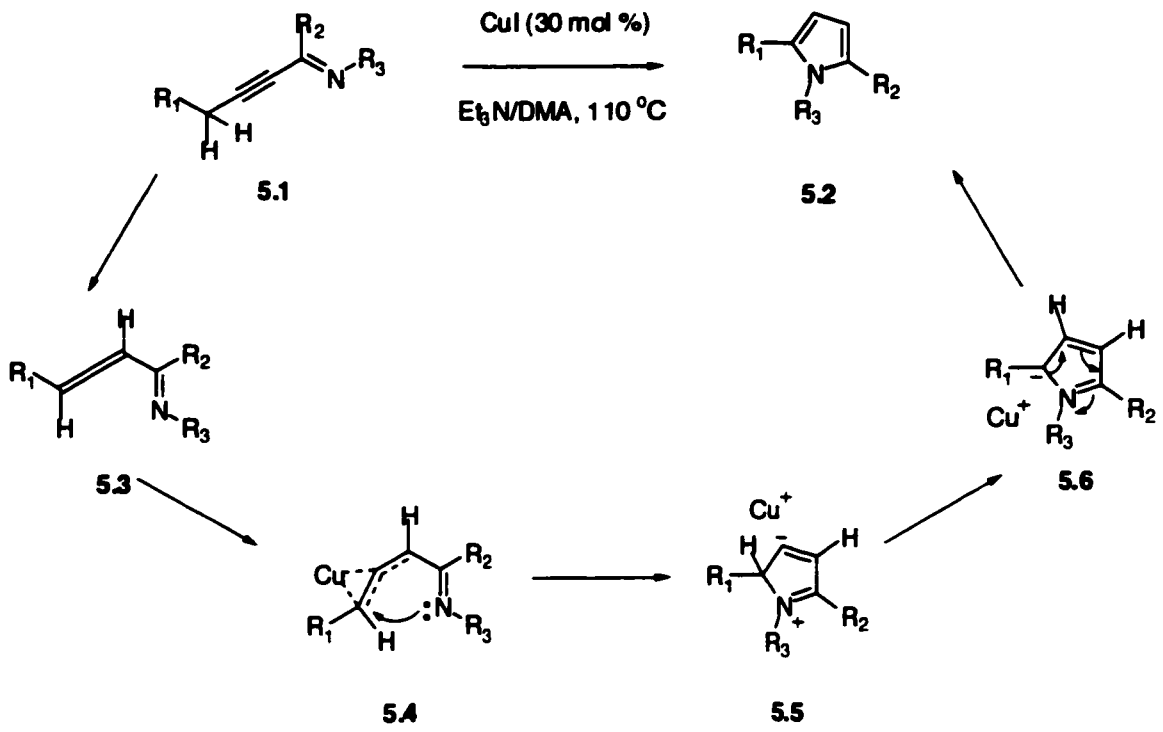
modulation (SERM),[143] anticonvulsant activities,[144] renin inhibition,[145] and amnesia reversal activity.[146]

Pyrrolinones have been prepared by catalytic methods which include the ruthenium catalyzed Alder-ene reaction[147] and ring closing metathesis,[148] the rhodium catalyzed hydrocarbonylation of alkenamides,[149] and the iron catalyzed carbonylation of allenyl imines.[150] Though many catalytic processes result in limited chirality, racemic pyrrolinones have been efficiently resolved by enzymatic kinetic resolution to their enantiomeric counterparts.[151]

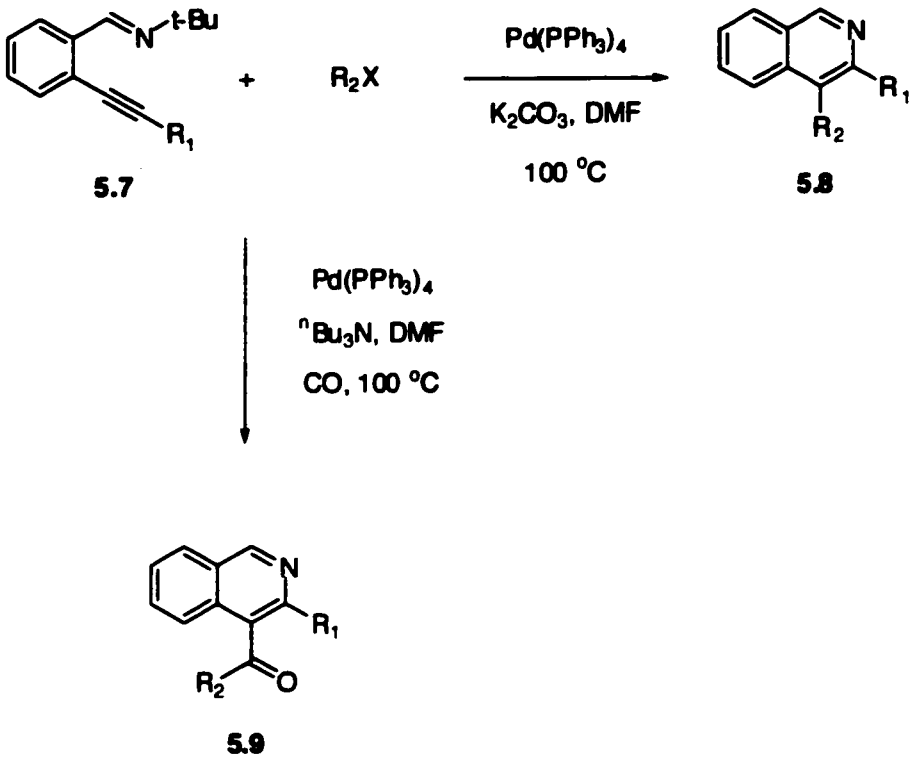
5.2 Aim of Research

Two groups have recently described the ability of alkynyl imines to form heterocyclic ring systems. Gevorgyan and coworkers demonstrated an efficient method for the construction of 2-monosubstituted and 2,5-disubstituted pyrroles, as well as fused aromatic heterocycles containing a pyrrole ring in 51 – 93 % yields.(Scheme 5-1).[152] It was proposed that the alkynyl imine (**5.1**) would undergo a base induced propargyl allenyl isomerization to form **5.3**, Cu promoted intramolecular nucleophilic attack transforms **5-3** to **5-5**, and rearrangement of **5.5** to the more stable **5.6** allows for lose of Cu leading to the cycloisomerization product (**5.2**).

Scheme 5-1. Route to Substituted Pyrroles



Larock and Dai prepared 3,4-disubstituted isoquinolines (**5.8**) and CO inserted 3,4-disubstituted isoquinolines (**5.9**) utilizing γ-imino alkynes.[153] The palladium catalyzed cross-coupling of N-*tert*-butyl-*ortho*-(1-alkynyl)benzaldimines (**5.7**) with excess aryl, allylic, and alkynyl halides (R_2X) afford **5.8** (Eq. 5-1) in 30 to 75 % yields. Likewise, placing **5.7** in combination with excess aryl halide and CO (1 atm) under similar conditions, generates 3-substiuted-4-aroylisoquinolines (**5.9**) in 31 – 76 % yields.



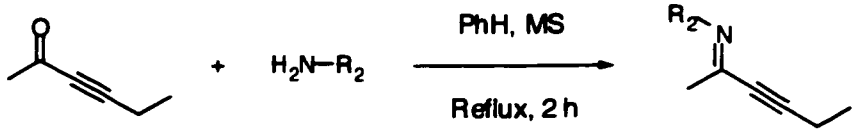
(5-1)

It was anticipated that the use of α-imino alkynes as functionalized alkynes for the reaction with CO/H_2 and **1.1** would afford heterocyclic pyrrolinone rings. The following section describes a novel chemo- and regioselective route to 4-carbaldehydepyrrolin-2-ones in 67 to 82 % yields by the zwitterionic rhodium complex (**1.1**) and triphenyl phosphite catalyzed cyclohydrocarbonylation/CO insertion of tri-substituted acetylenic imines.

5.3 Results and Discussion

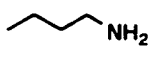
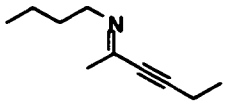
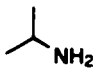
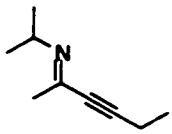
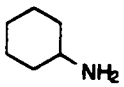
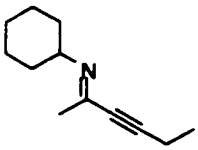
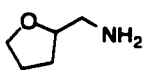
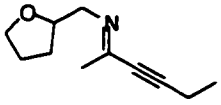
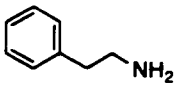
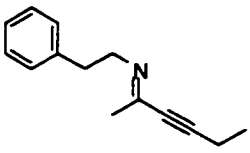
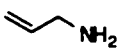
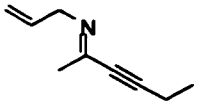
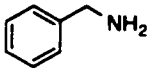
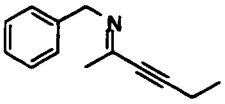
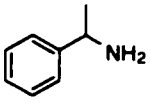
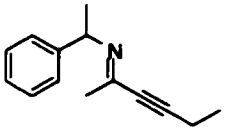
5.3.1 Synthesis of Starting Materials

There are many approaches to the preparation of alkynyl imines. In our study we utilized two routes: (a) the direct amination/dehydration of alkynones (Eq. 5-2, Table 5-1),[152] and (b) the cross-coupling reaction between imidoyl chlorides (**5.5**) and terminal alkynes (**5.15**) using catalytic amounts of $Pd(PPh_3)_2Cl_2$ and CuI (Eq. 5-3, Table 5-4).[154] Imidoyl chlorides (Eq. 5-4) were prepared by the direct reaction of secondary amides (**5.13**) with $SOCl_2$ (Table 5-2),[155] or by the reaction of acyl chlorides (**5.11**) with aza-Wittig reagents (**5.12**) (Table 5-3).[156] In this manner hex-3-yn-2-one was reacted with primary amines to form Schiff bases in 66 – 78 % yields. Imino alkynes (**5.16**) were also formed in 65 – 96 % yields, by the coupling of terminal alkynes (**5.15**) with imidoyl chlorides (**5.14**). These tri-substituted alkynyl imines (**5.16**) readily incorporate alkyl, alkoxy, vinyl and aryl groups in the R_1, R_2, and R_3 positions.

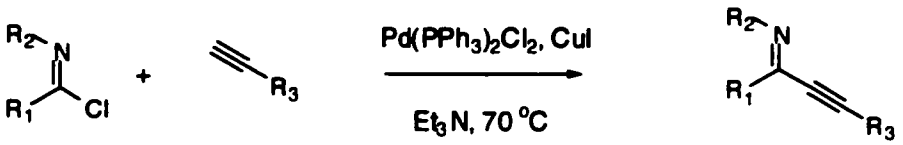


5.10 **5.16a - h** (5-2)

Table 5-1. α-Imino Alkynes Prepared by Amination of Hex-3-yn-2-one [a]

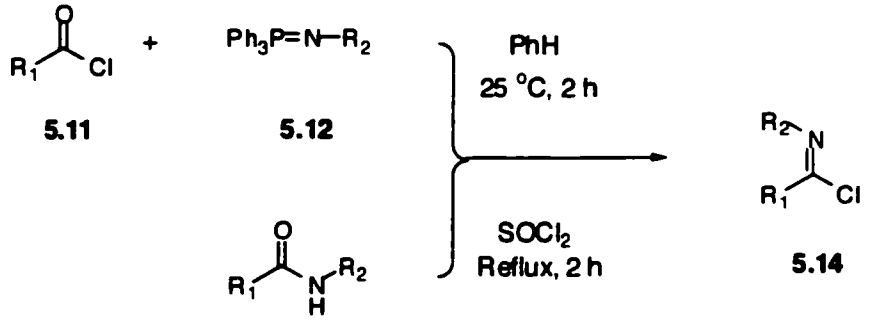
Entry	5.10	5.16	Isolated Yield (%) [b]
1			75
	5.10a	**5.16a**	
2			76
	5.10b	**5.16b**	
3			78
	5.10c	**5.16c**	
4			77
	5.10d	**5.16d**	
54			66
	5.10e	**5.16e**	
6			73
	5.10f	**5.16f**	
7			67
	5.10g	**5.16g**	
8			69
	5.10h	**5.16h**	

[a] Reaction conditions: 3-Hexyn-2-one, 25 mmol; amine (**5.10**), 28 mmol; PhH, 75 mL; molecular sieves (4 Å), 8 g; Reflux; 2 h. [b] The products were isolated by Kugelrohr distillation.



5.14 **5.15** **5.16i - y**

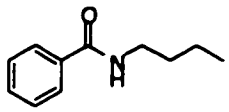
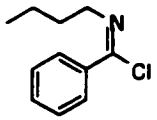
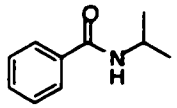
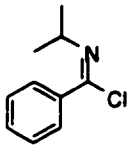
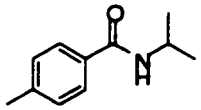
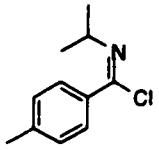
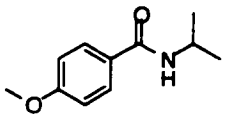
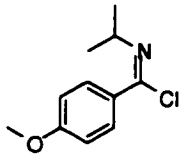
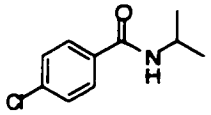
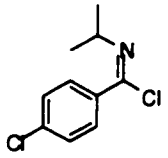
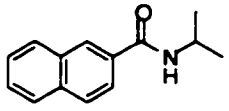
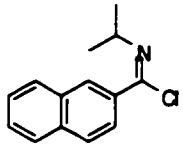
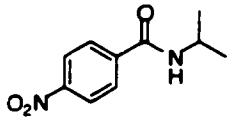
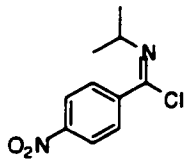
(5-3)



5.11 **5.12** **5.13** **5.14**

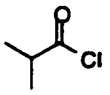
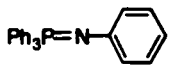
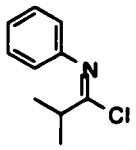
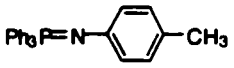
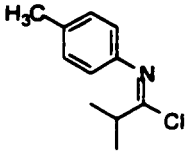
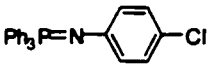
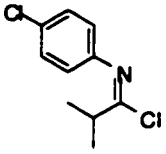
(5-4)

Table 5-2. Preparation of Imidolyl Chlorides From Secondary Amides [a]

Entry	5.13	5.14	Isolated Yield (%)[b]
1	 **5.13a**	 **5.14a**	88
2	 **5.13b**	 **5.14b**	84
3	 **5.13c**	 **5.14c**	92
4	 **5.13d**	 **5.14d**	83
5	 **5.13e**	 **5.14e**	88
6	 **5.13f**	 **5.14f**	69
7	 **5.13g**	 **5.14g**	91

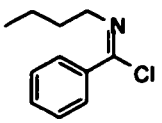
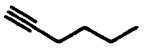
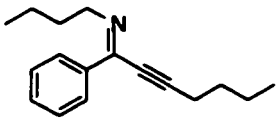
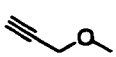
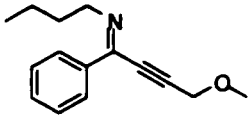
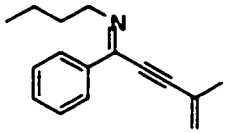
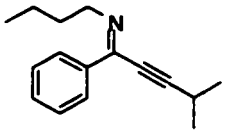
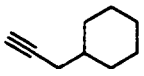
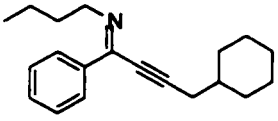
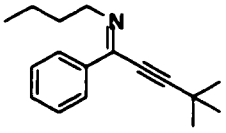
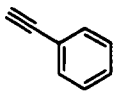
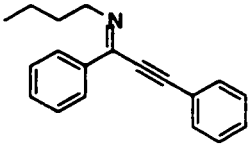
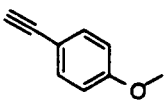
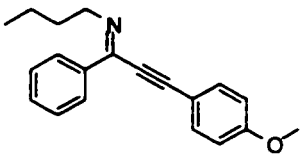
[a] Reaction conditions: Amide (**5.13**), 50 mmol; $SOCl_2$, 50 mL; reflux; 2 h; followed by evaporation of solvent. [b] The product was isolated by Kugelrohr distillation.

Table 5-3. Preparation of Imidoyl Chlorides From Acyl Chlorides [a]

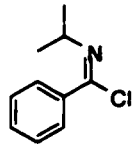
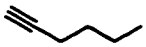
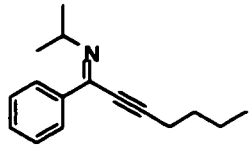
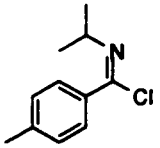
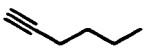
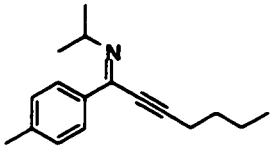
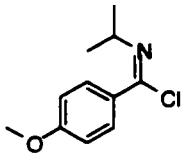
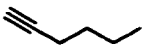
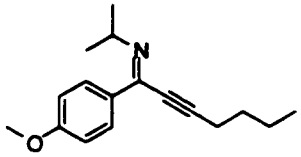
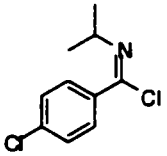
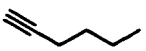
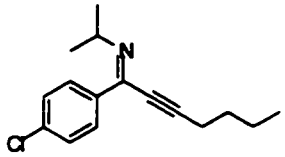
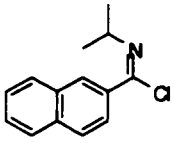
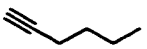
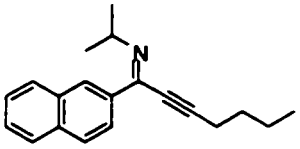
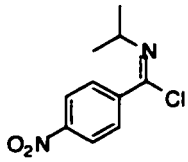
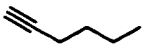
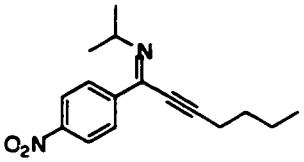
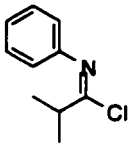
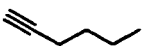
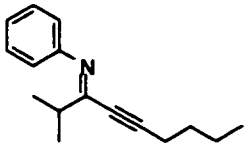
Entry	5.11	5.12	5.14	Isolated Yield (%) [b]
1				72
	5.11a	**5.12a**	**5.14h**	
2				74
		5.12b	**5.14i**	
3				69
		5.12c	**5.14j**	

[a] Reaction conditions: Acyl chloride (**5.11a**), 28 mmol; Aza-Wittig reagent (**5.12**), 30 mmol; PhH, 50 mL; 25 °C; 2 h; followed by evaporation of solvent. [b] The product was isolated by extraction with hexanes.

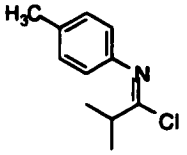
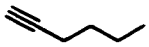
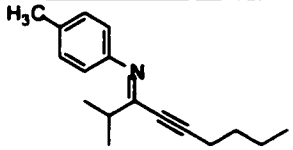
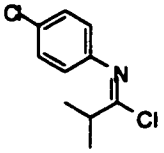
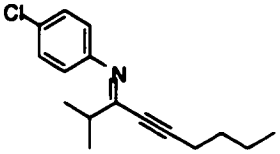
Table 5-4. Preparation of α-Imino Alkynes From Imidoyl Chlorides [a]

Entry	5.14	5.15	5.16	Isolated Yield [b] (%)
1	 **5.14a**	 **5.15a**	 **5.16i**	88
2		 **5.15b**	 **5.16j**	65
3		 **5.15c**	 **5.16k**	69
4		 **5.15d**	 **5.16l**	93
5		 **5.15e**	 **5.16m**	87
6		 **5.15f**	 **5.16n**	91
7		 **5.15g**	 **5.16o**	96
8		 **5.15h**	 **5.16p**	97

(Table 5-4. Continued)

Entry	5.5	5.6	5.7	Isolated Yield [b] (%)
9	 **5.14b**	 **5.15a**	 **5.16q**	94
10	 **5.14c**	 **5.15a**	 **5.16r**	93
11	 **5.14d**	 **5.15a**	 **5.16s**	82
12	 **5.14e**	 **5.15a**	 **5.16t**	77
13	 **5.14f**	 **5.15a**	 **5.16u**	93
14	 **5.14g**	 **5.15a**	 **5.16v**	77
15	 **5.14h**	 **5.15a**	 **5.16w**	92

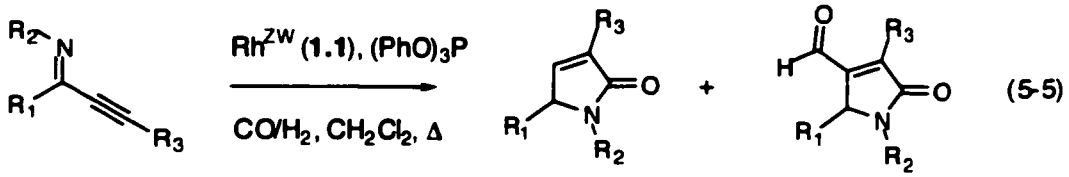
(Table 5-4. Continued)

Entry	5.5	5.6	5.7	Isolated Yield [b] (%)
16	 **5.14j**	 **5.15a**	 **5.16x**	93
17	 **5.14i**	 **5.15a**	 **5.16y**	96

[a] Reaction conditions: Imidoyl chloride (**5.14**), 20 mmol; alkyne (**5.15**), 25 - 30 mmol; $Pd(PPh_3)_2Cl_2$, 0.20 mmol (1.0 %); CuI, 0.20 mmol (1.0 %); Et_3N, 60 mL; 70 °C, 2 h. [b] The product was isolated by Kugelrohr distillation.

5.3.2 Reaction Optimization

The reaction of an alkynyl imine (**5.16**) with carbon monoxide and hydrogen in the presence of catalytic quantities of the zwitterionic rhodium complex (**1.1**) and triphenyl phosphite affords the pyrrolin-2-one (**5.17**) and the 4-carbaldehydepyrrolin-2-one (**5.18**) (Eq. 5-5).



(5-5)

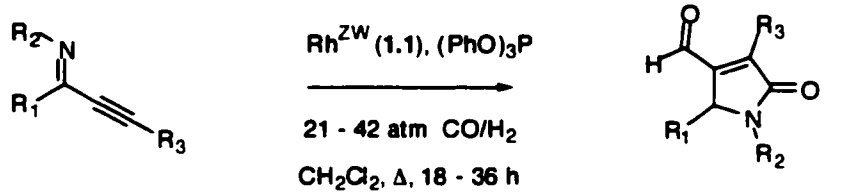
5.16 **5.17** **5.18**

The reaction is both temperature and pressure dependent. Using 1.5 mmol of **5.16b** with 2 mol % **1.1**, 8 mol % $(PhO)_3P$, 10 mL of CH_2Cl_2, and total pressures of 21 and 42 atm at optimum CO/H_2 ratios of 5:1 and 11:1 afford various mixtures of **5.17b** and **5.18b** (Table 5-5, entries 4, 7 and 8). Temperatures between 70 and 100 °C favor the production of **5.18b** over **5.17b** with some residual polymeric material (Table 5-5, entries 2 - 6). The longer the reaction takes place at these elevated temperatures the greater the abundance of **5.18b** (Table 5-5, entries 4 and 5). The temperature and time dependence of **5.18v** has led us to reason that **5.18b** likely arises from **5.17b** or an intermediate closely related to **5.17b**.

Table 5-5. Reaction Optimization Using 5.16b [a]

Entry	Rh^{ZW} (mol %)	$(PhO)_3P$ (mol %)	P (atm)	CO/H_2	T (°C)	t (h)	**5.17**: **5.18** [b]
1	2	0	21	5:1	80	20	-
2	2	8	21	5:1	70	20	64:36
3	2	8	21	5:1	80	20	49:51
4	2	8	21	5:1	90	20	22:78
5	2	8	21	5:1	90	40	16:84
6	2	8	21	5:1	100	20	3:97
7	2	8	42	5:1	90	20	33:67 [c]
8	2	8	42	11:1	90	20	14:86 [c]

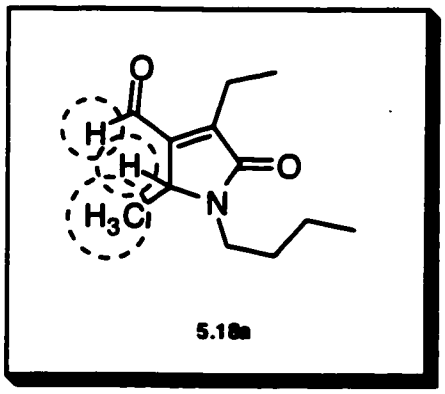
[a] Reaction conditions: **5.16b**, 1.5 mmol; CH_2Cl_2, 10 mL. [b] The reactions proceeded to full conversion (obtained by NMR), and the ratio of **5.17**:**5.18** was determined by ^1H NMR. Typically 10 to 20 % of a polymeric material accompanied **5.17** and **5.18**. [c] A substantial amount of polymeric material accompanied products **5.17** and **5.18**.



5.16 **5.18** (5-6)

5.3.3 NMR Determination of Regiochemistry

Enhancement of signals to non-bonded protons over short distances can be measured for distances up to 4 Å (0.4 nm) using NOE difference NMR spectroscopy. The position of the aldehyde was determined using product **5.18a** as an example of the aldehyde substituted pyrrolinone ring system (Fig. 5-1). Irradiation of the aldehydic ^{1}H at δ 9.71 (s, 1H) leads to a moderate enhancement of the methyl substituent at δ 2.38 (br, 3H) along with a weak enhancement to the methine ^{1}H at δ 3.30 (m, 1H). As well, the corresponding correlated spectroscopy spectrum (COSY) illustrated ^{1}H-^{1}H connectivities between the methyl at δ 2.38 and the methine multiplet at δ 3.30. Therefore the aldehyde substituent in **5.18a** is placed at position-4 of the pyrrolinone ring system as drawn below.



5.18a

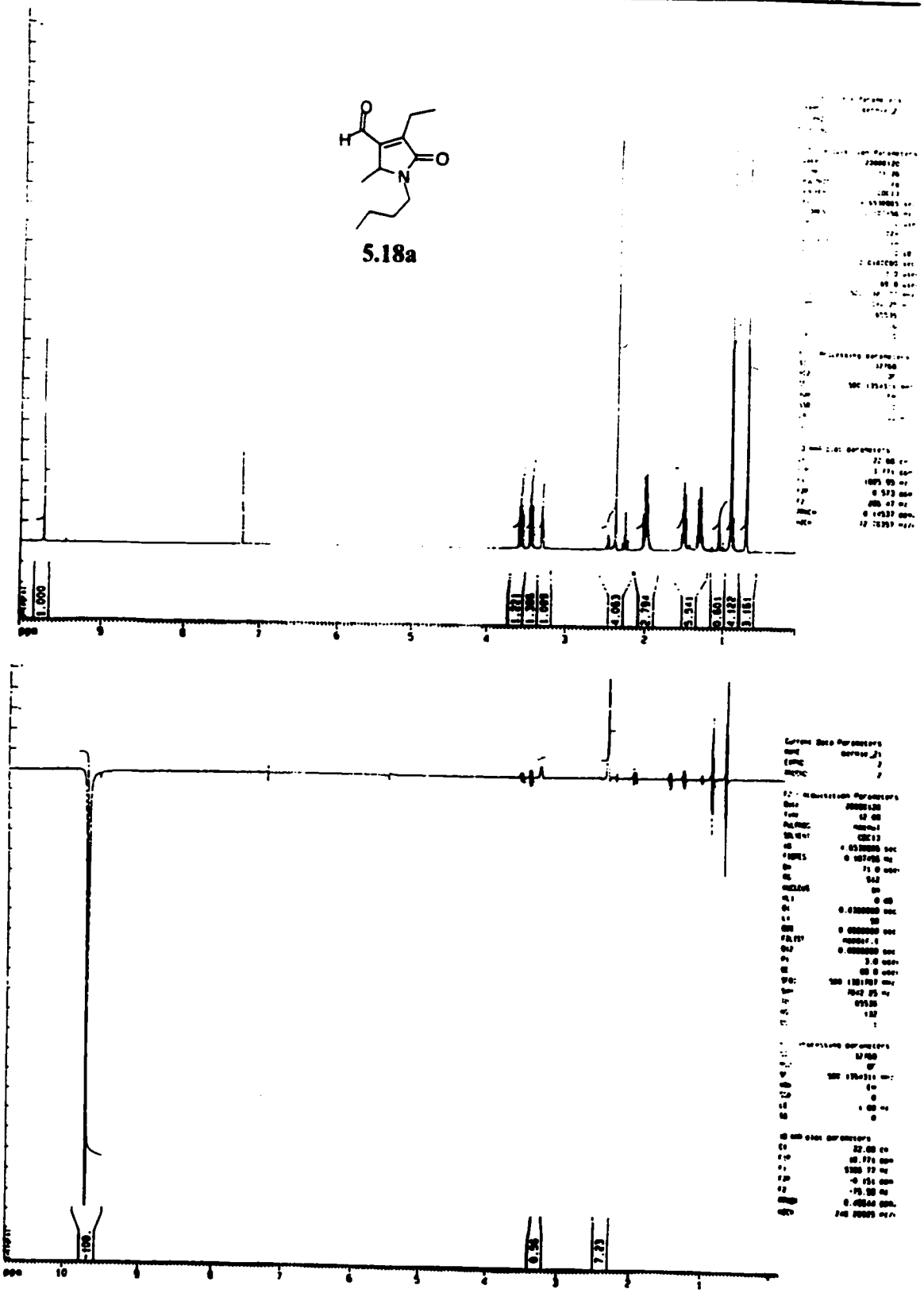
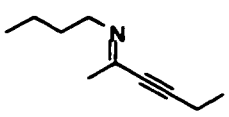
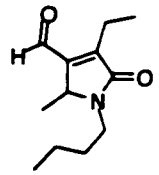
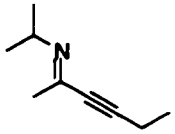
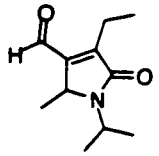
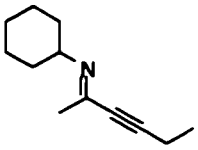
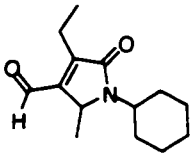
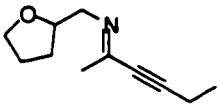
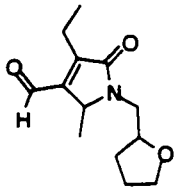
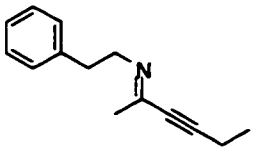
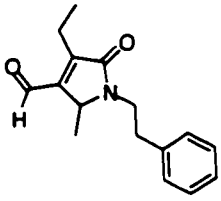


Figure 5-1. NOE Experiment on 5.18a

5.3.4 Cyclohydrocarbonylation Reactions of α-Imino Alkynes with Different R_2 Groups

The tandem cyclohydrocarbonylation/CO insertion of imino alkynes (Eq. 5-6) was evaluated by determining the dependence on R_2 (Table 5-6), R_3 (Table 5-7), and R_1 (Table 5-8). To initiate our investigation imino alkynes with R_1 = methyl, R_3 = ethyl, and R_2 groups containing n-butyl, isopropyl, cyclohexyl, and ethyl phenyl were found to react best by treating 1.5 mmol of **5.16** with 2 mol % of the zwitterionic rhodium complex (**1.1**), 8 mol % triphenyl phosphite, 10 mL of CH_2Cl_2, 18.5 atm CO, 3.5 atm of H_2 in a 45 mL autoclave for 18 to 36 hours at 100 °C. Placement of a minimum 2 carbon spacer between the imino nitrogen and a substituent within R_2 removes possible steric interference and allows the reaction to **5.18** to be complete within 18 hours (Table 5-6, entries 1 and 5). The addition of substituents to carbon 1 of R_2 required an increased reaction time of 24 hours when R_2 is isopropyl (Table 5-6, entry 2), and 36 hours when R_2 is cyclohexyl (Table 5-6, entry 3). Utilizing 2-methyltetrahydrofuran as R_2 (**5.16d**) preferentially leads to **5.18d** at 80 °C instead of 100 °C. Higher temperatures result in a dark discoloration of the reaction mixture and inhibiton of **5.18d**. The placement of allyl (**5.16f**), benzyl (**5.16g**), and methylbenzyl (**5.16h**) groups at R_2 result in products with no CO incorporation. Aromatic R_2 groups such as phenyl (**5.16w**), tolyl (**5.16x**), and 4-chlorophenyl (**5.16y**) revealed a complicated reaction mixture where **5.17** was minor, and **5.18** was no longer present.

Table 5-6. Tandem Cyclohydrocarbonylation/CO Insertion of α-Imino Alkynes with Different R_2 Groups [a]

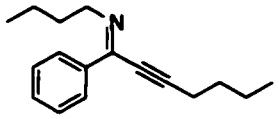
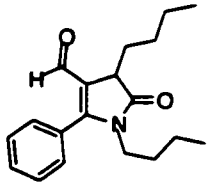
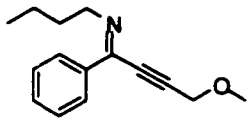
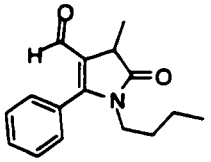
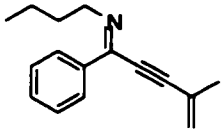
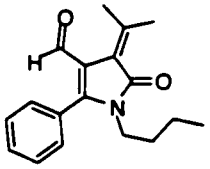
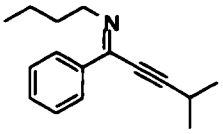
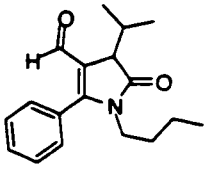
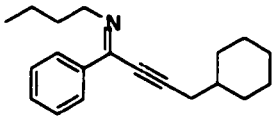
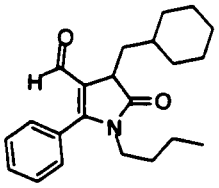
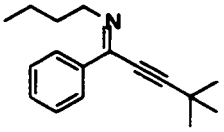
Entry	5.16	T (°C)	t (h)	5.18	Isolated Yield (%) [b]
1	 **5.16a**	100	18	 **5.18a**	82
2	 **5.16b**	100	24	 **5.18b**	79
3	 **5.16c**	100	36	 **5.18c**	80
4	 **5.16d**	80	36	 **5.18d**	73
5	 **5.16e**	100	18	 **5.18e**	75

[a] Reaction conditions: **5.16**, 1.5 mmol; **1.1**, 0.03 mmol (2 mol %); $(PhO)_3P$, 0.12 mmol (8 mol %); CH_2Cl_2, 10 mL; CO, 17.5 atm; H_2, 3.5 atm. [b] The reactions proceeded to full conversion (obtained by NMR), and the products were isolated by silica gel chromatography using 33:67 to 50:50 ethyl acetate:hexane as eluant.

5.3.5 Cyclohydrocarbonylation Reactions of α-Imino Alkyne with Different R_3 Groups

The unique transformation of **5.16** to **5.18** (Eq. 5-6), may be extended to α-imino alkynes where R_1 contains an aromatic unit. These unsaturates preferentially react at 90 °C with a total pressure of 42 atm and a CO/H_2 ratio being 1/1. To determine the scope at the alkynyl unit (R_3) we evaluated imino alkynes with R_1 = phenyl, and R_2 = ***n***-butyl. The R_3 group employed alkyl, alkoxy, vinyl, and aryl groups (Table 5-7). Interestingly, increasing the size of R_3 to n-butyl (**5.16i**), isopropyl (**5.16l**) and methylcyclohexyl (**5.16m**) has little influence on **5.18,** as all reactions are complete within 24 hours and have comparable yields ranging from 75 – 79 % (Table 5-7, entries 1, 4 and 5). Utilizing the ***tert***-butyl substituted α-imino alkyne (**5.16n**) causes the reaction to take place very slowly (Table 5-7, entry 6), even at temperatures exceeding 110 °C, while placement of a methoxy methyl group (**5.16j**) and vinyl (**5.16k**) at R_3 favor a reaction temperature of 75 °C. In particular, **5.16j** gives the demethoxylated product **5.18j** in 72 % yield (Table 5-7, entry 2), and **5.16k** gave the conjugated 3-isopropylidenepyrrolin-2-one **5.18k** in 67 % yield as expected (see Chapter 4) from our recent study on alkynones (Table 5-7, entry 3). Aromatic R_3 units consisting of phenyl (**5.16o**) and 4-methoxyphenyl (**5.16p**) favor five-membered pyrrolinones where the R_2 group (n-butyl) is cleaved and replaced by hydrogen.

Table 5-7. Tandem Cyclohydrocarbonylation/CO Insertion of α-Imino Alkynes with Different R_3 Groups [a]

Entry	5.16	T (°C)	t (h)	5.18	Isolated Yield (%) [b]
1	 **5.16i**	90	24	 **5.18i**	78
2	 **5.16j**	75	24	 **5.18j**	72
3	 **5.16k**	75	36	 **5.18k**	67
4	 **5.16l**	90	24	 **5.18l**	75
5	 **5.16m**	90	24	 **5.18m**	79
6	 **5.16n**	90	24	No Reaction	-

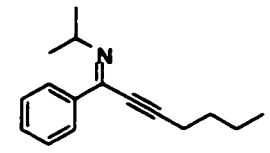
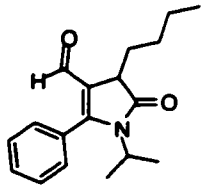
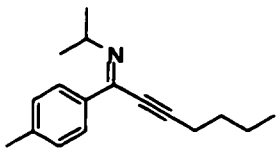
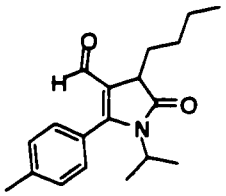
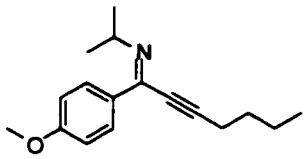
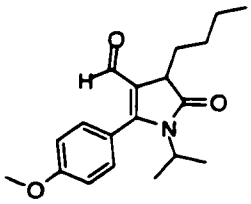
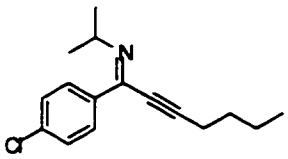
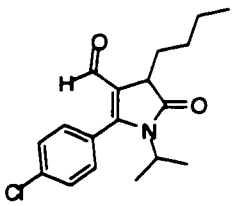
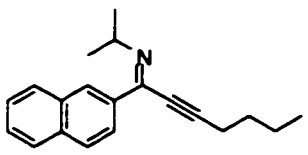
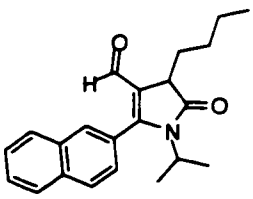
[a] Reaction conditions: **5.16**, 1.5 mmol; **1.1**, 0.03 mmol (2 mol %); $(PhO)_3P$, 0.12 mmol (8 mol %); CH_2Cl_2, 10 mL; CO, 38.5 atm; H_2, 3.5 atm. [b] The reactions proceeded to full conversion (obtained by NMR), and the products were isolated by using silica gel chromatography using 33:67 to 50:50 ethyl acetate:hexane as eluant

5.3.6 Cyclohydrocarbonylation Reactions of α-Imino Alkynes with Different Aromatic R_1 Groups

To evaluate the effect of substitution on the aromatic R_1 unit, the R_2 and R_3 substitutents used were isopropyl and n-butyl respectively, while the aromatic unit varied from phenyl (**5.16q**), to 4-tolyl (**5.16r**) and 4-anisoyl (**5.16s**) yielding **5.18q** to **5.18s** in 78 – 81 % (Table 5-8, entries 1- 3). Placement of an electron withdrawing group on the ring reduces the reactivity of **5.16**. Utilizing a 4-chlorophenyl substituent at R_1 (**5.16t**) gives **5.18t** in 72 % yield after 36 hours (Table 5-8, entry 4), and 4-nitrophenyl (**5.16v**) affords **5.17v** (64 % yield) as the major product after a reaction time of 18 hours. If **5.16v** is permitted to react for additional time the hydrogenation of the nitro group to an amine begins to compete with the production of **5.18** leading to a complicated reaction mixture. Increasing the size of the aryl group from phenyl (**5.16q**) to naphthyl **5.16u** requires a reaction time of 36 hours to obtain **5.18u** in 75 % yield (Table 5-8, entry 5).

Certain criteria appears evident for the preparation of 4-carbaldehydepyrrolin-2-ones (**5.18**). The R_1 unit may be alkyl or aryl, while R_2 and R_3 preferentially gives **5.18** when strong electron donating groups are used, as well as non-conjugating to the imino alkyne. Increasing the size of the R_1 and R_2 groups decrease the reactivity towards cyclization. Primary and secondary substituted R_3 groups have minimal reactivity differences, but placement of tertiary substituted groups appreciably reduce the reactivity of the imino alkyne.

Table 5-8. Tandem Cyclohydrocarbonylation/CO Insertion of α-Imino Alkynes with Substituted Aromatic R_1 Groups [a]

Entry	5.16	T (°C)	t (h)	5.18	Isolated Yield (%) [b]
1	 **5.16q**	90	24	 **5.18q**	80
2	 **5.16r**	90	24	 **5.18r**	81
3	 **5.16s**	90	24	 **5.18s**	78
4	 **5.16t**	90	36	 **5.18t**	72
5	 **5.16u**	90	36	 **5.18u**	75

[a] Reaction conditions: **5.16**, 1.5 mmol; **1.1**, 0.03 mmol (2 mol %); $(PhO)_3P$, 0.12 mmol (8 mol %); CH_2Cl_2, 10 mL; CO, 38.5 atm; H_2, 3.5 atm. [b] The reactions proceeded to full conversion (obtained by NMR), and the products were isolated by silica gel chromatography using 33:67 to 50:50 ethyl acetate:hexane as eluant.

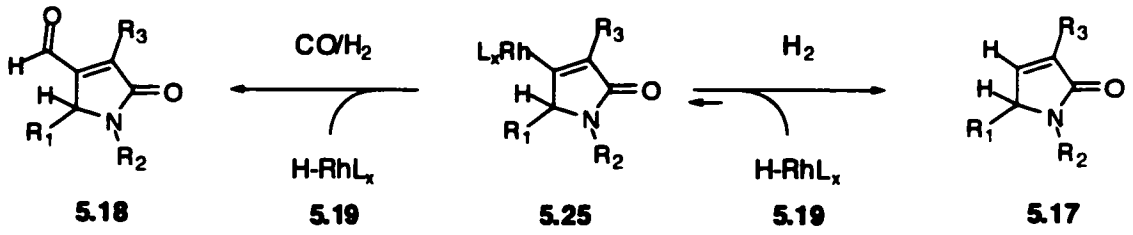
5.3.7 Mechanistic Aspects

In 1995, it was observed that catalytic amounts of the zwitterionic rhodium complex (**1.1**) and 1,4-bis(diphenylphosphino)butane readily hydrogenate imines in the presence of hydrogen and methanol.[49] In our reaction system we have placed an imine under hydroformylation conditions. As a result, there is potential for formamides to be produced which may lead to the cyclization we have observed. In order to determine whether or not the imine functional group initiated the cyclization with the alkyne in a CO and H_2 atmosphere we prepared *sec*-butylideneisopropylamine and isopropyl(1-phenylethylidene)amine and reacted them under our conditions. After 24 hours neither imine generated the expected formamides and only trace amounts of the hydrogenated counterparts were observed. The lack of formamides implied that cyclization to the core pyrrolinone ring should originate from the rhodium addition to the triple bond and a consequential acyl rhodium intermediate, or the presence of a triple bond adjacent to the imine functionality alters its reactivity to allow the rhodium to initially add to the imine.

In our reaction system the presence of both **5.17** and **5.18** led us to speculate that **5.18** may originate from **5.17**, or an intermediate related to **5.17** may lead to both **5.17** and **5.18** (Scheme 5-2). To test whether **5.18** originated from **5.17** we placed a number of pyrrolinones **5.17** (isolated prior to substrate optimization) back under a carbon monoxide/hydrogen atmosphere or a complete carbon monoxide atmosphere (see Section 8.5.6). Re-introduction of **5.17** utilizing the conditions noted for **5.16**, under a CO/H_2 or a CO atmosphere, resulted in low conversions to **5.18** after 24 hours (< 10 % conversion).

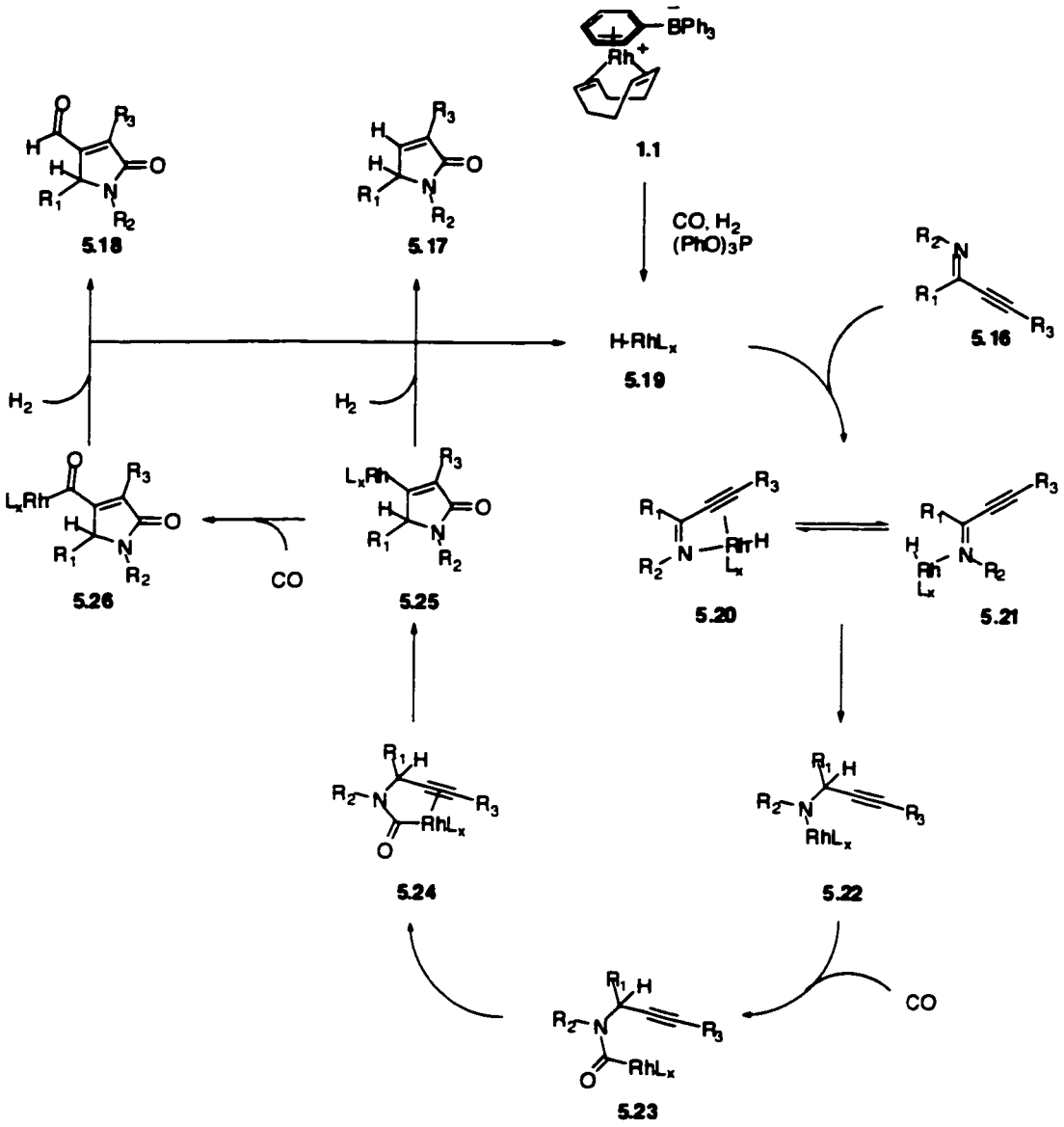
These results show that, in the conversion of α-imino alkynes to 4-carbaldehydepyrroli-2-ones, **5.17** is the minor and not the major route to **5.18**.

Scheme 5-2. A Possible Route to 5.17 and 5.18



A possible mechanism is outlined in Scheme 5-3. The active rhodium complex (**5.19**), generated from **1.1** (Scheme 5-3), binds to the acetylenic imine via the triple bond and the imine (**5.20**), or directly to the imine (**5.21**). Intramolecular hydrorhodation leads to **5.22** and subsequent carbonylation gives **5.23**. Reorientation of **5.23** to **5.24** promotes intramolecular cyclization across the triple bond to the 4-rhodiumpyrrolinone (**5.25**). Hydrogen addition to **5.25** creates the tri-substituted pyrrolinone **5.17** and regenerates the rhodium complex **5.19**. Alternatively, **5.25** undergoes CO insertion to generate **5.26**. Addition of H_2 generates the aldehyde substituted pyrrolinone ring **5.18** and regenerates the rhodium complex **5.19**.

Scheme 5-3. Proposed Mechanism



5.4 Conclusion

In conclusion we have described a unique preparation of tetra-substituted pyrrolinones. The unexpected tandem cyclohydrocarbonylation/CO insertion catalyzed by the zwitterionic rhodium complex **1.1** (η^6-$C_6H_5BPh_3$)$^-$Rh$^+$(1,5-COD) and triphenyl phosphite is both electronically and sterically controlled within the acetylenic imine. Utilizing a reasonable degree of control, these 4-carbaldehydepyrrolin-2-ones are readily prepared and have potential use as precursors toward important pharmacological applications.

CHAPTER 6

INVESTIGATIVE STUDIES TOWARD THE ZWITTERIONIC RHODIUM COMPLEX CATALYZED HYDROCARBONYLATION OF 2-ACETYLENIC THIAZOLES

6.1 Introduction

Sulfur and nitrogen containing heterocycles ranging from 5-, 6-, and 7-membered ring systems have received enormous attention due to their biological activities and pharmacological applications. The 5-membered thiazolidine and thiazole ring systems have use as protective agents against γ-radiation induced toxicity and mutagenesis,[157] the ability to treat cancer,[162] inhibit HIV protease,[163]as well as antitussive,[158] antibiotic,[159] anticonvulsant,[160] and antiasthmatic properties,[161] Those 5-membered heterocycles containing amido units, thiazolidinone and thiazolidinedione, have antimicrobial,[164] antipsychotic,[165] antiviral,[166] antihypoglycemic,[167] anti-inflammatory,[168] and antidiabetic properties.[169] Bicyclicthiazines act as dopamine receptor modulation agents,[170] hepatoprotective agents,[171] and serine protease inhibitors.[172] The 6-membered thiazinones are potent Na/H exchange inhibitors.[173] The 7-membered thiazepinones are important pharmacological compounds for the treatment of cancer, heart, and inflammatory diseases. These latter heterocycles aid in treating disease by acting as

inhibitors to angiotensin converting enzyme (ACE), neutral endopeptidase (NEP),[174] leukocyte adherence,[175] and the inhibition of calcium release in heart mitochondria.[176]

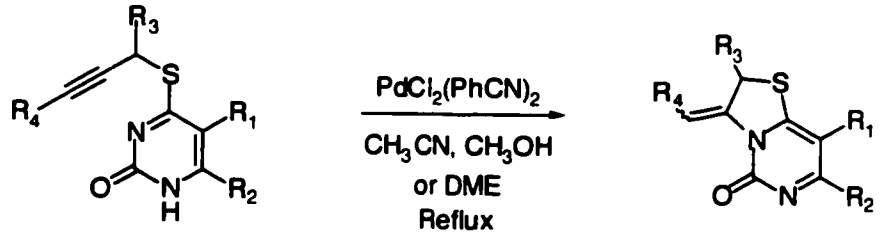
Transition metal complexes have been advantageously used as catalysts for ring expansion reactions,[177] and a number of synthetic applications have been simplified due to the availability of these materials. Rhodium complexes have been used for the catalytic synthesis of dithionanenones,[178] dioxacycloalkenones,[179] thiazolidines,[112] and diazepinediones.[180] Palladium reagents have provided the means to build isoquinolones,[181] tricyclic compounds,[182] pentadieneamides,[183] thiazenimines,[184] and iminocyclobutanes[185] by catalyzed reactions from appropriate reactants. Piperidinones,[186] mono- and trans- bicyclic-β-lactams,[187] and isoquinolines[188] were obtained by cobalt complexes. Metathesis catalysts were incorporated in the synthesis of bicyclic-β-lactams[189] as well as oxocene derivatives.[190]

6.2 Aim of Research

As a consequence of the earlier results on hydroformylation (Chapters 2 and 3) and cyclohydrocarbonylation (Chapters 4 and 5), it is clear that functional groups adjacent to a triple bond control the overall chemo- and regioselectivities for these reactions. We reasoned that utilizing the noted catalytic system on conjugated thiazolynes would result in a combination of the chemistry just described. Acetylenic

thiazoles incorporate the aromatic sulfur component of a thiophene ring (Chapter 3), and an imine-like fragment that would compare to a conjugated α-imino alkyne (Chapter 5). Consequently, it was anticipated that the resulting product would contain an unsaturated thiolactam.

Aromatic heterocyclic rings containing a nitrogen atom have been known to react with alkynes under metal catalyzed or thermolysis conditions to prepare fused ring systems in which the nitrogen is the connecting point for the alkynyl unit. In 1986, Yoshida and coworkers prepared thiazolopyrimidinones (**6.2**) in 57 – 88 % yields by Pd(II) catalyzed intramolecular nucleophilic addition of the amide to acetylene unit of propargylthiopyrimidinones **6.1** (Eq. 6-1).[191]



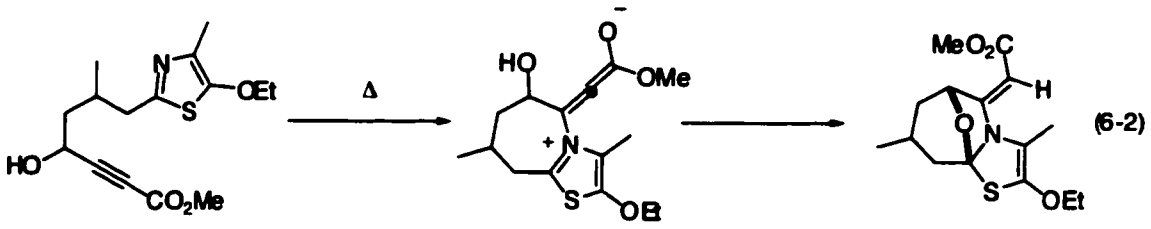
(6-1)

6.1

R_1, R_2, R_3, and R_4 = H and CH_3

6.2

As well, Jacobi and coworkers demonstrated the ability of non-conjugated acetylenic thiazoles (**6.3**) to cyclize first by Michael addition to give **6.4**, and then cycloisomerize to **6.5** in 30 to 50 % isolated yields (Eq. 6-2).[192]



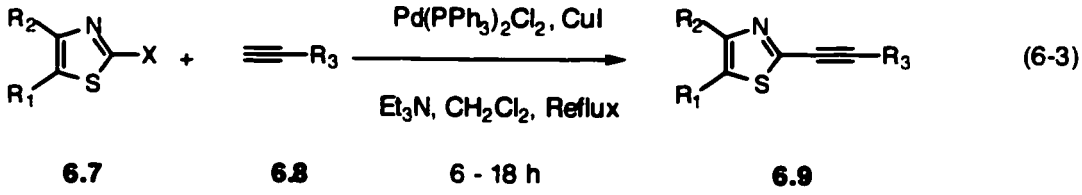
6.3 6.4 6.5 (6-2)

Our interest toward the placement of acetylenic thaizoles under hydroformylation conditions would appear valid and potentially useful to the pharmaceutical industry whether the 5-membered ring remains or a possible ring expansion to the 6- or 7-membered heterocyclic systems were obtained. The following sections describe our investigation on the novel zwitterionic rhodium catalyzed reaction of simple and functionalized acetylenic thiazoles with carbon monoxide and hydrogen to form hydrocarbonylation products in good to excellent yields, and chemo- and regioselectivities.

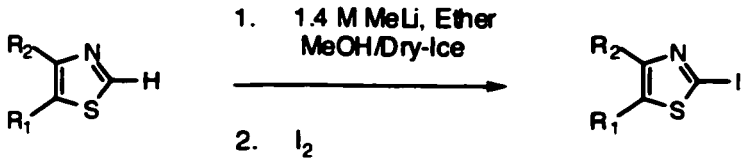
6.3 Results and Discussion

6.3.1 Synthesis of Starting Materials

The requisite acetylenic thiazoles (Eq. 6-3) are readily obtained in 56 to 95 % yields by the cross-coupling reaction of commercial 2-bromothiazole or presynthesized 2-iodothiazoles with terminal alkynes using catalytic quantities of $Pd(PPh_3)_2Cl_2$ and CuI under basic conditions (Table 6-1).[193] 2-Iodothiazoles were prepared by subsequent lithiation and iodination of both 4- and 4,5-substituted thiazoles (Eq. 6-4) (Table 6-2.).[194] In this manner, 2-acetylenic thiazoles were prepared which contained alkyl, vinyl, aryl, ether, chloroalkyl, and ester substituted groups attached to the heterocyclic ring or the acetylenic unit.

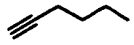
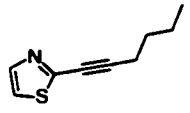
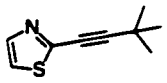
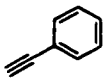
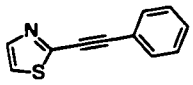
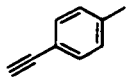
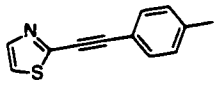
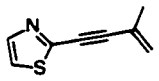
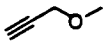
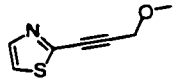
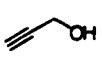
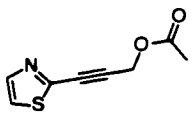


6.7 **6.8** **6.9** (6-3)

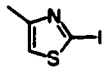
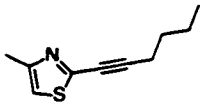
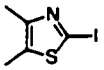
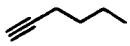
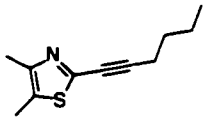
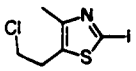
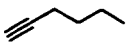
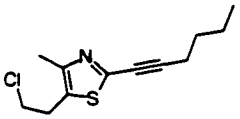
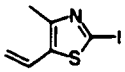
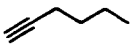
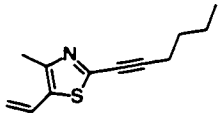
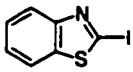
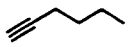
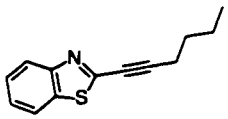


6.6 **6.7** (6-4)

Table 6-1. Preparation of 2-Acetylenic Thiazoles [a]

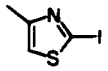
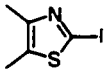
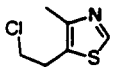
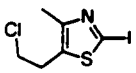
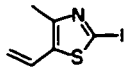
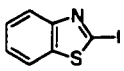
Entry	6.7	6.8	6.9	Isolated Yield (%) [b]
1	 **6.7a**	 **6.8a**	 **6.9a**	93
2		 **6.8b**	 **6.9b**	95
3		 **6.8c**	 **6.9c**	89
4		 **6.8d**	 **6.9d**	94
5		 **6.8e**	 **6.9e**	79
6 [e]		 **6.8f**	 **6.9f**	90
7 [e]		 **6.8g**	 **6.9g** [f]	56

(Table 6-1. Continued)

Entry	6.7	6.8	6.9	Isolated Yield (%) [b]
8				87
	6.7b [g]	**6.8a**	**6.9h**	
9				85
	6.7c [g]	**6.8a**	**6.9i**	
10				84
	6.7d [g]	**6.8a**	**6.9j**	
11				77
	6.7e [g]	**6.8a**	**6.9k**	
12				87
	6.7f [g]	**6.8a**	**6.9l**	

[a] Reaction conditions: Halothiazole (**6.7**), 20 mmol; alkyne (**6.8**), 25 - 30 mmol; $Pd(PPh_3)_2Cl_2$, 0.20 mmol (1.0 %); CuI, 0.20 mmol (1.0 %); Et_3N, 20 mL, CH_2Cl_2, 40 mL; reflux (65 °C); 18 h. [b] The products were isolated by silica gel chromatography using 0:100 to 5:95 MeOH:CH_2Cl_2 followed by Kugelrohr distillation. [e] Et_3N, 60 mL. [f] 3-Thiazol-2-yl-prop-2-yn-1-ol was directly converted to **6.9g** by the addition of 1 equivalent of acetic anhydride. [g] 6 h,

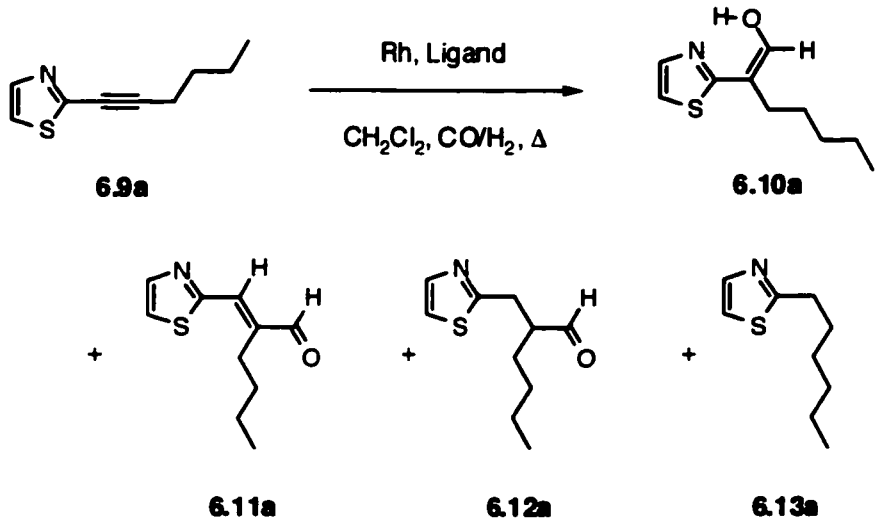
Table 6-2. Preparation of 2-Iodothiazoles [a]

Entry	6.6	6.7	Isolated Yield (%) [b]
1			56
	6.6b	**6.7b**	
2			54
	6.6c	**6.7c**	
3			63
	6.6d	**6.7d**	
4			51
	6.6e	**6.7e**	
5			57
	6.6f	**6.7f**	

[a] Reaction conditions: **6.6**, 50 mmol; Ether, 100 mL, 1.4 M MeLi, 40 mL; I_2, 60 mmol; Dry-Ice/MeOH. [b] The products were isolated by silica gel chromatography using CH_2Cl_2 as eluant, followed by sublimation.

6.3.2 Reaction Optimization

The reaction of an acetylenic thiazole **6.9** (1.5 – 3.0 mmol) with carbon monoxide (10.5 – 17.5 atm) and hydrogen (3.5 – 10.5 atm), in the presence of the zwitterionic rhodium complex **1.1** (2 mol %) and triphenyl phosphite (8 mol %), at 70 – 110 °C for 18 to 36 h, afforded the unexpected (*Z*)-thiazol-2-ylalk-1-en-1-ol (**6.10**) as the major product with the anticipated unsaturated aldehyde (**6.11**) and the saturated aldehyde analog (**6.12**) as by-products.



6.9a **6.10a** **6.11a** **6.12a** **6.13a** (6-5)

Given the novel results, the hydrocarbonylation of 2-acetylenic thiazoles was optimized by using 2-hex-1-ynylthiazole (**6.9a**) as a model substrate. Treating 1.5 mmol **6.9a** with 2 mol % **1.1**, 8 mol % $(PhO)_3P$, 10 mL of CH_2Cl_2, 14 atm CO, 7 atm H_2 in a 45 mL autoclave, from 70 to 110 °C resulted in a preference for **6.10a** ranging from 50 to 85 % after 20 h and the remainder consisting of a mixture of **6.11a** and **6.12a** (Table 6-3;

entries 1, 2, 4, and 6). Changing the pressure to 17.5 atm CO and 3.5 atm H_2 from 90 to 110 °C afforded a mixture of **6.10a** and **6.11a** in which the selectivity of **6.10a** was 77 to 87 % (Table 6-3; entries 3, 5 and 7). Applying a temperature of 110 °C, and a 1:1 ratio of CO/H_2 at a total pressure of 14 and 21 atm resulted in a selectivity for **6.10a** of 89 and 90 % respectively (Table 6-3, entries 8 and 9). Increasing the substrate (**6.9**) from 1.5 to 3.0 mmol, and the total volume from 10 to 20 mL CH_2Cl_2 at 110 °C affords **6.10a** in 83 % selectivity using 21 atm CO/H_2 in a 2:1 ratio (Table 6-3, entry 10), and **6.10a** in 88 % selectivity (86 % isolated yield) using a 1:1 ratio of CO/H_2 (Table 6-3, entry 11). The latter entry demonstrates that the (*Z*)-thiazol-2-ylalk-1-en-1-ol scale-up is readily achieved in a reasonable time frame using moderate temperatures and mild CO/H_2 pressures.

Table 6-3. Reaction Optimization Using 6.9a [a]

Entry	**6.9a** (mmol)	Pressure (atm)	$CO:H_2$	T (°C)	Conv. [b] (%)	**6.10**:**6.11**:**6.12** [c]	% of **6.10a** [d]
1	1.5	21	2:1	70	90	1:1:t	50
2		21	2:1	90	100	3:1:t	75
3		21	5:1	90	95	3.3:1:t	77
4		21	2:1	100	100	3.3:1:t	77
5		21	5:1	100	95	3.8:1:t	79
6		21	2:1	110	100	11:1:1	85
7		21	5:1	110	100	6.8:1:t	87
8		21	1:1	110	100	9.1:t:1	90
9		14	1:1	110	100	16:1:1	89
10	3.0	21	2:1	110	90	4.9:1:t	83
11		21	1:1	110	95	15:1:1	88

[a] Reaction conditions: **6.9a**, 1.5 - 3.0 mmol; **1.1**, 0.03 mmol (entries 1 - 9) - 0.06 mmol (entries 10,11) (2 mol %); $(PhO)_3P$, 0.12 mmol (entries 1 – 9) - 0.24 mmol (entries 10,11) (8 mol %); CH_2Cl_2, 10 mL (entries 1 – 9) - 20 mL (entries 10,11); 70 - 110 °C, 20 h. [b] The percent conversion was determined by ^1H NMR. [c] The ratio of **6.10**:**6.11**:**6.12** was determined by ^1H NMR. [d] The percentage of **6.10a** is based on the ratios of **6.10**:**6.11**:**6.12**.

Additional ligands and rhodium complexes were examined to determine the uniqueness of the present catalytic system incorporating the conditions of Table 6-3, entry 8. No reaction takes place with the zwitterionic rhodium complex **1.1** in the absence of an added ligand (Table 6-4, entries 1). Changing the ligand from $(PhO)_3P$ to $(iPrO)_3P$, Ph_3P and dppb gives **6.10a** in low selectivity and conversion with the addition of the hydrogenated thiazolyne **6.13a** (Table 6-4, entries 2 to 5). The rhodium complexes $Rh(CO)_2acac$, $[Cl(C_2H_4)_2Rh]_2$ and $[Cl(CO)_2Rh]_2$ favor **6.10a** in lower selectivity along with a mixture of the hydroformylated products **6.11a** and **6.12a** (Table 6-4, entries 6 to 8). No reaction occurred using catalytic quantities of $RhCl_3$ and $(PhO)_3P$ (Table 6-4, entries 9). The catalytic system comprised of the zwitterionic rhodium complex (**1.1**) and triphenyl phosphite is preferred for obtaining a thiazolylenol in excellent chemo- and regioselectivity, compared with other rhodium complexes and phosphorus ligands.

Table 6-4. Catalyst Optimization Using 6.9a [a]

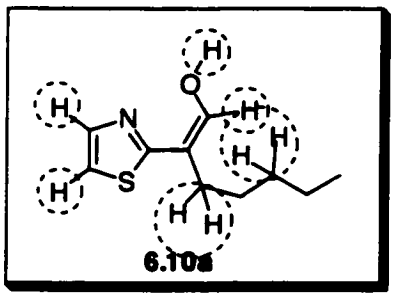
Entry	Rh	Ligand	Conv. [b] (%)	**6.10**:**6.11**:**6.12**:**6.13** [c]	% of **6.10a** [d]
1	Rh^{ZW}(**1.1**)	-	0	-	-
2	Rh^{ZW}(**1.1**)	$(PhO)_3P$	100	16:1:1:0	89
3	Rh^{ZW}(**1.1**)	$(iPrO)_3P$	90	3:1:t:1	60
4	Rh^{ZW}(**1.1**)	Ph_3P	35	3:t:2:6	27
5	Rh^{ZW}(**1.1**)	dppb [e]	10	mixture	-
6	$Rh(CO)_2acac$	$(PhO)_3P$	100	10:1:3:0	71
7	$[Cl(C_2H_4)_2Rh]_2$	$(PhO)_3P$	74	8:3:2:0	62
8	$[Cl(CO)_2Rh]_2$	$(PhO)_3P$	95	11:4:t:0	73
9	$RhCl_3$	$(PhO)_3P$	0	-	-

[a] Reaction conditions: **6.9a**, 1.5 mmol; **1.1**, 0.03 mmol (2 mol %); Ligand, 0.12 mmol (8 mol %); CH_2Cl_2, 10 mL; CO, 10.5 atm; H_2, 10.5 atm; 110 °C; 20 h. [b] The percent conversion was determined by ^1H NMR. [c] The ratio of **6.10**:**6.11**:**6.12**:**6.13** was determined by ^1H NMR [d] The percentage of **6.10a** is based on the ratios of **6.10**:**6.11**:**6.12**:**6.13**. [e] dppb, 0.06 mmol.

6.3.3 NMR Determination of Regiochemistry and Structure

Nuclear Overhauser and Exchange Spectroscopy (NOESY) is the gathering of all ^{1}H ^{1}H NOE effects in a molecule into a single spectrum. This simplifies the ability to solve the structures of large molecules with regions of fixed geometry.

Product **6.10a** is an excellent example of the thiazolylenol ring system. The NOESY spectrum (Fig. 6-1) illustrates a strong correlation between the acidic ^{1}H at δ 12.61 (br, 1H) and the olefinic ^{1}H at δ 6.87 (s, 1H), indicating a short ^{1}H ^{1}H distance. As well, no significant correlation between the olefinic proton at δ 6.87 (s, 1H) and the methylene at δ 2.27 (t, 2H, J = 7.0 Hz) was observed. Though, a significant correlation was observed between the olefinic ^{1}H at δ 6.87 (s, 1H) and the carbon 2 and 3 of the 2-substituted ***n***-pentyl chain δ 1.26 – 1.60 which could only result from a ***Z***-isomer of the newly formed double bond.



6.10a

The NOESY and corresponding COSY illustrated ^{1}H-^{1}H connectivities for the proton signals between δ 0.87 – 2.27 related to the ***n***-pentyl chain. As well, the olefin protons at δ 7.66 (d, 1H, J = 3.5 Hz) and δ 7.03 (d, 1H, J = 3.5 Hz) are only shifted slightly from

6.10a

Figure 6-1. NOESY Experiment on 6.10a

their original positions in the thiazole ring system of **6.9a**, δ 7.53 (d, 2H, J = 3.4 Hz) and δ 7.07 (d, 2H, J = 3.4 Hz), indicating they are still positioned next to the nitrogen and sulfur atoms. Therefore, the above observations illustrate that **6.10a** has structure shown above.

The ^{13}C NMR spectrum displays a chemical shift at δ 170.8 with a corresponding strong infrared stretching frequency of 1627 cm^{-1}. This chemical shift and infrared frequency are consistent with an unsaturated amide functionality.

The ^{13}C chemical shift at δ 170.8 is less consistent with the thiazol-2-ylenolic structure. The possibility of the chemical shift being due to the enolic carbon was dismissed since conjugated enolic carbons (where hydrogen bonding is a factor) are generally found > δ 160.[195] In addition, Pd/C catalyzed hydrogenation of the newly formed double bond resulted in the chemical shift at δ 170.8 shifting to δ 168.8 (see Section 8.7.5). As well, the carbon-2 of 2-substituted N-heterocyclic rings are generally found between δ 135 - 160. The chemical shift at δ 170.8 was not in complete agreement with the expected shift for the carbon-2 of the thiazole ring,[196] although, the carbon-2 of a heterocyclic ring involved in H-bonding would be expected to be shifted further downfield from its original position.

6.3.4 X-Ray Crystal Structure Determination

Park and Alper further studied the hydroformylation of 2-acetylenic N-heterocyclic aromatic rings.[197] In August 2002, they observed that upon placing 2-phenylethynylbenzothiazole (**6.9m**) under similar conditions to those just described (Eq. 6-6), a product resulted which upon standing produced a crystal with the structure found in Figure 6-2.

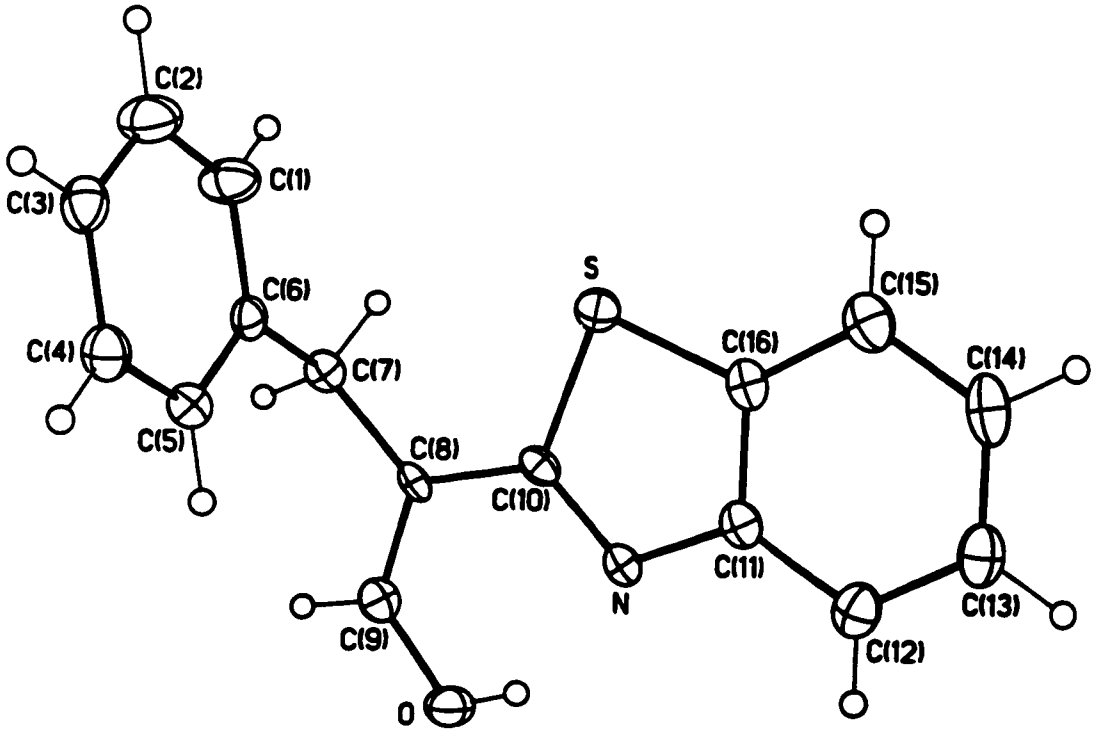
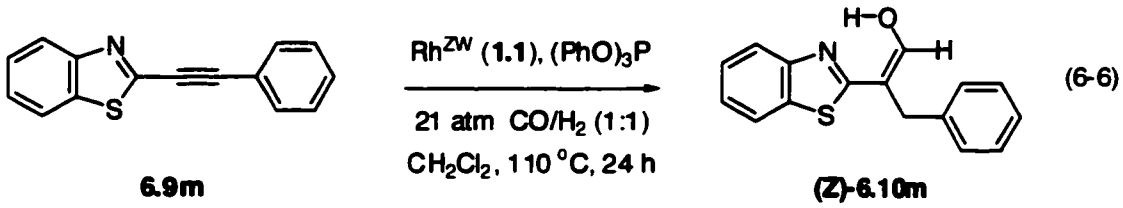


Figure 6-2. X-Ray Crystal Structure of 6.10m

The structure above is of the thiazol-2-ylenol (*Z*)-benzothiazol-2-yl-3-phenyl-propen-1-ol. The corresponding ^{1}H and ^{13}C NMR spectra for **6.10m**, is consistent with those found in our published results, and confirms that the product generated from placing acetylenic thiazoles under hydroformylation conditions is the (*Z*)-thiazol-2-ylalk-1-en-1-ol. An important note regards the ^{13}C NMR chemical shift at δ 170.8 which must results from the 2-position of the thiazole ring. Intramolecular hydrogen bonding of the thiazole ring to the enol functionality extends the range of the carbon-2 from N-heterocyclic aromatic rings from δ 135 – 170.

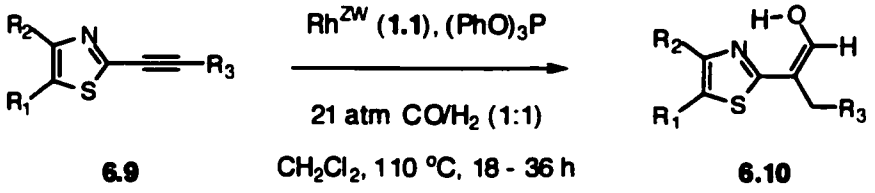


6.9m **(Z)-6.10m** (6-6)

The following sections describe the novel zwitterionic rhodium catalyzed reaction of simple and functionalized 2-acetylenic thiazoles with carbon monoxide and hydrogen to form (*Z*)-2-thiazol-2-ylalk-1-en-1-ols in 61 to 90 % yields with good to excellent chemo- and regioselectivities.

6.3.5 Hydrocarbonylation Enolation Reactions of Acetylenic Thiazoles with Different Substituents in the Acetylenic Unit

The scope of the acetylenic thiazole/thiazol-2-ylenol reaction was investigated using thiazolynes with modified alkyne components (Table 6-5) and altered thiazole rings (Table 6-6) employing the reaction conditions described in Table 6-3, entry 11 (Eq. 6-7).

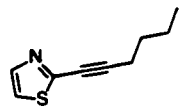
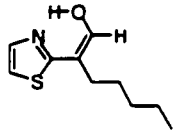
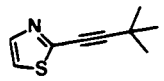
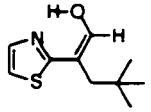
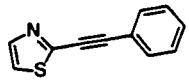
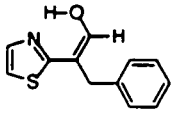
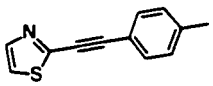
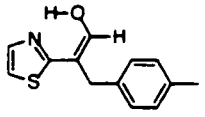
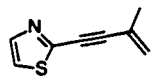
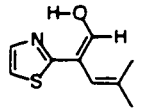
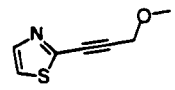
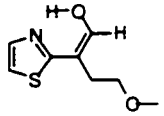
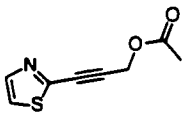
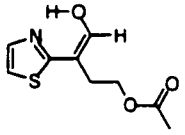


6.9 **6.10** (6-7)

Thiazolynes **6.9**, unsubstituted at the 4- and 5-position of the heterocycle (i.e. $R_1 = R_2 =$ H), and where the acetylenic unit contains an alkyl or aryl substituent (i.e. R_3), react under the noted conditions affording **6.10a – 6.10d** in 86 to 90 % isolated yields of the pure thiazolylenol (Table 6-5, entries 1 to 4). The (*Z*)-2-thiazol-2-ylalk-1-en-1-ols, **6.10e – 6.10g**, were obtained in 61 to 74 % isolated yields when the R_3 group of the alkyne unit was an alkyl ether, alkyl ester or vinyl substituent (Table 6-5, entries 5 to 7). Note that 2-(3-methylbut-3-en-1-ynyl)thiazole (**6.9e**) afforded only one thiazolylenol in 72 % yield (Table 6-5. entry 5). Effecting reactions of **6.9e – 6.9g** at 110 °C instead of 70 °C reduced the yields of **6.10e – 6.10g** and substantially increased the proportions of **6.11** and **6.12**. Therefore, these substrates react in a significantly temperature dependent fashion. The occurrence of more **6.11** and **6.12** using **6.9e – 6.9g** may be explained by

the ability of the rhodium catalyst to coordinate with ether, ester and vinyl functionalities prior to the intramolecular insertion of the catalyst to the triple bond of the thiazolyne. Prior coordination stimulates rhodium insertion to occur on either side of the triple bond as observed in previous studies (see Chapters 2 to 3). At lower temperature coordination of the metal to the thiazole ring is preferred to coordination of the metal to the competing functionality.

Table 6-5. Hydrocarbonylation Enolation Reactions of Acetylenic Thiazoles with Different Substituents in the Acetylenic Unit [a]

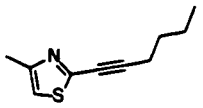
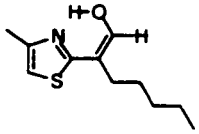
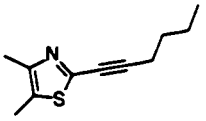
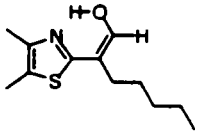
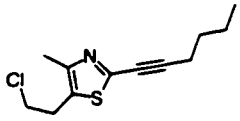
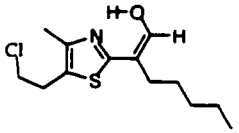
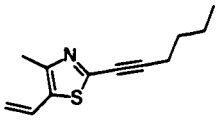
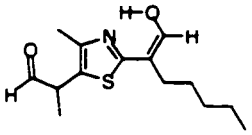
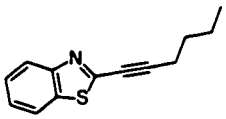
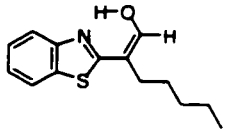
Entry	6.9	t (h)	6.10	Isolated Yield (%) [b]
1	 **6.9a**	24	 **6.10a**	86
2	 **6.9b**	36	 **6.10b**	89
3	 **6.9c**	18	 **6.10c**	90
4	 **6.9d**	18	 **6.5d**	87
5 [c]	 **6.4e**	24	 **6.10e**	72
6 [c]	 **6.9f**	24	 **6.10f**	74
7 [c]	 **6.9g**	24	 **6.10g**	61

[a] Reaction conditions: **6.9**, 3.0 mmol; **1.1**, 0.06 mmol (2 mol %); $(PhO)_3P$, 0.24 mmol (8 mol %); CH_2Cl_2, 20 mL; CO, 10.5 atm; H_2, 10.5 atm; 110 °C. [b] The reactions proceeded to full conversion (followed by NMR), and products were isolated by silica gel chromatography using 0:100 to 5:95 MeOH:CH_2Cl_2. [c] 70 °C.

6.3.6 Hydrocarbonylation Enolation Reactions of Acetylenic Thiazoles Containing Substituents at the 4-, and 4,5-Positions

The conversion of acetylenic thiazoles to (*Z*)-2-thiazol-2-ylalk-1-en-1-ols also proceeds nicely using substrates substituted at the 4-, or 4,5-positions of the reactant. The thiazol-2-ylenol, **6.10h**, was isolated in 83 % yield using **6.9h**, R_1 = H, R_2 = Me, and R_3 = *n*-Bu (Table 6-6, entry 1). Changing R_1 from H to methyl, chloroethyl, or vinyl afforded the thiazol-2-ylenol in 78 – 81 % yields (Table 6-6, entries 2 – 4). While the chloroethyl substituent is completely inert under the reaction conditions, the vinyl group reacts in a completely regioselective manner to form the branched chain aldehydic thiazolylenol. Finally, the hydrocarbonylation/enolation process is applicable to a benzothiazole – i.e. **6.9l** gave the benzothiazol-2-ylenol (**6.10l**) in 76 % isolated yield (Table 6-6, entry 5).

Table 6-6. Hydrocarbonylation Enolation Reactions of Acetylenic Thiazoles Containing Substituents at the 4-, and 4,5-Positions [a]

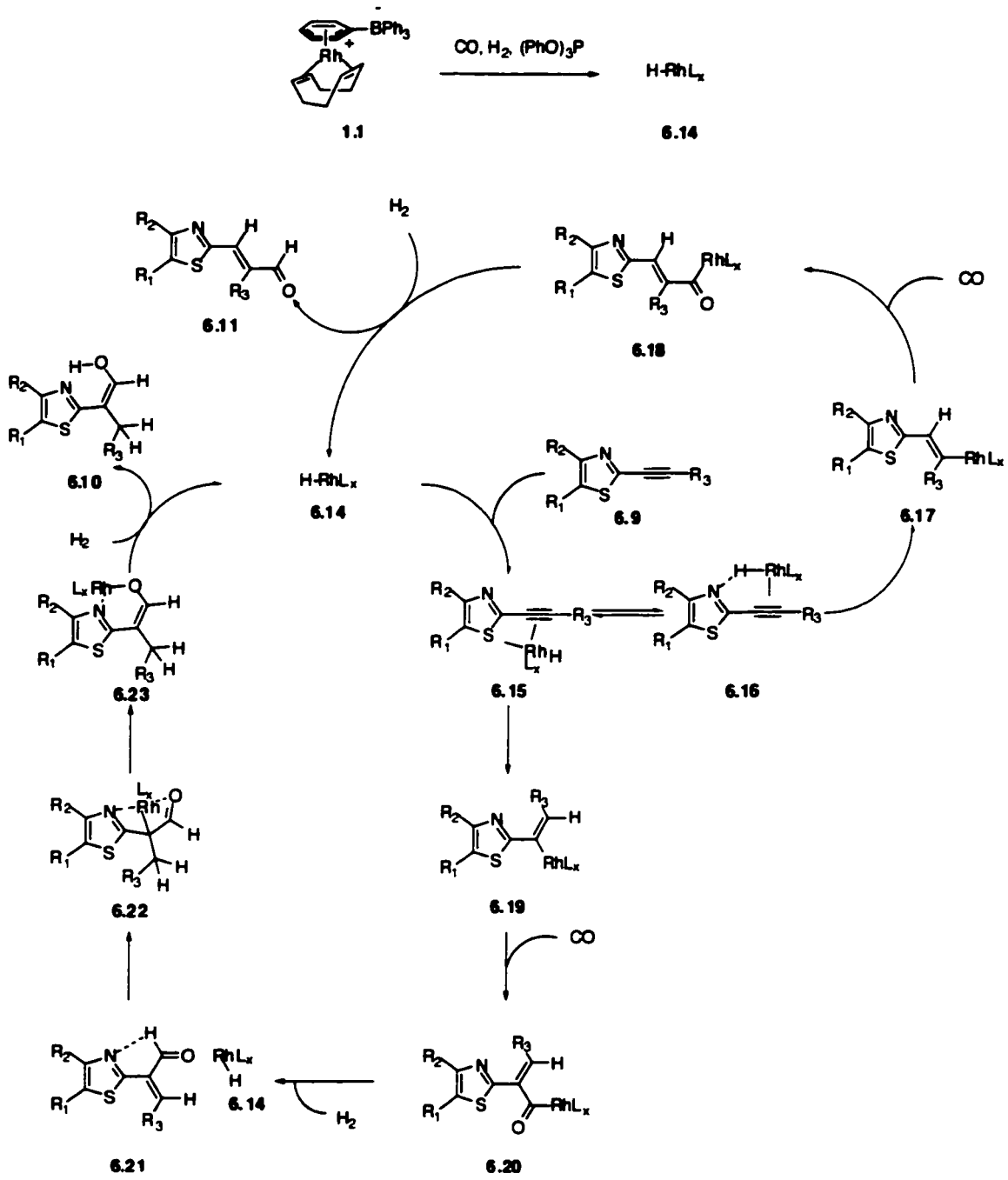
Entry	6.9	t (h)	6.10	Isolated Yield (%) [b]
1	 **6.9h**	24	 **6.10h**	83
2	 **6.9i**	18	 **6.10i**	78
3	 **6.9j**	18	 **6.10j**	79
4	 **6.9k**	18	 **6.10k**	81
5	 **6.9l**	18	 **6.10l**	76

[a] Reaction conditions: **6.9**, 3.0 mmol; **1.1**, 0.06 mmol (2 mol %); $(PhO)_3P$, 0.24 mmol (8 mol %); CH_2Cl_2, 20 mL; CO, 10.5 atm; H_2, 10.5 atm; 110 °C. [b] The reactions proceeded to full conversion (obtained by NMR), and products were isolated by silica gel chromatography using 0:100 to 5:95 MeOH:CH_2Cl_2.

6.3.7 Mechanistic Aspects

A possible mechanism for the conversion of acetylenic thiazoles to the (*Z*)-thiazol-2-ylalk-1-en-1-ols is outlined in Scheme 6-1. The active rhodium complex (**6.14**), formed from complex **1.1**, binds to the thiazolyne via the triple bond and a heteroatom (**6.15**) or possibly by H-bonding to the thiazole ring (**6.16**). Depending on the equilibrium between **6.15** and **6.16** two products will result. If **6.16** is favored, subsequent intramolecular insertion of the Rh-H bound to the alkyne would generate **6.17**. Carbonylation (**6.18**) of the latter and subsequent addition of hydrogen would give the hydroformylation product **6.11**. However, if **6.15** is favored, the intramolecular hydrorhodation would proceed in the opposite manner to form **6.19**, carbonylation of which would give **6.20**, and further hydrogen addition would generate **6.21** and the Rh-H **6.14**. Close proximity of the rhodium hydride to intermediate **6.21** initiates a second intramolecular hydrorhodation resulting in the formation of the aldehydic/Rh complex **6.22**. Favorable complexation between the thiazole ring, rhodium, and the aldehyde carbonyl initiates a rearrangenment of the aldehyde to the (*Z*)-enolic rhodium **6.23**. A final addition of hydrogen regenerates the rhodium complex **6.14** and affords the (*Z*)-2-thiazol-2-ylalk-1-en-1-ol (**6.10**), stabilized by intramolecular hydrogen bonding.

Scheme 6-1. Proposed Mechanism



6.4 Conclusion

In conclusion, a synthesis of (*Z*)-2-thiazol-2-ylalk-1-en-1-ols was discovered by the reaction of 2-acetylenic thiazoles with CO/H_2 in the presence of catalytic amounts of **1.1** and triphenyl phosphite. The process is general, and tolerates the presence of functional groups including ether, ester and chloro. The reactions are simple in execution and work-up, while thiazoles and enols are of significant intrinsic interest in drug design, incorporatioon of these heterocycles into organic synthetic strategies may lead to valuable pharmaceuticals.

CHAPTER 7

SYNTHESIS OF (*Z*)-2-BENZOXAZOL-2-YLALK-1-EN-1-OLS BY ZWITTERIONIC RHODIUM COMPLEX CATALYZED CHEMO- AND REGIOSELECTIVE HYDROCARBONYLATIVE ENOLATION OF 2-ACETYLENIC BENZOXAZOLES

7.1 Introduction

Oxazoles, like their thiazole counterpart, incorporate an important heterocyclic ring system that exhibits both high biological activity and potential for pharmacological applications. The core 5-membered O,N-heterocycle demonstrates cardioprotective[198] and adrenoceptor agonistic effects,[199] inhibition of lipid peroxidation,[200] inhibition of human placelet aggregation,[201] COX-2 inhibition,[202] telomerase inhibition,[203] and protein tyrosine phosphatase 1B inhibition.[204] Furthermore, they display analgesic,[205] antimigraine,[206] antitumor,[207] antimitotic,[208] antimicrobacterial,[209] antibacterial,[210] antihypertension,[211] anticancer,[212] antifungal,[213] and antihyperglycemic properties.[214]

In recent years particular interest has been bestowed upon natural products containing oxazolyl units. Particularly, the potent anticancer agent phorboxazole A,[215] the novel hypoglycemic agent SDZ PGU 693,[216] the potent antifungal agent preussin,[217] and the antiviral marine natural product (-)-hennoxazole A.[218]

Enolic functionalities play key roles in total synthetic applications. A recent synthesis of pulchellalactam, a tyrosine phosphatase inhibitor, utilized a key addition

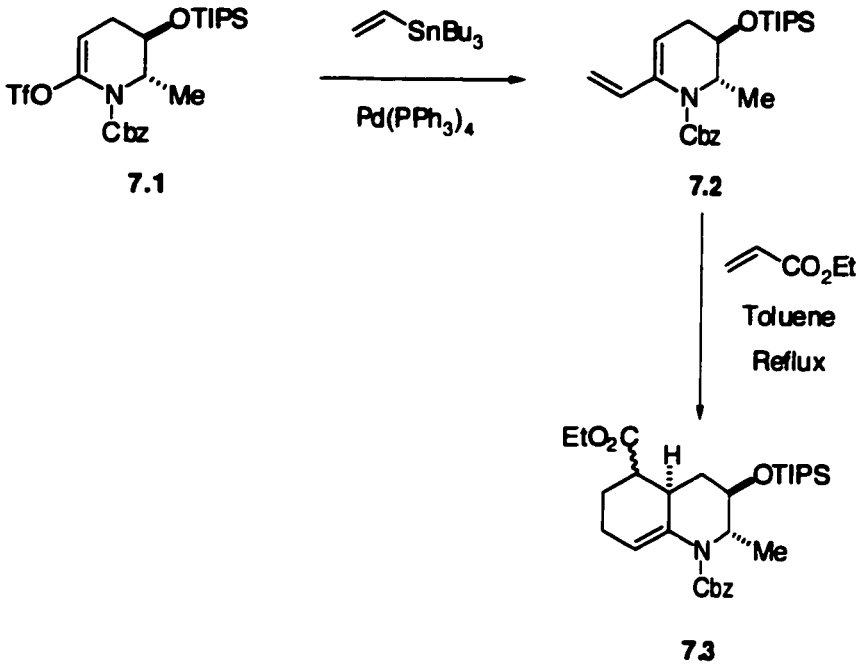
and elimination protocol of an enolic lactam.[219] The total synthesis of (-)-bafilomycin A1, a potent vascular ATPase inhibitor, used the Mukaiyama aldol reaction to initiate macrocyclization between an aldehyde and a TMS enol ether.[220] Boger's synthesis of (-)-roseophilin, the unnatural enantiomer of a naturally occurring antitumor antibiotic, enlisted a Diels-Alder reaction of an azadiene with an optically active enol ether.[221] The total synthesis of clavepictines A and B,[222] as well as desoxoprosophylline[223] included key cross-coupling reactions of enol triflates of N-protected lactams. In addition, a general route to 2,4,5-trisubstituted piperidines enabled the total syntheses of pseudodistomin B triacetate and pseudodistomin F to occur by Raney-Ni catalyzed hydrogenation of enol ethers.[224]

7.2 Aim of Research

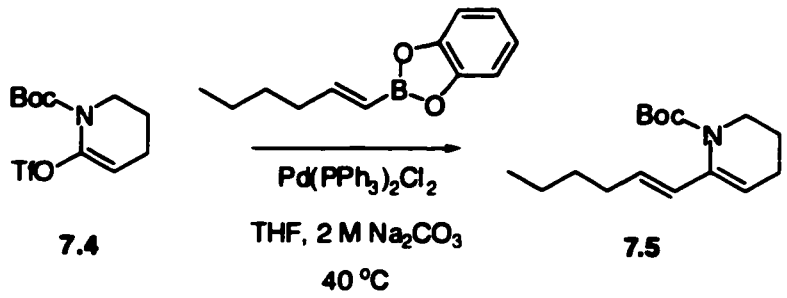
Oxazoles and enols have advantageously been used as building blocks for materials with pharmacological importance. Having these combined units within a molecule through a simple transformation resulting from the hydroformylation of acetylenic oxazoles would lead to materials that could be readily incorporated in synthetic strategies. The conversion of enols to enolic triflates would enable palladium catalyzed cross-coupling,[225] Suzuki coupling,[226] Stille coupling,[227] and Heck reactions to take place.[228] This material would also have the potential to be modified and chirality introduced by

asymmetric hydrogenation,[229] dihydroxylation,[230] aminohydroxylation,[231] and selenomethoxylation[232] of its newly formed double bond.

Scheme 7-1. Route to Bicyclic Piperidines

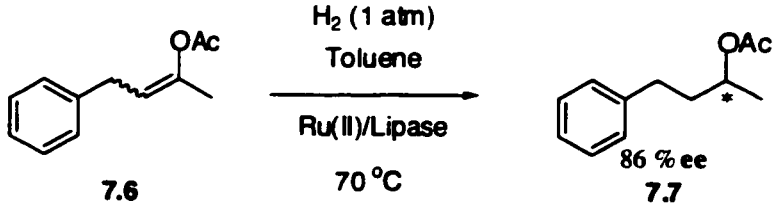


As an aside to Cha and coworkers approach to clavepictines,[222] Cha further studied the Stille coupling of enol triflates of N-acyl lactams to widen its applications in alkaloid synthesis. For example, triflate **7.1** underwent coupling with tributyl(vinyl)tin in the presence of catalytic amounts of $Pd(PPh_3)_4$ to afford diene **7.2** in 78 % yield (Scheme 7-1). The Diels-Alder reaction of **7.2** with ethyl acrylate provided **7.3** in a 1:1 ratio of the *endo* and *exo* diasteriomers in a combined yield of 79 %.



(7-1)

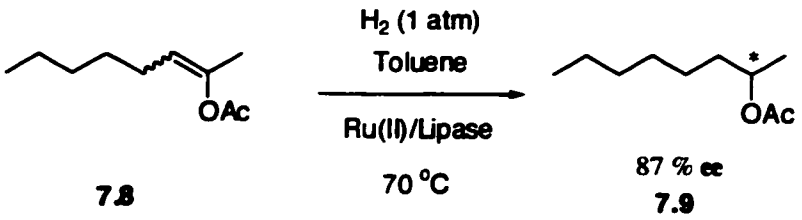
In addition, Occhiato and coworkers[226] studied the Suzuki coupling of the N-Boc protected vinyl triflate **7.4** with boron compounds. The Pd(II) coupled reaction of **7.4** with 2-[(*E*)—1-hexenyl]-1,3,2-benzodioxaborate provided the piperidine **7.5** in 82 % yield after 2 hours (Eq. 7-1). This extension of triflate chemistry further demonstrates the potential of an enol to generate more complex and useful components for organic synthesis.



(7-2)

In 2000, Kim and coworkers[229a] demonstrated the Ru(II)/lipase catalyzed asymmetric hydrogenation of both benzyl **7.6** (Eq. 7-2) and n-pentyl **7.8** (Eq. 7-3) substituted enol acetates to afford chiral acetates **7.7** and **7.9** in 85 to 91 % yields and 86 to 87 % **ee** respectively. Though, a phenyl substituted enol acetate was transformed to the corresponding chiral acetate in a low enantioselectivity of 47 %. The former

substituents are similar to those generated when 2-acetylenic thiazoles were transformed to (*E*)-2-thiazol-2-ylalk-1-en-1-ols.



7.8 7.9 (7-3)

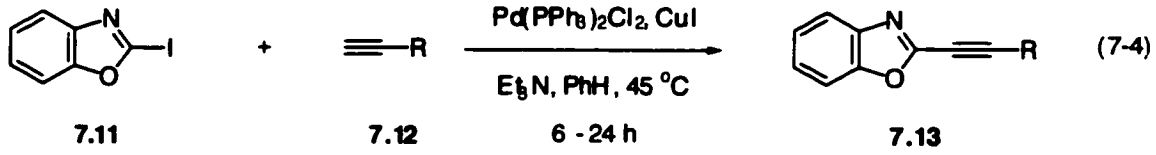
As a consequence of the results obtained in Chapter 6, it was anticipated that the novel transformation of an 2-alkynylheterocycle to a conjugated heterocyclic enol could be extended to acetylenic oxazoles in order to generate an additional example of this important transformation. Utilizing the present methodology from acetylenic thiazoles, to oxazoles, would provide a method for transforming an oxazole ring to an organic reagent capable of undergoing palladium catalyzed coupling, and potential chirality introduction to the newly formed enolic unit.

The following sections describe the novel zwitterionic rhodium catalyzed reaction of simple and functionalized acetylenic benzoxazoles with carbon monoxide and hydrogen to form 2-(*Z*)-2-benzoxazol-2-ylalk-1-en-1-ols in 37 to 87 % yields, and in moderate to excellent chemo- and regioselectivities.

7.3 Results and Discussion

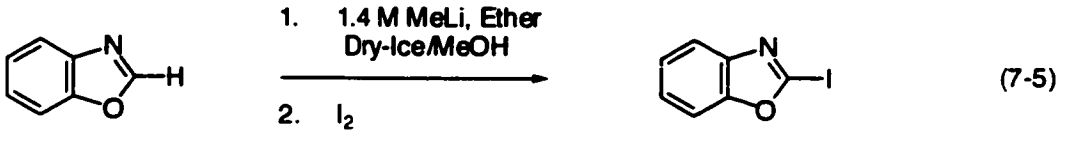
7.3.1 Synthesis of Starting Materials

The requisite acetylenic oxazoles (Eq. 7-4) were readily obtained, in 63 to 95 % yields, by the cross-coupling reaction of the presynthesized 2-iodobenzoxazole (**7.11**) with terminal alkynes using catalytic quantities of $Pd(PPh_3)_2Cl_2$ and CuI under basic conditions (Table 7-1).[193] In this manner, 2-acetylenic benzoxazoles were prepared which contained alkyl, vinyl, aryl, ether, and chloroalkyl substituted groups attached to the acetylenic unit.



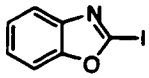
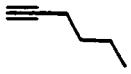
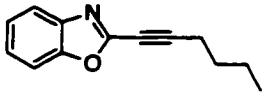
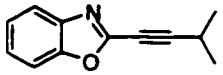
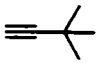
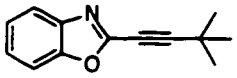
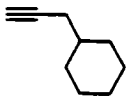
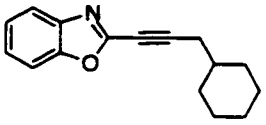
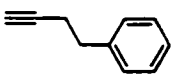
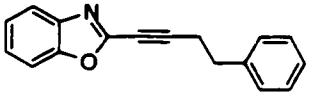
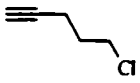
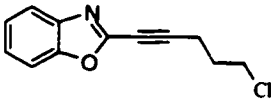
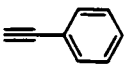
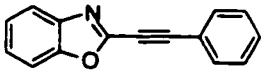
7.11 **7.12** 6 - 24 h **7.13** (7-4)

2-Iodobenzoxazole was prepared by lithiation and then iodination of benzoxazole in 72 % yield (Eq. 7-5).[233]

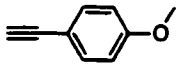
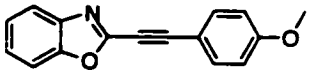
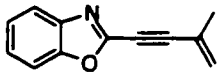
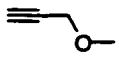
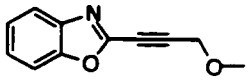
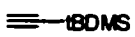
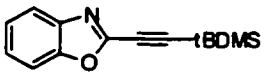
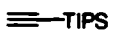
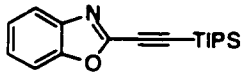


7.10 **7.11** (7-5)

Table 7-1. Preparation of 2-Acetylenic Benzoxazoles[a]

Entry	7.11	7.12	7.13	Isolated Yield (%)[b]
1				95
	7.11	**7.12a**	**7.13a**	
2				83
		7.12b	**7.13b**	
3				86
		7.12c	**7.13c**	
4				84
		7.12d	**7.13d**	
5				87
		7.12e	**7.13e**	
6				78
		7.12f	**7.13f**	
7				81
		7.12g	**7.13g**	

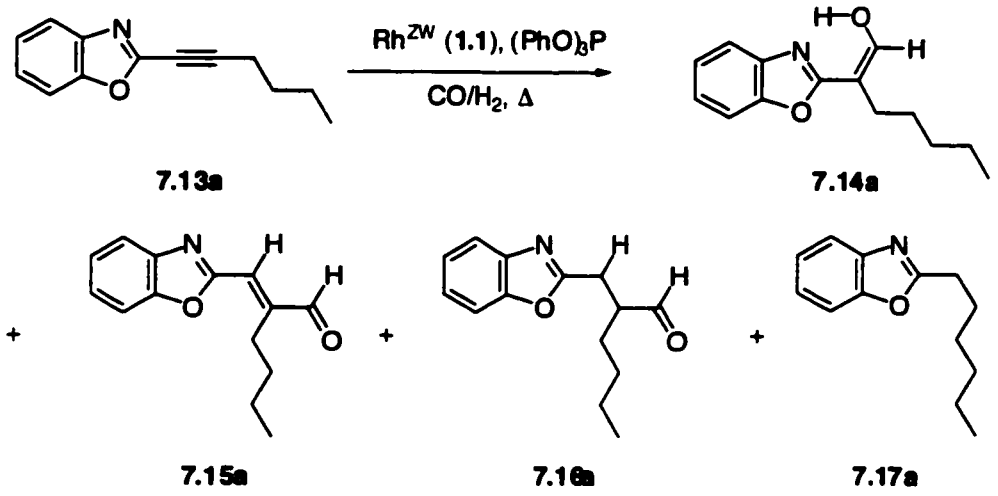
(Table 7-1. Continued)

Entry	7.11	7.12	7.13	Isolated Yield (%) [b]
8				90
		7.12h	**7.13h**	
9				63
		7.12i	**7.13i**	
10				65
		7.12j	**7.13j**	
11 [c]				75
		7.12k	**7.13k**	
12 [c]				79
		7.12l	**7.13l**	

[a] Reaction conditions: 2-Iodobenzoxazole (**7.11**), 20 mmol; alkyne (**7.12**), 25 - 30 mmol; $Pd(PPh_3)_2Cl_2$, 0.40 mmol (1.5 mol %); CuI, 0.80 mmol (3.0 mol %); Et_3N, 20 mL. PhH, 40 mL; 45 °C; 6 h. [b] The products were isolated by Kugelrohr distillation or by silica gel chromatography using CH_2Cl_2 as eluant. [c] 24 h.

7.3.2 Reaction Optimization

The reaction of an acetylenic benzoxazole **7.13** (1.5 – 3.0 mmol) with carbon monoxide and hydrogen in the presence of the zwitterionic rhodium complex **1.1** and triphenyl phosphite afforded the (*Z*)-2-benzoxazol-2-ylalk-1-en-1-ols (**7.14**) as the major product with the unsaturated aldehyde (**7.15**), the saturated aldehyde analog (**7.16**), and the hydrogenated alkyne (**7.17**) as by-products (Eq. 7-6).



7.13a **7.14a**

(7-6)

7.15a **7.16a** **7.17a**

The hydrocarbonylation and enolation of 2-acetylenic benzoxazoles was optimized using 2-hex-1-ynylbenzoxazole (**7.13a**) as a model substrate. Treating 1.5 mmol **7.13a** with 2 mol % **1.1**, 8 mol % $(PhO)_3P$, and CH_2Cl_2 as the optimum solvent (Table 7-1, entries 1 to 4) in a 45 mL autoclave at 100°C, **7.14a** was obtained in a 70 % selectivity. Upon decreasing the pressure from 42 to 14 atm CO/H_2 (7 atm H_2) at 100 °C resulted in a preference for **7.14a** ranging from 64 to 74 % after 21 h and the product

balance consisted of a mixture of **7.15a**, **7.16a** and **7.17a** (Table 7-2; entries 4 to 9). Changing the pressure to 7 atm CO and 3.5 atm H_2, and lowering the temperature from 110 to 60 °C resulted in a lowered selectivity of **7.14a** from 79 to 57 % (Table 7-2; entries 9 to 13), and with no conversion at 20 °C (Table 7-2, entry 14). Utilizing 3.0 mmol **7.13a** at 110 °C, and a 1:1 ratio of CO/H_2 at a total pressure of 14 and 21 atm gave **7.14a** in 78 and 79 % selectivity respectively (Table 7-2, entries 15 and 16). Increasing the substrate (**7.13a**) from 3.0 to 4.5 mmol at 110 °C affords **7.14a** in 78 % selectivity using 21 atm CO/H_2 in a 1:1 ratio (Table 7-2, entry 17). The latter entries demonstrate that both benzoxazol-2-yl and thiazol-2-ylalk-1-en-1-ols are readily obtained under identical conditions employing moderate temperatures and mild CO/H_2 pressures.

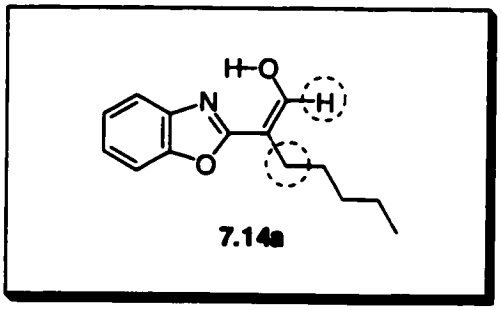
Table 7-2. Reaction Optimization Using 7.13a [a]

Entry	7.13a (mmol)	Solvent	P (atm)	$CO:H_2$	T (°C)	t (h)	Conv. (%)	7.14:7.15:7.16: 7.17 [b]
1	1.5	CH_3CN	28	3:1	100	21	80	64:20:7:8
2		PhH	28	3:1	100	21	62	64:25:4:8
3		THF	28	3:1	100	21	63	58:25:6:8
4		CH_2Cl_2	28	3:1	100	21	100	70:13:10:7
5		CH_2Cl_2	14	1:1	100	21	100	74:10:9:7
6		CH_2Cl_2	21	2:1	100	21	100	72:12:10:6
7		CH_2Cl_2	35	4:1	100	21	100	67:13:13:7
8		CH_2Cl_2	42	5:1	100	21	100	64:10:19:7
9		CH_2Cl_2	10.5	2:1	100	21	98	76:14:2:6
10		CH_2Cl_2	10.5	2:1	110	21	99	79:11:3:7
11		CH_2Cl_2	10.5	2:1	90	21	97	72:19:3:6
12		CH_2Cl_2	10.5	2:1	80	21	96	67:22:6:5
13		CH_2Cl_2	10.5	2:1	60	21	74	57:36:5:2
14		CH_2Cl_2	10.5	2:1	20	21	0	-
15	3.0 [c]	CH_2Cl_2	14	1:1	110	21	95	75:16:3:6
16		CH_2Cl_2	21	1:1	110	21	100	79:8:7:6
17	4.5 [d]	CH_2Cl_2	21	1:1	110	21	99	78:8:8:6

[a] Reaction conditions: **1.1**, 0.03 mmol (2 mol %); $(PhO)_3P$, 0.12 mmol (8 mol %); Solvent, 10 mL. [b] The ratio of **7.14**:**7.15**:**7.16**:**7.17** was determined by ^1H NMR. [c] **1.1**, 0.06 mmol (2 mol %); $(PhO)_3P$, 0.24 mmol (8 mol %), solvent, 20 mL. [d] **1.1**, 0.09 mmol (2 mol %); $(PhO)_3P$, 0.36 mmol (8 mol %), solvent, 20 mL.

7.3.3` *NMR Determination of Regiochemistry*

The NOE difference spectrum of **7.14a** (Fig. 7-1) illustrates, in contrast to the (*Z*)-2-thiazol-2-ylalk-1-en-1-ols, no correlation between the acidic ^{1}H at δ 11.90 (br, 1H) and the olefinic ^{1}H at δ 7.09 (s, 1H), indicating no ^{1}H ^{1}H correlation. No correlation indicated strong intramolecular hydrogen bonding of the protic hydrogen to the nitrogen from the oxazole ring. A significant correlation is found between the olefinic proton at δ 7.09 (s, 1H) and methylene at δ 2.38 (t, 2H, J = 7.4 Hz). As well, a strong effect was present between δ 2.38 (t, 2H, J = 7.4 Hz) and the olefinic ^{1}H at δ 7.09 (s, 1H), indicating they reside on the same side of the double bond at positions 1 and 2 (*Z*-isomer). The corresponding COSY illustrated ^{1}H-^{1}H connectivities for the proton signals between δ 0.88 – 2.40 related to the *n*-pentyl chain at position 2. In addition, the aromatic protons between δ 7.26 – 7.61 have shifted only slightly from their original positions in the benzoxazole ring of **7.13a** (see Section 8.7.2.2). Therefore, the benzene ring is still positioned next to the nitrogen and oxygen atoms, indicating that the above observations support **7.14a** as the structure for the product. This is consistent with the structure obtained by Park and Alper (Chapter 6).



7.14a

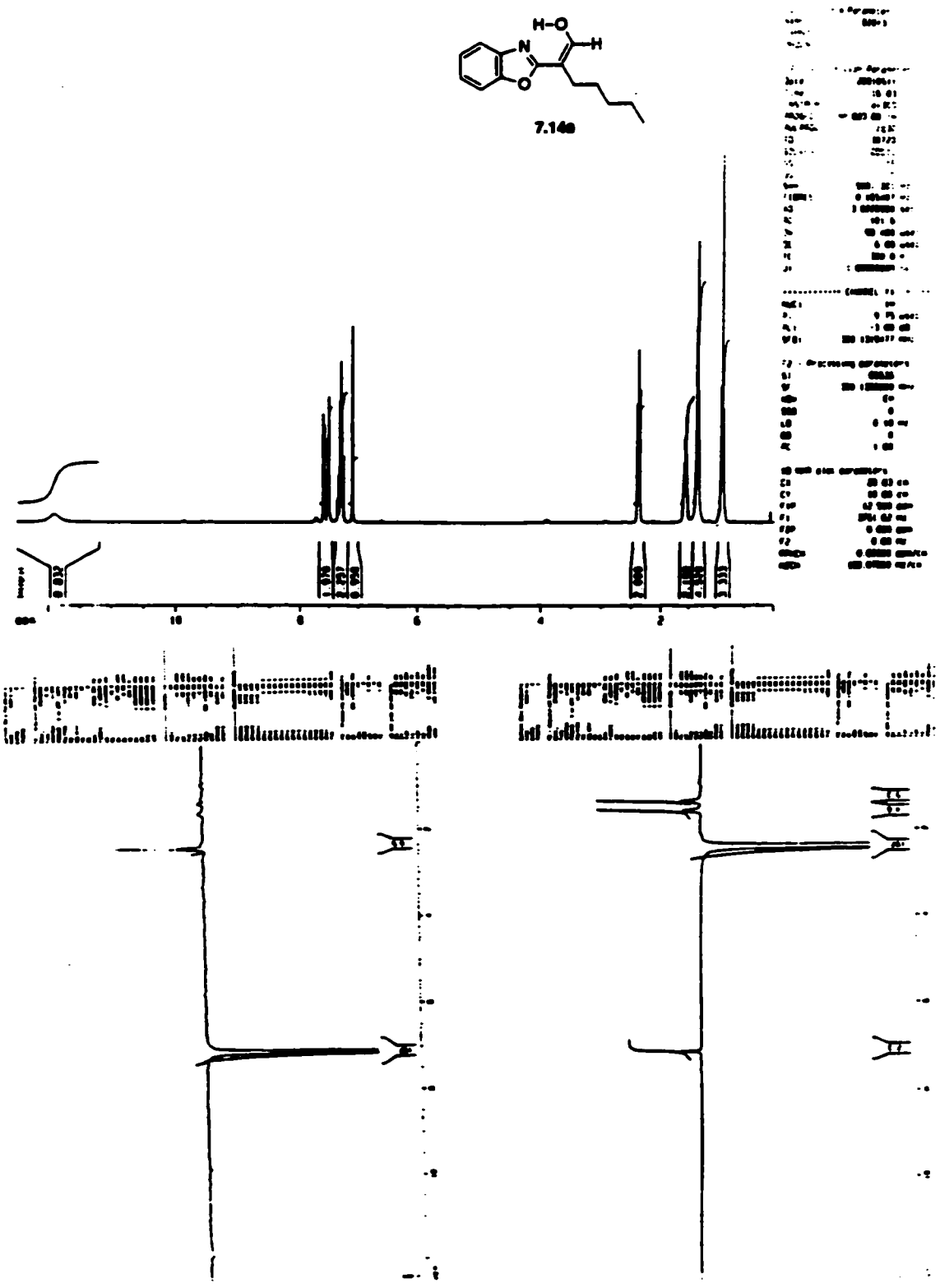
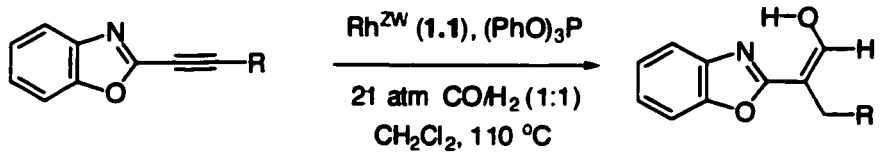


Figure 7-1. NOE Difference Experiment on 7.14a

7.3.4 Hydrocarbonylation Enolation Reactions of Acetylenic Benzoxazoles with Alkyl Substituents in the Acetylenic Unit [a]

The extent of the acetylenic benzoxazole/(*Z*)-2-benzoxazol-2-ylalk-1-en-1-ol reaction was investigated initially using 2-acetylenic benzoxazoles with aliphatic alkyne components (Table 7-3) and later incorporating functionalized alkynyl units (Table 7-4) employing the reaction conditions described in Table 7-2, entry 11 (Eq. 7-7).

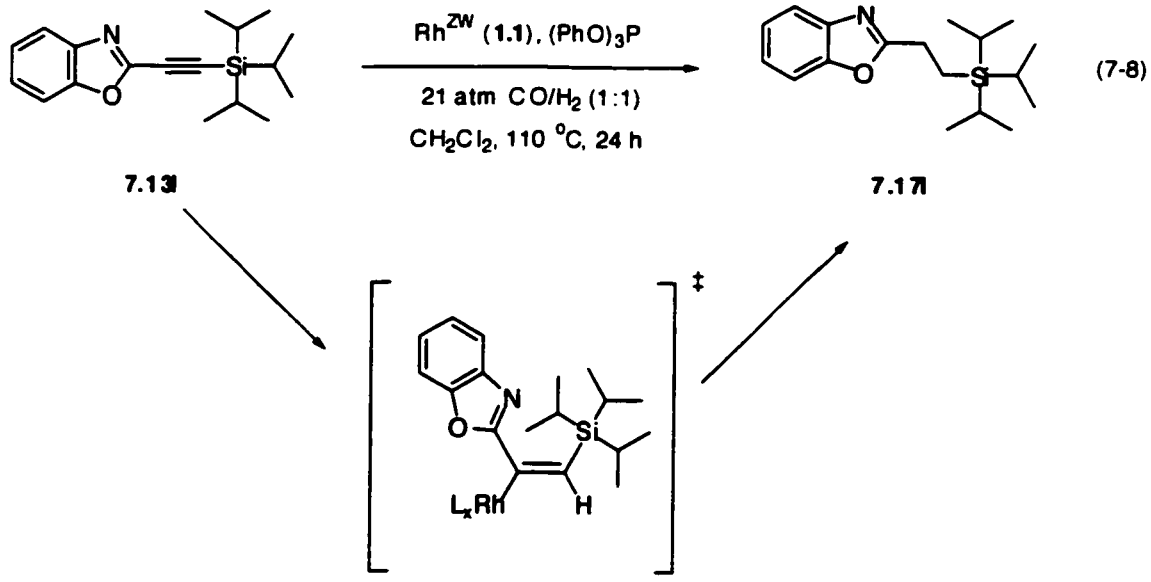


7.13 **7.14** (7-7)

Conversion of the α-carbon to the acetylenic unit from primary, to secondary, to tertiary results in increased selectivity for the benzoxazol-2-ylenol product with a consequential increase in reaction time. Use of ***n***-butyl as the R group (**7.13a**) on a 3 mmol basis affords **7.14a** in 76 % yield (the yield was 75 % using 4.5 mmol), and a reaction time of 21 hours (Table 7-3, entry 1). For consistency, all additional substrates were run with 3 mmol of substrate. Utilizing an ***iso***-propyl substituent (**7.13b**) affords **7.14b** in 83 % yield after 24 hours, and a ***tert***-butyl substituent (**7.13c**) gives **7.14c** in 87 % yield after 36 hours (Table 7-3, entries 2 and 3).

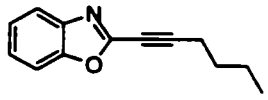
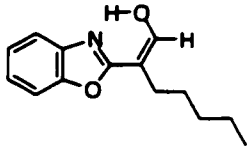
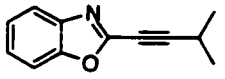
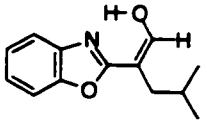
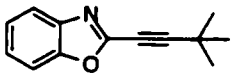
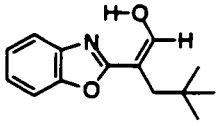
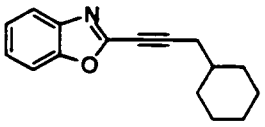
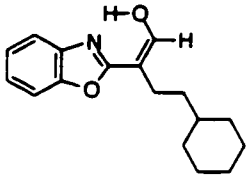
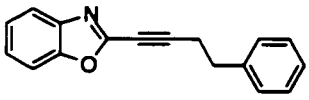
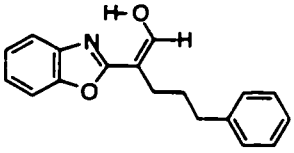
Applying increased substitution at the β- and γ-carbons to the triple bond results in a slight increase in selectivity over a straight chain alkyne **7.13a**. A methylcyclohexyl substituent (**7.13d**) affords **7.14d** in 78 % yield after 30 hours, and an ethylphenyl substituent (**7.13e**) gives **7.14e** in 80 % yield after 24 hours (Table 7-3, entries 4 and 5).

Excessive steric crowding near the alkynyl unit such as **7.13k** with a *tert*-butyldimethylsilyl (tBDMS) unit, and **7.13l** with a triisopropylsilyl (TIPS) unit inhibits carbonylation at the triple bond, and generates the alkyl substituted oxazoles **7.17k** and **7.17l** as major products (Eq.7-8). This result is likely influenced by increased crowding and destabilization of the rhodium intermediate due to interactions between the alkynyl substituent and benzoxazole ring in combination with the triphenylboron group from the zwitterionic rhodium complex (**1.1**).



(7-8)

Table 7-3. Hydrocarbonylation Enolation Reaction of Acetylenic Benzoxazoles with Alkyl Substituents at the Acetylenic Unit [a]

Entry	7.13	t (h)	7.14	Isolated Yield (%) [b]
1	 **7.13a**	21 21 [c]	 **7.14a**	76 75 [c]
2	 **7.13b**	24	 **7.14b**	83
3	 **7.13c**	36	 **7.14c**	87
4	 **7.13d**	30	 **7.14d**	78
5	 **7.13e**	21	 **7.14e**	80

[a] Reaction conditions: **7.13**, 3.0 mmol; **1.1**, 0.06 mmol (2 mol %); $(PhO)_3P$, 0.24 mmol (8 mol %); CH_2Cl_2, 20 mL; CO, 10.5 atm; H_2, 10.5 atm; 110 °C. [b] The reactions proceeded to full conversion (followed by NMR), and the products were isolated by silica gel chromatography using CH_2Cl_2. [c] **7.13a**, 4.5 mmol; **1.1**, 0.09 mmol (2 mol %); $(PhO)_3P$, 0.36 mmol (8 mol %); CH_2Cl_2, 20 mL; CO, 10.5 atm; H_2, 10.5 atm; 110 °C.

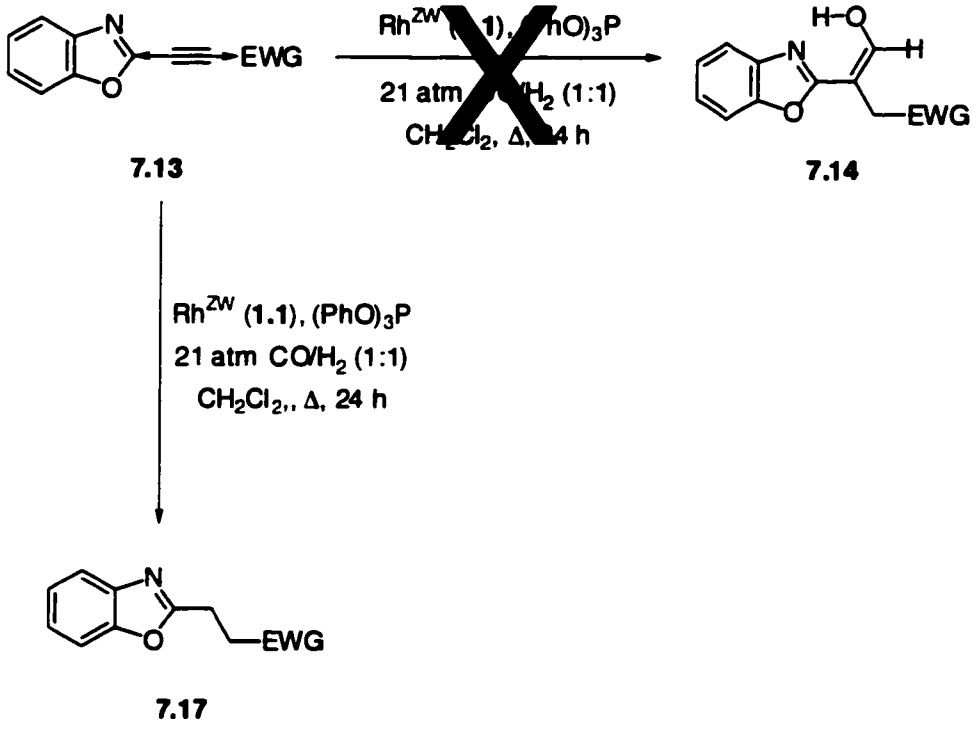
7.3.5 Hydrocarbonylation Enolation Reactions of Acetylenic Benzoxazoles Containing Functionalized Substituents in the Acetylenic Unit

The conversion of acetylenic benzoxazoles to (*Z*)-2-benzoxazol-2-ylalk-1-en-1-ols proceeds with some limitations using substrates incorporating functionalized alkynyl groups. A lowering of the reaction temperature to 90 °C aids in reducing the loss of selectivity and reactivity that occurs at 110°C in certain cases. For example, the presence of a 3-chloropropyl substituent (**7.13f**) results in 85 % conversion and 51 % yield of **7.14f** after 24 hours (Table 7-4, entry 1). At higher temperatures the loss of HCl promotes excessive decomposition of the rhodium complex.

When substituents capable of conjugating to the triple bond are employed, preference occurs for complete hydrogenation of the triple bond (**7.17**), and this is observed even at lower reaction temperatures and higher CO pressures. Applying the reaction to both phenyl (**7.13g**) and vinyl (**7.13i**) substituents led to trace amounts of the oxazolylenol; however, using a strong electron donating methoxy substituent in the alkynylbenzoxazole (**7.13h**) afforded the (*Z*)-2-benzoxazol-2-ylenol **7.14h** in 37 % yield (Table 7-4, entry 2).

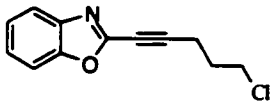
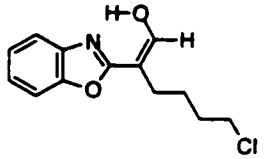
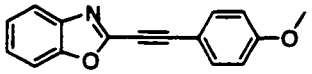
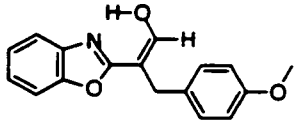
Electronegative substituted alkynes such as those containing methoxymethyl (**7.13j**), vinyl (**7.13i**), and phenyl (**7.13g**) groups inhibit ring formation and promote hydrogenation (**7.17**) (Eq. 7-9). The electron difficient oxazole ring possibly reduces the electron density of the acetylenic unit of the 2-position of the oxazole ring, making it

more susceptible to hydrogenation. In contrast, the less electronegative thiazole ring system provided the means for further carbonylative chemistry to take place with a greater variety of functionalized alkynes (Chapter 6). Oxygen, sulfur and carbon have electronegativities of 3.5, 2.4, and 2.5. Sulfur and carbon have similar electronegativities; therefore, sulfur has a negligible influence at the triple bond, while oxygen (differing by one electronegative unit) has a substantial influence at the acetylenic unit. The decreased electron density at the triple bond would create a weakly bound rhodium complex leading to reduced carbonylation and enhanced hydrogenation.



(7-9)

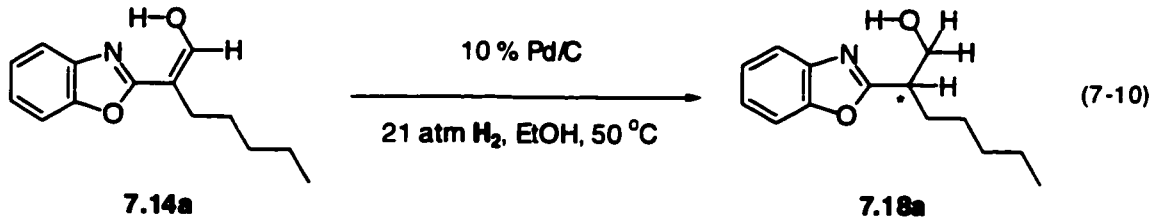
Table 7-4. Hydrocarbonylation Enolation Reactions of Acetylenic Benzoxazoles Containing Functionalized Substituents at the Alkynyl Units [a]

Entry	7.13	t (h)	7.14	Isolated Yield (%) [b]
1	 **7.13f**	24	 **7.14f**	51
2	 **7.13h**	24	 **7.14h**	37

[a] Reaction conditions: **7.13**, 3.0 mmol; **1.1**, 0.06 mmol (2 mol %); $(PhO)_3P$, 0.24 mmol (8 mol %); CH_2Cl_2, 20 mL; CO, 10.5 atm; H_2, 10.5 atm; 90 °C. [b] The reactions proceeded to full conversion (followed by NMR), and the products were isolated by silica gel chromatography using CH_2Cl_2 as eluant.

7.3.6 Stereofacial Hydrogenation of (Z)-2-Benzoxazol-2-ylalk-1-en-1-ols

Catalytic hydrogenation of **7.14a** with 10 % Pd/C was anticipated to afford the hydrogenated product **7.18a** (Eq. 7-10). Reaction of **7.14a** with H_2 in ethanol at 21 atm and 50 °C for 48 hours provided the desired 2-benzoxazol-2-ylalkan-1-ol (**7.18a**) in quantitative yield (see Section 8.7.5). This demonstrates that the hydrogenated enol may acquire potential chirality in 4 steps starting from benzoxazole, of which the latter 3 consecutive steps are catalytic in nature.



7.14a **7.18a** (7-10)

7.3.7 Mechanistic Aspects

It was speculated that the (*Z*)-benzoxazol-2-ylenol follows the same mechanistic profile proposed for the (*Z*)-thiazol-2-ylenols from acetylenic thiazoles (Chapter 6). The subsequent (*Z*)-benzoxazolylenol is the result of an initial zwitterionic rhodium catalyzed

hydroformylation at the triple bond followed by a final regioselective addition of hydrogen to the newly formed branched α,β-unsaturated aldehyde to the oxazolyl unit. The resulting enol functionality is stabilized by intramolecular H-bonding to the oxazole ring system.

7.4 Conclusion

In conclusion, the reaction of 2-acetylenic benzoxazoles with CO/H_2 in the presence of catalytic amounts of the zwitterionic rhodium complex **1.1** affords (*Z*)-2-benzoxazol-2-ylalk-1-en-1-ols. Although the process is limited primarily to benzoxazoles containing electron rich alkynyl substituents, the results extend the present technology to both sulfur and oxygen containing acetylenic N-heterocycles. The core enolic and oxazolyl units are important, and incrementing these materials into synthetic strategies may lead to enhancements for novel drug design.

CHAPTER 8

EXPERIMENTAL SECTION

8.1 General Experimental

All ^{1}H NMR and ^{13}C NMR were recorded on a Varian 200 and Bruker 300 MHz instruments, operating at 200 and 300 MHz for ^{1}H, and 50 and 75 MHz for ^{13}C respectively. NOESY and COSY experiments were performed on a Bruker 300 and 500 MHz spectrometers. NMR data are reported in chemical shifts relative to tetramethylsilane (TMS) as the internal standard, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet), integration and assignment. NMR spectra were run in $CDCl_3$ containing 0.03 % TMS. Proton spectra were referenced to 7.24 ppm and carbon to 77.0 ppm for $CDCl_3$. Infrared data were collected on a Bomem MB-100 FT-IR spectrometer. Liquid samples were run neat using sodium chloride disks. Solid samples were analyzed using fabricated KBr disks. Mass spectra were obtained on a VG 7070 E spectrometer, and the energy of ionization was 70 eV. Elemental analyses were performed by the elemental analysis service of M-H-W Laboratories, Phoenix, AZ. A Fisher-Johns apparatus was used for melting point determinations.

All air and /or moisture sensitive reactions were performed in glassware, flame dried under a a purge of dry nitrogen (passed through a drierite tower) or flame dried under vacuum followed by flushing with nitrogen. Solvents, solutions, and liquid reagents were transferred with syringes and double ended needles (cannulae) using

standard inert atmosphere techniques. Liquid substrates or reagents for small scale reactions were weighed. Air sensitive solids were handled using standard Schlenk techniques.

Chromatographic purifications were performed using flash grade silica, and when specified, a low nitrogen pressure was applied to the top of the column to enhance solvent elution. The volatiles were removed initially by an air aspirator controlled rotary evaporator , and the resulting liquids, oils or solids were placed briefly under high vacuum to remove any remaining volatiles. HPLC purifications were performed for analytical samples using a JAI recycling semi-prep HPLC and columns were packed with JAIGEL (polystyrene) or JORDI GEL (DVB). Chloroform (Omnisolv), tetrahydrofuran (BDH) and methanol (Omnisolv) were used as the eluants and an RI and UV detector were utilized to observe peak separation. An Aldrich based Kugelrohr was used for small scale vacuum distillations and sublimations.

Solvents were dried using the drying agents listed and the distilled under a dry atmosphere: benzene, toluene, diethyl ether, tetrahydrofuran and DME from sodium metal/benzophenone ketyl over nitrogen; dichloromethane, acetonitrile, methanol, and triethylamine from calcium hydride under nitrogen. UHP grade carbon monoxide, hydrogen, and argon were supplied by Air Products or Praxair.

Chemicals were purchased from Aldrich, Alfa Aesar, Lancaster, GFS Chemicals, and Strem Chemicals, and were used as received unless otherwise noted.

Autoclaves, gauges and gauge block assemblies were purchased from Parr Instrument Co..

All autoclaves were oven dried before use, and all gas lines were purged three times prior to charging the autoclave. Oil baths containing silicone oil (bp >140 °C/0.002 mm) was utilized as the medium for heating the autoclaves.

8.2 Experimental for Chapter 2

8.2.1 Materials

All 1-en-3-ynes were purchased form GFS Chemicals. Laboratory reagents and solvents were purchased from commercial sources. The zwitterionic rhodium complex (η^6-$C_6H_5BPh_3$)$^-Rh^+$(1,5-COD), **1.1**, was prepared as described by Schrock and Osborn.[1]

8.2.2 Synthesis of Starting Materials

8.2.2.1 Preparation of 5-acetyl-2,7-dimethyl-1-octen-3-yne (2.2d)

Enyne **2.2d** was prepared from 2,7-dimethyl-7-octen-5-yn-4-ol by the following procedure. A solution of triethylamine (20 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a stirred solution of 2,7- dimethyl-7-octen-5-yn-4-ol (10 mmol), acetyl chloride (20 mmol), and 4-dimethylaminopyridine (1.0 mmol) in CH_2Cl_2 (25 mL). After 2 hours the reaction mixture was treated with CH_2Cl_2 (50 mL), washed with 10 % HCl, saturated $NaHCO_3$, brine, and then dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation to afford a light yellow solution. The ester was further purified by silica gel chromatography using CH_2Cl_2 as eluant to give **2.2d** as a colourless liquid (90 % isolated yield).

5-Acetyl-2,7-dimethyl-1-octen-3-yne (2.2d). IR ν(CO) 1744 cm^{-1}; ^{1}H-NMR δ 5.50 (t, 1H, J = 7.4 Hz), 5.25 (d, 1H, *J* = 1.0 Hz), 5.20 (d, 1H, *J* = 1.0 Hz), 2.07 (s, 3H), 1.85 (s, 3H), 1.80 - 1.58 (m, 3H), 0.90 (d, 6H, J= 7.0 Hz); ^{13}C-NMR δ 170.6, 126.6,

123.2, 86.3, 63.7, 44.3, 25.4, 23.8, 23.1, 22.9, 21.6; ; MS (m/e) 194 [M^+]; EI HRMS calculated for $C_{12}H_{18}O_2$ [M^+] 194.13068, found 194.13074.

8.2.2.2 Preparation of 5-methoxy-2,7-dimethyl-1-octen-3-yne (2.2e).

Enyne **2.2e** was prepared from 2,7-dimethyl-7-octen-5-yn-4-ol by the following procedure. A solution of the alcohol (10 mmol) in pyridine (25 mL) was cooled to 0 °C, and treated with ***p***-toluenesulphonyl chloride (20 mmol). The reaction solution became brown with white crystals (pyridinium chloride). After the reaction was complete the mixture was added to 150 mL of ice-water. The tosylate appeared oily, and was taken up in ether. The aqueous layer was extracted three times with additional portions of ether. The collected fractions of ether were further washed with 10 % HCl, distilled water, brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a pale yellow solution of the tosylate.

Sodium (30 mmol) was dissolved in 50 mL of anhydrous methanol at 0 °C. A solution of the above tosylate in 5 mL anhydrous methanol was added slowly, and was allowed to react for 2 hours. The solution was poured into 150 mL of ice-water, and extracted with ether and dried over anhydrous $MgSO_4$. Evaporation of the ether afforded a clear yellow liquid. The liquid was further purified by silica gel chromatography using CH_2Cl_2 as eluant to give **2.2e** as a clear colourless liquid in 80 % isolated yield.

5-Methoxy-2,7-dimethyl-1-octen-3-yne (2.2e). ^{1}H-NMR δ 5.25 (d, 1H, J = 1.0 Hz), 5.17 (d, 1H, J = 1.0 Hz), 4.08 (t, 1H, J = 8.4 Hz), 3.38 (s, 3H), 1.87 (s, 3H), 1.58 (m, 2H), 1.22 (m, 1H), 0.90 (d, 6H); ^{13}C-NMR δ 127.0, 122.2, 87.8, 70.6, 66.7, 45.2, 25.2,

24.0, 23.2, 23.0; ; MS (m/e) 166 [M^+]; EI HRMS calculated for $C_{11}H_{18}O$ [M^+] 166.13576, found 166.13570.

8.2.2.3 Preparation of 1-(3-methoxy-1-propynyl)cyclohexene (2.2f)

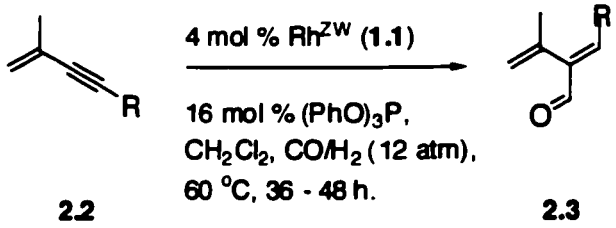
1-(3-Methoxy-1-propynyl)cyclohexene, **2.2f**, was prepared by the reaction of 1-ethynylcyclohexene with n-butyllithium followed by chloromethyl methyl ether. To a 250 mL round bottom flask purged with N_2 was added THF (20 mL) and 1-ethynylcyclohexene (20 mmol), and the mixture was cooled in a dry-ice/MeOH bath. An excess amount of 2.5 M BuLi (10 mL) was added over a 15 minute time period followed by chloromethyl methyl ether (22 mmol), and the reaction mixture was allowed to warm to room temperature. The reaction mixture was transferred to a separatory funnel, ether (300 mL) was added, and the organic layer was washed with water (100 mL) and brine (50 mL), dried over anhydrous $MgSO_4$, and evaporated. The product was further purified by Kugelrohr distillation to give **2.2f** as a clear colourless liquid in 80 % isolated yield.

1-(3-Methoxy-1-propynyl)cyclohexene (2.2f). colorless liquid; IR ν(C≡) 2219 cm^{-1}; ^{1}H-NMR δ 6.10 (m, 1H), 4.18 (s, 2H), 3.35 (s, 3H), 2.00 – 2.14 (m, 4H), 1.47 – 1.65 (m, 4H); ^{13}C-NMR δ 135.8, 120.7, 88.8, 82.6, 61.0, 58.0, 29.7, 26.1, 22.8, 22.0; MS (m/e) 150 [M^+]; EI HRMS calculated for $C_{10}H_{14}O$ [M^+] 150.10447, found 150.10447.

8.2.4 Hydroformylation of Conjugated Enynes: Optimization of Reaction Conditions.

To a 45 mL autoclave with a glass liner and stirring bar was placed the rhodium catalyst (0.24 mmol), ligand (0.96 mmol), 2,7-dimethyl-1-octen-3-yne (**2.2a**) (6 mmol), and solvent (10 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 6 atm, and then hydrogen was introduced up to a total pressure of 12 atm. The autoclave was placed in an oil bath and heated from 50 to 70 °C for 8 to 48 hours and then allowed to cool to room temperature. The autoclave was depressurized, and the solvent was removed by rotary evaporation. The resulting yellow residue was separated from the catalyst and polymeric material (if formed) by Kugelrohr distillation to give a clear colourless liquid. Product **2.3a** was further purified by silica gel chromatography using pentane:ether (90:10) as the developer to give the formyl diene **2.3a**. The results of reaction optimization are given in Table 2-1.

8.2.4 Hydroformylation of Conjugated Enynes.



2.2 **2.3**

To a 45 mL autoclave with a glass liner and stirring bar was placed the zwitterionic rhodium catalyst **1.1** (0.24 mmol), triphenyl phosphite (0.96 mmol), the conjugated enyne **2.2** (6 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 6 atm, and then hydrogen was introduced up

to a total pressure of 12 atm. The autoclave was placed in an oil bath at 60 °C for 48 hours and then allowed to cool to room temperature. The autoclave was depressurized, and the solvent was removed by rotary evaporation. The resulting yellow residue was separated from the catalyst and polymeric material (if formed) by Kugelrohr distillation to give a clear colourless liquid. Product **2.3** was further purified by silica gel chromatography using pentane:ether (90:10) as the developer to give the formyl dienes **2.3a – f** (Table 2-2).

***(E)*-2-(1-methylethenyl)-6-methyl-2-hepten-1-al (2.3a):** colorless liquid; IR ν(CO) 1690 cm^{-1}; ^{1}H-NMR δ 9.32 (s, 1H), 6.43 (t, 1H, J = 7.4 Hz), 5.15 (d, 1H, J = 1.0 Hz), 4.68 (d, 1H, J = 1.0 Hz), 2.34 (quintet, 2H, J = 7.4 Hz), 1.80 (s, 3H), 1.54 (m, 1H), 1.30 (quartet, 2H, J = 7.0 Hz), 0.83 (d, 6H, J = 6.6 Hz); ^{13}C-NMR δ 194.4, 155.8, 146.9, 138.9, 117.2, 38.5, 28.4, 28.1, 23.2, 22.9; EI MS (m/e) 166 [M^+]; EI HRMS calculated for $C_{11}H_{18}O$ [M^+] 166.13576, found 166.13541.

***(E)*-2-(1-methylethenyl)-2-penten-1-al (2.3b):** colorless liquid; IR ν(CO) 1690 cm^{-1}; ^{1}H-NMR δ 9.29 (s, 1H), 6.40 (t, 1H, J = 7.6 Hz), 5.10 (d, 1H, J = 1.0 Hz), 4.64 (d, 1H, J = 1.0 Hz), 2.30 (q, 2H, J = 7.6 Hz), 1.77 (s, 3H), 1.01 (t, 3H, J = 7.6 Hz); ^{13}C-NMR δ 194.4, 156.8, 146.5, 138.8, 117.1, 23.5, 23.1, 13.9; EI MS (m/e) 124 [M^+]; EI HRMS calculated for $C_8H_{12}O$ [M^+] 124.08882, found 124.08891.

***(E)*-2-(1-methylethenyl)-2-hepten-1-al (2.3c):** colorless liquid; IR ν(CO) 1690 cm^{-1}; ^{1}H-NMR δ 9.33 (s, 1H), 6.44 (t, 1H, J = 7.6 Hz), 5.14 (d, 1H, J = 1.0 Hz), 4.67 (d,

1H, J = 1.0 Hz), 2.34 (q, 2H, J = 7.2 Hz), 1.80 (s, 3H), 1.35 (m, 4H), 0.86 (t, 3H, J = 6.8 Hz); ^{13}C-NMR δ 194.4, 155.7, 147.1, 138.9, 117.3, 31.5, 29.9, 23.2, 23.0, 22.9, 14.4; EI MS (m/e) 152 [M^+]; EI HRMS calculated for $C_{10}H_{16}O$ [M^+] 152.12012, found 152.12311.

***(E)*-4-acetyl-2-(1-methylethenyl)-6-methyl-2-hepten-1-al (2.3d):** colorless liquid; IR ν_1(CO) 1742 cm^{-1} and ν_2(CO) 1695 cm^{-1}; ^{1}H-NMR δ 9.37 (s, 1H), 6.22 (d, 1H, J = 8.4 Hz), 5.66 (t, 1H, J = 8.4 Hz), 5.21 (d, 1H, J = 1.0 Hz), 4.78 (d, 1H, J = 1.0 Hz), 2.01 (s, 3H), 1.87 (s, 3H), 1.71 (m, 2H), 1.28 (m, 1H), 0.90 (d, 3H, J = 6.6 Hz), 0.88 (d, 3H, J = 6.6 Hz); 13C-NMR δ 193.9, 170.8, 150.3, 146.70, 138.8, 118.8, 70.3, 43.7, 25.1, 23.8, 22.8, 22.4, 21.6; FAB MS (m/e) 225.1413 [M+H]$^+$, calculated for $C_{13}H_{20}O_3$ [M+H]$^+$ 225.1413.

***(E)*-4-methoxy-2-(1-methylethenyl)-6-methyl-2-hepten-1-al (2.3e):** colorless liquid; IR ν(CO) 1695 cm^{-1}; ^{1}H-NMR δ 9.43 (s, 1H), 6.27 (d, 1H, J = 9.0 Hz), 5.22 (d, 1H, J = 1.0 Hz), 4.74 (d, 1H, J = 1.0 Hz), 4.18 (td, 1H, J_d = 4.4 Hz, J_t = 9.0 Hz), 3.25 (s, 3H), 1.87 (s, 3H), 1.60 (m, 2H), 1.19 (m, 1H), 0.89 (d, 6H, J = 6.6 Hz); ^{13}C-NMR δ 194.0, 154.2, 147.9, 138.6, 118.0, 76.5, 57.7, 44.8, 25.0, 24.0, 23.4, 22.6; EI MS (m/e) 196 [M^+]; EI HRMS calculated for $C_{12}H_{20}O_2$ [M^+] 196.14633, found 196.14782.

The spectral data for 2.3f is as follows: IR ν(CO) 1690 cm^{-1}; ^{1}H-NMR δ 9.32 (s, 1H), 6.40 (t, 1H, J = 5.8 Hz), 5.34 (m, 1H), 4.13 (d, 2H, J = 5.8 Hz), 3.28 (s, 3H), 2.36 (m, 1H), 2.17 (m, 1H), 1.98 (m, 2H), 1.56 (m, 4H); ^{13}C-NMR δ 194.2. The spectral data

for **2.3f** is as follows: IR ν(CO) 1690 cm^{-1}; ^{1}H-NMR δ 9.32 (s, 1H), 6.78 (s, 1H), 6.29 (m, 1H), 4.09 (s, 2H), 3.23 (s, 3H), 2.36 (m, 1H), 1.98 (m, 4H), 1.56 (m, 4H); ^{13}C-NMR δ 195.4. Mixture: EI MS (m/e) 180 [M^+]; EI HRMS calculated for $C_{11}H_{16}O_2$ [M^+] 180.115 03, found 180.11510.

8.3 Experimental for Chapter 3

8.3.1 Materials

2-Iodothiophene and 3-bromothiophene were purchased from Aldrich, and all terminal alkynes were purchased from GFS Chemicals. Tetrakis(triphenylphosphine)-palladium(0) was purchased from Strem Chemicals. 2-Iodobenzothiophene,[234] 3-iodobenzothiophene, [234] and the zwitterionic rhodium complex (η^6-$C_6H_5BPh_3$)$^-$Rh$^+$(1,5-COD) (**1.1**)[1] were prepared according to the literature methods.

8.3.2 Synthesis of Starting Materials

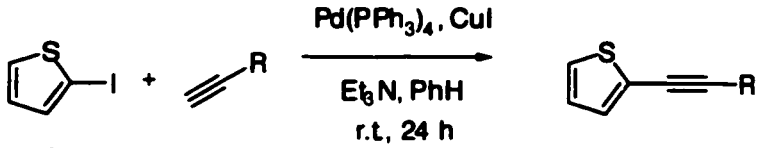
8.3.2.1 Preparation of 3-Thiophenoxy-1-propyne (3.3e):

To a 100 mL round bottom flask purged with N_2 was added CH_2Cl_2 (50 mL), thiophenol (30 mmol), 4-dimethylaminopyridine (33 mmol), and propargyl chloride (35 mmol) at room temperature. After 2 hours the reaction mixture was treated with CH_2Cl_2 (50 mL), washed with 10 % HCl, saturated $NaHCO_3$, brine, and then dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation, and the resulting liquid was further purified by Kugelrohr distillation to afford **3.3e** as a colorless liquid (95 % isolated yield).

3-Thiophenoxy-1-propyne (3.3e): IR ν(C≡CH) 3293 cm^{-1}, ν(C≡C) 2119 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43 - 7.47 (m, 2H), 7.24 - 7.36 (m, 3H), 3.60 (s, 2H), 2.23

(s, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 135.5, 130.6, 128.6, 80.5, 72.2, 23.1; EI MS (m/e) 148 [M^+]; HRMS calculated for C_9H_8S [M^+] 148.03467, found 148.03317.

8.3.2.2 General Procedure for the Pd/CuI Coupling of 2-Iodothiophene to a Terminal Alkyne.



3.2 **3.3** **3.4**

To a 100 mL round bottom flask purged with N_2 was added triethylamine (15 mL), the terminal alkyne (**3.3**) (25 - 30 mmol), PhH (50 mL), iodothiophene (**3.2**) (20 mmol), $Pd(PPh_3)_4$ (0.2 mmol), and CuI (0.5 mmol) at room temperature for 24 hours. Methanol (10 mL) was added, the solvent was evaporated. and diethyl ether (200 mL) was added to the resulting residue leading to the precipitation of $Et_3NH^+I^-$. This mixture was filtered, washed with 10 % HCl, distilled H_2O, brine, and dried over anhydrous $MgSO_4$ or Na_2SO_4. The ether solution was decolorized with activated charcoal, evaporated, and the resulting residue further purified by Kugelrohr distillation to give **3.4** (Table 3-1).

2-(Hex-1-ynyl)thiophene (3.4a): colorless liquid; IR ν(C≡C) 2225 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.14 (dd, 1H, J = 5.2, 1.2 Hz), 7.10 (dd, 1H, J = 3.4, 1.0 Hz), 6.91 (dd, 1H, J = 6.2, 3.6 Hz) 2.41 (t, 2H, J = 6.8 Hz), 1.39 - 1.62 (m, 4H), 0.93 (t, 3H, J = 7.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 131.5, 127.3, 126.4, 124.8, 95.1, 74.2, 31.2, 22.6, 20.0, 14.2; EI MS (m/e) 164 [M^+]; HRMS calculated for $C_{10}H_{12}S$ [M^+] 164.06597, found 164.06515.

2-(3-Tetrahydropyranyloxyprop-1-ynyl)thiophene (3.4b): colorless liquid; IR ν(C≡C) 2222 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.22 (dd, 1H, J = 4.8, 1.5 Hz), 7.18 (dd, 1H, J = 3.8, 1.0 Hz), 6.92 (dd, 1H, J = 4.8, 3.6 Hz), 4.84 (m, 0.75H), 4.78 (m, 0.25H) 4.47 (s, 1H), 4.44 (s, 1H), 3.58 (m, 1H), 3.55 (m, 1H), 1.45 - 1.85 (m, 4H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 133.0, 127.9, 127.5, 123.2, 97.5, 89.8, 79.7, 74.6, 62.5, 55.4, 54.5, 30.9, 25.9, 19.6; EI MS (m/e) 222 [M^+]; HRMS calculated for $C_{12}H_{14}O_2S$ [M^+] 222.07145, found 222.07211.

2-(3-Trimethylsilyloxyprop-1-ynyl)thiophene (3.4c): colorless liquid; IR ν(C≡C) 2224 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.21 (dd, 1H, J = 5.0, 1.0 Hz), 7.18 (dd, 1H, J = 3.6, 1.2 Hz), 6.93 (dd, 1H, J = 5.2, 3.8 Hz), 4.50 (s, 2H), 0.25 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 132.7, 128.9, 127.8, 127.5, 123.4, 92.1, 79.0, 52.2, 0.34; EI MS (m/e) 194 [M^+]; HRMS calculated for $C_{10}H_{14}OSiS$ [M^+] 210.05346, found 210.05346.

2-(3-Methoxyprop-1-ynyl)thiophene (3.4d): colorless liquid; IR ν(C≡C) 2221 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.19 - 7.25 (m, 2H), 6.95 (dd, 1H, J = 5.0, 3.6 Hz), 4.31 (s, 2H), 3.42 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 133.0, 127.9, 127.5, 123.4, 88.5, 80.2, 61.0, 58.3; EI MS (m/e) 152 [M^+]; HRMS calculated for C_8H_8OS [M^+] 152.02959, found 152.02832.

2-(3-Thiophenoxyprop-1-ynyl)thiophene (3.4e): colorless liquid; IR ν(C≡C) 2225 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.48 - 7.54 (m, 2H), 7.11 - 7.39 (m, 5H), 6.93 (dd, 1H, *J* = 6.0, 2.6 Hz), 3.85 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 135.6, 132.6, 131.4, 128.6, 127.8, 127.6, 127.5, 89.8, 24.8; EI MS (m/e) 230 [M^+]; HRMS calculated for $C_{13}H_{10}S_2$ [M^+] 230.02239, found 230.02452.

2-(3-Hydroxyprop-1-ynyl)thiophene (3.4f): colorless liquid; IR ν(OH) 3332 cm^{-1}, ν(C≡C) 2222 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.17 - 7.26 (m, 2H), 6.94 (dd, 1H, *J* = 6.0, 4.0 Hz). 4.48 (s, 2H), 2.19 (s, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 133.0, 128.0, 127.6, 91.8, 79.6, 52.3; EI MS (m/e) 138 [M^+]; HRMS calculated for C_7H_6OS [M^+] 138.01394, found 138.01307.

2-(2-Phenyleth-1-ynyl)thiophene (3.4i): white solid, mp 51-52 °C; IR ν(C≡C) 2203 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.49 - 7.55 (m, 2H), 7.26 - 7.38 (m, 5H), 7.01 (dd, 1H, *J* = 5.6, 3.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 132.6, 132.0, 129.0, 127.9, 127.7, 123.5, 93.7, 83.3; EI MS (m/e) 184 [M^+]; HRMS calculated for $C_{12}H_8S$ [M^+] 184.03467, found 184.03281.

2-(3-Methylbut-3-en-1-ynyl)thiophene (3.4j): colorless liquid; IR ν(C≡C) 2196 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.22 (m, 2H), 6.96 (dd, 1H, *J* = 4.2, 1.6 Hz), 5.39 (d, 1H, *J* = 3.2 Hz), 5.29 (d, 1H, *J* = 2.8 Hz), 1.95 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 132.4, 127.7, 127.6, 127.2, 123.9, 122.8, 82.7, 73.9, 23.7; EI MS (m/e) 148 [M^+]; HRMS calculated for C_9H_8S [M^+] 148.03467, found 148.03585.

3-(Hex-1-ynyl)thiophene (3.4k): colorless liquid; IR ν(C≡C) 2230 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.33 (dd, 1H, J = 3.0, 1.0 Hz), 7.21 (dd, 1H, J = 4.8, 3.0 Hz), 7.06 (dd, 1H, J = 5.0, 1.2 Hz), 2.38 (t, 2H, J = 7.0 Hz), 1.40 - 1.62 (m, 4H), 0.94 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 130.6, 128.1, 125.6, 123.6, 90.5, 76.1, 31.4, 22.6, 18.7, 14.3; EI MS (m/e) 164 [M^+]; HRMS calculated for $C_{10}H_{12}S$ [M^+] 164.06597, found 164.06591.

3-(2-Phenyleth-1-ynyl)thiophene (3.4l): white solid, mp 52 - 54 °C; IR ν(C≡C) 2226 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.55 (m, 3H), 7.35 (m, 4H), 7.23 (m, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 132.2, 130.5, 129.3, 129.0, 128.9, 127.3, 126.0, 123.8, 12.4, 122.9, 89.6, 85.2; EI MS (m/e) 184 [M^+]; HRMS calculated for $C_{12}H_8S$ [M^+] 184.03467, found 184.03416.

2-(Hex-1-ynyl)benzothiophene (3.4m): yellow oil; IR ν(C≡C) 2222 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.67 - 7.76 (m, 2H), 7.27 - 7.37 (m, 3H), 2.47 (t, 2H, J = 7.0 Hz) 1.39 - 1.69 (m, 4H), 0.96 (t, 3H, J = 6.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 140.4, 138.8, 128.3, 125.6, 125.2, 124.9, 124.1, 122.6, 97.4, 74.8, 31.7, 22.7, 20.2, 14.3; EI MS (m/e) 214 [M^+]; HRMS calculated for $C_{14}H_{14}S$ [M^+] 214.08162, found 214.08201.

3-(Hex-1-ynyl)benzothiophene (3.4n): colorless oil; IR ν(C≡C) 2224 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.93 (m, 1H), 7.83 (m, 1H), 7.50 (s, 1H), 7.32 - 7.47 (m, 2H), 2.51 (t, 2H, J = 6.8 Hz) , 1.48 - 1.70 (m, 4H), 0.98 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200

MHz, $CDCl_3$) δ 140.1, 139.4, 129.1, 125.4, 125.0, 123.6, 123.1, 119.7, 93.6, 74.7, 31.5, 22.7, 19.9, 14.3; EI MS (m/e) 214 [M^+]; HRMS calculated for $C_{14}H_{14}S$ [M^+] 214.08162, found 214.08194.

8.3.2.3 General Procedure for the Preparation of Propargyl Ester Thiophene Derivatives.

Triethylamine (2.8 mL, 20 mmol) was added dropwise to a stirred solution of 2-(3-hydroxyprop-1-ynyl)thiophene (**3.4f**) (1.38 g, 10 mmol), propionic or benzoic anhydride (12.5 mmol), and 0.12 g (1.0 mmol) of 4-dimethylaminopyridine in CH_2Cl_2 (40 mL). After 2 hours the reaction mixture was treated with CH_2Cl_2 (60 mL), washed with 10 % HCl, saturated $NaHCO_3$, brine, and then dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. The ester was further purified by silica gel chromatography using pentane:ether (90:10) as eluant (Table 3-1).

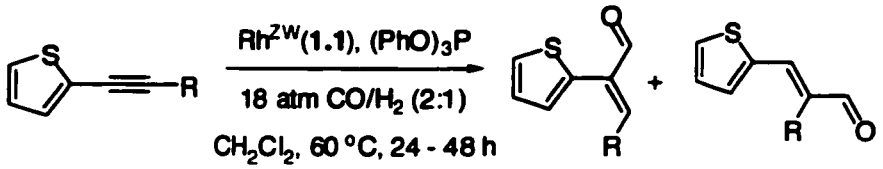
2-(3-Propionoxyprop-1-ynyl)thiophene (3.4g): colorless liquid; IR ν(C≡C) 2230 cm^{-1}, ν(C=O) 1744 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.20 - 7.27 (m, 2H), 6.94 (dd, 1H, J = 7.2, 2.4 Hz), 4.89 (s, 2H), 2.38 (q, 2H, J = 8.0 Hz), 1.15 (t, 3H, J = 7.7 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 174.3, 133.6, 128.4, 127.6, 122.6, 87.9, 80.3, 53.3, 28.0, 9.6; EI MS (m/e) 194 [M^+]; HRMS calculated for $C_{10}H_{10}O_2S$ [M^+] 194.04015, found 194.04172.

2-(3-Benzoxyprop-1-ynyl)thiophene (3.4h): colorless liquid; IR ν(C≡C) 2223 cm^{-1}, ν(C=O) 1723 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.06 - 8.11 (m, 2H), 7.39 - 7.60 (m, 3H), 7.23 - 7.29 (m, 2H), 6.97 (m, 1H) 5.15 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 166.5, 134.3, 134.1, 133.8, 133.7, 130.8, 130.5, 129.1, 128.5, 127.6, 122.6, 87.8, 80.8, 78.4, 53.9; EI MS (m/e) 242 [M^+]; HRMS calculated for $C_{14}H_{10}O_2S$ [M^+] 242.04015, found 242.04025.

8.3.3 Hydroformylation of Conjugated Thiophenynes: Optimization of Reaction Conditions.

To a 45 mL autoclave containing a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.12 mmol), triphenyl phosphite (0.48 mmol), the conjugated 2-(hex-1-ynyl)thiophene (**3.4a**) (3 mmol), and CH_2Cl_2 (10 to 20 mL). The autoclave was flushed three times with carbon monoxide, pressurized with 6 to 12 atm, and then hydrogen was introduced up to a total pressure of 12 to 18 atm. The autoclave was placed in an oil bath at 60 °C for 48 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through Celite, and the solvent was removed by rotary evaporation. The percent conversion and the ratio of **3.5a/3.6a/3.7a** were determined by the ratio of the aldehyde ^1H NMR signals. The resulting yellow residue was purified by silica gel chromatography using a pentane:ether 90:10 as the eluant to afford products **3.5a**. The results of optimization are described in Section 3.3.2.

8.3.4 Hydroformylation of Conjugated Thiophenynes.



3.4 **3.5** **3.6**

To a 45 mL autoclave containing a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.045 - 0.12 mmol), triphenyl phosphite (0.18 - 0.48 mmol), the conjugated thiophenyne **3.4** (3 mmol), and CH_2Cl_2 (20 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 12 atm, and then hydrogen was introduced up to a total pressure of 18 atm. The autoclave was placed in an oil bath at 60 °C for 24 to 48 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through Celite, and the solvent was removed by rotary evaporation. The resulting yellow residue was purified by silica gel chromatography using a pentane:ether gradient ranging from 90:10 to 75:25 as the eluant to afford products **3.5** and **3.6** (Tables 3-2, 3-3, and 3-4).

(*E*)-2-(2-Thienyl)hept-2-en-1-al (3.5a): colorless liquid; IR ν(C=O) 1694 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.40 (dd, 1H, J = 5.2, 1.2 Hz), 7.19 (dd, 1H, J = 3.6, 1.2 Hz), 7.09 (dd, 1H, J = 5.0, 3.6 Hz), 6.69 (t, 1H, J = 7.4 Hz), 2.60 (q, 2H, J = 7.2 Hz), 1.33 - 1.60 (m, 4H), 0.91 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ

193.5, 157.6, 136.8, 128.9, 127.4, 127.2, 31.6, 30.7, 23.1, 14.4; EI MS (m/e) 194 [M^+]; HRMS calculated for $C_{11}H_{14}OS$ [M^+] 194.07654, found 194.07837.

(*E*)-4-Tetrahydropyranyloxy-2-(2-thienyl)-but-2-en-1-al (3.5b): colorless liquid; IR ν(C=O) 1695 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.44, (dd, 1H, J = 5.0, 1.2 Hz), 7.07 - 7.16 (m, 2H), 6.79 (t, 1H, J = 5.6 Hz), 4.84 (d, 0.5H, J = 5.0 Hz), 4.76 (d, 0.5H, J = 5.2 Hz), 4.70 (m, 1H), 4.58 (d, 0.5 H, J = 5.8 Hz), 4.50 (d, 0.5H, J = 5.8 Hz), 3.85 (m, 1H), 3.55 (m, 1H), 1.46 - 1.82 (m, 4H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.8, 151.9, 135.8, 129.4, 128.5, 127.3, 99.5, 65.9, 63.0, 31.1, 26.0, 19.9; EI MS (m/e) 252 [M^+]; HRMS calculated for $C_{13}H_{16}O_3S$ [M^+] 252.08202, found 252.08198.

(*E*)-2-Methyltetrahydropyranyloxy-3-(2-thienyl)prop-2-en-1-al (3.6b): colorless liquid; IR ν(C=O) 1677 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.33 (dd, 1H, J = 5.4, 2.4 Hz), 7.54 (s, 1H), 7.52 (m, 1H), 7.15 (dd, 1H, J = 6.2, 3.6 Hz), 4.79 (m, 1H), 4.77 (s, 0.5H), 4.72 (s, 0.5H), 4.41 (s, 0.5H), 4.36 (s, 0.5H), 3.93 (m, 1H), 3.57 (m, 1H), 1.50 - 1.77 (m, 4H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.8, 145.7, 137.9, 135.2, 134.9, 133.4, 128.7, 99.7, 67.9, 59.4, 31.1, 25.9, 19.9; EI MS (m/e) 252 [M^+]; HRMS calculated for $C_{13}H_{16}O_3S$ [M^+] 252.08202, found 252.07931.

(*E*)-2-(2-Thienyl)-4-trimethylsilyloxybut-2-en-1-al (3.5c): colorless liquid; IR ν(C=O) 1698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.45 (dd, 1H, J = 4.0, 2.2 Hz), 7.09 - 7.13 (m, 2H), 6.72 (t, 1H, J = 5.2 Hz), 4.67 (d, 2H, J = 5.4 Hz), 0.06 (s, 9H);

^{13}C NMR (200 MHz, $CDCl_3$) δ 192.8, 155.0, 129.3, 128.4, 127.3, 61.4, 0.10; EI MS (m/e) 240 [M^+]; HRMS calculated for $C_{11}H_{16}O_2SiS$ [M^+] 240.06403, found 240.06224.

(*E*)-2-Methyltrimethylsilyloxy-3-(2-thienyl)prop-2-en-1-al (3.6c): colorless liquid, IR ν(C=O) 1679 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.64 (m, 1H), 7.54 (m, 1H), 7.46 (s, 1H), 7.15 (dd, 1H, *J* = 5.2, 3.8 Hz), 4.57 (s, 2H), 0.13 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.8, 145.4, 137.9, 137.8, 134.8, 133.5, 128.7, 64.5, 0.25; EI MS (m/e) 240 [M^+]; HRMS calculated for $C_{11}H_{16}O_2SiS$ [M^+] 240.06403, found 240.06186.

(*E*)-4-Methoxy-2-(2-thienyl)but-2-en-1-al (3.5d): colorless liquid, IR ν(C=O) 1696 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.43 (dd, 1H, *J* = 4.9, 1.4 Hz), 7.05 - 7.13 (m, 2H), 6.71 (t, 1H, . *J* = 5.4 Hz), 4.46 (d, 2H, *J* = 5.6 Hz), 3.40 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.7, 151.6, 136.1, 129.4, 128.5, 127.3, 70.9, 59.5; EI MS (m/e) 182 [M^+]; HRMS calculated for $C_9H_{10}O_2S$ [M^+] 182.04015, found, 182.04183.

(*E*)-2-Methylmethoxy-3-(2-thienyl)prop-2-en-1-al (3.6d): colorless liquid; IR ν(C=O) 1673 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.66 (dd, 1H, *J* = 5.0, 0.6 Hz), 7.56 (s, 1H), 7.49 (dd, 1H, *J* = 4.0, 1.0 Hz), 7.15 (dd, 1H, *J* = 4.9, 3.8 Hz), 4.37 (s, 2H), 3.39 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.8, 146.6, 137.8, 135.2, 134.8, 134.0, 128.7, 63.8, 58.9; EI MS (m/e) 182 [M^+]; HRMS calculated for $C_9H_{10}O_2S$ [M^+] 182.04015, found, 182.03884.

(*E*)-2-(2-Thienyl)-4-thiophenoxybut-2-en-1-al (3.5e): colorless oil; IR ν(C=O) 1693 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.43 (dd, 1H, *J* = 4.4, 1.8 Hz), 7.21 - 7.30 (m, 5H), 7.06 - 7.08 (m, 2H), 6.69 (t, 1H, *J* = 7.8 Hz), 3.98 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.8, 149.8, 137.7, 134.6, 131.2, 129.8, 129.6, 129.5, 128.4, 127.8, 127.4, 33.8; EI MS (m/e) 260 [M^+]; HRMS calculated for $C_{14}H_{12}OS_2$ [M^+] 260.03296, found 260.03262.

(*E*)-2-Methylthiophenoxy-3-(2-thienyl)pop-2-en-1-al (3.6e): colorless oil, IR ν(C=O) 1667 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.64 (dd, 1H, *J* = 5.2, 1.2 Hz), 7.42 - 7.48 (m, 4H), 7.12 - 7.31 (m, 4H), 4.13 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.1, 143.9, 137.8, 136.3, 134.8, 134.7, 133.4, 131.5, 129.5, 128.6, 127.5, 29.3; EI MS (m/e) 260 [M^+]; HRMS calculated for $C_{14}H_{12}OS_2$ [M^+] 260.03296, found 260.03094.

(*E*) 4-Propionoxy-2-(2-thienyl)but-2-en-1-al (3.5g): colorless liquid; IR ν_1(C=O) 1737 cm^{-1}, ν_2(C=O) 1698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.48 (dd, 1H, *J* = 5.2, 1.2 Hz), 7.16 (dd, 1H, *J* = 3.6, 1.2 Hz), 7.11 (dd, 1H, *J* = 4.8, 3.8 Hz), 6.65 (t, 1H, *J* = 5.8 Hz) 5.12 (d, 2H, *J* = 5.8 Hz), 2.40 (q, 2H, *J* = 7.6 Hz), 1.17 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.4, 174.6, 147.5, 137.0, 129.7, 129.0, 128.8, 127.5, 67.5, 28.0, 9.6; EI MS (m/e) 224 [M^+]; HRMS calculated for $C_{11}H_{12}O_3S$ [M^+] 224.05072, found 224.05045.

(*E*) 2-Methylpropionoxy-3-(2-thienyl)prop-2-en-1-al (3.6g): colorless liquid; IR ν_1(C=O) 1736 cm^{-1}, ν_2(C=O) 1678 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.55 (s, 1H),

7.61 (dd, 1H, J = 5.0, 0.8 Hz), 7.62 (s, 1H), 7.45 (dd, 1H, J = 3.8, 0.6 Hz), 7.14 - 7.19 (m, 1H), 5.05 (s, 2H), 2.32 (q, 2H, J = 7.6 Hz), 1.11 (t, 3H, J = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.1, 175.0, 146.3, 137.4, 135.5, 134.0, 132.5, 128.9, 56.7, 28.0, 9.7; EI MS (m/e) 224 [M^+]; HRMS calculated for $C_{11}H_{12}O_3S$ [M^+] 224.05072, found 224.05118.

(*E*) 4-Benzoxy-2-(2-thienyl)but-2-en-1-al (3.5h): colorless liquid; IR ν_1(C=O) 1722 cm^{-1}, ν_2(C=O) 1698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.04 - 8.09 (m, 2H), 7.41 - 7.62 (m, 4H), 7.22 (dd, 1H, J = 3.8, 1.2 Hz), 7.13 (dd, 1H, J = 5.0 , 3.6 Hz), 6.79 (t, 1H, J = 5.8 Hz), 5.36 (d, 2H, J = 5.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.4, 166.7, 147.3, 137.2, 134.1, 131.8, 130.4, 130.0, 129.8, 129.3, 129.1, 129.0, 127.5, 62.8; EI MS (m/e) 272 [M^+]; HRMS calculated for $C_{15}H_{12}O_3S$ [M^+] 272.05072, found 272.05082.

(*E*) 2-Methylbenzoxy-3-(2-thienyl)prop-2-en-1-al (3.6h): colorless liquid; IR ν_1(C=O) 1719 cm^{-1}, ν_2(C=O) 1679 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.96 - 7.01 (m, 2H), 7.70 (s, 1H), 7.62 - 7.65 (m, 1H), 7.33 - 7.51 (m, 4H), 7.15 (dd, 1H, J = 5.0, 3.8 Hz), 5.30 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.0, 167.1, 148.6, 137.4, 135.8, 134.7, 133.6, 132.4, 130.4, 129.0, 128.9, 57.2; EI MS (m/e) 272 [M^+]; HRMS calculated for $C_{15}H_{12}O_3S$ [M^+] 272.05072, found 272.05108.

(*E*)-3-Phenyl-2-(2-thienyl)prop-2-en-1-al (3.5i): colorless oil, IR ν(C=O) 1686 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.72 (s, 1H), 7.29 - 7.43 (m, 7H), 7.04 - 7.07 (m, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.4, 151.6, 135.3, 134.6, 131.0, 129.0, 128.1,

127.9; EI MS (m/e) 214 [M^+]; HRMS calculated for $C_{13}H_{10}OS$ [M^+] 214.04524, found 214.04524.

(*E*) 2-Phenyl-3-(2-thienyl)prop-2-en-1-al (3.6i): colorless oil, IR ν(C=O) 1674 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.60 (s, 1H), 7.43 - 7.50 (m, 3H), 7.32 - 7.36 (m, 1H), 7.18 - 7.27 (m, 3H), 6.99 (dd, 1H, J = 5.0, 3.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.4, 142.9, 140.0, 138.7, 135.0, 133.5, 132.8, 130.2, 129.8, 129.5, 127.8; EI MS (m/e) 214 [M^+]; HRMS calculated for $C_{13}H_{10}OS$ [M^+] 214.04524, found 214.04623.

4-Methyl-2-(2-thienyl)cyclopent-2-en-1-one (3.8): white solid, mp 53 - 55 °C; IR ν(C=O) 1698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.28 (dd, 1H, J = 5.2, 1.0 Hz), 7.03 (dd, 1H, J = 5.2, 3.8 Hz), 3.02 (m, 1H), 2.83 (d, 0.5H, J = 6.6 Hz), 2.74 (d, 0.5H, J = 6.4 Hz), 2.18 (d, 0.5H, J = 3.8 Hz), 2.08 (d, 0.5H, J = 4.0 Hz), 1.24 (d, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 160.9, 137.2, 133.5, 127.9, 126.5, 44.5, 34.0, 20.8; EI MS (m/e) 178 [M^+]; HRMS calculated for $C_{10}H_{10}OS$ [M^+] 178.04524, found 178.04621.

(*E*)-2-(1-Methylethenyl)-3-(2-thienyl)prop-2-en-1-al (3.6j): colorless liquid, IR ν(C=O) 1677 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.50 (dd, 1H, J = 5.0, 1.0 Hz), 7.38 - 7.42 (m, 1H), 7.33 (s, 1H), 7.06, 7.10 (m, 1H), 5.40 (d, 1H, J = 1.0 Hz), 5.04 (d, 1H, J = 1.0 Hz), 1.96 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.3, 147.0, 141.4, 139.1, 138.8, 134.7, 132.4, 128.0, 119.8, 27.3; EI MS (m/e) 178 [M^+]; HRMS calculated for $C_{10}H_{10}OS$ [M^+] 178.04524, found 178.04282.

(*E*)-2-(3-Thienyl)hept-2-en-1-al (3.5k): colorless liquid; IR ν(C=O) 1692 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.34 (dd, 1H, *J* = 4.8, 3.0 Hz), 7.29 (dd, 1H, *J* = 3.0, 1.4 Hz), 7.07 (dd, 1H, *J* = 5.0, 1.4 Hz), 6.66 (t, 1H, *J* = 7.6 Hz), 2.47 (q, 2H, *J* = 7.2 Hz), 1.29 - 1.55 (m, 4H), 0.89 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 194.3, 157.4, 139.0, 130.0, 129.0, 125.7, 125.5, 31.6, 30.4, 23.0, 10.4; EI MS (m/e) 194 [M^+]; HRMS calculated for $C_{11}H_{14}OS$ [M^+] 194.07654, found 194.07513.

(*E*)-3-Phenyl-2-(3-thienyl)prop-2-en-1-al (3.5l): colorless oil, IR ν(C=O) 1663 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.721 (s, 1H), 7.36 (s, 1H), 7.27 - 7.34 (m, 8H), 6.90 (dd, 1H, *J* = 4.4, 1.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 194.2, 151.0, 137.2, 134.9, 133.0, 131.0, 130.9, 129.2, 129.0, 128.8, 126.3, 126.2; EI MS (m/e) 214 [M^+]; HRMS calculated for $C_{13}H_{10}OS$ [M^+] 214.04524, found 214.04570.

(*E*) 2-Phenyl-3-(3-thienyl)prop-2-en-1-al (3.6l): colorless oil, IR ν(C=O) 1657 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.718 (s, 1H), 7.35 - 7.45 (m, 4H), 7.32 (s, 1H), 7.19 - 7.28 (m, 2H), 7.13 (dd, 1H, *J* = 5.0, 3.0 Hz), 6.66 (dd, 1H, *J* = 5.2, 1.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 194.3, 144.0, 141.1, 137.1, 134.4, 131.6, 129.9, 129.5, 129.0, 128.9, 128.8, 126.7; EI MS (m/e) 214 [M^+]; HRMS calculated for $C_{13}H_{10}OS$ [M^+] 214.04524, found 214.04424.

(*E*)-2-(2-Benzothienyl)hept-2-en-1-al (3.5m): colorless oil; IR ν(C=O) 1694 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.77 - 7.85 (m, 2H), 7.40 (s, 1H), 7.21

- 7.35 (m, 2H), 6.81 (t, 1H, J = 7.6 Hz), 2.65 (q, 2H, J = 7.2 Hz), 1.30 - 1.65 (m, 4H), 0.92 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.2, 159.1, 140.9, 138.9, 137.2, 130.5, 125.9, 124.9, 124.4, 122.6, 120.8, 31.6, 30.8, 23.1, 14.5; EI MS (m/e) 244 [M^+]; HRMS calculated for $C_{15}H_{16}OS$ [M^+] 244.09219, found 244.09229.

(*E*)-3-(2-Benzothienyl)-2-butylprop-2-en-1-al (3.6m): colorless oil; IR ν(C=O) 1677 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.80 - 7.87 (m, 2H), 7.56 (s, 1H), 7.41 (s, 1H), 7.37 - 7.40 (m, 2H), 2.67 (t, 2H, J = 7.6 Hz), 1.43 - 1.52 (m, 4H), 0.96 (t, 3H, J = 6.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 195.2, 142.7, 139.1, 138.6, 130.8, 126.8, 125.6, 125.1, 122.9, 30.2, 25.6, 23.9, 23.8, 14.6; EI MS (m/e) 244 [M^+]; HRMS calculated for $C_{15}H_{16}OS$ [M^+] 244.09219, found 244.09040.

(*E*)-2-(3-Benzothienyl)hept-2-en-1-al (3.5n): colorless oil; IR ν(C=O) 1691 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.85 - 7.90 (m, 1H), 7.32 - 7.44 (m, 3H), 7.26 (s, 1H), 6.99 (t, 1H, J = 7.6 Hz), 2.26 (q, 2H, J = 7.4 Hz), 1.21 - 1.50 (m, 4H), 0.82 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 193.6, 159.4, 140.5, 139.2, 138.8, 128.7, 126.6, 125.0, 124.0, 123.4, 123.2, 31.3, 30.7, 23.9, 14.4; EI MS (m/e) 244 [M^+]; HRMS calculated for $C_{15}H_{16}OS$ [M^+] 244.09219, found 244.08926.

(*E*)-3-(2-Benzothienyl)-2-butylprop-2-en-1-al (3.6n): colorless oil; IR ν(C=O) 1677 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.88 - 7.93 (m, 2H), 7.74 (s, 1H), 7.42 - 7.49 (m, 3H), 2.59 (t, 2H, J = 7.4 Hz), 1.37 - 1.57 (m, 4H), 0.93 (t, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 195.7, 144.5, 140.3, 140.0, 139.0, 128.5, 125.8, 125.6,

125.5, 123.5, 122.0, 30.7, 25.9, 23.7, 11.5; EI MS (m/e) 244 [M^+]; HRMS calculated for $C_{15}H_{16}OS$ [M^+] 244.09219, found 244.09201.

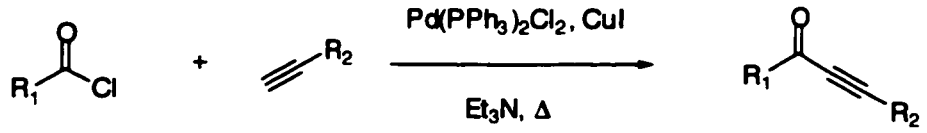
8.4 Experimental for Chapter 4

8.4.1 Materials

Hex-3-yn-2-one (**4.4a**), 4-phenylbut-3-yn-2-one (**4.4i**) and terminal alkynes were purchased from GFS Chemicals, and all acyl chlorides were purchased from Aldrich. Dichlorobis(triphenylphosphine)palladium(II) was purchased from Strem Chemicals. Other alkynones were prepared according to the procedure described by Hagihara and co-workers.[131] The zwitterionic rhodium complex (η^6-$C_6H_5BPh_3$)$^-Rh^+$(1,5-COD) (**1.1**) was prepared according to the procedure of Schrock and Osborn.[1]

8.3.5 Pd/CuI Catalyzed Acyl Chloride to Terminal Alkyne Coupling.

8.3.6



4.2 **4.3** **4.4**

To a 100 mL round bottom flask purged with N_2 was added triethylamine (40 mL), the terminal alkyne (**4.3**) (25 - 30 mmol), the acyl chloride (**4.2**) (20 mmol), $Pd(PPh_3)_2Cl_2$ (0.05 mmol), and CuI (0.25 mmol) at 50 °C or room temperature for 24 hours. Methanol (10 mL) was added, the solvent was evaporated. and diethyl ether (200 mL) was added to the resulting residue leading to the precipitation of $Et_3NH^+Cl^-$. This mixture was filtered, washed with 10 % HCl, distilled H_2O, brine, and dried over

anhydrous $MgSO_4$. The ether solution was evaporated, and the resulting residue was further purified by Kugelrohr distillation to give **4.4** (Table 4-1).

2-Methylnon-4-yn-3-one (4.4b): colorless liquid; IR ν(C≡C) 2211 cm^{-1}, ν(C=O) 1674 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.53 (septet, 1H, J = 6.8 Hz), 2.30 (t, 2H, J = 6.8 Hz), 1.31 - 1.54 (m, 4H), 1.69 (d, 6H, J = 7.0 Hz), 0.85 (t, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.9, 95.6, 80.3, 46.9, 43.5, 30.3, 22.5, 19.4, 18.5, 14.0; EI MS (m/e) 152 [M^+]; HRMS calculated for $C_{10}H_{16}O$ [M^+] 152.12012, found 152.11981.

5-Ethyldodec-7-yn-6-one (4.4c): colorless liquid; IR ν(C≡C) 2211 cm^{-1}, ν(C=O) 1669 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.24 (t, 2H, J = 6.8 Hz), 2.22 (quintet, 1H, J = 7.6 Hz), 1.10 - 1.58 (m, 12H), 0.71 - 0.83 (m, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.8, 94.9, 80.4, 56.6, 31.4, 29.8, 25.1, 23.2, 22.4, 19.1, 14.3, 13.9, 12.1; EI MS (m/e) 208 [M^+]; HRMS calculated for $C_{14}H_{24}O$ [M^+] 208.18272, found 208.18360.

1-Cyclohexylhept-2-yn-1-one (4.4d): colorless liquid; IR ν(C≡C) 2213 cm^{-1}, ν(C=O) 1671 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.34 (t, 2H, J = 7.0 Hz), 2.32 (m, 1H), 1.90 (m, 2H), 1.73 (m, 2H), 1.18 - 1.65 (m, 10H), 0.89 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.3, 95.5, 80.7, 52.8, 30.4, 28.9, 26.4, 26.0, 22.6, 19.2, 14.1; EI MS (m/e) 192 [M^+]; HRMS calculated for $C_{13}H_{20}O$ [M^+] 192.15142, found 192.15300.

2,2-Dimethylnon-4-yn-3-one (4.4e): colorless liquid; IR ν(C≡C) 2211 cm^{-1}, ν(C=O) 1671 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.30 (t, 2H, J = 6.6 Hz), 1.30 - 1.53

(m, 4H), 1.10 (s, 9H), 0.84 (t, 3H, J = 6.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 194.8, 96.1, 79.3, 45.2, 30.3, 26.6, 22.5, 19.2, 14.0; EI MS (m/e) 166 [M^+]; HRMS calculated for $C_{11}H_{18}O$ [M^+] 166.13576, found 166.13624.

1-Phenylhept-2-yn-1-one (4.4f): colorless liquid; IR ν(C≡C) 2201 cm^{-1}, ν(C=O) 1644 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.07 - 8.12 (m, 2H), 7.38 - 7.59 (m, 3H), 2.45 (t, 2H, J = 6.8 Hz), 1.40 - 1.66 (m, 4H), 0.91 (t, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 178.8, 137.5, 134.5, 130.1, 129.1, 97.4, 80.3, 30.4, 22.7, 19.5, 14.1; EI MS (m/e) 186 [M^+]; HRMS calculated for $C_{13}H_{14}O$ [M^+] 186.10446, found 186.10368.

1-(2-Furyl)hept-2-yn-1-one (4.4g): colorless liquid; IR ν(C≡C) 2210 cm^{-1}, ν(C=O) 1634 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.57 (dd, 1H, J = 2.2, 1.2 Hz), 7.24 (dd, 1H, J = 3.6, 1.2 Hz), 6.49 (dd, 1H, J = 3.2, 1.8 Hz), 2.39 (t, 2H, J = 6.6 Hz), 1.35 - 1.60 (m, 4H), 0.87 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 165.6, 153.8, 148.4, 121.3, 113.1, 96.1, 79.5, 30.3, 22.6, 19.4, 14.1; EI MS (m/e) 176 [M^+]; HRMS calculated for $C_{11}H_{12}O_2$ [M^+] 176.08373, found 176.08298.

2,2,6,-Tetramethylhept-4-yn-3-one (4.4h): colorless liquid; IR ν(C≡C) 2205 cm^{-1}, ν(C=O) 1673 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.22 (s, 9H), 1.10 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 194.8, 103.3, 77.7, 46.0, 45.1, 30.6, 26.6; EI MS (m/e) 166 [M^+]; HRMS calculated for $C_{11}H_{18}O$ [M^+] 166.13576, found 166.13576.

4-Methyl-1-phenylpent-1-yn-3-one (4.4j): colorless liquid; IR ν(C≡C) 2200 cm^{-1}, ν(C=O) 1670 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.52 - 7.57 (m, 2H), 7.30 - 7.43 (m, 3H), 2.73 (septet, 1H, J = 7.0 Hz), 1.23 (d, 6H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.9, 133.6, 131.2, 129.2, 120.9, 92.1, 87.4, 43.6, 18.7; EI MS (m/e) 172 [M^+]; HRMS calculated for $C_{12}H_{12}O$ [M^+] 172.08882, found 172.08747.

4-Ethyl-1-phenyloct-1-yn-3-one (4.4k): colorless liquid; IR ν(C≡C) 2198 cm^{-1}, ν(C=O) 1667 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.52 - 7.57 (m, 2H), 7.33 - 7.42 (m, 3H), 2.47 (quintet, 1H, J = 6.0 Hz), 1.47 - 1.86 (m, 4H), 1.23 - 1.32 (m, 4H), 0.84 - 0.95 (m, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.9, 133.6, 131.2, 129.2, 120.7, 91.6, 87.6, 56.8, 31.5, 30.0, 25.2, 23.3, 14.5, 12.3; EI MS (m/e) 228 [M^+]; HRMS calculated for $C_{16}H_{20}O$ [M^+] 228.15142, found 228.15183.

1-Cyclohexyl-3-phenylprop-2-yn-1-one (4.4l): colorless liquid; IR ν(C≡C) 2200 cm^{-1}, ν(C=O) 1666 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.51 - 7.57 (m, 2H), 7.30 - 7.42 (m, 3H), 2.47 (m, 1H), 2.00 - 2.10 (m, 2H), 1.22 - 1.80 (m, 8H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.0, 133.6, 131.2, 129.2, 120.8, 91.9, 87.8, 52.9, 31.5, 28.9, 26.4, 26.0; EI MS (m/e) 212 [M^+]; HRMS calculated for $C_{15}H_{16}O$ [M^+] 212.12012, found 212.12122.

4,4-Dimethyl-1-phenylpent-1-yn-3-one (4.4m): colorless liquid; IR ν(C≡C) 2199 cm^{-1}, ν(C=O) 1666 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.51 - 7.56 (m, 2H), 7.30 - 7.41 (m, 3H), 1.24 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 194.8, 133.5, 131.2, 129.2,

120.8, 92.8, 86.6, 45.5, 26.7; EI MS (m/e) 186 [M^+]; HRMS calculated for $C_{13}H_{14}O$ [M^+] 186.10446, found 186.10258.

1,3-Diphenylprop-2-yn-1-one (4.4n): white solid; mp 48 - 50 °C; IR ν(C≡C) 2200 cm^{-1}, ν(C=O) 1642 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.18 - 8.23 (m, 2H), 7.35 - 7.69 (m, 8H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 178.6, 137.5, 134.8, 133.7, 131.5, 130.2, 129.3, 129.0, 120.7, 93.8, 87.5; EI MS (m/e) 206 [M^+]; HRMS calculated for $C_{15}H_{10}O$ [M^+] 206.07316, found 206.07350.

1-Furyl-3-phenylprop-2-yn-1-one (4.4o): yellow solid; mp 49 - 51 °C; IR ν(C≡C) 2201 cm^{-1}, ν(C=O) 1632 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.56 - 7.64 (m, 3H), 7.30 - 7.46 (m, 4H), 2.47 (m, 1H), 6.55 (dd, 1H, J = 4.0, 2.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 165.3, 153.7, 148.7, 133.6, 131.5, 129.3, 121.7, 120.4, 113.3, 92.5, 86.8; EI MS (m/e) 196 [M^+]; HRMS calculated for $C_{13}H_8O_2$ [M^+] 196.05243, found 196.05326.

2,6-Dimethylhept-6-en-4-yn-3-one (4.4p): colorless liquid; IR ν(C≡C) 2194 cm^{-1}, ν(C=O) 1673 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.53 (d, 1H, J = 1.4 Hz), 5.46 (d, 1H, J = 1.2 Hz), 2.62 (septet, 1H, J = 6.8 Hz), 1.90 (s, 3H), 1.15 (d, 6H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.7, 127.9, 125.4, 93.0, 86.1, 43.6, 23.1, 18.5; EI MS (m/e) 136 [M^+]; HRMS calculated for $C_9H_{12}O$ [M^+] 136.08882, found 136..08998.

6-Ethyl-2-methyldec-1-en-3-yn-5-one (4.4q): colorless liquid; IR ν(C≡C) 2194 cm^{-1}, ν(C=O) 1669 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.53 (d, 1H, J = 1.2 Hz), 5.46 (d, 1H, J = 1.2 Hz), 2.37 (quintet, 1H, J = 6.8 Hz), 1.90 (s, 3H), 1.43 - 1.72 (m, 4H), 1.17 - 1.31 (m, 4H), 0.80 - 0.89 (m, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.9, 127.9, 125.5, 92.4, 86.4, 56.7, 31.3, 29.9, 25.1, 23.3, 23.1, 14.4, 12.2; EI MS (m/e) 192 [M^+]; HRMS calculated for $C_{13}H_{20}O$ [M^+] 192.15142, found 192.15142.

2,2,6-Trimethylhept-6-en-4-yn-3-one (4.4r): colorless liquid; IR ν(C≡C) 2192 cm^{-1}, ν(C=O) 1668 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.52 (d, 1H, J = 1.4 Hz), 5.46 (d, 1H, J = 1.2 Hz), 1.90 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 194.8, 127.7, 125.5, 93.6, 85.3, 45.4, 26.6, 23.1; EI MS (m/e) 150 [M^+]; HRMS calculated for $C_{10}H_{14}O$ [M^+] 150.10446, found 150.10618.

4-Methyl-1-phenylpent-4-en-2-yn-1-one (4.4s): yellow liquid; IR ν(C≡C) 2196 cm^{-1}, ν(C=O) 1644 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.08 - 8.14 (m, 2H), 7.41 - 7.62 (m, 3H), 5.67 (d, 1H, J = 1.4 Hz), 5.56 (d, 1H, J = 1.2 Hz), 2.00 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 178.6, 137.3, 134.7, 130.1, 129.2, 128.4, 125.5, 95.5, 86.2, 23.2; EI MS (m/e) 170 [M^+]; HRMS calculated for $C_{12}H_{10}O$ [M^+] 170.07316, found 170.07446.

6-Methoxy-2-methylhex-4-yn-3-one (4.4t): colorless liquid; IR ν(C≡C) 2211 cm^{-1}, ν(C=O) 1678 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.22 (s, 2H), 3.37 (s, 3H), 2.61 (septet, 1H, J = 7.0 Hz), 1.90 (s, 3H), 1.15 (d, 6H, J = 7.0 Hz); ^{13}C NMR (200 MHz,

$CDCl_3$) δ 192.0, 88.9, 84.9, 60.1, 58.6, 43.5, 18.3; EI MS (m/e) 140 [M^+]; HRMS calculated for $C_8H_{12}O_2$ [M^+] 140.08373, found 140.08373.

5-Ethyl-1-methoxynon-2-yn-4-one (4.4u): colorless liquid; IR ν(C≡C) 2211 cm^{-1}, ν(C=O) 1674 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.21 (s, 2H), 3.35 (s, 3H), 2.35 (quintet, 1H, J = 6.8 Hz), 1.41 - 1.75 (m, 4H), 1.16 - 1.27 (m, 4H), 0.79 - 0.87 (m, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 192.1, 88.3, 85.2, 60.1, 58.5, 56.5, 31.2, 29.9, 24.9, 23.2, 14.4, 12.1; EI MS (m/e) 196 [M^+]; HRMS calculated for $C_{12}H_{20}O_2$ [M^+] 196.14633, found 196.14767.

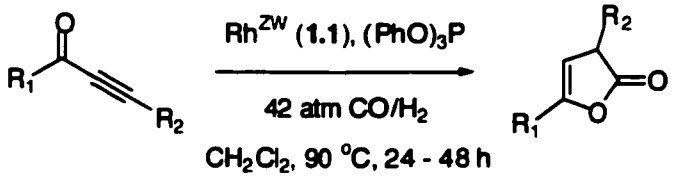
2,2-Dimethyl-6-methoxyhex-4-yn-3-one (4.4v): colorless liquid; IR ν(C≡C) 2207 cm^{-1}, ν(C=O) 1673 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.26 (s, 2H), 3.40 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 194.2, 89.6, 84.2, 60.2, 58.6, 45.2, 26.6; EI MS (m/e) 154 [M^+]; HRMS calculated for $C_9H_{14}O_2$ [M^+] 154.09938, found 154.09910.

4-Methoxy-1-phenylbut-2-yn-1-one (4.4w): yellow liquid; IR ν(C≡C) 2196 cm^{-1}, ν(C=O) 1644 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.08 - 8.13 (m, 2H), 7.41 - 7.62 (m, 3H), 4.35 (s, 2H), 3.45 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 178.0, 136.9, 134.9, 130.2, 129.2, 90.6, 84.8, 60.4, 58.8; EI MS (m/e) 174 [M^+]; HRMS calculated for $C_{11}H_{10}O_2$ [M^+] 174.06808, found 174.06787.

8.4.3 Cyclohydrocarbonylation of α-Keto Alkynes: Optimization of Reaction Conditions.

To a 45 mL autoclave with a glass liner and stirring bar was placed the zwitterionic rhodium complex (**1.1**) (0.03 mmol), ligand (0.12 - 0.48 mmol), the α-keto alkyne **4.4e** (1.5 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 17.5 - 38.5 atm, and then hydrogen was introduced up to a total pressure of 21 - 42 atm. The autoclave was placed in an oil bath at 60 - 120 °C for 24 to 48 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through celite, and the solvent was removed by rotary evaporation. The percent conversion and the ratio of **4.5e/4.6e/4.7e** were determined by ^1H NMR. The optimization results are given in Tables 4-2 and 4-3.

8.4.4 Cyclohydrocarbonylation of α-Keto Alkynes where R_2 is an Alkyl Chain



4.4 **4.5**

To a 45 mL autoclave with a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.03 mmol), triphenyl phosphite (0.48 mmol), the α-keto alkyne **4.4** (1.5 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 38.5 atm, and then hydrogen was introduced up to

a total pressure of 42 atm. The autoclave was placed in an oil bath at 90 °C for 24 to 48 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through celite, and the solvent was removed by rotary evaporation. The resulting residue was purified by Kugelrohr distillation, flash silica gel chromatography, or crystallization to afford products **4.5** (see Tables 4-4).

3-Ethyl-5-methyl-2(3H)-furanone (4.5a): colorless liquid; IR ν(C=O) 1797 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.08 (d, 1H, J = 4.6 Hz), 3.12 (m, 1H), 1.93 (s, 3H), 1.68 (m, 2H), 0.89 (t, 3H, J = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 180.1, 150.8, 104.1, 46.9, 24.5, 14.5, 11.4; EI MS (m/e) 126 [M^+]; HRMS calculated for $C_7H_{10}O_2$ [M^+] 126.06808, found 126.06610.

3-Butyl-5-isopropyl-2(3H)-furanone (4.5b): colorless liquid; IR ν(C=O) 1797 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.07 (d, 1H, J = 2.4 Hz), 3.18 (td, 1H, J = 7.6, 2.5 Hz), 2.54 (septet, 1H, J = 6.8 Hz), 1.76 (m, 1H), 1.58 (m, 1H), 1.25 - 1.36 (m, 2H), 1.12 (d, 6H, J = 6.6 Hz), 0.88 (t, 3H, J = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 180.5, 161.8, 101.6, 45.4, 31.2, 29.4, 28.3, 23.0, 19.9, 14.4; EI MS (m/e) 182 [M^+]; HRMS calculated for $C_{11}H_{18}O_2$ [M^+] 182.13068, found 182.13083.

3-Butyl-5-(3-heptyl)-2(3H)-furanone (4.5c): colorless liquid; IR ν(C=O) 1798 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.11 (d, 1H, J = 1.8 Hz), 3.21 (td, 1H, J = 7.2, 2.0 Hz), 2.16 (quintet, 1H, J = 7.0 Hz), 1.14 - 1.78 (m, 14H), 0.80 - 0.93 (m, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 180.6, 158.6, 104.6, 45.3, 41.5, 31.8, 31.2, 30.0, 29.9, 29.3, 25.4,

23.2, 23.0, 14.4, 12.0; EI MS (m/e) 238 [M^+]; HRMS calculated for $C_{15}H_{26}O_2$ [M^+] 238.19328, found 238.19644.

3-Butyl-5-cyclohexyl-2(3H)-furanone (4.5d): colorless liquid; IR ν(C=O) 1797 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.04 (d, 1H, J = 2.2 Hz), 3.16 (m, 1H), 2.22 (m, 1H), 1.51 - 1.91 (m, 6H), 1.17 - 1.37 (m, 10H), 0.87 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 180.5, 160.9, 101.7, 45.3, 37.5, 31.2, 30.2, 29.3, 26.6, 26.2, 23.0, 14.4; EI MS (m/e) 222 [M^+]; HRMS calculated for $C_{14}H_{22}O_2$ [M^+] 222.16198, found 222.16438.

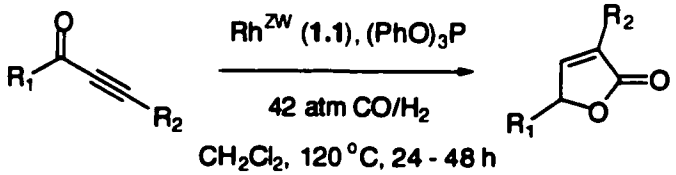
3-Butyl-5-t-butyl-2(3H)-furanone (4.5e): colorless liquid; IR ν(C=O) 1798 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.02 (d, 1H, J = 2.2 Hz), 3.14 (m, 1H), 1.74 (m, 1H), 1.54 (m, 1H), 1.28 (m, 2H), 1.10 (s, 9H), 0.83 (t, 3H, J = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 180.5, 164.2, 100.7, 45.5, 32.8, 29.2, 27.7, 27.0, 23.0, 14.4; EI MS (m/e) 196 [M^+]; HRMS calculated for $C_{12}H_{20}O_2$ [M^+] 196.14633, found 196.14856.

3-Butyl-5-phenyl-2(3H)-furanone (4.5f): white solid; mp 47 - 49 °C; IR ν(C=O) 1775 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.57 - 7.62 (m, 2H), 7.37 - 7.41 (m, 3H), 5.81 (d, 1H, J = 2.8 Hz), 3.44 (td, 1H, J = 5.4, 2.6 Hz), 1.74 (m, 1H), 1.61 - 1.93 (m, 2H), 1.29 - 1.48 (m, 4H), 0.90 (t, 3H, J = 7.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 179.4, 153.4, 130.1, 129.3, 129.0, 125.4, 103.2, 46.2, 31.3, 29.4, 23.1, 14.4; EI MS (m/e) 216 [M^+]; HRMS calculated for $C_{14}H_{16}O_2$ [M^+] 216.11503, found 216.11467.

3-Butyl-5-phenyl-2(5H)-furanone (4.6f): colorless liquid; IR ν(C=O) 1759 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.32 - 7.37 (m, 3H), 7.21 - 7.27 (m, 2H), 7.07 (d, 1H, J = 1.6 Hz), 5.85 (d, 1H, J = 1.8 Hz), 2.33 (t, 2H, J = 6.8 Hz), 1.28 - 1.64 (m, 4H), 0.91 (t, 3H, J = 7.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 174.6, 148.2, 135.9, 134.6, 129.7, 129.4, 127.0, 82.8, 30.1, 25.5, 22.9, 14.4; EI MS (m/e) 216 [M^+]; HRMS calculated for $C_{14}H_{16}O_2$ [M^+] 216.11503, found 216.11662.

3-Butyl-5-furyl-2(5H)-furanone (4.6g): colorless liquid; IR ν(C=O) 1760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.39 (dd, 1H, J = 2.2, 1.4 Hz), 7.03 (dd, 1H, J = 3.4, 2.2 Hz), 6.34 (d, 1H, J = 1.2 Hz), 5.85 (dd, 1H, J = 3.6, 1.4 Hz), 2.33 (t, 2H, J = 6.8 Hz), 1.31 - 1.61 (m, 4H), 0.91 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 173.8, 148.4, 144.4, 144.2, 136.5, 111.3, 110.7, 75.8, 30.2, 25.6, 22.8, 14.4; EI MS (m/e) 206 [M^+]; HRMS calculated for $C_{12}H_{14}O_3$ [M^+] 206.09423, found 206.09561.

8.4.5 Cyclohydrocarbonylation of α-Keto Alkynes where R_2 is an Aryl Group



4.4 **4.6**

To a 45 mL autoclave with a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.03 mmol), triphenyl phosphite (0.48 mmol), the α-keto alkyne **4.4** (1.5 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times

with carbon monoxide, pressurized to 38.5 atm, and then hydrogen was introduced up to a total pressure of 42 atm. The autoclave was placed in an oil bath at 120 °C for 24 to 48 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through celite, and the solvent was removed by rotary evaporation. The resulting residue was purified by Kugelrohr distillation, flash silica gel chromatography, or crystallization to afford products **4.6** (see Tables 4-5).

5-Methyl-3-phenyl-2(5H)-furanone (4.6i): colorless liquid; IR ν(C=O) 1756 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.85 - 7.80 (m, 2H), 7.52 (d, 1H, J = 1.8 Hz), 7.35 - 7.42 (m, 3H), 5.14 (qd, 1H, J = 6.8, 1.6 Hz), 1.49 (d, 3H, J = 6.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 172.3, 149.6, 131.9, 130.1, 129.9, 129.2, 127.6, 77.3, 19.7; EI MS (m/e) 174 [M^+]; HRMS calculated for $C_{11}H_{10}O_2$ [M^+] 174.06808, found 174.06854.

5-Isopropyl-3-phenyl-2(5H)-furanone (4.6j): white solid; mp 86 - 88 °C; IR ν(C=O) 1730 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.81 - 7.86 (m, 2H), 7.54 (d, 1H, J = 2.0 Hz), 7.34 - 7.42 (m, 3H), 4.82 (dd, 1H, J = 6.8, 2.0 Hz), 2.05 (octet, 1H, J = 6.8 Hz), 1.03 (d, 6H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 172.4, 147.2, 132.8, 130.1, 129.2, 127.6, 85.7, 32.7, 18.6, 18.3; EI MS (m/e) 202 [M^+]; HRMS calculated for $C_{13}H_{14}O_2$ [M^+] 202.09938, found 202.10117.

5-(3-Heptyl)-3-phenyl-2(5H)-furanone (4.6k): colorless oil; IR ν(C=O) 1753 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.81 - 7.86 (m, 2H), 7.55 (d, 1H, J = 2.8 Hz), 7.34 - 7.42 (m, 3H), 5.05 (dd, 1H, J = 5.0, 2.4 Hz), 1.70 (m, 1H), 1.27 - 1.48 (m, 8H), 0.84 -

0.98 (m, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 172.5, 148.0, 132.6, 130.2, 129.2, 127.6, 83.3, 43.7, 29.9, 29.7, 29.2, 23.4, 22.7, 14.6, 12.2; EI MS (m/e) 258 [M^+]; HRMS calculated for $C_{17}H_{22}O_2$ [M^+] 258.16198, found 258.16338.

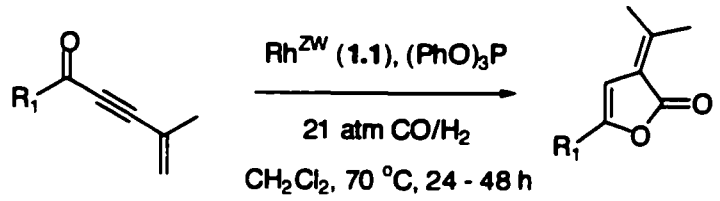
5-Cyclohexyl-3-phenyl-2(5H)-furanone (4.61): white solid; mp 101 - 103 °C; IR ν(C=O) 1728 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.80 - 7.85 (m, 2H), 7.56 (d, 1H, J = 1.8 Hz), 7.36 - 7.43 (m, 3H), 4.83 (dd, 1H, J = 5.8, 1.6 Hz), 1.66 - 1.86 (m, 5H), 1.10 - 1.30 (m, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 172.3, 147.4, 132.5, 130.3, 129.8, 129.2, 127.6, 85.2, 42.3, 29.2, 28.9, 26.7, 26.4, 26.3; EI MS (m/e) 242 [M^+]; HRMS calculated for $C_{16}H_{18}O_2$ [M^+] 242.13068, found 242.13194.

5-t-Butyl-3-phenyl-2(5H)-furanone (4.6m): white solid; mp 116 - 118 °C; IR ν(C=O) 1725 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.83 - 7.86 (m, 2H), 7.54 (s, 1H), 7.37 - 7.41 (m, 3H), 4.71 (s, 1H), 1.02 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 172.4, 146.6, 133.3, 130.2, 129.9, 129.2, 127.6, 88.9, 36.0, 26.2; EI MS (m/e) 216 [M^+]; HRMS calculated for $C_{14}H_{16}O_2$ [M^+] 216.11503, found 216.11695.

3,5-Diphenyl-2(5H)-furanone (4.6n): white solid; mp 110 - 112 °C; IR ν(C=O) 1760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.87 - 7.93 (m, 2H), 7.61 (d, 1H, J = 2.0 Hz), 7.29 - 7.45 (m, 8H), 6.00 (d, 1H, J = 2.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 172.4, 148.1, 135.4, 131.5, 130.1, 129.9, 129.7, 129.3, 127.8, 127.2, 82.2; EI MS (m/e) 236 [M^+]; HRMS calculated for $C_{16}H_{12}O_2$ [M^+] 236.08372, found 236.08386.

5-Furyl-3-phenyl-2(5H)-furanone (4.6o): yellow solid; mp 105 - 107 °C; IR ν(C=O) 1758 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.87 - 7.93 (m, 2H), 7.61 (d, 1H, J = 2.0 Hz), 7.29 - 7.45 (m, 8H), 6.00 (d, 1H, J = 2.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 171.6, 147.9, 144.6, 144.0, 133.3, 130.3, 129.7, 129.4, 127.9, 111.4, 111.0, 75.1; EI MS (m/e) 226 [M^+]; HRMS calculated for $C_{14}H_{10}O_3$ [M^+] 226.06299, found 226.06474.

8.4.6 Cyclohydrocarbonylation of α-Keto Alkynes where R_2 is a 1-Methylethenyl Group



4.4 **4.8**

To a 45 mL autoclave with a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.03 mmol), triphenyl phosphite (0.12 mmol), the α-keto alkyne **4.4** (1.5 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 17.5 atm, and then hydrogen was introduced up to a total pressure of 21 atm. The autoclave was placed in an oil bath at 70 °C for 24 to 48 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through celite, and the solvent was removed by rotary evaporation. The resulting residue was purified by Kugelrohr distillation, flash silica gel chromatography, or crystallization to afford products **4.8** (see Tables 4-6).

3-Dimethylmethylene-5-isopropyl-2-furanone (4.8p): colorless liquid; IR ν(C=O) 1760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.72 (s, 1H), 2.62 (septet, 1H, J = 7.6 Hz), 2.30 (s, 3H), 2.01 (s, 3H), 1.15 (d, 6H, J = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 168.5, 161.2, 151.7, 123.5, 99.6, 28.5, 24.7, 21.1, 20.1; EI MS (m/e) 166 [M^+]; HRMS calculated for $C_{10}H_{14}O_2$ [M^+] 166.09938, found 166.09952.

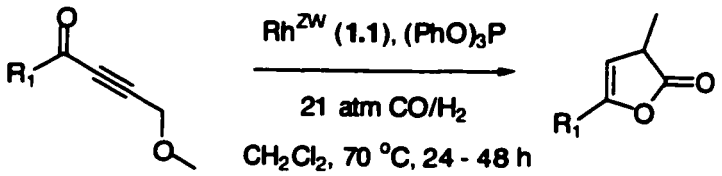
3-Dimethylmethylene-5-(3-heptyl)-2-furanone (4.8q): colorless liquid; IR ν(C=O) 1764 cm^{-1}: ^1H NMR (200 MHz, $CDCl_3$) δ 5.75 (s, 1H), 2.31 (s, 3H), 2.23 (quintet, 1H, J = 7.2 Hz), 2.01 (s, 3H), 1.39 (m, 4H), 1.17 - 1.34 (m, 4H), 0.80 - 0.88 (m, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 169.6, 158.4, 151.4, 123.4, 102.5, 41.8, 32.2, 30.0, 25.8, 24.8, 23.5, 23.2, 21.1, 14.6, 12.3; EI MS (m/e) 222 [M^+]; HRMS calculated for $C_{14}H_{22}O_2$ [M^+] 222.16198, found 222.16056.

5-t-Butyl-3-dimethylmethylene-2-furanone (4.8r): colorless liquid; IR ν(C=O) 1768 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.68 (s, 1H), 2.29 (s, 3H), 2.00 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 168.6, 163.6, 151.8, 98.7, 99.6, 33.0, 27.9, 24.7, 21.1; EI MS (m/e) 180 [M^+]; HRMS calculated for $C_{11}H_{16}O_2$ [M^+] 180.11503, found 180.11268.

3-Dimethylmethylene-5-phenyl-2-furanone (4.8s): white solid; mp 111 - 113 °C; IR ν(C=O) 1752 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.60 - 7.65 (m, 2H), 7.32 - 7.40 (m, 3H), 6.43 (s, 1H), 2.37 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 167.7,

161.2, 154.2, 151.9, 130.0, 129.3, 125.2, 124.0, 100.9, 25.0, 21.5; EI MS (m/e) 166 [M^+]; HRMS calculated for $C_{13}H_{14}O_2$ [M^+] 166.09938, found 166.09952.

8.4.7 Cyclohydrocarbonylation of α-Keto Alkynes where R_2 is a Methylmethoxy Group



4.4 **4.5**

To a 45 mL autoclave with a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.03 mmol), triphenyl phosphite (0.12 mmol), the α-keto alkyne **4.4** (1.5 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 17.5 atm, and then hydrogen was introduced up to a total pressure of 21 atm. The autoclave was placed in an oil bath at 70 °C for 24 to 48 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through celite, and the solvent was removed by rotary evaporation. The resulting residue was purified by Kugelrohr distillation, flash silica gel chromatography, or crystallization to afford products **4.5** (see Tables 4-7).

5-Isopropyl-3-methyl-2(3H)-furanone (4.5t): colorless liquid; IR ν(C=O) 1797 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.07 (d, 1H, J = 1.8 Hz), 3.22 (qd, 1H, J = 7.6, 2.0 Hz), 2.53 (septet, 1H, J = 6.8 Hz), 1.29 (d, 3H, J = 7.6 Hz), 1.12 (d, 6H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 181.1, 161.5, 103.4, 40.2, 28.3, 19.8, 16.5; EI MS (m/e) 140 [M^+]; HRMS calculated for $C_8H_{12}O_2$ [M^+] 140.08373, found 140.08246.

5-(3-Heptyl)-3-methyl-2(3H)-furanone (4.5u): colorless liquid; IR ν(C=O) 1796 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.11 (d, 1H, J = 2.2 Hz), 3.21 (qd, 1H, J = 7.4, 2.2 Hz), 2.15 (quintet, 1H, J = 6.8 Hz), 1.41 - 1.55 (m, 4H), 1.28 (d, 3H, J = 7.6 Hz), 1.16 - 1.25 (m, 4H), 0.79 - 0.86 (m, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 181.2, 158.3, 106.3, 41.3, 40.0, 31.6, 29.9, 25.2, 23.2, 16.8, 14.6, 12.0; EI MS (m/e) 196 [M^+]; HRMS calculated for $C_{12}H_{20}O_2$ [M^+] 196.14633, found 196.14631.

5-t-Butyl-3-methyl-2(3H)-furanone (4.5v): colorless liquid; IR ν(C=O) 1792 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.05 (d, 1H, J = 2.2 Hz), 3.22 (qd, 1H, J = 7.6, 2.2 Hz), 1.30 (d, 3H, J = 7.6 Hz), 1.15 (s, 9H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 180.5, 163.4, 101.8, 39.7, 32.2, 27.0, 15.9; EI MS (m/e) 154 [M^+]; HRMS calculated for $C_9H_{14}O_2$ [M^+] 154.09938, found 154.10027.

3-Methyl-5-phenyl-2(5H)-furanone (4.6w): colorless liquid; IR ν(C=O) 1759 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.32 - 7.37 (m, 3H), 7.52 (d, 1H, J = 1.8 Hz), 7.21 - 7.26 (m, 2H), 7.11 (d, 1H, J = 1.6 Hz), 5.85 (d, 1H, J = 1.6 Hz), 1.97 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 174.2, 148.3, 135.2, 129.5, 129.0, 126.4, 82.0, 28.9, 10.6; EI MS (m/e) 174 [M^+]; HRMS calculated for $C_{11}H_{10}O_2$ [M^+] 174.06808, found 174.06996.

8.5 Experimental for Chapter 5

8.5.1 Materials

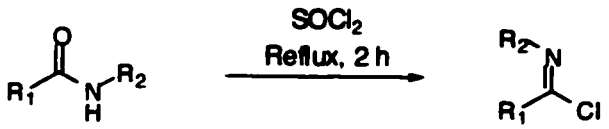
All acyl chlorides and primary amines were purchased from Aldrich, and all terminal alkynes were purchased from GFS Chemicals.. Dichloro-bis(triphenylphosphine)palladium(II) was purchased from Strem Chemicals. The zwitterionic rhodium complex (η^6-$C_6H_5BPh_3$)$^-Rh^+$(1,5-COD) (**1.1**) was prepared according to the procedure of Schrock and Osborn.[1]

8.5.1 Synthesis of Starting Materials

8.5.2.1 General Procedure for the Preparation of Secondary Amides from Acyl Chlorides and Primary Amines.

To a 250 mL round bottom flask fitted with a reflux condenser was added the acyl chloride (50 mmol), Et_3N (75 mmol), and $CHCl_3$ (100 mL). The primary amine (55 mmol) was added drop-wise through the condenser, and the reaction flask was allowed to stir for an additional 30 minutes. The solvent was removed by rotary evaporation followed by addition of ethyl acetate (200 mL) leading to the solvation of the secondary amide and the precipitation of $Et_3NH^+Cl^-$. This mixture was filtered, the filtrate evaporated, and the resulting solid washed with hexanes (200 mL), and collected and dried by suction filtration to give **5.13a – 5.13g** .

8.5.2.2 General Procedure for the Preparation of Imidoyl Chlorides from Secondary Amides.



5.13 **5.14**

To a 100 mL round bottom flask was added the secondary amide (**5.13**) (50 mmol) and $SOCl_2$ (50 mL) followed by heating to reflux. After 2 hours the excess $SOCl_2$ was removed by rotary evaporation, and the resulting residue was further purified by Kugelrohr distillation to give the imidoyl chlorides **5.14a – 5.14g** (Table 5-2).

N-Butylbenzimidoyl chloride (5.14a): colorless liquid; IR ν(C=N) 1668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, 2H, J = 6.7 Hz), 7.39 – 7.48 (m, 3H), 3.78 (t, 2H, J = 6.9 Hz), 1.79 (quintet, 2H, J = 7.7 Hz), 1.53 (sextet, 2H, J = 7.7 Hz), 1.04 (t, 3H, J = 7.4 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 141.1, 135.9, 130.9, 128.8, 128.1, 53.8, 31.8, 20.6, 13.8; EI MS (m/z) 160 [M^+ - Cl]; HRMS calculated for $C_{11}H_{14}NCl$ [M^+ - Cl] 160.11262, found 160.11455.

N-Isopropylbenzimidoyl chloride (5.14b): colorless liquid; IR ν(C=N) 1669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, 2H, J = 8.0 Hz), 7.40 – 7.46 (m, 3H), 4.20 (septet, 1H, J = 6.3 Hz), 1.32 (d, 6H, J = 6.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 139.3, 136.0, 130.9, 129.0, 128.8, 128.1, 54.8, 22.6; EI MS (m/z) 146 [M^+ - Cl]; HRMS calculated for $C_{10}H_{12}NCl$ [M^+ - Cl] 146.09694, found 146.09770.

N-Isopropyl-4-methylbenzimidoyl chloride (5.14c): colorless liquid; IR ν(C=N) 1669 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, 2H, J = 8.3 Hz), 7.20 (d, 2H, J = 8.6 Hz), 4.17 (septet, 1H, J = 6.3 Hz), 2.39 (s, 3H), 1.29 (d, 6H, J = 6.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 141.3, 139.3, 133.4, 124.0, 128.9, 54.7, 22.7, 21.3; EI MS (m/z) 160 [M^+ - Cl]; HRMS calculated for $C_{11}H_{14}NCl$ [M^+ - Cl] 160.11262, found 161.11310.

N-Isopropyl-4-methoxybenzimidoyl chloride (5.14d): colorless liquid; IR ν(C=N) 1673 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, 2H, J = 8.8 Hz), 6.87 (d, 2H, J = 8.9 Hz), 4.18 (septet, 1H, J = 6.3 Hz), 3.79 (s, 3H), 1.32 (d, 6H, J = 6.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 162.8, 131.3, 126.7, 114.6, 113.6, 55.4, 54.8, 22.2; EI MS (m/z) 176 [M^+ - Cl]; HRMS calculated for $C_{11}H_{14}NOCl$ [M^+ - Cl] 176.10754, found 176.10460.

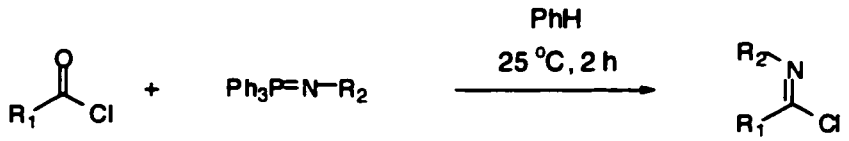
N-Isopropyl-4-chlorobenzimidoyl chloride (5.14e): colorless liquid; IR ν(C=N) 1666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, 2H, J = 8.6 Hz), 7.34 (d, 2H, J = 8.8 Hz), 4.14 (septet, 1H, J = 6.3 Hz), 1.28 (d, 6H, J = 6.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 138.1, 137.2, 134.4, 130.1, 128.3, 54.9, 22.6; EI MS (m/z) 215 [M^+]; HRMS calculated for $C_{10}H_{11}NCl_2$ [M^+] 215.02685, found 215.02640.

N-Isopropyl-naphthalene-2-carboximidoyl chloride (5.14f): colorless liquid; IR ν(C=N) 1656 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.14 (d, 1H, J = 8.7 Hz), 7.93 (d, 1H, J = 6.7 Hz), 7.81 – 7.85 (m, 2H), 7.52 – 7.57 (m, 2H), 4.29 (septet, 1H, J = 6.3 Hz), 1.39 (d, 6H, J = 6.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 139.6, 134.5, 133.2,

130.0, 129.8, 129.0, 128.6, 127.2, 126.4, 125.2, 55.0, 22.7; EI MS (m/z) 196 [M^+ - Cl]; HRMS calculated for $C_{14}H_{14}NCl$ [M^+ - Cl] 196.11262, found 196.11490.

N-Isopropyl-4-nitrobenzimidoyl chloride (5.14g): colorless liquid; IR ν(C=N) 1662 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, 2H, J = 9.0 Hz), 8.13 (d, 2H, J = 9.0 Hz), 4.14 (septet, 1H, J = 6.3 Hz), 1.26 (d, 6H, J = 6.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.2, 141.3, 137.7, 129.8, 123.3, 55.4, 22.4; EI MS (m/z) 191 [M^+ - Cl]; HRMS calculated for $C_{10}H_{11}N_2O_2Cl$ [M^+ - Cl] 191.08205, found 191.08040.

8.5.2.3 General Procedure for the Preparation of Imidoyl Chlorides From Acyl Chlorides and Aza-Wittig Reagents.



5.11 **5.12** **5.14**

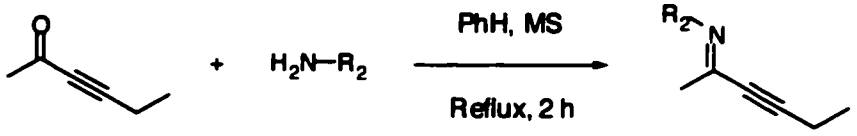
To a 250 mL round bottom flask fitted with a reflux condenser was added benzene (150 mL), PPh_3Br_2 (30 mmol), the aryl amine (30 mmol), triethylamine (75 mmol), and allowed to reflux overnight. After the reaction mixture was cooled $Et_3NH^+Br^+$ was filtered, and the filtrate evaporated to dryness. To the resulting aza-Wittig reagent was added benzene (50 mL), isobutyryl chloride (28 mmol), and allowed to react at room temperature. After 2 hours the solvent was evaporated and the resulting mixture was extracted with hexanes (100 mL). The hexanes solution was evaporated by rotary evaporation to give **5.14h – 5.14j** (Table 5-3).

2-Methyl-N-phenylpropionimidoyl chloride (5.14h): colorless liquid; IR ν(C=N) 1695 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, 2H, J = 7.1 Hz), 7.15 (t, 1H, J = 7.4 Hz), 6.88 (d, 2H, J = 7.3 Hz), 2.95 (septet, 1H, J = 6.8 Hz), 1.35 (d, 6H, J = 6.8 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 147.1, 132.0, 128.6, 124.6, 120.0, 41.5, 20.2; EI MS (m/z) 146 [M^+ - Cl]; HRMS calculated for $C_{10}H_{12}NCl$ [M^+ - Cl] 146.09694, found 146.08530.

2-Methyl-N-*p*-tolylpropionimidoyl chloride (5.14i): colorless liquid; IR ν(C=N) 16954 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, 2H, J = 8.0 Hz), 6.81 (d, 2H, J = 8.2 Hz), 2.95 (septet, 1H, J = 6.8 Hz), 2.35 (s, 3H), 1.35 (d, 6H, J = 6.8 Hz) ; ^{13}C NMR (300 MHz, $CDCl_3$) δ 144.5, 134.1, 131.9, 129.2, 120.0, 41.4, 20.8, 20.1; EI MS (m/z) 160 [M^+ - Cl]; HRMS calculated for $C_{11}H_{14}NCl$ [M^+ - Cl] 160.11262, found 162.11320.

N-(4-Chlorophenyl)-2-methylpropionimidoyl chloride (5.14j): colorless liquid; IR ν(C=N) 1666 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, 2H, J = 8.8 Hz), 6.81 (d, 2H, J = 8.8 Hz), 2.92 (septet, 1H, J = 6.8 Hz), 1.33 (d, 6H, J = 6.8 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 153.1, 145.6, 130.1, 128.8, 121.6, 41.6, 20.1; EI MS (m/z) 215 [M^+]; HRMS calculated for $C_{10}H_{11}NCl_2$ [M^+] 215.02685, found 215.02654.

8.5.2.4 General Procedure for the Preparation of Acetylenic Imines from Hex-3-yn-2-one and Primary Amines.



5.10 **5.16a - h**

To a 250 mL round bottom flask fitted with a reflux condenser was added hex-3-yn-2-one (25 mmol), benzene (75 mL) and 4 Å molecular sieves (8 g). The primary amine **5.10** (28 mmol) was added drop-wise through the condenser followed by heating the flask to reflux for 2 hours. This mixture was cooled to room temperature, filtered, the filtrate evaporated, and the resulting solution was further purified by Kugelrohr distillation to give **5.16a – 5.16h** (Table 5-1).

Butyl-(1-methylpent-2-ynylidene)amine (5.16a): colorless liquid; IR ν(C≡C) 2215 cm^{-1}, ν(C=N) 1618 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.40 (t, 2H, J = 7.4 Hz), 2.27 (q, 2H, J = 7.5 Hz), 2.01 (s, 3H), 1.48 (quintet, 2H, J = 7.4 Hz), 1.24 (sextet, 2H, J = 7.4 Hz), 1.09 (t, 3H, J = 7.5 Hz), 0.82 (t, 3H, J = 7.4 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.2, 99.4, 74.7, 32.4, 27.4, 20.4, 13.7, 13.3, 12.7; EI MS (m/z) 151 [M^+]; HRMS calculated for $C_{10}H_{17}N$ [M^+] 151.13610, found 151.13656.

Isopropyl-(1-methylpent-2-ynylidene)amine (5.16b): colorless liquid; IR ν(C≡C) 2214 cm^{-1}, ν(C=N) 1614 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.78 (septet, 1H, J = 6.2 Hz), 2.21 (q, 2H, J = 7.6 Hz), 1.96 (s, 3H), 1.05 (t, 3H, J = 7.6 Hz), 0.98 (d, 6H, J =

6.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 147.8, 98.7, 74.4, 55.0, 27.5, 23.0, 13.2, 12.6; EI MS (m/z) 137 [M^+]; HRMS calculated for $C_9H_{15}N$ [M^+] 137.12045, found 137.12167.

Cyclohexyl-(1-methylpent-2-ynylidene)amine (5.16c): colorless liquid; IR ν(C≡C) 2215 cm^{-1}, ν(C=N) 1619 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.42 (m, 1H), 2.22 (q, 2H, J = 7.4 Hz), 1.95 (s, 3H), 1.48 – 1.85 (m, 4H), 1.14 – 1.32 (m, 6H), 1.05 (t, 3H, J = 7.64 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 147.9, 98.4, 74.6, 63.6, 33.1, 27.5, 25.4, 24.6, 13.2, 12.6; EI MS (m/z) 177 [M^+]; HRMS calculated for $C_{12}H_{19}N$ [M^+] 177.15175, found 177.14983.

(1-Methylpent-2-ynylidene)(tetrahydrofuran-2-yl)amine (5.16d): colorless liquid; IR ν(C≡C) 2215 cm^{-1}, ν(C=N) 1619 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.91 (quintet, 1H, J = 6.2 Hz), 3.66 (quintet, 1H, J = 6.2 Hz), 3.54 (q, 1H, J = 6.8 Hz), 2.17 (q, 2H, J = 7.4 Hz), 1.94 (s, 3H), 1.60 – 1.87 (m, 4H), 0.98 (t, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 151.4, 99.7, 78.3, 74.6, 67.6, 59.8, 29.0, 27.3, 25.1, 13.0, 12.4; EI MS (m/z) 179 [M^+]; HRMS calculated for $C_{11}H_{17}N$ [M^+] 179.13101, found 179.13355.

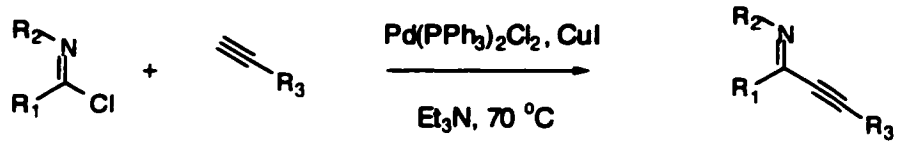
(1-Methylpent-2-ynylidene)phenethylamine (5.16e): colorless liquid; IR ν(C≡C) 2212 cm^{-1}, ν(C=N) 1615 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.18 – 7.28 (m, 5H), 3.78 (t, 2H, J = 7.8 Hz), 2.91 (t, 2H, J = 7.8 Hz), 2.32 (q, 2H, J = 7.4 Hz), 2.13 (s, 3H), 1.16 (t, 3H, J = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 151.0, 140.1, 128.6, 128.1, 125.7, 99.8, 74.6, 57.1, 36.7, 27.5, 13.3, 12.7; EI MS (m/z) 199 [M^+]; HRMS calculated for $C_{14}H_{17}N$ [M^+] 199.13610, found 199.13760.

Allyl-(1-methylpent-2-ynylidene)amine (5.16f): colorless liquid; IR ν(C≡C) 2216 cm^{-1}, ν(C=N) 1615 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.79 – 5.99 (m, 1H), 4.96 – 5.14 (m, 2H), 4.06 (d, 2H, J = 6.0 Hz), 2.29 (q, 2H, J = 7.4 Hz), 2.06 (s, 3H), 1.11 (t, 3H, J = 7.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 150.9, 135.4, 115.1, 99.8, 74.4, 57.9, 27.2, 12.9, 12.4; EI MS (m/z) 135 [M^+]; HRMS calculated for $C_9H_{13}N$ [M^+] 135.10480, found 135.10434.

Benzyl-(1-methylpent-2-ynylidene)amine (5.16g): colorless liquid; IR ν(C≡C) 2215 cm^{-1}, ν(C=N) 1614 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.30 – 7.34 (m, 5H), 4.76 (s, 2H), 2.41 (q, 2H, J = 7.6 Hz), 2.22 (s, 3H), 1.22 (t, 3H, J = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 151.3, 139.7, 128.2, 127.9, 126.6, 100.2, 74.9, 59.7, 27.7, 13.3, 12.8; EI MS (m/z) 185 [M^+]; HRMS calculated for $C_{13}H_{15}N$ [M^+] 185.12045, found 185.11989.

(1-Methylpent-2-ynylidene)(1-phenylethyl)amine (5.16h): colorless liquid; IR ν(C≡C) 2216 cm^{-1}, ν(C=N) 1608 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.17 – 7.45 (m, 5H), 5.03 (q, 1H, J = 6.6 Hz), 2.37 (q, 2H, J = 7.6 Hz), 2.20 (s, 3H), 1.51 (d, 2H, J = 6.6 Hz), 1.20 (t, 3H, J = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 148.8, 144.9, 127.9, 126.4, 126.2, 99.2, 74.7, 63.5, 27.5, 23.2, 13.1, 12.5; EI MS (m/z) 199 [M^+]; HRMS calculated for $C_{14}H_{17}N$ [M^+] 199.13610, found 199.13535.

8.5.2.5 General Procedure for the Pd/CuI Catalyzed Imidoyl Chloride to Terminal Alkyne Coupling.



5.14 **5.15** **5.16i - y**

To a 100 mL round bottom flask purged with N_2 was added triethylamine (40 mL), the terminal alkyne (**5.15**) (25 - 30 mmol), the imidoyl chloride (**5.14**) (20 mmol), $Pd(PPh_3)_2Cl_2$ (0.20 mmol), and CuI (0.25 mmol) at 70 ° C for 2 hours. Diethyl ether (40 mL) was added to the flask leading to the precipitation of $Et_3NH^+Cl^-$. This mixture was filtered, the filtrate evaporated, and the resulting residue was further purified by Kugelrohr distillation to give **5.16i – 5.16y** (Table 5-4).

Butyl(1-phenylhept-2-ynylidene)amine (5.16i): yellow liquid; IR ν(C≡C) 2211 cm^{-1}, ν(C=N) 1595 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 – 8.03 (m, 2H), 7.37 – 7.39 (m,3H), 3.82 (t, 2H, J = 7.1 Hz), 2.50 (t, 2H, J = 7.0 Hz), 1.73 (quintet, 2H, J = 7.1 Hz), 1.61 (quintet, 3H, J = 7.2 Hz), 1.41 – 1.53 (m, 4H), 0.97 (t, 3H, J = 7.3 Hz), 0.96 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.7, 138.0, 129.9, 128.0, 127.3, 100.6, 73.9, 32.7, 30.4, 22.0, 20.7, 19.0, 14.0, 13.5; EI MS (m/z) 241 [M^+]; HRMS calculated for $C_{17}H_{23}N$ [M^+] 241.18305, found 241.18072.

Butyl(4-methoxy-1-phenylbut-2-ynylidene)amine (5.16j): yellow liquid; IR ν(C≡C) 2208 cm^{-1}, ν(C=N) 1595 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99 – 8.03 (m, 2H), 7.31 – 7.37 (m,3H), 4.34 (s, 2H), 3.83 (t, 2H, J = 7.0 Hz), 3.42 (s, 3H), 1.73 (quintet,

2H, J = 7.4 Hz), 1.45 (sextet, 2H, J = 7.4 Hz), 0.96 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.4, 137.1, 130.0, 128.0, 127.1, 94.4, 78.6, 59.7, 57.6, 56.0, 32.5, 20.5, 13.8; EI MS (m/z) 229 [M^+]; HRMS calculated for $C_{15}H_{19}NO$ [M^+] 229.14666, found 229.14789.

Butyl(4-methyl-1-phenylpent-4-en-2-ynylidene)amine (5.16k): yellow liquid; IR ν(C≡C) 2199 cm^{-1}, ν(C=N) 1592 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 8.05 (m, 2H), 7.39 – 7.42 (m,3H), 5.55 (d, 1H, J = 1.7 Hz), 5.45 (d, 1H, J = 1.5 Hz), 3.87 (t, 2H, J = 7.0 Hz), 2.03 (s, 3H), 1.77 (quintet, 2H, J = 7.5 Hz), 1.47 (sextet, 2H, J = 7.5 Hz), 1.00 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.2, 137.5, 130.1, 128.1, 127.2, 125.7, 124.5, 99.1, 80.5, 56.1, 32.6, 23.0, 20.7, 13.9; EI MS (m/z) 225 [M^+]; HRMS calculated for $C_{16}H_{19}N$ [M^+] 225.15175, found 225.15039.

Butyl(4-methyl-1-phenylpent-2-ynylidene)amine (5.16l): yellow liquid; IR ν(C≡C) 2213 cm^{-1}, ν(C=N) 1595 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 8.03 (m, 2H), 7.36 – 7.39 (m,3H), 3.82 (t, 2H, J = 7.0 Hz), 2.86 (septet, 1H, J = 6.9 Hz), 1.74 (quintet, 2H, J = 7.5 Hz), 1.44 (sextet, 2H, J = 7.2 Hz), 1.31 (d, 6H, J = 6.9 Hz), 0.98 (t, 3H, J = 7.4 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.6, 137.9, 129.9, 128.0, 127.3, 105.7, 73.0, 55.8, 32.6, 22.6, 21.1, 20.7, 13.9; EI MS (m/z) 227 [M^+]; HRMS calculated for $C_{16}H_{21}N$ [M^+] 227.16740, found 227.16796.

Butyl(4-cyclohexyl-1-phenylbut-2-ynylidene)amine (5.16m): yellow liquid; IR ν(C≡C) 2213 cm^{-1}, ν(C=N) 1595 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 8.06 (m,

2H), 7.37 – 7.41 (m,3H), 3.85 (t, 2H, J = 7.2 Hz), 2.40 (d, 2H, J = 6.5 Hz), 1.70 – 1.90 (m, 8H), 1.47 (sextet, 2H, J = 7.5 Hz), 1.09 – 1.32 (m, 5H), 1.00 (t, 3H, J = 7.4 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.7, 138.0, 129.9, 127.9, 127.3, 99.5, 74.8, 56.0, 37.1, 32.6, 27.0, 26.1, 20.7, 13.9; EI MS (m/z) 281 [M^+]; HRMS calculated for $C_{20}H_{27}N$ [M^+] 281.21435, found 281.21268.

Butyl(4,4-dimethyl-1-phenylpent-2-ynylidene)amine (5.16n): yellow liquid; IR ν(C≡C) 2216 cm^{-1}, ν(C=N) 1595 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 8.05 (m, 2H), 7.36 – 7.41 (m,3H), 3.83 (t, 2H, J = 7.0 Hz), 1.74 (quintet, 2H, J = 7.2 Hz), 1.47 (sextet, 2H, J = 7.4 Hz), 1.38 (s, 9H), 1.00 (t, 3H, J = 7.4 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.6, 137.9, 129.8, 127.9, 127.2, 108.3, 72.3, 55.7, 32.5, 30.5, 28.1. 20.6, 13.9; EI MS (m/z) 241 [M^+]; HRMS calculated for $C_{17}H_{23}N$ [M^+] 241.18305, found 241.18306.

Butyl(1,3-diphenylprop-2-ynylidene)amine (5.16o): yellow oil; IR ν(C≡C) 2203 cm^{-1}, ν(C=N) 1595 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 – 8.13 (m, 2H), 7.59 – 7.62 (m, 2H), 7.40 – 7.45 (m, 6H), 3.96 (t, 2H, J = 7.0 Hz), 1.81 (quintet, 2H, J = 7.0 Hz), 1.50 (sextet, 2H, J = 7.5 Hz), 1.01 (t, 3H, J = 7.4 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.8, 138.1, 132.5, 130.7, 130.0, 129.0, 128.7, 127.8, 122.1, 98.6, 82.0, 56.8, 33.2, 21.2, 14.5; EI MS (m/z) 261 [M^+]; HRMS calculated for $C_{19}H_{19}N$ [M^+] 261.15175, found 261.15178.

Butyl[3-(4-methoxyphenyl)-1-phenylprop-2-ynylidene]amine (5.16p): yellow oil; IR ν(C≡C) 2198 cm^{-1}, ν(C=N) 1603 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 – 8.16 (m, 2H), 7.53 (d, 2H, J = 7.1 Hz), 7.42 – 7.47 (m, 3H), 6.91 (d, 2H, J = 7.1 Hz), 3.99 (t, 2H, J = 7.0 Hz), 3.79 (s, 3H), 1.84 (quintet, 2H, J = 7.2 Hz), 1.54 (sextet, 2H, J = 7.4 Hz), 1.05 (t, 3H, J = 7.4 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 160.5, 150.4, 137.7, 133.6, 130.0, 128.4, 127.2, 114.0, 113.4, 98.6, 80.8,. 56.0, 55.1, 32.7, 20.7, 13.9; EI MS (m/z) 291 [M^+]; HRMS calculated for $C_{20}H_{21}NO$ [M^+] 291.16231, found 291.15940.

Isopropyl(1-phenylhept-2-ynylidene)amine (5.16q): yellow liquid; IR ν(C≡C) 2205 cm^{-1}, ν(C=N) 1594 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 – 8.03 (m, 2H), 7.35 – 7.40 (m, 3H), 4.22 (septet, 1H, J = 6.3 Hz), 2.49 (t, 2H, J = 7.1 Hz), 1.61 (quintet, 2H, J = 6.9 Hz), 1.49 (sextet, 2H, J = 7.1 Hz), 1.26 (d, 6H, J = 6.3 Hz), 0.96 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 148.5, 138.1, 129.8, 127.9, 127.4, 99.8, 73.7, 55.7, 30.3, 23.3, 21.9, 18.9, 13.4; EI MS (m/z) 227 [M^+]; HRMS calculated for $C_{16}H_{21}N$ [M^+] 227.16740, found 227.16659.

Isopropyl(1-*p*-tolylhept-2-ynylidene)amine (5.16r): yellow liquid; IR ν(C≡C) 2204 cm^{-1}, ν(C=N) 1590 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, 2H, J = 8.0 Hz), 7.18 (d, 2H, J = 7.9 Hz), 4.22 (septet, 1H, J = 6.3 Hz), 2.49 (t, 2H, J = 7.1 Hz), 2.37 (s, 3H), 1.64 (quintet, 2H, J = 7.1 Hz), 1.51 (sextet, 2H, J = 7.1 Hz), 1.26 (d, 6H, J = 6.3 Hz) 0.97 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 148.4, 139.9, 135.5, 128.6, 127.3, 99.5, 73.8, 55.6, 30.3, 23.4, 21.9, 21.2, 18.9, 13.4; EI MS (m/z) 241 [M^+]; HRMS calculated for $C_{17}H_{23}N$ [M^+] 241.18305, found 241.18199.

Isopropyl[1-(4-methoxyphenyl)hept-2-ynylidene]amine (5.16s): yellow liquid; IR ν(C≡C) 2204 cm^{-1}, ν(C=N) 1606 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, 2H, J = 8.9 Hz), 6.86 (d, 2H, J = 8.9 Hz), 4.16 (septet, 1H, J = 6.3 Hz), 3.77 (s, 3H), 2.46 (t, 2H, J = 7.1 Hz), 1.58 (quintet, 2H, J = 7.2 Hz), 1.47 (sextet, 2H, J = 7.2 Hz), 1.22 (d, 6H, J = 6.3 Hz) 0.94 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 161.0, 147.7, 131.0, 128.8, 113.2, 99.4, 73.7, 55.4, 55.1, 30.3, 23.4, 21.9, 18.8, 13.4; EI MS (m/z) 257 [M^+]; HRMS calculated for $C_{17}H_{23}NO$ [M^+] 257.17796, found 257.18002.

Isopropyl[1-(4-chlorophenyl)hept-2-ynylidene]amine (5.16t): yellow liquid; IR ν(C≡C) 2204 cm^{-1}, ν(C=N) 1591 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, 2H, J = 8.8 Hz), 7.32 (d, 2H, J = 8.8 Hz), 4.17 (septet, 1H, J = 6.3 Hz), 2.47 (t, 2H, J = 7.1 Hz), 1.60 (quintet, 2H, J = 7.0 Hz), 1.47 (sextet, 2H, J = 7.2 Hz), 1.22 (d, 6H, J = 6.3 Hz) 0.94 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 147.3, 136.6, 135.9, 128.7, 128.1, 100.2, 73.3, 55.8, 30.3, 23.3, 21.9, 18.9, 13.4; EI MS (m/z) 261 [M^+]; HRMS calculated for $C_{16}H_{20}NCl$ [M^+] 261.12843, found 261.12842.

Isopropyl[1-(naphthalene-2-yl)hept-2-ynylidene]amine (5.16u): yellow oil; IR ν(C≡C) 2216 cm^{-1}, ν(C=N) 1584 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.27 (dd, 1H, J = 8.7, 1.7 Hz), 7.96 (dd, 1H, J = 5.9, 3.6 Hz), 7.83 – 7.87 (m, 2H), 7.48 – 7.54 (m, 2H), 4.36 (septet, 1H, J = 6.3 Hz), 2.57 (t, 2H, J = 7.0 Hz), 1.69 (quintet, 2H, J = 6.9 Hz), 1.57 (sextet, 2H, J = 7.1 Hz), 1.31 (d, 6H, J = 6.3 Hz), 1.03 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 148.5, 135.6, 134.2, 132.8, 128.7, 128.2, 127.6, 127.5, 126.6,

126.0, 124.1, 100.0, 73.8, 55.9, 30.3, 23.4, 21.9, 19.0, 13.5; EI MS (m/z) 277 [M^+]; HRMS calculated for $C_{20}H_{23}N$ [M^+] 277.18305, found 277.18157.

Isopropyl[1-(4-nitrophenyl)hept-2-ynylidene]amine (5.16v): yellow oil; IR ν(C≡C) 2205 cm^{-1}, ν(C=N) 1576 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, 2H, J = 9.0 Hz), 8.11 (d, 2H, J = 9.0 Hz), 4.18 (septet, 1H, J = 6.3 Hz), 2.49 (t, 2H, J = 7.1 Hz), 1.62 (quintet, 2H, J = 7.3 Hz), 1.46 (sextet, 2H, J = 7.1 Hz), 1.22 (d, 6H, J = 6.3 Hz), 0.93 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 148.6, 146.6, 143.5, 128.3, 123.1, 101.4, 73.0, 56.3, 30.2, 23.2, 22.0, 18.9, 13.4; EI MS (m/z) 272 [M^+]; HRMS calculated for $C_{16}H_{20}N_2O_2$ [M^+] 272.15248, found 272.15421.

(1-Isopropylhept-2-ynylidene)phenylamine (5.16w): yellow liquid; IR ν(C≡C) 2215 cm^{-1}, ν(C=N) 1609 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (t, 2H, J = 7.4 Hz), 7.04 (t, 1H, J = 7.4 Hz), 6.90 (d, 2H, J = 7.3 Hz), 2.75 (septet, 1H, J = 6.9 Hz), 2.17 (t, 2H, J = 7.0 Hz), 1.31 (quintet, 2H, J = 6.8 Hz), 1.24 (d, 6H, J = 6.9 Hz), 1.16 (sextet, 2H, J = 7.0 Hz), 0.78 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 160.7, 151.7, 128.2, 123.8, 120.2, 99.5, 74.8, 38.9, 29.8, 21.4, 19.9, 18.7, 13.3; EI MS (m/z) 227 [M^+]; HRMS calculated for $C_{16}H_{21}N$ [M^+] 227.16740, found 227.16798.

(1-Isopropylhept-2-ynylidene)-*p*-tolylamine (5.16x): yellow liquid; IR ν(C≡C) 2216 cm^{-1}, ν(C=N) 1604 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, 2H, J = 8.3 Hz), 6.84 (d, 2H, J = 8.3 Hz), 2.74 (septet, 1H, J = 6.8 Hz), 2.30 (s, 3H), 2.20 (t, 2H, J = 6.9 Hz), 1.32 (quintet, 2H, J = 6.9 Hz), 1.23 (d, 6H, J = 6.8 Hz), 1.21 (sextet, 2H, J = 7.3

Hz), 0.81 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 160.3, 148.9, 133.2, 128.7, 120.2, 99.3, 74.8, 39.0, 29.8, 21.4, 20.8, 19.9, 18.7, 13.3; EI MS (m/z) 241 [M^+]; HRMS calculated for $C_{17}H_{23}N$ [M^+] 241.18305, found 241.18407.

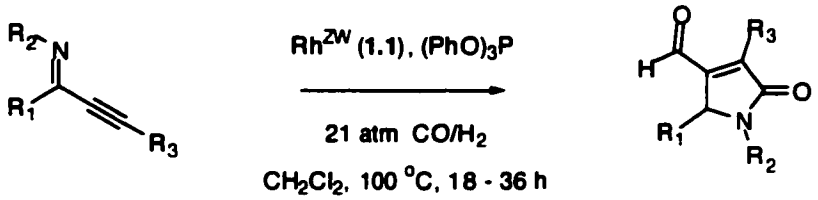
(4-Chlorophenyl)(1-isopropylhept-2-ynylidene)amine (5.16y): yellow liquid; IR ν(C≡C) 2216 cm^{-1}, ν(C=N) 1607 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, 2H, J = 8.6 Hz), 6.81 (d, 2H, J = 8.6 Hz), 2.71 (septet, 1H, J = 6.9 Hz), 2.18 (t, 2H, J = 6.9 Hz), 1.31 (quintet, 2H, J = 7.0 Hz), 1.20 (d, 6H, J = 6.9 Hz), 1.16 (sextet, 2H, J = 7.0 Hz), 0.79 (t, 3H, J = 7.1 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 161.6, 150.3, 129.1, 128.3, 121.7, 100.3, 74.7, 38.9, 29.8, 21.5, 19.9, 18.7, 13.3; EI MS (m/z) 261 [M^+]; HRMS calculated for $C_{16}H_{20}NCl$ [M^+] 261.12843, found 261.12629.

8.5.3 Cyclohydrocarbonylative/CO Insertion of Acetylenic Imines: Optimization of Reaction Conditions.

To a 45 mL autoclave containing a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.03 mmol), triphenyl phosphite (0.12 mmol), acetylenic imine **5.16b** (1.5 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times with carbon monoxide, pressurized from 17.5 to 38.5 atm followed by the introduction of hydrogen to a total pressure of 21 to 42 atm. The autoclave was placed in an oil bath at 80 to 100 °C for 20 hours, and then was allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture was filtered through

Celite, and the solvent was removed by rotary evaporation. The percent conversion and the ratio of **5.17b/5.18b** were determined by ^{1}H NMR. The results on reaction optimization are given in Table 5-5.

8.5.4 General Procedure for the Cyclohydrocarbonylative/CO Insertion of Acetylenic Imines Where R_1 is an Alkyl Group.



5.16 **5.18**

To a 45 mL autoclave containing a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.03 mmol), triphenyl phosphite (0.12 mmol), acetylenic imine **5.16** (1.5 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times with carbon monoxide, pressurized from 17.5 atm followed by the introduction of hydrogen to a total pressure of 21 atm. The autoclave was placed in an oil bath at 80 to 100 °C for 18 to 36 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through Celite, and the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel chromatography using a ethyl acetate:hexanes gradient ranging from 33:67 to 50:50 as the eluant to afford **5.18** (Table 5-6).

3-Ethyl-5-methyl-1-isopropyl-3-pyrrolin-2-one (5.17b): colorless liquid; IR ν(C=O) 1683 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.47 (d, 1H, J = 1.9 Hz), 4.05 (septet, 1H, J = 6.5 Hz), 3.78 (qd, 1H, J = 6.9, 1.9 Hz), 2.28 (q, 2H, J = 7.4 Hz), 1.33 (d, 6H, J = 6.3 Hz), 1.12 (d, 3H, J = 6.9 Hz), 1.11 (t, 3H, J = 7.5 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 171.0, 159.6, 118.1, 45.4, 21.7, 20.1, 19.9, 11.1, 8.5; EI MS (m/z) 167 [M^+]; HRMS calculated for $C_{10}H_{17}NO$ [M^+] 167.13101, found 167.13306.

3-Ethyl-5-methyl-1-phenethyl-3-pyrrolin-2-one (5.17e): colorless liquid; IR ν(C=O) 1683 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.29 (m, 5H), 6.47 (d, 1H, J = 1.9 Hz), 3.96 (t, 1H, J = 7.4 Hz), 3.78 (qd, 1H, J = 6.9, 1.9 Hz), 3.26 (t, 1H, J = 7.4 Hz), 2.82 – 2.88 (m, 2H), 2.28 (q, 2H, J = 7.4 Hz), 1.12 (d, 3H, J = 6.9 Hz), 1.11 (t, 3H, J = 7.5 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 171.0, 140.5, 139.8, 139.1, 128.7, 128.5, 126.3, 56.1, 41.4, 36.1, 18.8, 16.7, 11.7; EI MS (m/z) 229 [M^+]; HRMS calculated for $C_{15}H_{15}NO$ [M^+] 229.14666, found 229.14360.

1-Butyl-4-carbaldehyde-3-ethyl-5-methyl-3-pyrrolin-2-one (5.18a): colorless liquid; IR ν_1(C=O) 1727 cm^{-1}, ν_2(C=O) 1644 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.71 (s, 1H), 3.55 (t, 1H, J = 7.7 Hz), 3.45 (t, 1H, J = 7.7 Hz), 3.30 (m, 1H), 2.38 (br, 3H), 2.01 (m, 2H), 1.52 (q, 2H, J = 7.7 Hz), 1.32 (sextet, 2H, J = 7.7 Hz), 0.92 (t, 3H, J = 7.4 Hz), 0.71 (t, 3H, J = 7.5 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 182.9, 180.1, 159.9, 118.8, 46.0, 40.5, 31.9, 22.5, 20.7, 14.3, 11.4, 9.6; EI MS (m/z) 209 [M^+]; HRMS calculated for $C_{12}H_{19}NO_2$ [M^+] 209.14158, found 209.14173.

4-Carbaldehyde-3-ethyl-1-isopropyl-5-methyl-3-pyrrolin-2-one (5.18b): colorless liquid; IR ν_1(C=O) 1725 cm^{-1}, ν_2(C=O) 1641 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.61 (s, 1H), 4.05 (septet, 1H, J = 6.5 Hz), 3.17 (m, 1H), 2.32 (br, 3H), 1.92 (m, 2H), 1.35 (d, 3H, J = 6.2 Hz), 1.33 (d, 3H, J = 6.3 Hz), 0.61 (t, 3H, J = 7.5 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 182.3, 179.6, 159.6, 118.1, 45.4, 21.7, 20.1, 19.9, 11.1, 8.5; EI MS (m/z) 195 [M^+]; HRMS calculated for $C_{11}H_{17}NO_2$ [M^+] 195.12593, found 195.12707.

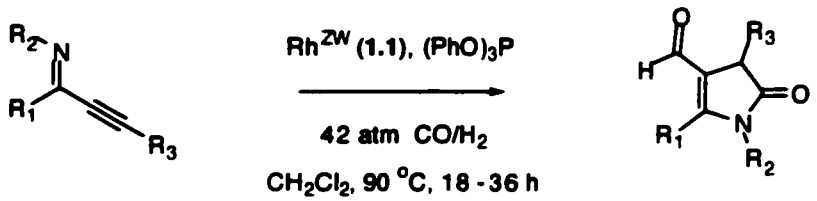
4-Carbaldehyde-1-cyclohexyl-3-ethyl-5-methyl-3-pyrrolin-2-one (5.18c): colorless liquid; IR ν_1(C=O) 1723 cm^{-1}, ν_2(C=O) 1642 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.67 (s, 1H), 3.59 (m, 1H), 3.23 (m, 1H), 2.36 (br, 3H), 1.57 – 2.22 (m, 8H), 1.18 – 1.30 (m, 4H), 0.65 (t, 3H, J = 7.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 182.5, 179.8, 159.8, 118.2, 54.1, 45.5, 29.9, 29.7, 26.0, 24.9, 21.9, 11.4, 8.6; EI MS (m/z) 235 [M^+]; HRMS calculated for $C_{14}H_{21}NO_2$ [M^+] 235.15723, found 235.15558.

4-Carbaldehyde-3-ethyl-5-methyl-1-(tetrahydrofuran-2-ylmethyl)-3-pyrrolin-2-one (5.18d): yellow liquid; IR ν_1(C=O) 1726 cm^{-1}, ν_2(C=O) 1642 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.67 (s, 1H), 3.95 (m, 1H), 3.59 – 3.82 (m, 3H), 3.26 – 3.46 (m, 2H), 2.39 (br, 3H), 1.75 – 2.09 (m, 6H), 0.68 (t, 3H, J = 7.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 182.6, 179.8, 160.6, 118.0, 77.1, 68.0, 45.4, 44.1, 29.0, 25.5, 21.8, 11.0, 9.1; EI MS (m/z) 237 [M^+]; HRMS calculated for $C_{13}H_{19}NO_3$ [M^+] 237.13649, found 237.13525.

4-Carbaldehyde-3-ethyl-5-methyl-1-phenethyl-3-pyrrolin-2-one (5.18e): yellow liquid; IR ν_1(C=O) 1725 cm^{-1}, ν_2(C=O) 1642 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.10 – 7.27 (m, 5H), 3.62 – 3.79 (m, 2H), 2.90 (m, 1H),. 2.86 (t, 2H, J = 6.6 Hz), 1.99 (q, 2H, J = 7.4 Hz), 1.95 (br, 3H), 0.74 (t, 3H, J = 7.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 182.4, 179.5, 159.4, 137.8, 129.8, 128.9, 127.0, 118.0, 45.4, 42.1, 35.1, 21.8, 10.3, 9.3; EI MS (m/z) 257 [M^+]; HRMS calculated for $C_{16}H_{19}NO_2$ [M^+] 257.14158, found 257.14301.

1,3-Dibutyl-4-carbaldehyde--5-phenyl-4-pyrrolin-2-one (5.18i): yellow liquid; IR ν_1(C=O) 1727 cm^{-1}, ν_2(C=O) 1649 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.12 (s, 1H), 7.44 – 7.48 (m, 3H), 7.32 – 7.38 (m, 2H), 3.31 – 3.43 (m, 3H), 1.98 (q, 2H, J = 7.2 Hz), 1.18 – 1.28 (m, 6H), 1.03 (sextet, 2H, J = 7.7 Hz), 0.79 (t, 3H, J = 7.1 Hz), 0.65 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 184.6, 179.3, 161.7, 130.3, 128.8, 128.5, 126.9, 119.9, 44.6, 40.1, 30.3, 28.3, 26.7, 22.3, 19.3, 13.5, 13.0; EI MS (m/z) 299 [M^+]; HRMS calculated for $C_{19}H_{25}NO_2$ [M^+] 299.18853, found 299.18708. Anal. calcd for $C_{19}H_{25}NO_2$: C, 76.22; H, 8.42; N, 4.68. Found: C, 76.10; H, 8.30; N, 4.46 .

8.5.5 General Procedure for the Cyclohydrocarbonylative/CO Insertion of Acetylenic Imines Where R_1 is an Aryl Group.



5.16 **5.18**

To a 45 mL autoclave containing a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.03 mmol), triphenyl phosphite (0.12 mmol), acetylenic imine **5.16** (1.5 mmol), and CH_2Cl_2 (10 mL). The autoclave was flushed three times with carbon monoxide, pressurized from 38.5 atm followed by the introduction of hydrogen to a total pressure of 42 atm. The autoclave was placed in an oil bath at 75 to 90 °C for 18 to 36 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through Celite, and the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel chromatography using a ethyl acetate:hexanes gradient ranging from 33:67 to 50:50 as the eluant to afford **5.18** (Tables 5-7 and 5-8).

1-Butyl-3-isopropylidene-5-phenyl-4-pyrrolin-2-one (5.17k): yellow liquid; IR ν(C=O) 1687 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.40 (m, 5H), 5.74 (s, 1H), 3.58 (t, 2H, J = 7.4 Hz), 2.44 (s, 3H), 2.05 (s, 3H), 1.36 (quintet, 2H, J = 7.4 Hz), 1.14 (sextet, 2H, J = 7.2 Hz), 0.75 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 168.7, 150.4,

142.6, 132.3, 129.8, 128.5, 127.7, 120.0, 100.9, 40.2, 31.1, 24.0, 20.7, 19.9, 13.6; EI MS (m/z) 255 [M^+]; HRMS calculated for $C_{17}H_{21}NO$ [M^+] 255.16231, found 255.16115.

3-Butyl-5-(4-chlorophenyl)-1-isopropyl-3-pyrrolin-2-one (5.17t): yellow liquid; IR ν(C=O) 1684 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, 2H, J = 8.5 Hz), 7.08 (d, 2H, J = 8.4 Hz), 6.42 (d, 1H, J = 1.7 Hz), 4.92 (d, 1H, J = 1.8 Hz), 4.13 (septet, 1H, J = 6.9 Hz), 2.27 (t, 2H, J = 6.9 Hz), 1.50 (quintet, 2H, J = 7.2 Hz), 1.33 (sextet, 2H, J = 7.3 Hz), 1.19 (d, 6H, J = 6.9 Hz), 0.88 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 172.1, 139.7, 139.0, 136.0, 133.9, 128.9, 128.6, 62.9, 44.8, 29.5, 25.1, 22.4, 21.2, 20.7, 13.8; EI MS (m/z) 291 [M^+]; HRMS calculated for $C_{17}H_{22}NOCl$ [M^+] 291.13899, found 291.13583.

3-Butyl-1-isopropyl 5-(naphthalen-2-yl)-3-pyrrolin-2-one (5.17u): yellow oil; IR ν(C=O) 1680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.82 (m, 3H), 7.72 (s, 1H), 7.43 – 7.51 (m, 2H), 7.11 – 7.23 (m, 1H), 6.51 (d, 1H, J = 1.7 Hz), 5.13 (d, 1H, J = 1.7 Hz), 4.20 (septet, 1H, J = 6.9 Hz), 2.35 (t, 2H, J = 7.4 Hz), 1.52 (quintet, 2H, J = 7.4 Hz), 1.37 (sextet, 2H, J = 7.5 Hz), 1.20 (d, 6H, J = 6.9 Hz), 0.91 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 172.1, 139.9, 138.9, 134.7, 133.2, 129.7, 128.5, 127.7, 126.7, 126.3, 125.5, 124.2, 120.0, 63.8, 44.8, 29.5, 25.1, 22.3, 21.2, 20.7, 13.8; EI MS (m/z) 307 [M^+]; HRMS calculated for $C_{21}H_{25}NO$ [M^+] 307.19361, found 307.19552.

3-Butyl-1-isopropyl 5-(4-nitrophenyl)-3-pyrrolin-2-one (5.17v): yellow oil; IR ν(C=O) 1684 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, 2H, J = 8.7 Hz), 7.35 (d, 2H, J

= 8.7 Hz), 6.45 (d, 1H, J = 1.7 Hz), 5.06 (d, 1H, J = 1.8 Hz), 4.17 (septet, 1H, J = 6.9 Hz), 2.27 (t, 2H, J = 7.1 Hz), 1.50 (quintet, 2H, J = 7.2 Hz), 1.33 (sextet, 2H, J = 7.3 Hz), 1.20 (d, 6H, J = 6.9 Hz), 0.87 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 172.1, 147.8, 145.4, 139.8, 139.0, 128.0, 124.1, 62.6, 45.1, 29.4, 25.1, 22.3, 21.4, 20.8, 13.8; EI MS (m/z) 302 [M^+]; HRMS calculated for $C_{17}H_{22}N_2O_3$ [M^+] 302.16304, found 302.16390.

1-Butyl-4-carbaldehyde-3-methyl-5-phenyl-4-pyrrolin-2-one (5.18j): yellow liquid; IR ν_1(C=O) 1730 cm^{-1}, ν_2(C=O) 1648 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.51 – 7.53 (m, 3H), 7.39 – 7.41 (m, 2H), 3.39 – 3.42 (m, 3H), 1.47 (d, 3H, J = 7.6 Hz), 1.32 (q, 2H, J = 7.4 Hz), 1.08 (sextet, 2H, J = 7.3 Hz), 0.72 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.0, 180.3, 161.7, 130.7, 129.2, 128.9, 127.2, 122.2, 40.4, 40.0, 30.7, 19.6, 14.9, 13.4; EI MS (m/z) 257 [M^+]; HRMS calculated for $C_{16}H_{19}NO_2$ [M^+] 257.14158, found 257.14055.

1-Butyl-4-carbaldehyde-3-isopropylidene-5-phenyl-4-pyrrolin-2-one (5.18k): yellow liquid; IR ν_1(C=O) 1730 cm^{-1}, ν_2(C=O) 1648 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.16 (s, 1H), 7.46 – 7.49 (m, 3H), 7.33 – 7.36 (m, 2H), 3.43 (t, 2H, J = 7.5 Hz), 2.50 (s, 3H), 2.46 (s, 3H), 1.33 (quintet, 2H, J = 7.5 Hz), 1.10 (sextet, 2H, J= 7.6 Hz), 0.70 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 184.3, 167.3, 161.3, 160.8, 130.2, 129.5, 128.6, 128.0, 127.7, 121.6, 115.3, 40.6, 30.9, 28.0, 23.7, 19.7, 13.3; EI MS (m/z) 283 [M^+]; HRMS calculated for $C_{18}H_{21}NO_2$ [M^+] 283.15723, found 283.15525.

1-Butyl-4-carbaldehyde-3-isopropyl-5-phenyl-4-pyrrolin-2-one (5.18l): yellow liquid; IR ν_1(C=O) 1726 cm^{-1}, ν_2(C=O) 1649 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.46 – 7.52 (m, 3H), 7.35 – 7.38 (m, 2H), 3.47 (m, 1H), 3.35 (d, 1H, J = 3.3 Hz), 2.63 (septet, 1H, J = 6.9 Hz), 1.36 (m, 1H), 1.28 (quintet, 2H, J = 6.9 Hz), 1.18 (d, 3H, J = 7.0 Hz), 1.07 (sextet, 2H, J = 7.5 Hz), 0.86 (d, 3H, J = 7.0 Hz), 0.67 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.0, 178.5, 162.9, 130.6, 129.1, 128.8, 127.3, 119.8, 50.5, 40.3, 30.7, 29.2, 19.7, 19.4, 17.5, 13.3; EI MS (m/z) 285 [M^+]; HRMS calculated for $C_{18}H_{23}NO_2$ [M^+] 285.17288, found 285.17165. Anal. calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.61; H, 8.08; N, 4.74 .

1-Butyl-4-carbaldehyde-3-cyclohexylmethyl-5-phenyl-4-pyrrolin-2-one (5.18m): yellow liquid; IR ν_1(C=O) 1727 cm^{-1}, ν_2(C=O) 1649 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 1H), 7.47 – 7.54 (m, 3H), 7.34 – 7.38 (m, 2H), 3.29 – 3.50 (m, 3H), 1.78 – 1.94 (m, 2H), 1.51 – 1.68 (m, 7H), 0.90 – 1.36 (m, 8H), 0.71 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.0, 179.9, 161.5, 130.6, 129.1, 128.8, 127.4, 121.3, 43.0, 40.0, 36.8, 34.7, 33.9, 32.9, 30.6, 26.4, 26.2, 26.1, 19.7, 13.4; EI MS (m/z) 339 [M^+]; HRMS calculated for $C_{22}H_{29}NO_2$ [M^+] 339.21983, found 339.21833. Anal. calcd for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.64; H, 8.75; N, 4.01 .

3-Butyl-4-carbaldehyde-1-isopropyl-5-phenyl-4-pyrrolin-2-one (5.18q): yellow liquid; IR ν_1(C=O) 1726 cm^{-1}, ν_2(C=O) 1648 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.46 – 7.51 (m, 3H), 7.31 – 7.36 (m, 2H), 3.69 (septet, 1H, J = 6.9 Hz),), 3.38 (t, 1H, J = 5.5 Hz), 2.00 (m, 2H), 1.34 (d, 3H, J = 6.9 Hz), 1.28 (d, 3H, J = 6.9 Hz),

1.11 – 1.26 (m, 4H), 0.82 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.0, 179.9, 162.8, 130.5, 129.3, 129.0, 128.8, 127.6, 120.2, 46.8, 45.3, 28.6, 26.7, 22.5, 20.0, 19.6, 13.8; EI MS (m/z) 285 [M^+]; HRMS calculated for $C_{18}H_{23}NO_2$ [M^+] 285.17288 found 285.17136. Anal. calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91. Found: C, 75.91; H, 7.92; N, 4.84 .

3-Butyl-4-carbaldehyde-1-isopropyl-5-*p*-tolyl-4-pyrrolin-2-one (5.18r): yellow liquid; IR ν_1(C=O) 1727 cm^{-1}, ν_2(C=O) 1648 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.30 (d, 2H, J = 8.2 Hz), 7.23 – 7.25 (m, 2H), 3.73 (septet, 1H, J = 6.9 Hz), 3.40 (t, 1H, J = 5.2 Hz), 2.42 (s, 3H), 1.98 – 2.07 (m, 2H), 1.36 (d, 3H, J = 6.9 Hz), 1.30 (d, 3H, J = 6.9 Hz), 1.10 – 1.26 (m, 4H), 0.84 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.3, 180.1, 163.2, 140.9, 129.5, 129.3, 128.9, 124.6, 120.2, 46.8, 45.3, 28.7, 26.7, 22.6, 21.4, 20.0, 19.6, 13.8; EI MS (m/z) 299 [M^+]; HRMS calculated for $C_{19}H_{25}NO_2$ [M^+] 299.18853 found 299.18709.

3-Butyl-4-carbaldehyde-1-isopropyl-5-(4-methoxyphenyl)-4-pyrrolin-2-one (5.18s): yellow liquid; IR ν_1(C=O) 1725 cm^{-1}, ν_2(C=O) 1646 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.25 – 7.27 (m, 2H), 7.00 (d, 2H, J = 8.9 Hz), 3.85 (s, 3H), 3.76 (septet, 1H, J = 6.9 Hz),), 3.39 (m, 1H), 2.00 (m, 2H), 1.37 (d, 3H, J = 6.9 Hz), 1.31 (d, 3H, J = 6.8 Hz), 1.10 – 1.26 (m, 4H), 0.84 (t, 3H, J = 7.3 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.3, 180.1, 163.0, 161.3, 130.9, 130.5, 120.3, 119.5, 114.3, 55.4, 46.7, 45.4, 28.7, 26.8, 22.6, 20.0, 19.7, 13.9; EI MS (m/z) 315 [M^+]; HRMS calculated for

$C_{17}H_{25}NO_3$ [M^+] 315.18344 found 315.18192. Anal. calcd for $C_{17}H_{25}NO_3$: C, 72.35; H, 7.99; N, 4.44. Found: C, 72.17; H, 7.93; N, 4.36 .

3-Butyl-4-carbaldehyde-1-isopropyl-5-(4-chlorophenyl)-4-pyrrolin-2-one (5.18t): yellow oil; IR ν_1(C=O) 1726 cm^{-1}, ν_2(C=O) 1649 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.10 (s, 1H), 7.50 (d, 2H, J = 8.7 Hz), 7.28 – 7.33 (m, 2H), 3.69 (septet, 1H, J = 6.9 Hz),), 3.41 (t, 1H, J = 5.4 Hz), 1.97 - 2.07 (m, 2H), 1.36 (d, 3H, J = 6.9 Hz), 1.31 (d, 3H, J = 6.9 Hz), 1.10 – 1.27 (m, 4H), 0.84 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 184.6, 179.8, 161.3, 137.0, 130.7, 130.4, 129.8, 129.3, 126.1, 120.7, 46.9, 45.4, 28.7, 26.8, 22.6, 20.1, 19.8, 13.9; EI MS (m/z) 319 [M^+]; HRMS calculated for $C_{18}H_{22}NO_2Cl$ [M^+] 319.13391 found 319.13476.

3-Butyl-4-carbaldehyde-1-isopropyl-5-(2-naphthalenyl)-4-pyrrolin-2-one (5.18u): yellow oil; IR ν_1(C=O) 1725 cm^{-1}, ν_2(C=O) 1647 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.17 (s, 1H), 7.88 – 7.99 (m, 4H), 7.53 – 7.63 (m, 2H), 7.36 – 7.42 (m, 1H), 3.77 (septet, 1H, J = 6.8 Hz),), 3.44 – 3.51 (m, 1H), 2.00 - 2.14 (m, 2H), 1.16 – 1.45 (m, 10H), 0.89 (t, 1.5H, J = 6.7 Hz), 0.87 (t, 1.5H, J = 6.6 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 185.3, 185.1, 180.0, 162.9, 162.8, 133.7, 132.5, 129.8, 129.6, 128.9, 128.8, 128.3, 127.9, 127.4, 125.4, 125.0, 124.9, 120.6, 47.1, 47.0, 45.5, 28.9, 28.7, 26.9, 26.8, 22.6, 20.1, 20.0, 19.8, 19.6, 13.9; EI MS (m/z) 335 [M^+]; HRMS calculated for $C_{22}H_{25}NO_2$ [M^+] 35.18853 found 335.18905. Anal. calcd for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 79.00; H, 7.15; N, 3.87 .

8.5.6 General Procedure for Re-introducing 5.17 to a CO/H_2 or CO Atmosphere

To a 45 mL autoclave containing a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.02 mmol), triphenyl phosphite (0.08 mmol), pyrrolin-2-one **5.17** (1.0 mmol), and CH_2Cl_2 (7 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 38.5 atm followed by the introduction of hydrogen to a total pressure of to 42 atm, or pressurized to 42 atm with only CO. The autoclave was placed in an oil bath at 90 °C for 24 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture was filtered through Celite, and the solvent was removed by rotary evaporation. The percent conversion to **5.18** was then evaluated by ^{1}HNMR.

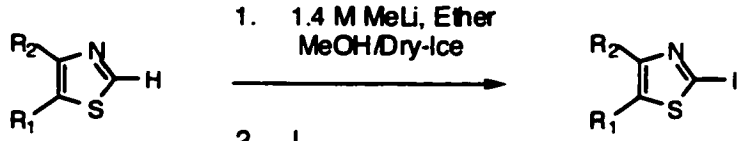
8.6 Experimental for Chapter 6

8.6.1 Materials

2-Bromothiazole was purchased from Alfa Aesar, all thiazoles were purchased from Aldrich, and terminal alkynes were purchased from GFS Chemicals. The rhodium complexes chlorobis(ethylene)rhodium(I) dimer, chlorodicarbonylrhodium(I) dimer, dicarbonylrhodium(I) acetoacetonate, and rhodium(III) chloride as well as dichlorobis(triphenylphosphine)palladium(II) were purchased from Strem Chemicals. The zwitterionic rhodium complex (η^6-$C_6H_5BPh_3$)$^-Rh^+$(1,5-COD) (**1.1**) was prepared according to the procedure of Schrock and Osborn.[1]

8.6.2 Synthesis of Starting Materials

8.6.2.1 General Procedure for the Preparation of Substituted 2-Iodothiazoles.



6.6 **6.7**

To a 250 mL round bottom flask purged with N_2 was added ether (100 mL) and the thiazole (50 mmol), and the mixture was cooled in a dry-ice/MeOH bath. An excess amount of 1.4 M MeLi (40 mL) was added over a 15 minute time period followed by I_2 (60 mmol), and the reaction mixture was allowed to warm to room temperature. The reaction mixture was transferred to a separatory funnel, ether (300 mL) was added, and

then the organic layer was washed with water (100 mL) and brine (50 mL), dried over anhydrous $MgSO_4$, and evaporated. The product (**6.7**) was isolated by silica gel chromatography using CH_2Cl_2 as eluant, and further purified by sublimation (Table 6-2).

2-Iodo-4-methylthiazole (6.7b): tan solid; mp 62 - 64 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.80 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 155.3, 119.8, 99.4, 16.9; EI MS (m/z) 225 [M^+]; HRMS calculated for C_4H_4NSI [M^+] 224.91092, found 224.91157.

2-Iodo-4,5-dimethylthiazole (6.7c): tan solid; mp 85 – 87 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.30 (s, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 150.8, 132.7, 95.0, 14.5, 11.0; EI MS (m/z) 239 [M^+]; HRMS calculated for C_5H_6NSI [M^+] 238.92657, found 238.92819.

5-(2-Chloroethyl)-4-methylthiazole: To a 100 mL round bottom flask was added 4-methyl-5-thiazoleethanol (60 mmol) and $SOCl_2$ (40 mL), and the mixture was heated to reflux. After 2 hours the excess $SOCl_2$ was removed by rotary evaporation, and the resulting solid was washed with three 50 mL portions of ether. The solid was dissolved in distilled water (50 mL) and transferred to a 500 mL separatory funnel with 200 mL additional ether. Saturated $NaHCO_3$ was added until the pH was 10, and no color remained in the aqueous layer. The organic layer was separated, dried over anhydrous $MgSO_4$, and the solvent was removed by rotary evaporation. The residue was further purified by Kugelrohr distillation to give a colorless liquid (96 % isolated yield).

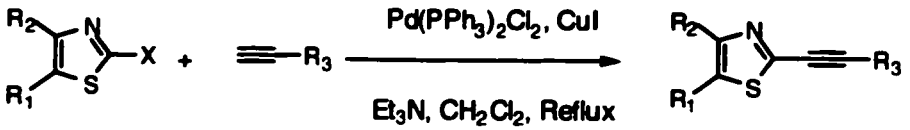
^{1}H NMR (200 MHz, $CDCl_3$) δ 8.52 (s, 1H), 3.57 (t, 2H, J = 7.0 Hz), 3.12 (t, 2H, J = 7.0 Hz), 2.32 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 149.9, 149.8, 126.9, 44.1, 29.4, 14.7; EI MS (m/z) 161 [M^+]; HRMS calculated for C_6H_8NClS [M^+] 161.00660, found 161.00601.

5-(2-Chloroethyl)-2-iodo-4-methylthiazole (6.7d): tan solid, mp 105 – 107 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.59 (t, 2H, J = 6.8 Hz), 3.14 (t, 2H, J = 6.8 Hz), 2.33 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 151.9, 133.7, 97.1, 43.9, 29.5, 14.9; EI MS (m/z) 287 [M^+]; HRMS calculated for C_6H_7NClSI [M^+] 286.90324, found 286.90092.

2-Iodo-4-methyl-5-vinylthiazole (6.7e): tan solid; mp 73 – 75 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.68 (dd, 1H, J= 17.2, 10.8 Hz), 5.32 (d, 1H, J = 17.2 Hz), 5.23 (d, 1H, J = 11.0 Hz), 2.37 (s, 3H), ^{13}C NMR (200 MHz, $CDCl_3$) δ 151.5, 137.2, 125.5, 117.2, 97.6, 15.0; EI MS (m/z) 251 [M^+]; HRMS calculated for C_6H_6NSI [M^+] 250.92657, found 250.92684.

2-Iodobenzothiazole (6.7f): tan solid; 79 – 81 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.00 (dd, 1H, J = 6.0, 2.0 Hz), 7.79 (dd, 1H, J = 7.0, 1.8 Hz), 7.37 (m, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 154.1, 139.0, 126.3, 125.5, 122.3, 120.4, 105.8; EI MS (m/z) 261 [M^+]; HRMS calculated for C_7H_4NSI [M^+] 260.91092, found 260.90951.

8.6.2.2 General Procedure for the Pd/CuI Coupling of 2-Halothiazoles to Alkynes.



6.7 **6.8** 6 - 18 h **6.9**

To a 100 mL round bottom flask purged with N_2 was added triethylamine (20 mL), the terminal alkyne (**6.8**) (25 - 30 mmol), CH_2Cl_2 (40 mL), the 2-halothiazole (**6.7**) (20 mmol), $Pd(PPh_3)_2Cl_2$ (0.2 mmol), CuI (0.2 mmol), and the mixture was heated to reflux (65 °C) for 6 - 18 hours. Ether (50 mL) was added to the reaction mixture leading to the precipitation of $Et_3NH^+X^-$. The resulting mixture was filtered, evaporated, isolated by silica gel chromatography using a MeOH:CH_2Cl_2 gradient ranging from 0:100 to 5:95. and further purified if necessary by Kugelrohr distillation to give **6.9** (Table 6-1).

2-Hex-1-ynylthiazole (6.9a): colorless liquid; IR ν(C≡C) 2230 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.53 (d, 1H, J = 3.4 Hz); 7.07 (d, 1H, J = 3.4 Hz), 2.24 (t, 2H, J = 7.0 Hz), 1.20 – 1.43 (m, 4H), 0.72 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 148.8, 142.5, 119.4, 95.7, 73.7, 29.6, 21.5, 18.7, 13.0; EI MS (m/z) 165 [M^+]; HRMS calculated for $C_9H_{11}NS$ [M^+] 165.06122, found 165.06099.

2-(3,3-Dimethylbut-1-ynyl)thiazole (6.9b): colorless liquid; IR ν(C≡C) 2229 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.58 (d, 1H, J = 3.2 Hz), 7.11 (d, 1H, J = 3.4 Hz), 1.17 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 149.0, 142.6, 119.5, 103.1, 72.4, 30.0, 27.8; EI MS (m/z) 165 [M^+]; HRMS calculated for $C_9H_{11}NS$ [M^+] 165.06122, found 165.05867.

2-Phenylethynylthiazole (6.9c): yellow liquid; IR ν(C≡C) 2207 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.78 (d, 1H, J = 3.2 Hz), 7.50 – 7.54 (m, 2H), 7.29 – 7.33 (m, 4H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 143.3, 131.6, 129.3, 128.9, 128.5, 128.2, 128.1, 121.1, 120.6, 93.6, 82.0; EI MS (m/z) 185 [M^+]; HRMS calculated for $C_{11}H_7NS$ [M^+] 185.02992, found 185.02834.

2-*p*-Tolylethynylthiazole (6.9d): white solid; mp 59 – 61 °C; IR ν(C≡C) 2211 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.76 (d, 1H, J = 3.2 Hz), 7.41 (d, 2H, J = 8.0 Hz), 7.26 (d 1H, J = 3.2 Hz), 7.09 (d, 2H, J = 7.8 Hz), 2.27 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 143.2, 139.6, 131.5, 129.0, 128.8, 120.4, 118.0, 94.0, 81.6, 21.3; EI MS (m/z) 199 [M^+]; HRMS calculated for $C_{12}H_9NS$ [M^+] 199.04557, found 199.04293.

2-(3-Methylbut-3-en-1-ynyl)thiazole (6.9e): yellow liquid; IR ν(C≡C) 2202 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.83 (d, 1H, J = 3.2 Hz), 7.38 (d, 1H, J = 3.2 Hz), 5.55 (d, 1H, J = 1.7 Hz), 5.45 (d, 1H, J = 1.7 Hz), 2.01 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 148.2, 143.1, 125.1, 124.5, 120.5, 94.5, 80.9, 22.3; EI MS (m/z) 149 [M^+]; HRMS calculated for C_8H_7NS [M^+] 149.02992, found 149.03097.

2-(3-Methoxyprop-1-ynyl)thiazole (6.9f): colorless liquid; IR ν(C≡C) 2231 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.74 (d, 1H, J = 3.2 Hz), 7.29 (d, 1H, J = 3.4 Hz), 4.28 (s, 2H), 3.37 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 147.8, 143.3, 120.8, 90.0, 79.1,

59.9, 57.8; EI MS (m/z) 153 [M^+]; HRMS calculated for C_7H_7NOS [M^+] 153.02483, found 153.02558.

2-(3-Acetylprop-2-ynyloxy)thiazole (6.9g): colorless liquid; IR ν(C≡C) 2241 cm^{-1},ν(C=O) 1747 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.60 (d, 1H, J = 3.2 Hz), 7.22 (d, 1H, J = 3.4 Hz), 4.71 (s, 2H), 1.89 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 169.3, 146.8, 143.1, 121.0, 87.5, 78.6, 51.5, 20.0; EI MS (m/z) 181 [M^+]; HRMS calculated for $C_8H_7NO_2S$ [M^+] 181.01975, found 181.02181.

2-Hex-1-ynyl-4-methylthiazole (6.9h): colorless liquid; IR ν(C≡C) 2231 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.71 (s, 1H), 2.34 (t, 2H, J = 6.8 Hz), 2.32 (s, 3H), 1.34 – 1.54 (m, 4H), 0.83 (t, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 152.7, 148.4, 114.2, 95.7, 74.0, 29.8, 21.8, 18.9, 16.7, 13.3; EI MS (m/z) 179 [M^+]; HRMS calculated for $C_{10}H_{13}NS$ [M^+] 179.07687, found 179.07768.

2-Hex-1-ynyl-4,5-dimethylthiazole (6.9i): colorless liquid; IR ν(C≡C) 2229 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.38 (t, 2H, J = 6.8 Hz), 2.28 (s, 3H), 2.26 (s, 3H), 1.39 – 1.58 (m, 4H), 0.87 (t, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 148.6, 144.5, 127.4, 95.0, 74.2, 30.1, 21.9, 19.1, 14.5, 13.5, 11.2; EI MS (m/z) 193 [M^+]; HRMS calculated for $C_{11}H_{15}NS$ [M^+] 193.09252, found 193.09234.

5-(2-Chloroethyl)-2-hex-1-ynyl-4-methylthiazole (6.9j): colorless liquid; IR ν(C≡C) 2229 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 3.58 (t, 2H, J = 7.2 Hz), 3.11 (t, 2H, J

= 6.8 Hz), 2.37 (t, 2H, J = 6.8 Hz), 2.29 (s, 3H), 1.37 – 1.53 (m, 4H), 0.86 (t, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 149.7, 146.0, 128.2, 95.8, 74.0, 44.0, 29.9, 29.6, 21.8, 19.0, 14.8, 13.4; EI MS (m/z) 241 [M^+]; HRMS calculated for $C_{12}H_{16}NClS$ [M^+] 241.06920, found 241.06734.

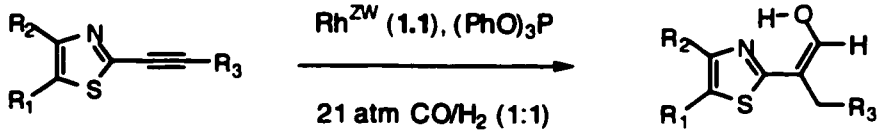
2-Hex-1-ynyl-4-methyl-5-vinylthiazole (6.9k): yellow liquid; IR ν(C≡C) 2228 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.58 (dd, 1H, J = 17.2, 10.4 Hz), 5.59 (d, 1H, J = 17.2 Hz), 5.06 (d, 1H, J = 10.4 Hz), 2.30 (t, 2H, J = 7.0 Hz), 2.24 (s, 3H), 1.30 – 1.49 (m, 4H), 0.79 (t, 3H, J = 7.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 149.7, 145.2, 131.7, 125.9, 115.8, 96.3, 74.1, 29.7, 21.6, 18.9, 14.8, 13.2; EI MS (m/z) 205 [M^+]; HRMS calculated for $C_{12}H_{15}NS$ [M^+] 205.09252, found 205.09341.

2-Hex-1-ynylbenzothiazole (6.9l): yellow oil; IR ν(C≡C) 2229 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.99 (d, 1H, J = 8.8 Hz), 7.78 (d, 1H, J = 6.6 Hz), 7.33 – 7.49 (m, 2H), 2.48 (t, 2H, J = 7.0 Hz), 1.41 – 1.69 (m, 4H,), 0.92 (t, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 152.7, 149.2, 135.0, 126.4, 125.8, 123.3, 121.1, 98.8, 74.6, 29.9, 22.0, 19.3, 13.5; EI MS (m/z) 215 [M^+]; HRMS calculated for $C_{13}H_{13}NS$ [M^+] 215.07687, found 215.07539.

8.6.3 Hydrocarbonylative Enolation of Conjugated Thiazolynes: Optimization of Reaction Conditions.

To a 45 mL autoclave containing a glass liner and stirring bar was placed the rhodium complex (0.03 - 0.06 mmol), ligand (0.12 - 0.24 mmol), acetylenic thiazole **6.9a** (1.5 - 3 mmol), and CH_2Cl_2 (10 - 20 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 7 – 17.5 atm followed by the introduction of hydrogen to a total pressure of 14 - 21 atm. The autoclave was placed in an oil bath at 70 - 110 °C for 20 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture was filtered through Celite, and the solvent was removed by rotary evaporation. The percent conversion and the ratio of **6.10**:**6.11**:**6.12**:**6.13** were determined by ^1H NMR The results on reaction optimization are given in Tables 6-3 and 6-4.

8.6.4 General Procedure for the Hydrocarbonylative Enolation of Conjugated Thiazolynes.



6.9 **6.10**

To a 45 mL autoclave containing a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.06 mmol), triphenyl phosphite (0.24 mmol),

acetylenic thiazole **6.9** (3 mmol), and CH_2Cl_2 (20 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 10.5 atm followed by the introduction of hydrogen to a total pressure of 21 atm. The autoclave was placed in an oil bath at 110 °C for 18 to 36 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture filtered through Celite, and the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel chromatography using a MeOH:CH_2Cl_2 gradient ranging from 0:100 to 5:95 as the eluant to afford product **6.10** (Tables 6-5 and 6-6).

(*Z*)-2-Thiazol-2-ylhept-1-en-1-ol (6.10a): colorless liquid; IR ν(S-C=N) 1626 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.61 (s, 1H), 7.66 (d, 1H, J = 3.4 Hz), 7.03 (d, 1H, J = 3.6 Hz), 6.87 (s, 1H), 2.27 (t, 2H, J = 6.8 Hz), 1.47 – 1.60 (m, 2H), 1.26 – 1.36 (m, 4H), 0.87 (t, 3H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 170.8, 149.9, 144.4, 114.4, 107.1, 31.5, 30.5, 28.7, 28.7, 22.4, 14.0; EI MS (m/z) 197 [M^+]; HRMS calculated for $C_{10}H_{15}NOS$ [M^+] 197.08743, found 197.08876.

(*Z*)-2-Butyl-3-thiazol-2-ylpropenal (6.11a): colorless liquid; IR ν(C=O) 1685 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.99 (d, 1H, J = 3.2 Hz), 7.55 (d, 1H, J = 3.2 Hz), 7.39 (s, 1H), 2.72 (t, 2H, J = 7.4 Hz), 1.36 – 1.45 (m, 4H), 0.89 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 194.5, 162.0, 145.1, 144.6, 139.5, 122.6, 29.7, 25.2, 23.0, 13.8; EI MS (m/z) 195 [M^+]; HRMS calculated for $C_{10}H_{13}NOS$ [M^+] 195.07178, found 195.07199.

(*Z*)-4,4-Dimethyl-2-thiazol-2-ylpent-1-en-1-ol (6.10b): colorless liquid; IR ν(S-C=N) 1619 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 13.01 (br, 1H), 7.61 (d, 1H, J = 3.2 Hz), 7.03 (d, 1H, J = 3.2 Hz), 6.89 (s, 1H), 2.20 (s, 2H), 0.90 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 172.4, 152.9, 139.8, 113.9, 104.3, 44.2, 32.4, 29.6; EI MS (m/z) 197 [M^+]; HRMS calculated for $C_{10}H_{15}NOS$ [M^+] 197.08743, found 197.08783.

(*Z*)-3-Phenyl-2-thiazol-2-ylpropen-1-ol (6.10c): yellow liquid; IR ν(S-C=N) 1627 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.91 (br, 1H), 7.72 (d, 1H, J = 3.4 Hz), 7.30 – 7.37 (m, 5H), 7.08 (d, 1H, J = 3.6 Hz), 7.07 (s, 1H), 3.71 (s, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 170.6, 151.6, 140.0, 138.7, 128.5, 128.3, 126.5, 114.9, 106.2, 36.4; EI MS (m/z) 217 [M^+]; HRMS calculated for $C_{12}H_{11}NOS$ [M^+] 217.05613, found 217.05522.

(*Z*)-2-Thiazol-2-yl-*p*-tolylpropen-1-ol (6.10d): yellow liquid; IR ν(S-C=N) 1627 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.80 (br, 1H), 7.72 (d, 1H, J = 3.4 Hz), 7.28 (d, 2H, J = 8.0 Hz), 7.18 (d, 2H, J = 8.2 Hz), 7.09 (s, 1H), 7.08 (d, 1H, J = 3.6 Hz), 3.68 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 170.0, 151.4, 139.9, 136.0, 135.6, 129.0, 128.4, 114.8, 106.3, 35.9, 20.9; EI MS (m/z) 231 [M^+]; HRMS calculated for $C_{13}H_{13}NOS$ [M^+] 231.07178, found 231.07116.

(*Z*)-4-Methyl-2-thiazol-2-ylpenta-1,3-dien-1-ol (6.10e): yellow liquid; IR ν(S-C=N) 1614 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.43 (br, 1H), 7.64 (d, 1H, J = 3.4 Hz), 7.03 (d, 1H, J = 3.4 Hz), 6.89 (s, 1H), 5.74 (s, 1H), 1.82 (s, 3H), 1.72 (s, 3H); ^{13}C NMR

(200 MHz, $CDCl_3$) δ 170.9, 152.1, 140.2, 138.6, 117.9, 114.8, 106.1, 25.6, 19.4; EI MS (m/z) 181 [M^+]; HRMS calculated for $C_9H_{11}NOS$ [M^+] 181.05613, found 181.05572.

(*Z*)-4-Methoxy-2-thiazol-2-ylbut-1-en-1-ol (6.10f): colorless liquid; IR ν(S-C=N) 1626 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.75 (br, 1H), 7.67 (d, 1H, J = 3.4 Hz), 7.10 (d, 1H, J = 3.6 Hz), 6.95 (s, 1H), 3.63 (t, 2H, J = 7.2 Hz), 3.33 (s, 3H), 2.56 (t, 2H, J = 7.0 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 170.5, 151.6, 140.4, 114.4, 103.8, 71.7, 58.6, 30.9; EI MS (m/z) 185 [M^+]; HRMS calculated for $C_8H_{11}NO_2S$ [M^+] 185.05105, found 185.05066.

(*Z*)-1-Acetyl-3-thiazol-2-ylbut-3-ene (6.10f): colorless liquid; IR ν(S-C=N) 1739 cm^{-1}, ν(C=O) 1627 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.82 (br, 1H), 7.70 (d, 1H, J = 3.6 Hz), 7.14 (d, 1H, J = 3.4 Hz), 6.99 (s, 1H), 4.23 (f, 2H, J = 6.8 Hz), 2.64 (t, 2H, J = 7.0 Hz), 2.05 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 170.9, 169.9, 152.0, 143.8, 140.4, 114.5, 102.9, 63.0, 29.9, 20.9; EI MS (m/z) 213 [M^+]; HRMS calculated for $C_9H_{11}NO_3S$ [M^+] 213.04596, found 213.04697.

(*Z*)-2-(4-Methylthiazol-2-yl)hept-1-en-1-ol (6.10h): colorless liquid; IR ν(S-C=N) 1627 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.78 (br, 1H), 6.88 (s, 1H), 6.63 (s, 1H), 2.39 (s, 3H), 2.24 (t, 2H, J = 7.4 Hz), 1.51 – 1.58 (m, 2H), 1.27 – 1.34 (m, 4H), 0.88 (t, 3H, J = 6.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 170.0, 150.5, 150.0,108.9, 107.0, 31.4, 30.2, 28.8, 22.4, 16.7, 14.0; EI MS (m/z) 211 [M^+]; HRMS calculated for $C_{11}H_{17}NOS$ [M^+] 211.10308, found 211.10110.

(*Z*)-2-(4,5-Dimethylthiazol-2-yl)hept-1-en-1-ol (6.10i): colorless liquid; IR ν(S-C=N) 1628 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.78 (br, 1H), 6.90 (s, 1H), 2.36 (s, 3H), 2.31 (s, 3H), 2.23 (t, 2H, J = 7.0 Hz), 1.59 – 1.63 (m, 2H), 1.32 – 1.39 (m, 4H), 0.95 (t, 3H, J = 6.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 166.0, 149.5, 145.3, 121.5, 106.6, 31.3, 30.1, 28.8, 22.3, 14.1, 13.9, 10.9; EI MS (m/z) 225 [M^+]; HRMS calculated for $C_{12}H_{19}NOS$ [M^+] 225.11873, found 225.12050.

(*Z*)-2-[5-(2-Chloroethyl)-4-methylthiazol-2-yl]hept-1-en-1-ol (6.10j): yellow oil; IR ν(S-C=N) 1626 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.60 (br, 1H), 6.85 (s, 1H), 3.64 (t, 2H, J = 7.4 Hz), 3.15 (t, 2H, J = 7.2 Hz), 2.30 (s, 3H), 2.20 (t, 2H, J = 7.2 Hz), 1.49 – 1.60 (m, 2H), 1.25 – 1.32 (m, 4H), 0.87 (t, 3H, J = 6.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 167.6, 150.1, 147.0, 122.7, 106.8, 44.3, 31.4, 30.2, 29.6, 28.8. 22.4, 14.6, 14.0; EI MS (m/z) 273 [M^+]; HRMS calculated for $C_{13}H_{20}NOClS$ [M^+] 273.09541, found 273.09470.

(*Z*)-2-[2-(2-Hydroxy-1-pentylvinyl)-4-methylthiazol-5-yl]propanal (6.10k): yellow oil; IR ν(C=O) 1731 cm^{-1}, ν(S-C=N) 1625 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.58 (br, 1H), 9.62 (d, 1H, J = 1.4 Hz), 6.90 (s, 1H), 3.93 (qd, 1H, J = 7.2, 1.6 Hz), 2.38 (s, 3H), 2.26 (t, 2H, J = 7.0 Hz), 1.48 – 1.61 (m, 2H), 1.50 (d, 3H, J = 7.0 Hz), 1.30 – 1.39 (m, 4H), 0.92 (t, 3H, J = 6.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 198.8, 169.2, 150.6, 148.0, 123.9, 107.5, 45.7, 32.0, 30.9, 29.4, 23.0, 16.3, 15.5, 14.6; EI MS (m/z) 267 [M^+]; HRMS calculated for $C_{14}H_{21}NO_2S$ [M^+] 267.12930, found 267.13017.

(*Z*)-2-Benaothiazol-2-yl)hept-1-en-1-ol (6.10l): yellow oil; IR ν(S-C=N) 1621 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 13.25 (s, 1H), 7.74 (d, 2H, J = 8.2 Hz), 7.43 – 7.51 (m, 1H), 7.27 – 7.34 (m, 1H), 7.23 (s, 1H), 2.37 (t, 2H, J = 7.6 Hz), 1.62 – 1.73 (m, 2H), 1.36 – 1.45 (m, 4H), 0.97 (t, 3H, J = 6.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 171.0, 155.6, 151.4, 131.8, 127.0, 124.7, 122.0, 120.9, 107.6, 32.0, 30.9, 29.8, 23.1, 14.7; EI MS (m/z) 247 [M^+]; HRMS calculated for $C_{14}H_{17}NOS$ [M^+] 247.10308, found 247.10076. Anal. calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.93; N, 5.66. Found: C, 68.25; H, 6.95; N, 5.84.

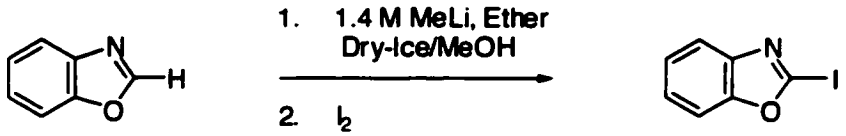
8.7 Experimental for Chapter 7

8.7.1 Materials

Benzoxazole was purchased from Aldrich, and terminal alkynes were purchased from GFS Chemicals. The zwitterionic rhodium complex (η^6-$C_6H_5BPh_3$)$^-Rh^+$(1,5-COD) (**1.1**) was prepared according to the procedure of Schrock and Osborn.[1]

8.7.2 Synthesis of Starting Materials

8.6.2.1 General Procedure for the Preparation of 2-Iodobenzoxazole (7.10).

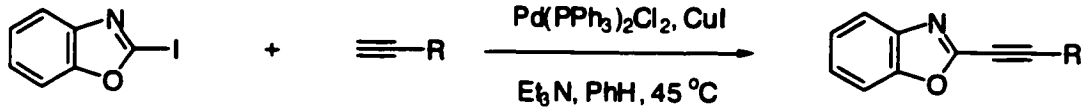


7.10 **7.11**

To a 500 mL round bottom flask purged with N_2 was added ether (200 mL) and benzoxazole (65 mmol). The mixture was cooled in a dry-ice/MeOH bath, and an excess amount of 1.4 M MeLi (50 mL) was added over a 15 minute time period. After allowing the mixture to react for a 30 minute time period, I_2 (60 mmol) was added, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was transferred to a separatory funnel, ether (300 mL) was added, the organic layer was washed with water (100 mL) and brine (50 mL), dried over anhydrous $MgSO_4$, and evaporated. The product (**7.11**) was isolated by silica gel chromatography using CH_2Cl_2 as eluant in 72 % yield.

2-Iodobenzoxazole (7.11): white solid; 90 – 92 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, 1H, J = 6.6, 2.6 Hz), 7.49 (dd, 1H, J = 6.6, 2.6 Hz), 7.22 – 7.29 (m, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 154.0, 142.6, 125.3, 124.7, 119.3, 110.1, 108.3; EI MS (m/z) 245 [M^+]; HRMS calculated for C_7H_4NOI [M^+] 244.93376, found 244.93520.

8.7.2.2 General Procedure for the Pd/CuI Coupling of 2-Iodobenzoxazole to Alkynes.



7.11 **7.12** 6 - 24 h **7.13**

To a 100 mL round bottom flask purged with N_2 was added triethylamine (20 mL), the terminal alkyne (**7.12**) (25 - 30 mmol), CH_2Cl_2 (40 mL), 2-iodobenzoxazole (**7.11**) (20 mmol), $Pd(PPh_3)_2Cl_2$ (0.2 mmol), CuI (0.2 mmol), and the mixture was heated to 45 °C for 6 - 24 hours. Ether (50 mL) was added to the reaction mixture leading to the precipitation of $Et_3NH^+I^-$. The resulting mixture was filtered, evaporated, isolated by silica gel chromatography using CH_2Cl_2 as the eluant, and further purified if necessary by Kugelrohr distillation to give **7.13** (Table 7-1).

2-Hex-1-ynylbenzoxazole (7.13a): colorless oil; IR ν(C≡C) 2244 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, 1H, J = 6.7, 2.4 Hz), 7.45 (dd, 1H, J = 6.7, 2.4 Hz), 7.28 – 7.36 (m, 2H), 2.47 (t, 2H, J = 7.2 Hz), 1.62 (quintet, 2H, J = 7.2 Hz), 1.48 (sextet, 2H, J = 7.2 Hz), 0.92 (t, 3H, J = 7.3 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 150.0, 147.7, 140.8,

125.9, 124.7, 120.1, 110.4, 96.4, 69.4, 29.7, 21.9, 19.0, 13.5; EI MS (m/z) 199 [M^+]; HRMS calculated for $C_{13}H_{13}NO$ [M^+] 199.09971, found 199.09856.

2-(3-Methylbut-1-ynyl)benzoxazole (7.13b): colorless oil; IR ν(C≡C) 2248 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, 1H, J = 6.7, 2.4 Hz), 7.44 (dd, 1H, J = 6.7, 2.4 Hz), 7.27 – 7.35 (m, 2H), 2.82 (septet, 1H, J = 6.9 Hz), 1.28 (d, 6H, J = 6.9 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 150.0, 147.7, 140.8, 125.9, 124.7, 120.1, 110.4, 101.0, 68.7, 21.9, 21.1; EI MS (m/z) 185 [M^+]; HRMS calculated for $C_{12}H_{11}NO$ [M^+] 185.08406, found 185.08444.

2-(3,3-Dimethylbut-1-ynyl)benzoxazole (7.13c): colorless oil; IR ν(C≡C) 2227, 2252 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.66 (dd, 1H, J = 6.6, 2.6 Hz), 7.44 (dd, 1H, J = 6.6, 2.6 Hz), 7.28 – 7.36 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 150.0, 147.7, 140.8, 125.9, 124.7, 120.1, 110.4, 103.5, 68.1, 30.0, 28.1; EI MS (m/z) 199 [M^+]; HRMS calculated for $C_{13}H_{13}NO$ [M^+] 199.09971, found 199.09982.

2-(3-Cyclohexylprop-1-ynyl)benzoxazole (7.13d): colorless oil; IR ν(C≡C) 2242 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, 1H, J = 6.6, 2.4 Hz), 7.46 (dd, 1H, J = 6.6, 2.4 Hz), 7.28 – 7.37 (m, 2H), 2.38 (d, 2H, J = 6.7 Hz), 1.84 – 1.88 (m, 2H), 1.58 – 1.76 (m, 4H), 1.00 – 1.32 (m, 5H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 150.0, 147.7, 140.8, 125.9, 124.7, 120.1, 110.3, 95.4, 70.3, 36.8, 32.6, 27.0, 25.9; EI MS (m/z) 239 [M^+]; HRMS calculated for $C_{16}H_{17}NO$ [M^+] 239.13101, found 239.13046.

2-(4-Phenylbut-1-ynyl)benzoxazole (7.13e): yellow oil; IR ν(C≡C) 2243 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, 1H, J = 6.6, 2.6 Hz), 7.47 (dd, 1H, J = 6.6, 2.6 Hz), 7.23 – 7.39 (m, 7H), 2.98 (t, 2H, J = 7.5 Hz), 2.78 (t, 2H, J = 7.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 150.1, 147.7, 140.8, 139.6, 128.6, 128.4, 126.6, 126.0, 124.9, 120.3, 110.5, 95.3, 70.1, 34.0, 21.5; EI MS (m/z) 247 [M^+]; HRMS calculated for $C_{17}H_{13}NO$ [M^+] 247.09971, found 247.09975.

2-(5-Chloropent-1-ynyl)benzoxazole (7.13f): colorless oil; IR ν(C≡C) 2246 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 (dd, 1H, J = 6.6, 2.4 Hz), 7.43 (dd, 1H, J = 6.6, 2.4 Hz), 7.27 – 7.33 (m, 2H), 3.65 (t, 2H, J = 6.7 Hz), 2.65 (t, 2H, J = 6.7 Hz), 2.05 (quintet, 2H, J = 6.7 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.9, 147.1, 140.6, 126.0, 124.4, 120.1, 110.3, 93.9, 70.1, 43.4, 30.9, 16.6; EI MS (m/z) 219 [M^+]; HRMS calculated for $C_{12}H_{10}NOCl$ [M^+] 219.04509, found 219.04524.

2-Phenylethynylbenzoxazole (7.13g): white solid; 94 – 96 °C; IR ν(C≡C) 2224 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.74 (dd, 1H, J = 6.8, 2.4 Hz), 7.64 – 7.66 (m, 2H), 7.48 – 7.54 (m, 1H), 7.34 – 7.44 (m, 5H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 150.3, 147.7, 141.1, 132.4, 130.3, 128.6, 126.3, 125.0, 120.4, 120.2, 110.6, 93.4, 77.5; EI MS (m/z) 219 [M^+]; HRMS calculated for $C_{15}H_9NO$ [M^+] 219.06841, found 219.06837.

2-(4-Methoxyphenyl)benzoxazole (7.13h): white solid; 105 – 107 °C; IR ν(C≡C) 2217 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, 1H, J = 6.5, 2.4 Hz), 7.57 (d, 2H, J = 8.7 Hz), 7.49 (dd, 1H, J = 6.5, 2.4 Hz), 7.33 – 7.36 (m, 2H), 6.88 (d, 2H, J = 8.7

Hz), 3.80 (s,); ^{13}C NMR (300 MHz, $CDCl_3$) δ 161.6, 150.6, 148.4, 141.5, 134.6, 126.4, 125.3, 120.6, 114.7, 112.4, 110.9, 94.4, 55.8; EI MS (m/z) 249 [M^+]; HRMS calculated for $C_{16}H_{11}NO_2$ [M^+] 249.07898, found 249.07650.

2-(3-Methylbut-3-en-1-ynyl)benzoxazole (7.13i): colorless oil; IR ν(C≡C) 2219 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (dd, 1H, J = 6.6, 2.6 Hz), 7.48 (dd, 1H, J = 6.6, 2.6 Hz), 7.28 – 7.36 (m, 2H), 5.65 (d, 1H, J = 3.2 Hz), 5.52 (d, 1H, J = 3.2 Hz), 2.00 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.2, 147.5, 140.9, 127.0, 126.2, 124.9, 124.7, 120.3, 110.5, 94.3, 76.2, 22.3; EI MS (m/z) 183 [M^+]; HRMS calculated for $C_{12}H_9NO$ [M^+] 183.06841, found 183.06575.

2-(3-Methoxyprop-1-ynyl)benzoxazole (7.13j): colorless oil; IR ν(C≡C) 2240 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, 1H, J = 6.8, 2.6 Hz), 7.46 (dd, 1H, J = 6.8, 2.6 Hz), 7.27 – 7.35 (m, 2H), 4.34 (s, 2H), 3.44 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.5, 147.1, 141.0, 126.9, 125.4, 120.9, 111.0, 90.3, 75.1, 60.2, 58.5; EI MS (m/z) 187 [M^+]; HRMS calculated for $C_{11}H_9NO_2$ [M^+] 187.06333, found 187.06096.

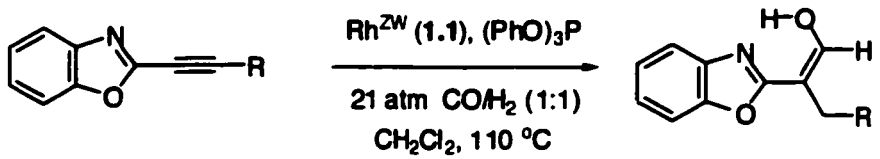
2-(*tert*-Butyldimethylsilanylethynyl)benzoxazole (7.13k): white solid; 53 – 54 °C; IR ν(C≡C) 2174 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, 1H, J = 6.8, 2.5 Hz), 7.49 (dd, 1H, J = 6.8, 2.5 Hz), 7.34 – 7.39 (m, 2H), 1.00 (s, 9H), 0.23 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.1, 146.9, 140.7, 126.5, 125.1, 120.5, 110.6, 100.4, 92.1, 26.0, 16.6, -5.13; EI MS (m/z) 257 [M^+]; HRMS calculated for $C_{15}H_{19}NOSi$ [M^+] 257.12359, found 257.12421.

2-(Triisopropylsilanylethynyl)benzoxazole (7.13l): colorless oil; IR ν(C≡C) 2172 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (dd, 1H, J = 6.7, 2.5 Hz), 7.46 (dd, 1H, J = 6.7, 2.5 Hz), 7.29 – 7.35 (m, 2H), 1.13 (br, 21H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 150.4, 147.3, 141.1, 126.8, 125.4, 120.8, 110.9, 99.2, 93.8, 18.9, 11.4; EI MS (m/z) 299 [M^+]; HRMS calculated for $C_{18}H_{25}NOSi$ [M^+] 299.17054, found 299.16933.

8.7.3 Hydrocarbonylative Enolation of Conjugated Benzoxazolynes: Optimization of Reaction Conditions.

To a 45 mL autoclave containing a glass liner and stirring bar was placed the rhodium complex (0.03 - 0.06 mmol), $(PhO)_3P$ (0.12 - 0.24 mmol), 2-acetylenic benzoxazole **7.13a** (1.5 - 3 mmol), and CH_2Cl_2 (10 - 20 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 7 – 17.5 atm followed by the introduction of hydrogen to a total pressure of 14 - 21 atm. The autoclave was placed in an oil bath at 60 - 110 °C for 20 hours, and then was allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture was filtered through Celite, and the solvent was removed by rotary evaporation. The percent conversion and the ratio of **7.14**:**7.15**:**7.16**:**7.17** were determined by ^1H NMR The results on reaction optimization are given in Table 7-2.

8.7.4 General Procedure for the Hydrocarbonylative Enolation of Conjugated Benzoxazolynes.



7.13 **7.14**

To a 45 mL autoclave containing a glass liner and stirring bar was placed the zwitterionic rhodium complex **1.1** (0.06 mmol), triphenyl phosphite (0.24 mmol), acetylenic benzoxazole **7.13** (3 mmol), and CH_2Cl_2 (20 mL). The autoclave was flushed three times with carbon monoxide, pressurized to 10.5 atm followed by the introduction of hydrogen to a total pressure of 21 atm. The autoclave was placed in an oil bath at 110 °C for 20 to 36 hours, and then was allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture was filtered through Celite, and the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel chromatography using CH_2Cl_2 as the eluant to afford product **7.14** (Tables 7-3 and 7-4).

(*Z*)-2-Benzoxazol-2-ylhept-1-en-1-ol (7.14a): yellow oil; IR ν(O-C=N) 1631 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.90 (br, 1H), 7.59 (dd, 1H, J = 6.6, 2.3 Hz), 7.51 (dd, 1H, J = 6.6, 2.3 Hz), 7.26 – 7.48 (m, 2H), 7.09 (s, 1H), 2.38 (t, 2H, J = 7.4 Hz), 1.57 (quintet, 2H, J = 7.4 Hz), 1.31 – 1.37 (m, 4H), 0.90 (t, 3H, J = 7.2 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 165.6, 155.2, 148.3, 139.8, 124.6, 124.1, 118.1, 110.4, 101.3, 31.2, 29.5, 27.1, 22.4. 14.8; EI MS (m/z) 231 [M^+]; HRMS calculated for $C_{14}H_{17}NO_2$ [M^+]

231.12593, found 231.12717. Anal. calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.84; H, 7.22; N, 6.21.

(*Z*)-2-Benzoxazol-2-yl-4-methylpent-1-en-1-ol (7.14b): yellow oil; IR ν(O-C=N) 1630 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.00 (br, 1H), 7.60 (dd, 1H, J = 6.6, 2.4 Hz), 7.50 (dd, 1H, J = 6.6, 2.4 Hz), 7.26 – 7.34 (m, 2H), 7.09 (s, 1H), 2.26 (d, 2H, J = 7.2 Hz), 1.91 (nanotet, 1H, J = 7.0 Hz), 0.95 (d, 6H, J = 6.8 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 165.7, 156.2, 148.3, 139.8, 124.6, 124.1, 118.1, 110.3, 100.1, 36.3, 28.0, 22.1; EI MS (m/z) 217 [M^+]; HRMS calculated for $C_{13}H_{15}NO_2$ [M^+] 217.11028, found 217.11182.

(*Z*)-2-Benzoxazol-2-yl-4,4-dimethylpent-1-en-1-ol (7.14c): white solid; 90 – 92 °C; IR ν(O-C=N) 1630 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 12.30 (br, 1H), 7.58 (dd, 1H, J = 6.6, 2.4 Hz), 7.49 (dd, 1H, J = 6.6, 2.4 Hz), 7.26 – 7.35 (m, 2H), 7.10 (s, 1H), 2.34 (s, 2H), 0.92 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 166.0, 157.8, 147.9, 139.6, 124.5, 124.0, 117.8, 110.2, 98.1, 39.6, 31.7, 29.0; EI MS (m/z) 231 [M^+]; HRMS calculated for $C_{14}H_{17}NO_2$ [M^+] 231.12593, found 231.12649.

(*Z*)-2-Benzoxazol-2-yl-4-cyclohexylbut-1-en-1-ol (7.14d): yellow oil; IR ν(O-C=N) 1631 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 11.85 (br, 1H), 7.59 (dd, 1H, J = 6.6, 2.4 Hz), 7.50 (dd, 1H, J = 6.6, 2.4 Hz), 7.26 – 7.35 (m, 2H), 7.09 (s, 1H), 2.40 (t, 2H, J = 7.4 Hz), 1.68 – 1.80 (m, 5H), 0.90 – 1.48 (m, 8H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 165.6, 155.1, 148.3, 139.8, 124.6, 124.1, 118.1, 110.4, 101.6, 37.5, 37.1, 33.2, 26.7, 26.3, 24.5;

EI MS (m/z) 271 [M^+]; HRMS calculated for $C_{17}H_{21}NO_2$ [M^+] 271.15723, found 271.15523.

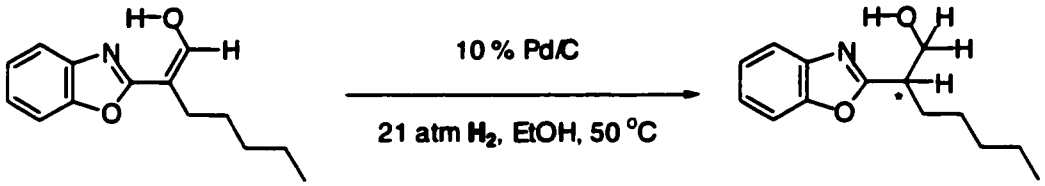
(*Z*)-2-Benzoxazol-2-yl-5-phenylpent-1-en-1-ol (7.14e): yellow oil; IR ν(O-C=N) 1630 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 11.93 (br, 1H), 7.62 (dd, 1H, J = 6.6, 2.4 Hz), 7.53 (dd, 1H, J = 6.6, 2.4 Hz), 7.21 – 7.38 (m, 7H), 7.13 (s, 1H), 2.73 (t, 2H, J = 7.4 Hz), 2.48 (t, 2H, J = 7.2 Hz), 1.97 (quintet, 2H, J = 7.4 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 165.5, 155.6, 148.3, 142.0, 139.8, 128.4, 128.3, 125.8, 124.7, 124.2, 118.2, 110.4, 100.9, 35.2, 31.2, 26.8; EI MS (m/z) 279 [M^+]; HRMS calculated for $C_{18}H_{17}NO_2$ [M^+] 279.12593, found 279.12642.

(*Z*)-2-Benzoxazol-2-yl-6-chlorohex-1-en-1-ol (7.14f): yellow oil; IR ν(O-C=N) 1631 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 12.00 (br, 1H), 7.59 (dd, 1H, J = 6.6, 2.4 Hz), 7.51 (dd, 1H, J = 6.6, 2.4 Hz), 7.22 – 7.34 (m, 2H), 7.11 (s, 1H), 3.56 (t, 2H, J = 6.8 Hz), 2.42 (t, 2H, J = 7.0 Hz), 1.82 (quintet, 2H, J = 7.0 Hz), 1.73 (quintet, 2H, J = 7.0 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.2, 155.5, 148.2, 139.7, 124.7, 124.3, 118.1, 110.4, 100.6, 44.7, 31.9, 27.1, 26.5; EI MS (m/z) 251 [M^+]; HRMS calculated for $C_{13}H_{14}NO_2Cl$ [M^+] 251.07131, found 251.07239.

(*Z*)-2-Benzooxazol-2-yl-3-(4-methoxy-phenyl)-propen-1-ol (7.14h): yellow oil; IR ν(O-C=N) 1633 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 12.02 (br, 1H), 7.59 (dd, 1H, J = 6.6, 2.4 Hz), 7.45 (dd, 1H, J = 6.6, 2.4 Hz), 7.21 – 7.34 (m, 4H), 7.20 (s, 1H), 6.82 (d, 2H, J = 8.7 Hz), 3.76 (s, 3H), 3.69 (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.2, 158.1,

156.2, 148.3, 139.7, 131.6, 129.4, 124.7, 124.2, 118.1, 113.8, 110.5, 101.1, 55.2, 32.1; EI MS (m/z) 281 [M^+]; HRMS calculated for $C_{17}H_{15}NO_3$ [M^+] 281.10519, found 281.10502.

8.7.5 General Procedure for the Stereofacial Hydrogenation of (Z)-Benzoxazol-2-ylalk-1-en-1-ols



7.14a **7.18a**

To a 45 mL autoclave containing a glass liner and stirring bar was placed 10 % Pd/C (0.05 mmol Pd), benzoxazolylalkenol **7.14a** (1.0 mmol), and 99 % ethanol (5 mL). The autoclave was pressurized with hydrogen to a total pressure of 21 atm. The autoclave was placed in an oil bath at 50 °C for 48 hours, and then allowed to cool to room temperature. The autoclave was depressurized, the reaction mixture was filtered through Celite, and the solvent was removed by rotary evaporation to afford product **7.18a**.

2-Benzoxazol-2-ylheptan-1-ol (7.18a): colorless oil; IR ν(N-H) 3359 cm^{-1}, ν(O-C=N) 1613 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (dd, 1H, J = 6.2, 3.0 Hz), 7.44 (dd, 1H, J = 6.2, 3.0 Hz), 7.24 – 7.29 (m, 2H), 3.97 (d, 2H, J = 7.0 Hz), 3.52 (br, 1H), 3.18 (quintet, 1H, J = 6.8 Hz), 1.75 – 1.86 (m, 2H), 1.25 – 1.36 (m, 6H), 0.82 (t, 3H, J = 7.2 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 168.6, 150.4, 140.7, 124.6, 124.2, 119.5, 110.4,

63.5, 42.4, 31.6, 29.7, 26.8, 22.4, 13.9; EI MS (m/z) 233 [M^+]; HRMS calculated for $C_{14}H_{19}NO_2$ [M^+] 233.14158, found 233.13833. Anal. calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.27; H, 8.06; N, 5.89.

References and Notes

1. Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* **1970**, *9*, 2339.

2. Shapley, J. R.; Schrock, R. R.; Osborn; J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816.

3. Schrock, R. R.; Osborn; J. A. *J. Chem. Soc., Chem. Commun.* **1970**, 567.

4. (a) Nolte, H. J.; Gafner, G.; Haines, L. M. *J. Chem. Soc., Chem. Commun.* **1969**, 1406. (b) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2134.

5. Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 4450.

6. Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1990**, *112*, 3674.

7. Alper, H.; Zhou, J.-Q. *J. Org. Chem.* **1992**, *57*, 3729.

8. (a) Neibecker, D.; Réau, R. *New J. Chem.* **1991**, *15*, 279. (b) Tanaka, M.; Hayashi, T.; Ogata, I. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2351. (c) Matsumoto, M.; Tamura, M. *J. Mol. Catal.* **1982**, *16*, 195.

9. Alper, H.; Zhou, J.-Q. *J. Chem. Soc., Chem. Commun.* **1993**, 316.

10. (a) Carretero, J. C.; Arrayas, R. G.; Buezo, N. D.; Garrido, J. L.; Alonso, I.; Adrio, J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *153*, 259. (b) de la Pradilla, R. F.; Mendez, P.; Priego, J.; Viso, A. *J. Chem. Soc., Perkin Trans 1* **1999**, 1247. (c) Lautens, M.; Edwards, L. G. *Tetrahedron Lett.* **1989**, *30*, 6813.

11. March, J. in *Advanced Organic Chemistry*, 4th Ed.; John Wiley and Sons, New York, **1992**, pp 352 - 356.

12. Corey, E. J.; Weigel, L. P.; Chamberlin, R.; Cho, H.; Hua, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 6615.

13. Totland, K.; Alper, H. *J. Org. Chem.* **1993**, *58*, 3326.

14. Park, H. S.; Alberico, E.; Alper, H. *J. Am. Chem. Soc.* **1999**, *121*, 11697.

15. Zhou, J.-Q.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1991**, 233.

16. Zhou, J.-Q.; Alper, H. *J. Org. Chem.* **1992**, *57*, 3328.

17. Lin, Y.-S.; El Ali, B.; Alper, H. *Tetrahedron Lett.* **2001**, *42*, 2423.

18. (a) Metzner, P.; Thuillier, A. *Sulfur Reagents in Organic Synthesis*, Academic Press, London, 1994. (b) Minami, T.; Motoyoshiya, J. *Synthesis* **1992**, 333. c) Cadogan, J. I. G. *Organophosphorus Reagents in Organic Synthesis*, Academic Press, London, 1979.

19. For recent examples related to sulfones, see: (a) Ravindran, B.; Sakthivel, K.; Suresh, C. G.; Pathak, T. *J. Org. Chem.* **2000**, *65*, 2637. (b) Overkleeft, H. S.; Bos, P. R.; Hekking, B. G.; Gordon, E. J.; Ploegh, H. L.; Kessler, B. M. *Tetrahedron Lett.* **2000**, *41*, 6005. (c) Joyeau, R.; Maoulida, C.; Guillet, C.; Frappier, F.; Teixeira, A. R. L.; Schrevel, J.; Santana, J.; Grellier, P. *Eur. J. Med. Chem.* **2000**, *35*, 257. (d) Clark, R. B.; Pearson, W. H. *Org. Lett.* **1999**, *1*, 349. e) Schmidtke, G.; Holzhutter, H. G.; Bogyo, M.; Kairies, N.; Groll, M.; (e) Giuli, R.; Emch, S.; Groettrup, M. *J. Biol. Chem.* **1999**, *274*, 35734. (f) Xia, L. H.; Kilb, J. Wex, H.; Li, Z. Q.; Lipyansky, A.; Breuil, V.; Stein, L.; Palmer, J. T.; Dempster, D. W.; Bromme, D. *Biol. Chem.* **1999**, *380*, 679. (g) Bogyo, M.; Shin, S.; Mcmaster, J. S.; Ploegh, H. L. *Chem. & Biol.* **1998**, *5*, 307. (h) Caturla, F.; Nájera, C. *Tetrahedron Lett.* **1996**, *37*, 2833. i) Smith, D. C.; Fuchs, P. L. *J. Org. Chem.* **1995**, *60*, 2692.

20. For examples related to phosphonates, see: (a) Thomas, A. A.; Sharpless, K. B. *J. Org. Chem.* **1999**, *64*, 8379. (b) Stowasser, B.; Budt, K.-H.; Li, J.-Q.; Peyman,

A.; Ruppert, D. *Tetrahedron Lett.* **1992**, *33*, 6625. (c) Patel, D. V.; Rielly-Gauvin, K.; Ryono, D. E. *Tetrahedron Lett.* **1990**, *31*, 5587. (d) Patel, D. V.; Rielly-Gauvin, K.; Ryono, D. E. *Tetrahedron Lett.* **1990**, *31*, 5591. (e) Zygmunt, J. *Tetrahedron* **1985**, *41*, 4979. (f) Engel, R. *Chem. Rev.* **1977**, *77*, 349.

21. Lin, Y.-S.; El Ali, B.; Alper, H. *J. Am. Chem. Soc.* **2001**, *123*, 7719.

22. Zhou, J.-Q.: Alper, H. *Organometallics* **1994**, *13*, 1586.

23. (a) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332. (b) Ojima, I.; Ingallina, P.; Donovan, R. J.; Close, N. *Organometallics* **1991**, *10*, 38.

24. Matsuda, I.; Fukuta, Y.; Tsuchashi, T.; Nagashima, H.; Itoh, K. *Organometallics* **1997**, *16*, 4327.

25. (a) Matsuda, I.; Ogiso, A.; Sato, S. *J. Am. Chem. Soc.* **1990**, *112*, 6120. (b) Matsuda, I.; Sakakibara, J.; Nagashima, H. *Tetrahedron Lett.* **1991**, *32*, 7431. (c) Ojima, I.; Donovan, R. J.; Shay, W. R. *J. Am. Chem. Soc.* **1992**, *114*, 6580. (d) Ojima. I.; Tzamarioudaki, M.; Tsai, C. Y. *J. Am. Chem. Soc.* **1994**, *116*, 3643.

26. Monteil, F.; Matsuda, I.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4419.

27. Aronica, L. A.; Caporusso, A. M.; Salvadori, P.; Alper, H. *J. Org. Chem.* **1999**, *64*, 9711.

28. Tius, M. A.; Pal, S. K. *Tetrahedron Lett.* **2001**, *42*, 2605.

29. (a) Martin, J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. I* **1981**, 2415. (b) Martin, J.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1976**, 679.

30. Pillot, J.; Donogues, J.; Calas, R. J. *J. Chem. Res. Synop.* **1977**, 268

31. Fleming, I.; Perry, D. A. *Tetrahedron* **1981**, *37*, 4034.

32. Jong, M. E.; Gaede, B. *Tetrahedron* **1979**, *35*, 621.

33. Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, *66*, 2377.

34. Jones, T. K.; Denmark, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 2642.

35. Monteil, F.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1995**, 1601.

36. (a) Shirakawa, E.; Yamamoto, Y.; Nakao, Y.; Tsuchimoto, T.; Hiyama, T. *Chem. Commun.* **2001**, 1926. (b) Roser, C.; Albers, R.; Sander, W. *Eur. J. Org. Chem.* **2001**, 269. (c) Shirakawa, E.; Nakao, Y.; Yoshida, H.; Hiyama, T. *J. Am. Chem. Soc.* **2000**, *122*, 9030. (d) Marshall, J. A.; Welmaker, G. S.; Gung, B. W. *J. Am. Chem. Soc.* **1991**, *113*, 647. (e) Capperucci, A.; Degl'Innocenti, A.; Faggi, C.; Reginato, G.; Ricci, A.; Dembech, P.; Seconi, G. *J. Org. Chem.* **1989**, *54*, 2966. (f) Chan. P. C. M.; Chong, J. M. *J. Org. Chem.* **1988**, *53*, 5584.

37. Goldberg, Y.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1994**, 1209.

38. (a) Masuda, T. J. *Synth. Org. Chem. Japan* **1985**, *43*, 744. (b) Park, J. S.; Serwon, S.; Langner, A.; Ehrlich, P. *J. Polym. Sci.: Part A: Polym. Chem.* **1989**, *27*, 4281. (c) Billingham, N. C.; Calvert, P. D. *Adv. Polym. Sci.* **1989**, *90*, 3.

39. Simonoscu, C. I.; Percec, V.; Dumitrsku, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497.

40. Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci.: Part A: Polym. Chem.* **1987**, *25*, 1027.

41. Douglas, W. E.; Overend, A. S. *J. Organomet. Chem.* **1993**, *444*, C62.

42. Haupt, H. J.; Ortmann, U. *Anorg. Allg. Chem.* **1993**, *619*, 1209.

43. Trost, B. M.; Fleming, I. in *Comprehensive Organic Synthesis*, Vol. 8, Perganon, Oxford, **1992**, Ch. 3.12.

44. (a) Fogg, D. E.; James, B. R.; Kilner, M. *Inorg. Chim. Acta* **1994**, *222*, 85. (b) Langley, C. J.; Goodwin, T. J.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1625. (c) Brune, H. A.; Unsin, J.; Hemmer, R.; Reichnardt, M. *J. Organomet. Chem.* **1989**, *369*, 335. (d) Bhaduri, S.; Sapre, N.; Sharma, K.; Jones, P. J.; Carpenter, G. *J. Chem. Soc., Dalton Trans.* **1990**, 1305. (e) Basu, A.; Bhaduri, S.; Sapre, N.; Sharma, K.; Jones, P. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1126.

45. (a) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562. (b) Willoughby, C. A.; Buchwald, S. L. *J. Org. Chem.* **1993**, *58*, 7627. (c) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952. (d) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11703.

46. (a) Spindler, F.; Pugin, B.; Blaser, H.-U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 558. (b) Chan, Y. N. C.; Osborn, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9400. (c) Chan, Y. N. C.; Meyer, D.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1990**, 869.

47. (a) Burk, M. J.; Feaster, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 6266. (b) Burk, M. J.; Martinez, J. P.; Feaster, J. E.; Cosford, N. *Tetrahedron* **1994**, *50*, 4399. (c) Kang, G. –J., Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1466. (d) Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P.; Kang, G. –J.; Herb, G.; Thorburn, I. S.; Spogharich, R. *J. Mol. Catal.* 1990, *62*, 243. (e) Becalski, A., G.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kang, G. –J.; Rettig, S. *Inorg. Chem.* **1991**, *30*, 5002. (f) Ball, G. E.; Cullen, W. R.; Fryzuk, M. D.; Henderson, W. J.; James, B. R.; MacFarlane, K. S. *Inorg. Chem.* **1994**, *33*, 1464. (g) Bakos, J.; Tóth, I.; Heil, B.; Markó, L. *J.*

Organomet. Chem. **1985**, *279*, 23. (h) Bakos, J.; Tóth, I.; Heil, B.; Szalontai, G.; Párkányi, L.; Fülöp, V. *J. Organomet. Chem.* **1989**, *370*, 263. (i) Lensink, C.; de Vries, J. G. *Tetrahedron: Asymmetry* **1992**, *3*, 235. (j) Lensink, C.; de Vries, J. G. *Tetrahedron: Asymmetry* **1993**, *4*, 215.

48. (a) Levi, A.; Modena, G.; Scorrano, G. *J. Chem. Soc., Chem. Commun.* **1975**, 6. (b) Oppolzer, W.; Wills, M.; Starkemann, C.; Bernardinelli, G. *Tetrahedron Lett.* **1990**, *31*, 4117.

49. Zhou, Z.; James, B. R.; Alper, H. *Organometallics* **1995**, *14*, 4209.

50. Amaratunga, S.; Alper, H. *J. Organomet. Chem.* **1995**, *488*, 25.

51. Alper, H.; Hashem, K.; Heveling, J. *Organometallics* **1982**, *1*, 775.

52. Cuny, G.D.; Buchwald, S.L. *J. Am. Chem. Soc.* **1993**, *115*, 2066.

53. Johnson, J.R.; Cuny, G.D.; Buchwald, S.L. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1760.

54. (a) Hidai, M.; Fukuoka, A.; Koyasu, Y.; Uchida, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 516. (b) Hidai, M.; Fukuoka, A.; Koyasu, Y.; Uchida, Y. *J. Mol. Catal.* 1986, *35*, 29. (c) Hidai, M.; Matsuzaka, H. *Polyhedron* **1988**, *7*, 2369. (d) Ishii, Y.; Sato, M.; Matsuzaka, H.; Hidai, M. *J. Mol. Catal.* 1989, *54*, L13.

55. Ishii, Y.; Miyashita, K.; Kamita, K.; Hidai, M. *J. Am. Chem. Soc.* **1997**, *119*, 6448.

56. Bärfacker, L.; Hollmann, C.; Eilbracht, P. *Tetrahedron* **1998**, *54*, 4493.

57. Jain, N. F.; Cirillo, P. F.; Schaus, J. V.; Panck, J. S. *Tetrahedron Lett.* **1995**, *36*, 8723.

58. Eguchi, M.; Zeng, Q.; Korda, A.; Ojima, I. *Tetrahedron Lett.* **1993**, *34*, 915.

59. (a) Ojima, I.; Vu, A. T.; McCullagh, J. V.; Kinoshita, A. *J. Am. Chem. Soc.* **1999**, *121*, 3230. (b) Ojima, I.; Zhu, J.; Vidal, E. S.; Kass, D. F. *J. Am. Chem. Soc.* **1998**, *120*, 6690.

60. (a) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1993**, 12, 11. (b) Doyle, M. P.; Shanklin, M. S. *Organometallics* **1994**, *13*, 1081.

61. Alonso, M. A.; Casares, J. A.; Espinet, P.; Vallés, E.; Soulantica, K. *Tetrahedron Lett.* **2001**, *42*, 5697

62. Bonafoux, D.; Ojima, I. Org. Lett. 2001, 3, 1303..

63. Ojima, I.; Vidal, E. S. *Organometallics* **1999**, *18*, 5103.

64. (a) Inomata, K.; Toda, S.; Kinoshita, H. *Chem. Lett.* **1990**, 1567. (b) Bergbreiter, D. K.; Chen, B.; Weatherforf, D. *J. Mol. Catal.* 1992, *74*, 409.

65. El Ali, B.; Vasopollo, G.; Alper, H. *J. Org. Chem.* **1993**, *58*, 4739.

66. Zargarian, D.; Alper, H. *Organometallics* **1993**, *12*, 712.

67. Amer, B.; Alper, H. *J. Organomet. Chem.* **1990**, *383*, 573.

68. (a) Arzouanian, H.; Petrignami, J. F.;Alper, H. *Tetrahedron Lett.* **1986**, *27*, 5979. (b) Wang, J. X.; Alper, H. *J. Org. Chem.* **1986**, *51*, 275. (c) Alper, H.; Petrignami, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 1154

69. (a) Tsuji, J. *Palladium Reagents and Catalysis*; Wiley: New York, **1995**. (b) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation*; Plenum Press: New York, **1991**. (c) Bohn, C.; Beller, M. *Transition Metals for Fine Chemistry and Organic Synthesis*; VCH: Weinheim-Germany, **1998**.

70. (a) Jayasree, S.; Seayed, A.; Gupte, S. P.; Chaudhari, V. *Cat. Lett.* **1999**, *58*, 213. (b) El Ali, B.; Alper, H. . *J. Mol. Catal.* 1991, *67*, 29. (c) El Ali, B.; Alper, H. . *J.*

Mol. Catal. 1995, *96*, 197. (d) Drent, A.; Budzelaar, M. *J. Organomet. Chem.* **1993**, *455*, 247.

71. El Ali, B.; Tijani, J.; El-Ghanam, A. M. *Tetrahedron Lett.* **2001**, *42*, 2385.

72. (a) Akao, M.; Sugawara, S.; Amino, K.; Inoue, Y. *J. Mol. Catal.* 2000, *157*, 117. (b) Alper, H.; Maldonado, M. S.; Lin, I. J. B. *J. Mol. Catal.* 1988, *49*, L27. (c) Knifton, F. *J. Mol. Catal.* 1977, *2*, 293.

73. Alper, H.; Despeyroux, B.; Woell, J. B. *Tetrahedron Lett.* **1983**, *24*, 5691.

74. (a) Heck, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 2712. (b) Chiusoli, G. P. Ventturello, C.; Merzoni, S. *Chem. Ind.* **1968**, 977.

75. (a) Son, S. U.; Park, S. –J.; Lee, S. I.; Chumg, Y. K. *Perkin 1* **2000**, 141. (b) Lee, B. Y.; Chung, Y. K.; Jeong, N.; Lee, Y.; Hwang, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 8793. (c) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc., Perkins Trans. 1* 1973, 975. (d) Baxter, R. J.; Knox, G. R.; Pauson, P. L.; Spicer, M. D. *J. Organomet. Chem.* **1999**, *579*, 90.

76. (a) Shibata, T.; Yamashita, K.; Ishida, H.; Takagi, K. *Org. Lett.* **2001**, *3*, 1217. (b) MacWhorter, S. E.; Sampath, V.; Olmstead, M. M.; Schore, N. E. *J. Org. Chem.* **1988**, *53*, 203.

77. (a) Gabriele, B.; Salemo, G.; Costa, M.; Chiusoli, G. P. *Tetrahedron Lett.* **1999**, *40*, 989. (b) Joh, T.; Nagata, H.; Takahashi, S. *Inorg. Chim. Acta* **1994**, *220*, 45. (c) Mise, T.; Hong, P.; Yamazaki, H. *J. Org. Chem.* **1983**, *48*, 238. (d) Joh, T.; Nagata, H.; Takahashi, S. *Chem. Lett.* **1992**, 1305.

78. (a) Rudler, H.; Parlier, A.; Rudler, M.; Vaissermann, J. *J. Organomet. Chem.* **1998**, *567*, 101. (b) Kang, H. Y.; Cho, Y. S.; Koh, H. Y.; Chang, M. H. *Tetrahedron Lett.* **1991**, *32*, 2779.

79. Hicks, F. A.; Kahlaoni, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 5881.

80. Takeuchi, R.; Yasue, H. *J. Org. Chem.* **1993**, *58*, 5386.

81. Hong, P.; Mise, T.; Yamazakim, H. *J. Organomet. Chem.* **1991**, *412*, 291.

82. Arzoumanian, H.; Jean, M.; Nuel, D.; Cabrera, A.; Garcia Gutierrez, J. L.; Rosas, N. *Organometallics* **1995**, *14*, 5438.

83. Xiao, W.-J..; Alper, H. *J. Org. Chem.* **1997**, *62*, 3422.

84. Huh, F. –T.; Orita, A.; Alper, H. *J. Org. Chem.* **1993**, *58*, 6956.

85. Arzoumanian, H.; Jean, M.; Nuel, D.; Cabrera, A.; Garcia, J. L.; Rosas, N. *Organometallics* **1997**, *16*, 2726.

86. Kalinin, V. N.; Shostakovskii, M. V.; Ponomarev, A. B. *Tetrahedron Lett.* **1990**, *31*, 4073.

87. Xiao, W. –J.; Alper, H. . *J. Org. Chem.* **1999**, *64*, 9646.

88. An, Z.; Catallani, M.; Chiusoli, G. P. *J. Organomet. Chem.* 1990, *397*, C31.

89. (a) Okuro, K.; Furune, M.; Miura, M.; Nomura, M. . *J. Org. Chem.* **1992**, *57*, 4754. (b) Inoue, Y.; Taniguchi, M.; Hashimoto, H.; Ohuchi, K.; Imaizumi, S. *Chem. Lett.* **1988**, 81.

90. Okuro, K. Alper, H. *J. Org. Chem.* **1997**, *62*, 1566.

91. Larksarp, C.; Alper, H. *Org. Lett.* **1999**, *1*, 1619.

92. Larksarp, C.; Alper, H. *J. Org. Chem.* **1999**, *64*, 9194.

93. El Ali, B.; Alper, H. *Synlett* **2000**, 161.

94. (a) Trost, B. M.; Fleming, I. in *Comprehensive Organic Synthesis*, Vol. 4, Perganon, Oxford, **1991**, pp. 913 - 950; (b) Elschenbroich, C.; Salzer, A. *in Organometallics: A Concise Introduction*, 2nd Ed., VCH Publishers, New York, **1992**, pp. 434 - 437; (c) Cornils, B; Herrmann, W. A. in *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1, VCH Publishers, **1996**, pp.29 - 111.

95. (a) Fell, B.; Beutler, M. *Tetrahedron Lett.* **1972**, 3455. (b) Botteghi, C.; Salomon, C. *Tetrahedron Lett.* **1974**, 4285. (c) Greenfield, H.; Wotiz, J. H.; Wender, I. *J. Org. Chem.* **1957**, *22*, 542. (d) Wuts, P. G. M.; Ritter, A. R. *J. Org. Chem.* **1989**, *54*, 5180. (e) Campi, E.M.; Jackson, W. R.; Nilsson, Y. *Tetrahedron Lett.* **1991**, *32*, 1093. (f) Nombel, P.; Lugan, N.; Mulla, F.; Lavigne, G. *Organometallics* **1994**, *13*, 4673.

96. Doyama, K.; Joh, T.; Takahashi, S. *Tetrahedron Lett.* **1996**, *27*, 4497.

97. Doyama, K.; Joh, T.; Shiohara, T.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4353.

98. Campi, E. M.; Jackson, W. R. *Aust. J. Chem.* **1989**, *42*, 471.

99. Xu, W.; Alper, H.; *Macromolecules* **1996**, *29*, 6695.

100. Gevorgyan, V.; Takeda, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11313.

101. Stang, P. J.; Diederich, F. in *Modern Acetylene Chemistry*, VCH Publishers, New York, **1995**, Chapter 7.

102. (a) O'Shea, D. F.; Sharp, J.T. *J. Chem. Soc., Perkins Trans. 1*, **1997**, 3025. (b) Kimura, M.; Ezoc, A.; Shibata, K.; Tamaru, Y. *J. Am. Chem. Soc.* **1998**, *120*,

4033. (c) Barluenga, J.; Canteli, R. M.; Flórez, J.; Gutiérrez-Rodriquez, A.; Martin, E. *J. Am. Chem. Soc.* **1998**, *120*, 2514.

103. Sauvêtre, R.; Normant, J. F. *Tetrahedron Lett.* **1982**, *23*, 4325.

104. Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Rühter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698.

105. Stevens, M. P. in *Polymer Chemistry: An Introduction*, 2nd Ed., Oxford University Press, New York, **1990**, Chapter 6.

106. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. in *Spectrometric Identification of Organic Compounds*, 5th Ed.; John Wiley and Sons, New York, **1991**, Chapter 6.

107. (a) Dubois, M. R. *Chem. Rev.* **1989**, *89*, 1. (b) Hegedus, L. L.; McCabe, R. W. In *Catalyst Poisoning*; Marcel Dekker: New York, **1984**. (c) Hutton, A. T. In *Comprehensive Coordination Chemistry*; Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Perganon: Oxford, **1984**; Vol. 5, p 1151.

108. (a) Joule, J. A.; Mills, K.; Smith, G. F. In *Heterocyclic Chemistry, 3rd Edition*; Chapman and Hall: London, **1995**. (b) Meyers, A. I. In *Heterocycles in Organic Chemistry*; Taylor, E.C.; Weissberger, A., Eds; John Wiley and Sons:: New York, 1974. (c) Paquette, L. A. In *Principles of Modern Heterocyclic Chemistry*, W. A. Benjamin Inc.: New York, **1968**.

109. (a) Krohn, K.; Kirst, H. A.; Maag, H., Eds. In *Antibiotics and Antivirial Compounds*; VCH Publishers Inc.: New York, **1993**. (b) Lednicer, D.; Mitscher, L. A. In *Organic Chemistry of Drug Synthesis*; John Wiley and Sons: New York, **1977**.

110. (a) Choi, W.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1189. (b) Ng, S. C.; Chan, H. S. O.; Wong,, P. M. L.; Tan, K. L.; Tanb, B. T. G. *Polymer* **1998**, *39*, 4963. (c) Longridge, J. J.; Rawson, J. M. *Polyhedron* **1998**, *17*, 1871.

111. Aldea, R.; Alper, H. *J. Org. Chem.* **1995**, *60*, 8365.

112. Khumtaveeporn, K.; Alper, H. *J. Am. Chem. Soc.* **1994**, *116*, 5662.

113. Xiao, W.-J.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **1998**, *63*, 2609.

114. Xiao, W.-J..; Alper, H. *J. Org. Chem.* **1998**, *63*, 7939.

115. Xiao, W.-J.; Vasapollo, G.; Alper, H. *J. Org. Chem.* **1999**, *64*, 2080.

116. Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V. In *Comprehensive Heterocyclic Chemistry II*; Perganon: Oxford, **1996**, Vol. 2, p 679.

117. (a) Carpita, A.; Lezzi, A.; Rossi, R.; Marchetti, F.; Merlino, S. *Tetrahedron* **1985**, *41*, 621. (b) Rossi, R.; .Carpita, A.; Lezzi, A. *Tetrahedron* **1984**, *40*, 2773. (c) Sakamoto, T; Shiraiwa, M.; Kondo, Y.; Yamanaka, H. *Synthesis* **1983**, 312 (d) Ames, D. E.; Bull, D.; Takundwa, C. *Synthesis* **1981**, 364. (e) D'Auria, M.; De Mico, A.; D'Onofrio, F.; Piancatelli, G. *J. Org. Chem.* **1987**, *52*, 5243.

118. (a) Boivin, J.; Huppe, S.; Zard, S. Z. *Tetrahedron Lett.* **1996**, *37*, 8735. (b) Degl'Innocenti, A.; Funicello, M.; Scafato, P.; Spagnolo, P. *Tetrahedron Lett.* **1997**, *38*, 2171. (c) Varney, M. D.; Romines, W. H.; Palmer, C. L., PCT Int. Appl. WO 9,640,674, **1996**. (d) Tanaka, H.; Fukuzumi, K.; Togawa, T.; Banno, K.; Ushiro, T.; Morii, M.; Nakatani, T., PCT Int. Appl. WO 9,633,195, **1996**. (e) Chan, M. F.; Raju, B. G.; Kois, A.; Verner, E. J.; Wu, C.; Castillo, R. S.;

Yalamoori, V.; Balaji, V. N., US Patent 5,594,021, **1997**. (f) Labadie, S. S. *Synth. Commun.* **1998**, *28*, 2531.

119. (a) Li, Y.; Thiemann, T.; Sawada, T.; Mataka, S.; Tashiro, M. *J. Org. Chem.* **1997**, *62*, 7926. (b) Katritzky, A. R.; Serdyuk, L.; Xie, L.; Ghiviriga, I. *J. Org. Chem.* **1997**, *62*, 6215. (c) Hoerndler, C.; Hansen, H. J. *Helv. Chimica Acta* **1997**, *80*, 2520. (d) Kaye, P. T.; Molema, W. E. *Chem. Commun.* **1998**, 2479. (e) Cossy, J.; Rakotoarisoa, H.; Kahn, P.; Desmurs, J. -R. *Tetrahedron Lett.* **1998**, *39*, 9671. (f) Jones, R. C. F.; Patel, P.; Hirst, S. C.; Smallridge, M. J. *Tetrahedron* **1998**, *54*, 6191. (g) Höppe, H. A., Lloyd-Jones, G. C.; Murray, M.; Peakman, T. M.; Walsh, K. E. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1545.

120. (a) Boldi, A. M.; Johnson, C. R.; Eissa, H. O. *Tetrahedron Lett.* **1999**, *40*, 619. (b) Lu, T. -J.; Cheng, S. -M.; Sheu, L. -J. *J. Org. Chem.* **1998**, *63*, 2738. (c) Shiraishi, H.; Nishitani, T.; Sakaguchi, S.; Ishii. Y. *J. Org. Chem.* **1998**, *63*, 6234. (d) Yoshimatsu, M.; Oguri, K.; Ikeda, K.; Gotoh, S. *J. Org. Chem.* **1998**, *63*, 4475.

121. (a) Chang, C. -T.; Chen, K. -M; Liu, W. -H.; Lin, F. -I.; Wu, R. -T., U.S. Patent 5,602,170, **1997**. (b) Chang, C. -T.; Chen, K. -M; Liu, W. -H.; Lin, F. -I.; Wu, R. -T., U.S. Patent 5,747,525, **1998**. (c) Ebermann, R.; Alth, G.; Kreitner, M.; Kubin, A. *J. Photochem. Photobiol., B* **1996**, *36*, 95. (d) Wierzbicky, M.; Sauveur, F.; Bonnet, J.; Tordjman, C., Fr. Demande FR 2,752,576, **1998**. (e) Asari, T.; Okamoto, S.; Kono, S., Japanese Patent 10,316,673, **1998.**

122. (a) Walter, H., PCT Int. Appl. WO 9,733,890, **1997**. (b) Morita, K.; Murabayashi, A., Japanese Patent 09,095,482, **1997**. (c) Kanehira, K.; Tagawa,

H.; Shiono, M., Japanese Patent 09, 104,682, **1997**. (d) Fischer, R.; Dumas, J.; Bretschneider, T.; Gallenkamp, B.; Lieb, F.; Wernthaler, K.; Erdelen, C.; Wachendorff-Neumann, U.; Mencke, N.; Turberg, A., Ger. Offen DE 19,527,190, **1996**. (e) Theobald, H.; Harries, V.; Kardorff, U.; Baeuerle, P.; Goetz, G., PCT Int. Appl. WO 9,314,079, **1993.**

123. Sargent, A. L.; Titus, E. P. *Organometallics* **1998**, *17*, 65.

124. (a) Rao, Y. S. *Chem. Rev.* **1976**, 625. (b) Barton, D.; Nakanishi, K.; Meth-Cohn, O. in *Comprehensive Natural Products Chemistry*, Vol. 8, Elsevier Science Ltd., Oxford, **1999**, pp. 378 - 385. (c) Rao, G. V.; Cain, R. B. *J. Chem. Soc., Perkin Trans I* **1996**, 2111. (d) Handa, S. *Tetrahedron: Asymmetry* **1996**, *7*, 1281. (e) Knight, D. W. *Contemp. Org. Synth.* **1994**, *1*, 287.

125. (a) Alper, H.; Leonard, D. *Tetrahedron Lett.* **1985**, *26*, 5639. (b) Alper, H.; Leonard, D. *J. Chem. Soc., Chem. Commun.* **1985**, 511. (c) Alper, H.; Hamel, N. *J. Chem. Soc., Chem. Commun.* **1990**, 135. (d) El Ali, B.; Okuro, K.; Vasapollo, G.; Alper, H. *J. Am. Chem. Soc.* **1996**, *118*, 4264. (e) Brunner, M.; Alper, H. *J. Org. Chem.* **1997**, *62*, 7565. (f) Cao, P.; Zhang, X. *J. Am. Chem. Soc.* **1999**, *121*, 7708.

126. (a) Cowell, A.; Stille, J. K. *Tetrahedron Lett.* **1979**, 133. (b) Inoue, Y.; Ohuchi, K.; Yen, I. -F.; Imaizumi, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3518. (c) El Ali, B.; Alper, H. *J. Org. Chem.* **1991**, *56*, 5357. (d) Matsushita, K.; Komori, T.; Oi, S.; Inoue, Y. *Tetrahedron Lett.* **1994**, *35*, 5889. (e) Gabriele, B.; Costa, M.; Salerno, G.; Chiusoli, G. P. *J. Chem. Soc., Chem. Commun.* **1994**, 1429. (f) Mandai, T.; Tsujiguchi, Y.; Matsuoka, S.; Saito, S.; Tsuji, J. *J. Organomet. Chem.* **1995**, *488*,

127. (g) Xiao, W. -J.; Alper, H. *J. Org. Chem.* **1997**, *62*, 3422. (h) Gabriele, B.; Salerno, G.; De Pascali, F.; Costa, M.; Chiusoli, G. P. *J. Chem. Soc., Perkin Trans. 1* **1997**, 147. (i) Allevi, P.; Ciuffreda, P.; Anastasia, M. *Tetrahedron: Asymmetry* **1997**, *8*, 93. (j) Dupont, J.; Donato, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 949. (k) Ogawa, A.; Kawabe, K. -I.; Kawakami, J. -I.; Mihara, M.; Hirao, T. *Organometallics* **1998**, *17*, 3111.

127. (a) Joh, T.; Doyama, K.; Onitsuka, K.; Shiohara, T.; Takahashi, S. *Organometallics* **1991**, *10*, 2493. (b) Copéret, C.; Sugihara, T.; Wu, G.; Shimoyama, I.; Negishi, E, -I. *J. Am. Chem. Soc.* **1995**, *117*, 3422. (c) Trost, B. M.; Fleming, I. in *Comprehensive Organic Synthesis*, Vol. 5, Pergamon, Oxford, **1991**, pp. 1136 - 1138.

128. Rossi, R.; Bellina, F.; Biagetti, M.; Mannina, L. *Tetrahedron Lett.* **1998**, *39*, 7599.

129. Agbossou, F.; Carpentier, J. -F.; Mortreux, A. *Chem. Rev.* **1995**, *95*, 2485.

130. Kawaguchi, T.; Yasuta, S.; Inoue, Y. *Synthesis* **1996**, 1431.

131. Tohda, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1977**, 777.

132. Hauptmann, H.; Mader, M. *Synthesis* **1978**, 307.

133. Hirao, T.; Misu, D.; Agawa, T. *Tetrahedron Lett.* **1986**, *27*, 933.

134. (a) Rao, A. V. R.; Reddy, S. P.; Reddy, E. R. *J. Org. Chem.* **1986**, *51*, 4158. (b) Wadsworth, D. H.; Geer, S. M.; Detty, M. R. *J. Org. Chem.* **1987**, *52*, 3662.

135. (a) Ma, D.; Ma; J.; Ding, W.; Dai, L. *Tetrahedron: Asymmetry* **1996**,*7*, 2365. (b) Jouin, P.; Castro, B. *J. Chem. Soc. Perkin Trans. 1* **1987**, 1177.

136. (a) Casiraghi, G.; Spanu, P.; Rassu G.; Pinna, L.; Ulgheri, F. *J. Org. Chem.* **1994**, *59*, 2906. (b) Klaver, W. J.; Hiemstra, H.; Speckamp, W. N. *J. Am. Chem. Soc.* **1989**, *111*, 2588.

137. (a) Iwasawa, N.; Maeyama, K. *J. Org. Chem.* **1997**, 62, 1918. (b) Shiraki, R.; Sumino, A.; Tadano, K.; Ogawa, S. *J. Org. Chem.* **1996**, *61*, 2845.

138. Wiedhopf, R. M.; Trumbull, E. R.; Cole, J. R. *J. Pharm. Sci.* **1973**, *62*, 1206.

139. Bosch, J.; Roca, T.; Catena, J. –L.; Llorens, O.; Pérez, J. –J.; Lagunas, C.; Fernández, A. G.; Miquel, I.; Fernández-Serrat, A.; Farrerons, C. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1745.

140. Smith, III, A. B.; Hirschmann, R.; Pasternak, A.; Guzman, M. C.; Yokoyama, A.; Sprengeler, P. A.; Darke, P. L.; Emini, E. A.; Schleif. W. A. *J. Am. Chem. Soc.* **1995**, *117*, 11113.

141. Spaltenstein, A.; Almond, M. R.; Bock, W. J.; Cleary, D. G.; Furfine, E. S.; Hazen, R. J.; Kazmierski, W. M.; Salituro, F. G.; Tung, R. D.; Wright, L. L. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 1159.

142. (a) Ogiso, T.; Iwaki, M.; Tanino, T.; Ikeda, K.; Paku, T.; Horibe, Y.; Suzuki, H. *J. Pharm. Sci.* **1998**, 87, 594. (b) Pinza, M.; Farina, C.; Cerri, A.; Pfeiffer, U.; Riccaboni, M. T.; Banfi, S.; Biagetti, R.; Pozzi, O.; Magnani, M.; Dorigotti, L. *J. Med. Chem.* **1993**, *36*, 4214.

143. Grese, T. A.; Pennington, L. D.; Sluka, J. P.; Adrian, M. D.; Cole, H. W.; Fuson, T. R.; Magee, D. E.; Phillips, D. L.; Rowley, E. R.; Shetler, P. K.; Short, L. L.; Venugopalan, M.; Yang, N. N.; Sato, M.; Glasebrook, A. L.; Bryant, H. U. *J. Med. Chem.* **1998**, *41*, 1272.

144. (a) Reddy, P. A.; Hsiang, B. C. H.; Latifi, T. N.; Hill, M. W.; Woodward, K. E.; Rothman, S. M.; Ferrendelli, J. A.; Covey, D. F. *J. Med. Chem.* **1996**, *39*, 1898. (b) Yong, A. K.; Stemp, G.; Blackburn, T. P.; Buckingham, R. E.; Chan, W. N.; Evans, J. M.; Hadley, M. S.; Thompson, M.; Upton, N.; Stean, T. O.; *Bioorg. Med. Chem. Lett.* **1995**, *5*, 1163.

145. Williams, P. D.; Perlow, D. S.; Payne, L. S.; Holloway, M. K.; Siegl, P. K. S.; Schorn, T. W.; Lynch, R. J.; Strouse, J. F.; Vlasuk, G. P.; Hoogsteen, K.; Springer, J. P.; Bush, L.; Halgren, T. A.; Richards, A. D.; Kay, J.; Veber, D. F. *J. Med. Chem.* **1991**, *34*, 887.

146. Butler, D. E.; Leonard, J. D.; Caprathe, B. W.; L'Italien, Y. J.; Pavia, M. R.; Hershenson, F. M.; Poschel, P. H.; Marriott, J. G. *J. Med. Chem.* **1987**, *30*, 498.

147. Trost, B. M.; Roth, G. J. *Org. Lett.* **1999**, *1*, 67.

148. Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324.

149. Ojima, I.; Korda, A.; Shay, W. R. *J. Org. Chem.* **1991**, *56*, 2024.

150.) Sigman, M. S.; Eaton, B. E. *J. Org. Chem.* **1994**, *59*, 7488.

151. (a) Cuiper, A. D.; Kouwijzer, M. L. C. E.; Grootenhuis, P. D. J.; Kellogg, R. M.; Feringa, B. L. *J. Org. Chem.* **1999**, *64*, 9529. (b) van der Deen, H.; Cuiper, A. D.; Hof, R. P.; van Oeveren, A.; Ferimha, B. L.; Kellogg, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 3801.

152. Kel'in, A. V.; Sromek, A. W.; Gevorgyan, V. *J. Am. Chem. Soc.* **2001**, *123*, 2074.

153. Dai, G.; Larock, R.C. *Org. Lett.* 2001, *3*, 4035.

154. (a) Lin, S. -Y.; Sheng, H. -Y.; Huang, Y. -Z. Synthesis 1991, 235. (b) Faust, R.; Göbelt, B. *Tetrahedron Lett.* **1997**, *38*, 8017.

155. Kantlehner, W.; Mergen, W. W. In Comprehensive Organic Functional Group Transformations; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Tarrytown, NY, **1995**; Vol. 5, Chapter 17.

156. (a) Shi, C.; Wang, K. K. *J. Org. Chem.* **1998**, *63*, 3517. (b) Shi, C.; Zhang, Q.; Wang, K. K. *J. Org. Chem.* **1999**, *64*, 925.

157. Wilmore, B. H.; Cassidy, P. B.; Warters, R. L.; Roberts, J. C. *J. Med. Chem.* **2001**, *44*, 2661.

158. Domenico, R.; Spinelli, S.; Gallico, L.; Fiocchi, L.; Lotto, A.; Menta, E.; Borghi, A.; Rosa, C. D.; Tognella, S. *J. Med. Chem.* **1995**, *38*, 508.

159. Bagley, M. C.; Bashford, K. E.; Hesketh, C. L.; Moody, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 3301.

160. Andurkar, S. V.; Beguin, C.; Stables, J. P.; Kohn, H. *J. Med. Chem.* **2001**, *44*, 1475.

161. Ballart, B.; Marti, J.; Velasco, D.; Lopez-Calahorra, F.; Pascual, J.; Garcia, M. L.; Cabre, F.; Mauleon, D. *Eur. J. Med. Chem.* **2000**, *35*, 439.

162. Gu, X. –H.; Wan, X. –Z.; Jiang, B. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 569.

163. Mimoto, T.; Kato, R.; Takaku, H.; Nojima, S.; Terashima, K.; Misawa, S.; Fukazawa, T.; Ueno, T.; Sato, H.; Shintani, M.; Kiso, Y.; Hayachi, H. *J. Med. Chem.* **1999**, *42*, 1789.

164. Kucukguzel, S. G.; Oruc, E. E.; Rollas, S.; Sahin, F.; Ozbek, A. *Eur. J. Med. Chem.* **2002**, *37*, 197.

165. Hrib, N. J.; Jurcak, J. G.; Bregna, D. E.; Burgher, K. L.; Hartman, H. B.; Kafka, S.; Kerman, L. L.; Kongsamut, S.; Roehr, J. E. *J. Med. Chem.* **1996**, *39*, 4044.

166. Graciet, J. C.; Niddam, V.; Gamberoni, M.; Trabaus, C.; Dessolin, J.; Medou, M.; Mourier, N.; Zoulim, F.; Borel, C. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 1775.

167. Yanagisawa, H.; Takamura, M.; Yamada, E.; Fujita, S.; Fujiwara, T.; Yachi, M.; Isobe, A.; Hagisawa, Y. *Bioorg. Med. Chem. Lett.* **2000**, *10*, 373.

168. Prabhaker, C.; Madhusudhan, G.; Sahadev, K.; Reddy, C. M.; Sarma, M. R.; Reddy, G. O.; Chakrabarti, R.; Rao, C. S.; Kumar, T. D.; Rajagopalan, R. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 2725.

169. Tanis, S. P.; Parker, T. T.; Colca, J. R.; Fisher, R. M.; Kletzein, R. F. *J. Med. Chem.* **1996**, *39*, 5053.

170. Khalil, E. M.; Pradhan, A.; Ojala, W. H.; Gleason, W. B.; Mishra, R. K.; Johnson, R. L. *J. Med. Chem.* **1999**, *42*, 2977.

171. Tamura, S. Y.; Goldman, E. A.; Brunck, T. K.; Ripka, W. C.; Semple, J. E. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 331.

172. Hasegawa, M.; Nakayama, A.; Yokohama, S.; Hosokami, T., Kurebayashi, Y.; Ikeda, T.; Shimoto, Y.; Ide, S.; Honda, Y.; Suzuki, N. *Chem Pharm. Bull.* **1995**, *43*, 1125.

173. Kiec-Kononowicz, K.; Karolak-Wojciechowska, J.; Muller, C. E.; Schumacher, B.; Pekala, E.; Szymanska, E. *Eur. J. Med. Chem.* **2001**, *36*, 407.

174. (a) Amblard, M.; Daffix, I.; Bedos, P.; Bergé, G; Pruneau, D.; Paquet, J. –L.; Luccarini, J. –M.; Bélichard, P.; Dodey, P.; Martinez, J. *J. Med. Chem.* **1999**, *42*, 4185. (b) Amblard, M.; Daffix, I.; Bergé, G; Calmès, M.; Dodey, P.; Pruneau, D.; Paquet, J. –L.; Luccarini, J. –M.; Bélichard, P.; Martinez, J. *J. Med. Chem.* **1999**, *42*, 4193. (c) Robl, J. A.; Sun, C. –Q.; Stevenson, J.; Ryono, D. E.; Simpkins, L.

M.; Cimarusti, M. P.; Dejneka, T.; Slusarchyk, W. A.; Chao, S.; Stratton, L.; Misra, R. N.; Bednarz, M. S.; Asaad, M. M.; Cheung, H. S.; Abboa-Offei, B. E.; Smith, P. L.; Mathers, P. D.; Fox, M; Schaeffer, T. R.; Seymour, A. A.; Trippodo, N. C. *J. Med. Chem.* **1997**, *40*, 1570.

175. Boschelli, D. H.; Connor, D. T.; Kramer, J. B.; Unangst, P. C. US Patent 5,489,586, **1996.**

176. (a) Medh, J. D.; Rex, K. A.; Benedict, C. R.; Sordahl, L.A. *J. Cardiovasc. Pharmacol.* **1991**, *18*, 473. (b) Kawai, A.; Inoue, H.; Narita, H.; Nagao, T. European Patent 416,479, **1991.**

177. Khumtaveeporn, K.; Alper, H. *Acc. Chem. Res.* **1995**, *28*, 414.

178. Mori, T.; Sawada, Y.; Oku, A. *J. Org. Chem.* **2000**, *65*, 3620.

179. (a) Mori, T.; Oku, A. *Chem. Commun.* **1999**, 1339. (b) Oku, A.; Murai, N.; Baird, J. *J. Org. Chem.* **1997**, *62*, 2123.

180. Ohno, M.; Noda, M.; Yamamoto, Y.; Eguchi, S. *J. Org. Chem.* **1999**, *64*, 707.

181. Jeong, I. –Y.; Nagao, Y. *Tetrahedron Lett.* **1998**, *39*, 8677.

182. (a) Holzapfel, C. W.; Marais, L. *Tetrahedro Lett.* **1997**, *38*, 8585. (b) Umehara, M.; Honnami, H.; Hishida, S.; Kawata, T.; Ohba, S.; Zen, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 562.

183. Satake, A.; Ishii, H.; Shimizu, I.; Inoue, Y.; Hasegawa, H.; Yamamoto, A. *Tetrahedron* **1995**, *51*, 5331.

184. Baeg, J. –O.; Alper, H. *J. Org. Chem.* **1995**, *60*, 3092.

185. Nguyen, P. T.; Palmer, W. S.; Woerpel, K. A. *J. Org. Chem.* **1999**, *64*, 1843.

186. Wang, M. D.; Alper, H. *J. Am. Chem. Soc.* **1992**, *114*, 7018.

187. (a) Davoli, P.; Moretti, I.; Prati, F.; Alper, H. . *J. Org. Chem.* **1999**, *64*, 518. (b) Piotti, M. E.; Alper, H. *J. Am. Chem. Soc.* **1996**, *118*, 111.

188. Grotjahn, D. B.; Vollhardt, K. P. C. *Synthesis*, **1993**, 579.

189. Barrett, A. G. M.; Ahmed, M.; Baker, S. P.; Baugh, S. P. D.; Braddock, D. C.; Procopiou, P. A.; White, A. J. P.; Williams, D. J. . *J. Org. Chem.* **2000**, *65*, 3716.

190. Crimmins, M. T.; Tabet, E. A. *J. Am. Chem. Soc.* **2000**, *122*, 5473.

191. Mizotani, M.; Sanemitsu, Y.; Tamaru, Y.; Yoshida, Z. *Tetrahedron* **1986**, *42*, 305.

192. Jacobi, P. A.; Egbertson, M.; Frechette, R. F.; Miao, C.; Weiss, K. T. *Tetrahedron* **1988**, *44*, 3327.

193. Diederich, F.; Stang, PJ. In *Metal-catalyzed Cross-coupling Reactions*; Wiley-VCH: Weinheim, 1998; pp 203 – 229.

194. Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *J. Org. Chem.* **1988**, *53*, 1748.

195. Osmialowski, B.; Kolehmainen, E.; Nissinen, M.; Krygowski, T. M.; Gawinecki, R. *J. Org. Chem.* **2002**, *67*, 3339.

196. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. in *Spectrometric Identification of Organic Compounds*, 5th Ed.; John Wiley and Sons, New York, **1991**, Chapter 5.

197. Park, S. B.; Alper, H. *University of Ottawa*, **August 2002**, Unpublished Work.

198. Gomoll, A. W.; Ogletree, M. L. *Eur. J. Pharm.* **1994**, *271*, 471.

199. Wong, W. C.; Sun, W.; Cui, W.; Chen, Y.; Forray, C.; Vaysse, P. J.; Branchek, T. A.; Gluchowski, C. *J. Med. Chem.* **2000**, *43*, 1699.

200. Huh, P. W.; Belayev, L.; Zhao, W.; Clemens, J. A.; Panetta, J. A.; Busto R.; Ginsberg, M. D. *Eur. J. Pharm.* **2000**, *389*, 79.

201. Mousa, S. A.; Forsythe, M.; Bozarth, J.; Youssef, A.; Wityak, J.; Olson. R.; Sielecki, T. *J. Cardiov. Pharm.* **1998**, *32*, 736.

202. Hashimoto, H.; Imamura, K.; Haruta, J. –I.; Wakitani, K. *J. Med. Chem.* **2002**, *45*, 1511.

203. Kim, M. –Y.; Vankayalapati, H.; Shin-Ya, K.; Wierzba, K.; Hurley, L.H. *J. Am. Chem. Soc.* **2002**, *124*, 2098.

204. Malamas, M. S.; Sredy, J.; Gunawan, I.; Mihan, B.; Sawicki, D. R.; Seestaller. L.; Sullivan, D.; Flam, B. R. *J. Med. Chem.* **2000**, *43*, 995.

205. Boyd, R. E.; Press, J. B.; Rasmussen, C. R.; Raffa, R. B.; Codd, E. E.; Connelly, C. D.; Bennett, D. J.; Kirifides, A. L.; Gardocki, J. F.; Reynolds, B.; Hortenstein, J. T.; Reitz, A. B. *J. Med. Chem.* **1999**, *42*, 5064.

206. Jandu, K. S.; Barrett, V.; Brockwell, M.; Cambridge, D.; Farrant, D. R.; Foster, C.; Giles, H.; Glen, R. C.; Hill, A. P.; Hobbs, H.; Honey, A.; Martin, G. R.; Salmon, J.; Smith, D.; Woollard, P.; Selwood, D. L. *J. Med. Chem.* **2001**, *44*, 681.

207. (a) Li, Q.; Woods, K. W.; Claiborne, A.; Gwaltney, S. L.; Barr, K. J.; Liu, G.; Gehrke, L.; Credo, R. B.; Hui, Y. H.; Lee, J.; Warner, R. B.; Kovar, P.; Nukkala, M. A.; Zielinski, N. A.; Tahir, S. K.; Fitzgerald, M.; Kim, K. H.; Marsh, K.; Frost, D.; Ng, S. –C.; Rosenberg, S.; Sham, H. L. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 465. (b) Nam, N. H.; Kim, Y.; You, Y. J.; Hong, D. H.; Kim, H. M.; Ahn, B. Z. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 3073.

208. Szczepankiewicz, B. G.; Liu, G.; Jae, H. S.; Tasker, A. S.; Gunawardana, I. W.; von Geldem, T. W.; Gwallney, S. L.; Wu-Wong, J. R.; Gehrke, L.; Chiou, W. J.; Credo, R. B.; Alder, J. D.; Nukkala, M. A.; Zielinski, N. A.; Jarvis, K.; Mollison,

K. W.; Frost, D. J.; Bauch, J. L.; Hui, Y. H.; Claiborne, A. K.; Li, Q.; Rosenberg, S. H. *J. Med. Chem.* **2001**, *44*, 4416.

209. (a) Weidner-Wells, M. A.; Boggs, C. M.; Foleno, B. D.; Wira, E.; Bush, K.; Goldschmidt, R. M.; Hlasta, D. J. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 1829. (b) Artico, M.; Mai, A.; Sbardella, G.; Massa, S.; Lampis, G.; Deidda, D.; Pompei, R. *Bioorg. Med. Chem. Lett.* **1998**, *8*, 1493.

210. (a) Genin, M. J.; Allwine, D. A.; Anderson, D. J.; Barbachyn, M. R.; Emmert, D. E.; Garmon, S. A.; Graber, D. R.; Grega, K. C.; Hester, J. B.; Hutchinson, D. K.; Morris, J.; Reischer, R. J.; Ford, C. W.; Zurenko, G. E.; Hamel, J. C.; Schaadt, R. D.; Stapert, D.; Yagi, B. H. *J. Med. Chem.* **2000**, *43*, 953. (b) Pae, A. N.; Kim, S. Y.; Kim, H. Y.; Joo, H. J.; Cho, Y. S.; Choi, K. I.; Choi, J. H.; Koh, H. Y. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 2685.

211. Sakai, M. T.; Hara, J.; Goto, K.; Yamaguchi, I. *J. Cardiov. Pharm.* **2000**, *36*, S95.

212. Uckun, F. M.; Forsyth, C. J.; Parker, H. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 1181.

213. Fernandez, R.; Dherbomez, M.; Letourneux, Y.; Nabil, M.; Verbist, J. F.; Biard, J. F. *J. Nat. Prod.* **1999**, *62*, 678.

214. Henke, B. R.; Blanchard, S. G.; Brackeen, M. F.; Brown, K. K.; Cobb, J. E.; Collins, J. L.; Harrington, W. W.; Hashim, M. A.; Hull-Ryde, E. A.; Kaldor, I.; Kliewer, S. A.; Lake, D. H.; Leesnitzer, L. M.; Lehmann, J. M.; Orband-Miller, L. A.; Miller, J. F.; Mook, R. A.; Noble, S. A.; Oliver, W.; Parks, D. J.; Plunket, K. D.; Szewcyk, J. R.; Willson, T. M. *J. Med. Chem.* **1998**, *41*, 5020.

215. (a) White, D. J.; Kranemann, C. L.; Kuntiyong, P. *Org. Lett.* **2001**, *3*, 4003. (b) Smith, A. B.; Minbiole, K. P.; Verhoest, P. R.; Schelhaas, M. *J. Am. Chem. Soc.* **2001**, *123*, 10942. (c) Huang, H.; Panek, J. S. *Org. Lett.* **2001**, *3*, 1693.

216. Desai, R. C. *J. Org. Chem.* **2001**, *66*, 4939,

217. Lee, K. Y.; Kim, Y. H.; Oh, C. Y.; Ham, W. H. *Org. Lett.* **2000**, *2*, 4041.

218. Yokokawa, F.; Asano, T.; Shioiri, T. *Org. Lett.* **2000**, *2*, 4169.

219. Li, W. -R.; Lin, S. T.; Hsu, N. -M.; Chem, M. -S. *J. Org. Chem.* **2002**, *67*, 4702.

220. Scheidt, K. A.; Bannister, T. D.; Tasaka, A.; Wendt, M. D.; Savall, B. M.; Fegley, G. J.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 6981.

221. Boger, D. L.; Hong, J. *J. Am. Chem. Soc.* **2001**, *123*, 8515.

222. Ha, J. D.; Cha, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 10012.

223. Luker, T.; Hiemstra, H.; Speckamp, W. N. *J. Org. Chem.* **1997**, *62*, 3592.

224. Ma, D.; Sun, H. *J. Org. Chem* **2000**, *65*, 6009.

225. (a) Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001. (b) Piber, M.; Jensen, A. E.; Rottlaender, M.; Knochel, P. *Org. Lett.* **1999**, *1*, 1323.

226. (a) Occhiato, E. G.; Trabocchi, A.; Guama, A. *J. Org. Chem.* **2001**, *66*, 2459. (b) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020.

227. (a) Maguire, M. P.; Sheets, K. R.; McVety, K.; Spada, A. P.; Zilberstein, A. *J. Med. Chem.* **1994**, *37*, 2129. (b) Sandosham, J.; Undheim, , K. *Heterocycles* **1994**, *37*, 501.

228. Gibertson, S. R. Fu, Z. *Org. Lett.* **2001**, *3*, 161.

229. (a) Jung, H. M.; Koh, J. H.; Kim, M. –J.; Park, J. *Org. Lett.* **2000**, *2*, 2487. (b) Lotz, M.; Ireland, T.; Perea, J. J. A.; Knochel, P. *Tetrahedron: Asymmetry* **1999**, *10*, 1839. (c) Jiang, Q.; Xiao, D.; Zhang, Z.; Chao, P.; Zhang, X. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 516.

230. Ojima, I. In *Catalytic Asymmetric Synthesis*; VCH Publishers: New York, 1993; pp 6 – 19 and 245 – 260.

231. (a) Li, G.; Chang, H. –T.; Sharpless, K. B. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 451. (b) Bruncko, M.; Schlingloff, G.; Sharpless, K. B. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1483. (c) Goossen, L. J.; Liu, H.; Dress, K. R.; Sharpless, K. B. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1080.

232. (a) Déziel, R.; Goulet, S.; Grenier, L.; Bordeleau, J.; Bernier, J. *J. Org. Chem.* **1993**, *58*, 3619. (b) Déziel, R.; Malenfant, E.; Thibault, C.; Fréchette, S.; Gravel, M. *Tetrahedron Lett.* **1997**, *38*, 4753. (c) Back, T. G.; Nan, S. *J. Chem. Soc., Perkin Trans. I* **1998**, 3123.

233. (a) Hodges, J. C.; Patt, W. C.; Connolly, C. J. *J. Org. Chem.* **1991**, *56*, 449. (b) Whitney, S. E.; Rickborn, B. *J. Org. Chem.* **1991**, *56*, 3058.

234. Gaeriner, R. *J. Am. Chem. Soc.* **1952**, *74*, 4950.

Claims to Original Research

1. Use of the zwitterionic rhodium complex (η^6-$C_6H_5BPh_3$)$^-Rh^+$(1,5-COD)/$(PhO)_3P$ catalyst system to achieve regioselective hydroformylation of functionalized and non-functionalized conjugated enynes to their formyl dienes.
2. Use of the zwitterionic rhodium complex **1.1**/$(PhO)_3P$ catalyst system for the first regioselective hydroformylation of highly functionalized 2-acetylenic thiophenes. α,β-Unsaturated aldehydes branched to the thiophene ring was the major isomer for all substrates examined.
3. Incorporating the zwitterionic rhodium complex **1.1** for the chemo- and regioselective cyclohydrocarbonylation of α-keto alkynes affording 2-, 2(3*H*)-, and 2(5*H*)-furanones depending on the substituents of the original alkynone using hydroformylation conditions.
4. Tandem cyclohydrocarbonylation/CO insertion of α-imino alkynes to afford tetra-substituted 4-carbaldehydepyrrolino-2-ones by the zwitterionic rhodium **1.1** catalysis utilizing hydroformylation type conditions
5. The zwitterionic rhodium complex **1.1** catalyzed chemo- and regioselective hydrocarbonylative enolation of 2-acetylenic thiazoles to (*Z*)-2-thiazol-2-ylalk-1-en-1-ols under mild hydroformylation conditions.
6. Chemo- and regioselective hydrocarbonylative enolation of 2-acetylenic benzoxazoles to (*Z*)-2-thiazol-2-ylalk-1-en-1-ols by zwitterionic rhodium complex **1.1** catalysis under mild hydroformylation conditions.

Publication List

1. B. G. Van den Hoven, S. B. Park, and H. Alper, Zwitterionic Rhodium Catalyzed Hydroformylation of Acetylenic Thiazoles and Oxazoles: A Correction, and the Unusual Formation of Enols Stabilized by Intramolecular Hydrogen Bonding, *In Preparation.*
2. B. G. Van den Hoven and H. Alper, Innovative Synthesis of 4-Carbaldehydepyrrolin-2-ones by Zwitterionic Rhodium Catalyzed Chemo- and Regioselective Tandem Cyclohydrocarbonylation/CO Insertion of α-Imino Alkynes, *J. Am. Chem. Soc.* **2001**, *123*, 10214.
3. B. G. Van den Hoven and H. Alper, Remarkable Synthesis of 2-(***Z***)-6-(***E***)-4***H***-[1,4]-Thiazepin-5-ones by Zwitterionic Rhodium Catalyzed Chemo- and Regioselective Cyclohydrocarbonylative Ring Expansion of Acetylenic Thiazoles, *J. Am. Chem. Soc.* **2001**, *123*, 1017.
4. B. G. Van den Hoven, B. El Ali and H. Alper, Chemo- and Regioselective Cyclohydrocarbonylation of α-Keto Alkynes Catalyzed by a Zwitterionic Rhodium Complex and Triphenyl Phosphite, *J. Org.. Chem.* **2000**, *65*, 4131.
5. B. G. Van den Hoven and H. Alper, The First Regioselective Hydroformylation of Acetylenic Thiophenes Catalyzed by a Zwitterionic Rhodium Complex and Triphenyl Phosphite, *J. Org. Chem.* **1999**, *64*, 9640.
6. B. G. Van den Hoven and H. Alper, Regioselective Hydroformylation of Enynes Catalyzed by a Zwitterionic Rhodium Complex and Triphenyl Phosphite, *J. Org. Chem.* **1999**, *64*, 3964.