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UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

Table of Contents

Abstract

This thesis comprises research on the regioselective carbonylation and related reactions involving various unsaturated organic substances such as alkenes, alkynes, allylic esters, alcohols and amines, open chain and cyclic α,β-unsaturated esters using cationic, neutral and zwitterionic rhodium(I) complexes as catalysts. New methods for the preparation of valuable functionally substituted derivatives have been developed.

Acknowledgements

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Finally, I would especially like to thank my parents, my wife, Xiaoying, my son, Yiyuan, and my close friends, Prof. Yaozeng Huang, Prof. Lixin Dai and Mr. Peiji for their constant support and encouragement throughout my studies.

List of Abbreviations

Ac	acetyl
acac	acetylacetone
2,2'-Bipy	2,2'-bipyridyl
COD	1,5-cyclooctadiene
dba	dibenzylideneacetone
DOP	dioctyl phthalate
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
Et	ethyl
IR	infrared
L	ligand
Me	methyl
MS	mass spectrum
NMR	nuclear magnetic resonance
NOE	Nuclear Overhauser Effect
pfb	perfluorobutyrate
Ph	phenyl
i-PrOH	isopropanol
PTC	phase-transfer catalysis
r.t.	room temperature
TDA-1	tris(2,6-dioxaheptyl)amine
THF	tetrahydrofuran
TMS	tetramethylsilane

List of Tables

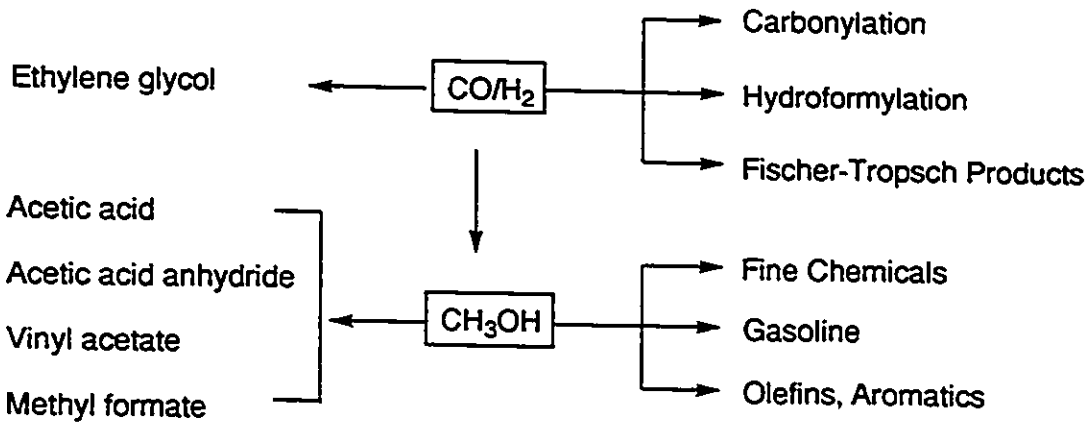
Chapter 1

Introduction to Carbonylation Chemistry

1-1. History and Background of Carbonylation Chemistry

Since the characterization of ferrocene in the early 1950's, organometallic chemistry has developed to become a distinct and very large part of chemical research[1]. In recent years, with the growth of interest in organotransition metal chemistry, it is clear that many transition metals, their compounds and in particular their organometallic derivatives are potentially important catalysts and reagents for organic syntheses and industrial processes. A number of industrial processes have been induced that are based on homogeneous transition metal catalysts. Among the large scale industrial processes using transition metal catalysts, some involve direct carbonylation of organic substrates, i.e. the introduction of a carbonyl group into a molecule by insertion of carbon monoxide.

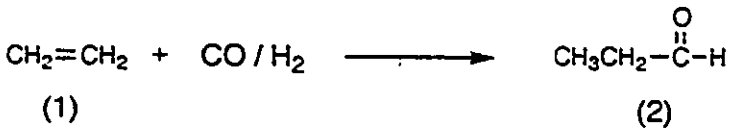
The carbonylation of active organic substrates catalyzed by transition metal complexes has been extensively investigated. Research has been carried out on the establishment of chemical technology that enables the production of some chemicals directly from carbon monoxide and hydrogen in the presence of appropriate catalysts. The use of carbon monoxide and hydrogen as building blocks in this chemistry is shown in Scheme 1-1.[2]



Scheme 1-1

The use of carbon monoxide as a "one-carbon unit" has considerable potential in organic synthesis and a variety of new carbonylation reactions are currently being explored which may eventually become commercial processes. For example, acetic acid is now manufactured by the direct carbonylation of methanol in the presence of a homogeneous rhodium catalyst.[3] Linear alcohols used in the synthesis of biodegradable detergents are derived from terminal alkenes via hydroformylation with carbon monoxide and hydrogen catalyzed by cobalt complexes.[4]

The first well-defined carbonylation reaction was discovered fifty years ago by Otto Roelen[5] working in the lab of Ruhrchemie A. G. during an investigation into the mechanism of the high pressure, cobalt-catalyzed Fischer-Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen. He found that the reaction of ethene (1) with CO/H_2 led to the formation of propanal (2) in high yield under typical conditions of Fischer-Tropsch synthesis(Scheme 1-2). Later it was shown that the actual catalyst is a soluble cobalt carbonyl species with the reaction taking place in a homogeneous phase.[6-8]



Scheme 1-2

This reaction was named "hydroformylation" as it resulted in the net addition of formaldehyde to the double bond. Since the discovery of this reaction, hydroformylation has developed into a valuable industrial method and consequently has been the most intensively studied of all carbonylation reactions.

Roelen's discovery was quickly followed by the work of Reppe and co-workers during 1939-45[9,10] which showed that many types of organic carbonyl compounds could be obtained from unsaturated hydrocarbons via stoichiometric or catalytic reactions.

About a quarter century after Roelen's research, the essentials of carbonylation chemistry had remained the same as in Roelen and Reppe's time. With a few exceptions, reactions still required the use of high temperature, high pressure, expensive autoclave

equipment, large quantities of highly toxic, volatile and unstable catalysts ($Ni(CO)_4$, $Fe(CO)_5$, $Co_2(CO)_8$) and instead of a single major product, usually gave a complex mixture of compounds requiring separation.

In 1960s, the work by Wilkinson[11], Heck[12], and Tsuji[13] led to the discovery of stable and highly active catalysts based on organophosphine complexes of rhodium and palladium. In addition, there were significant advances involving the application of new techniques such as phase transfer catalysis which resulted in many carbonylation reactions effected at low temperature and pressures using only catalytic amounts of transition metal catalysts such as $Co_2(CO)_8$, some Pd and Rh complexes.[14,15] These results have promoted the development of carbonylation chemistry rapidly in both academic reseach and industrial processes.

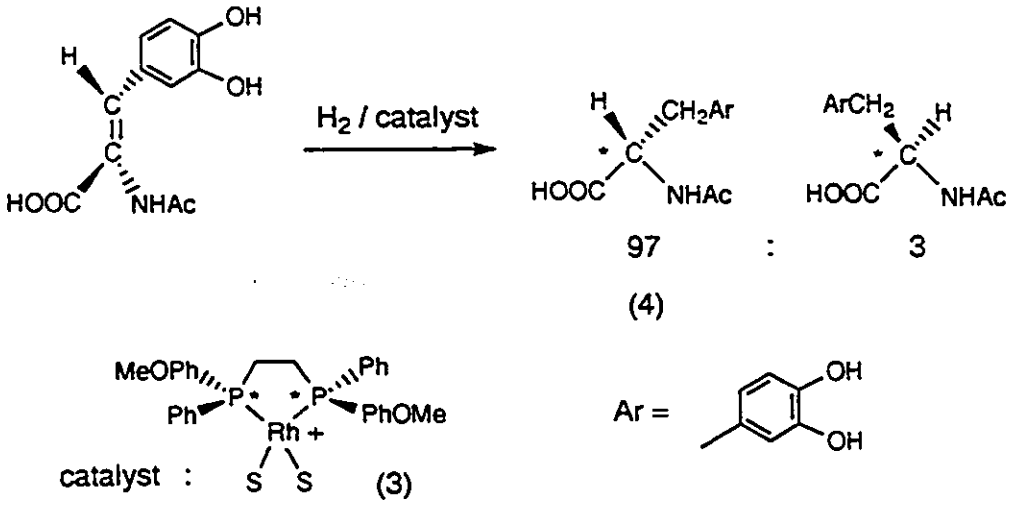
1-2. Carbonylation Chemistry

1-2-1. Homogeneous Catalysis of Hydrogenation and Hydroformylation[16]

Catalytic processes are classified as either homogeneous or heterogeneous, the distinction is based on the solubility and type of active site of the catalyst. Homogeneous catalysts are soluble in the reaction medium and their active site is a metal atom in a molecular complex. Heterogeneous catalysts are insoluble in the reaction medium and

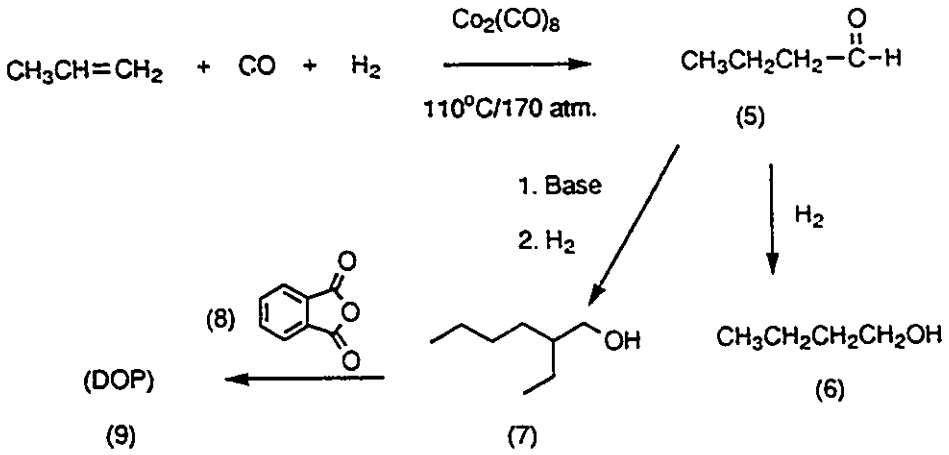
the active site is located on a solid surface.[17] Due to the higher selectivity and lower energy requirements of homogeneous catalysis, it is becoming much more economically significant in order to reduce the rising cost in energy and natural resources.

In 1964, it was discovered that a solution of a $RhCl(PPh_3)_3$ (called Wilkinson's catalyst), can catalyze the hydrogenation of olefins at room temperature and atmospheric pressure.[18] Wilkinson and coworkers studied the selective characteristics of this complex in detail and carried out the first extensive study of the mechanism of hydrogenation[19] and hydrofomylation of olefins.[20, 21] Since that time, many other studies have contributed to our understanding of this remarkably selective and synthetically useful catalyst. Asymmetric hydrogenation has been studied since the beginning of the 1970's. If a catalyst $[L_2RhS_2]^+$ (3) bearing a chiral diphosphine ligand is used, a prochiral unsaturated molecule can be hydrogenated to chiral products and high optical purity can be achieved in many cases.[22] A commercial application of asymmetric hydrogenation is the manufacture of L-Dopa (4), which is effective in the treatment of Parkinson's disease.[23]



Scheme 1-3

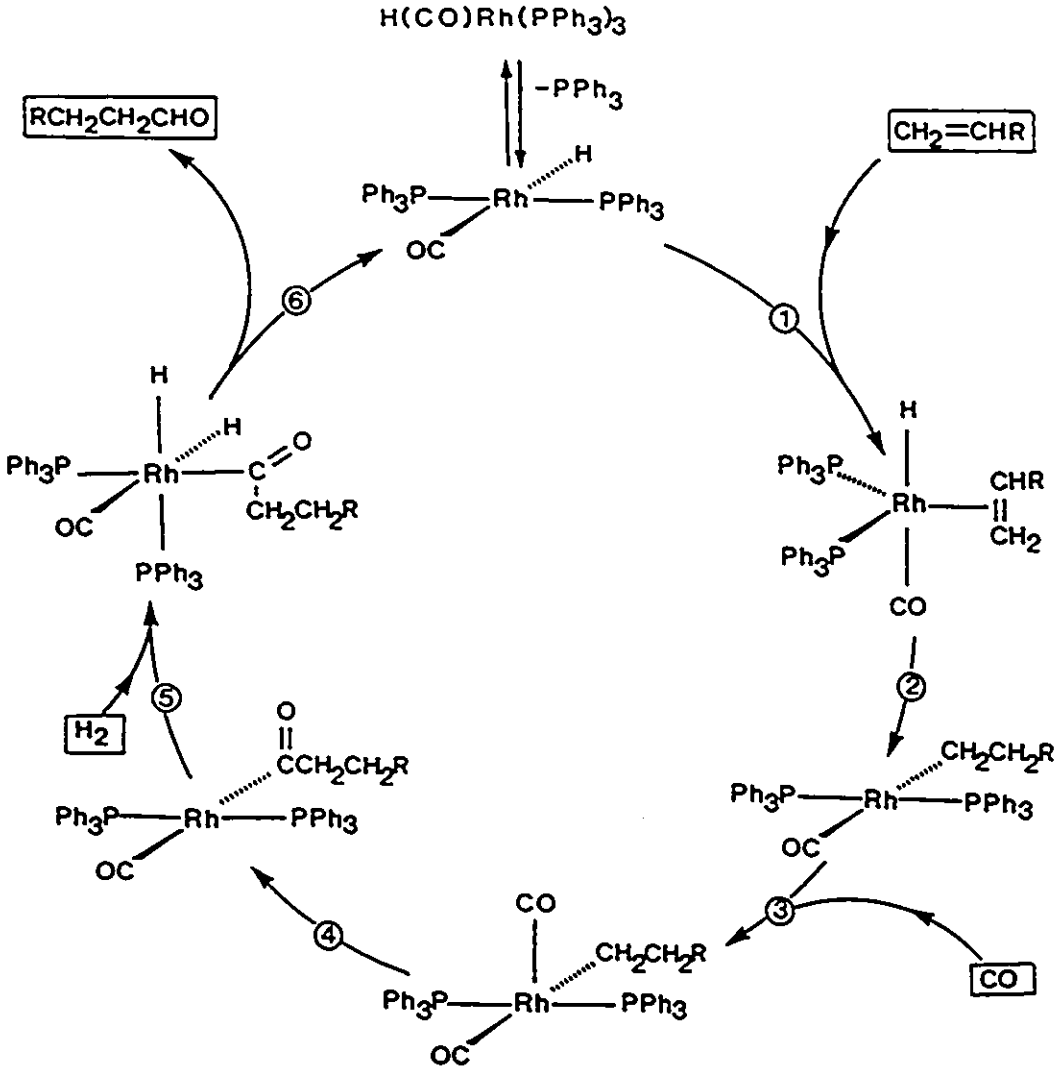
The most important industrial application of the hydroformylation reaction using a homogeneous cobalt catalyst is the preparation of butyraldehyde (5) from propylene and synthesis gas.[24] The n-butyraldehyde is then hydrogenated to n-butanol(6) which is used extensively as an industrial solvent, or the n-butyraldehyde undergoes aldol condensation and subsequent hydrogenation to afford 2-ethylhexanol (7) which can react with phthalic anhydride (8) to form dioctyl phthalate (DOP) (9) used as a plasticiser for polyvinylchloride resins (Scheme 1-4). The terminal aldehydes (C_{13}-C_{15}) prepared by hydroformylation are hydrogenated to the alcohols which are applied in the manufacture of biodegradable detergents.[25]



Scheme 1-4

The above reactions are homogeneously catalyzed by a number of transition-metal carbonyl complexes. Cobalt was the most widely used catalytic metal in early investigations, but rhodium has attracted much more interest in recent years due to its higher reactivity.[26,27] Recently, Union Carbide has utilized $HRh(CO)(PPh_3)_3$ (10) instead

of $Co_2(CO)_8$ as the catalyst[28] in the hydroformylation process, which can be carried out under very mild conditions (Scheme 1-5).



Scheme 1-5

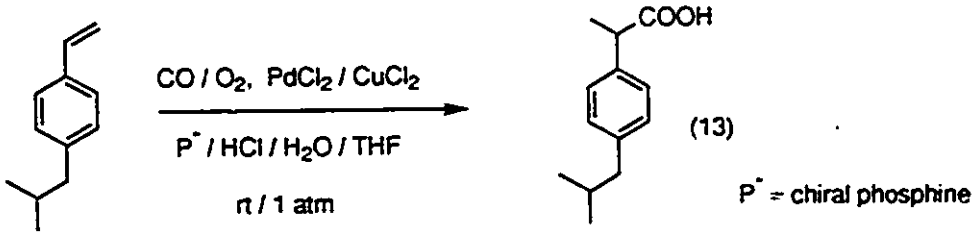
1-2-2. Reppe Carbonylation

Reppe-type reactions refer to the carbonylation of alkenes and alkynes with the simultaneous addition of HX (X=NR, OR, halogen etc.) to the unsaturated center. The catalysts employed in these reactions are $Co_2(CO)_8$, $Ni(CO)_4$, $Fe(CO)_5$ and Pd complexes. An example of a commercial Reppe reaction is the production of acrylic ester (12) from acetylene (11), CO and ROH.[29]

$$\underset{(11)}{HC{\equiv}CH} + CO + ROH \xrightarrow{Ni(CO)_4} \underset{(12)}{CH_2{=}CHCOOR}$$

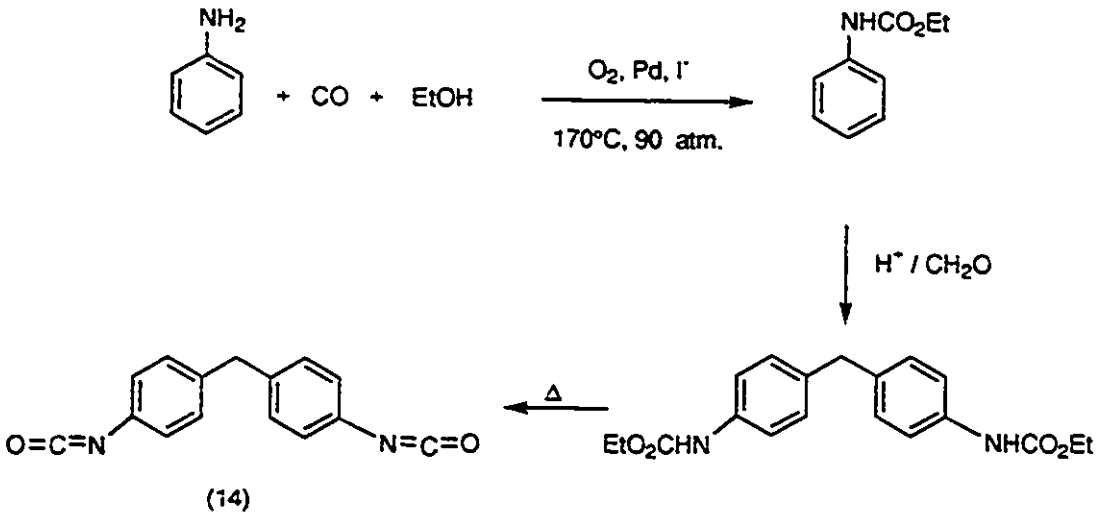
Scheme 1-6

Based on organopalladium chemistry [Pd(II)-Pd(O)],[30-32] the hydroesterification and hydrocarboxylation of olefins to branched carboxylic esters can be effected under exceptionally mild conditions affording branched chain products in high yield.[33] The application of this catalytic system in the preparation of nonsteroidal anti-inflammatory agents including ibuprofen has been successful. In the presence of a chiral phosphine ligand, an optically active ibuprofen (13) was obtained in fair enantiomeric excess[34](Scheme 1-7).



Scheme 1-7

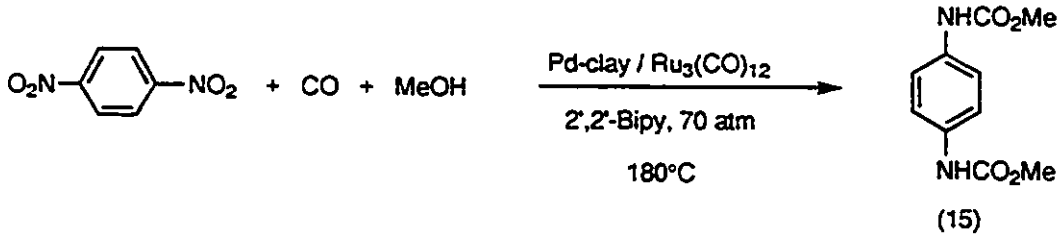
Aliphatic and aromatic amines, under carbonylation conditions, are transformed to urethanes. This chemistry has been successfully applied in the synthesis of methylenediphenyldiisocyanate (MDI) (14), an important intermediate for polyurethane manufacture[35] (Scheme 1-8).



(14)

Scheme 1-8

Also, Alper and Valli recently found a novel method to prepare the dicarbamate (15) directly by carbonylation of 1,4-dinitrobenzene (Scheme 1-9).[36]

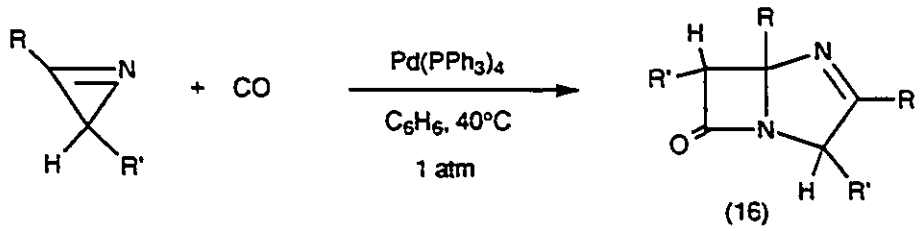


(15)

Scheme 1-9

1-2-3. Metal Catalyzed Ring Expansion Reactions

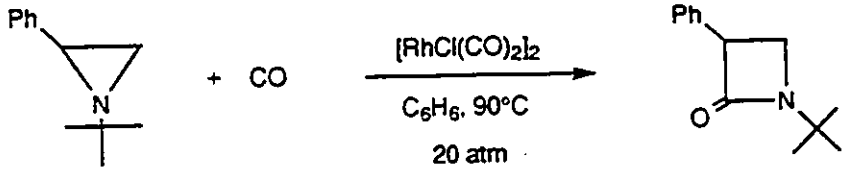
Insertion of carbon monoxide into nitrogen heterocycles affords lactams[37] while lactones are formed from oxygen heterocycles.[38] In 1981, Alper and co-workers discovered a one step synthesis of β-lactams (16) via ring expansion of aziridines using $Pd(PPh_3)_4$ as the catalyst (Scheme 1-10).[37]



(16)

(Scheme 1-10)

The synthesis of monocyclic β-lactams from aziridines can be attained by the incorporation of carbon monoxide using an appropriate metal catalyst. The first example comprises Rh(I) catalyzed direct, regiospecific, ring expansion of aziridines e.g. (17) to β-lactams e.g. (18) (Scheme 1-11).[39,40]. The latter was obtained in quantitative yield.



(17) (18)

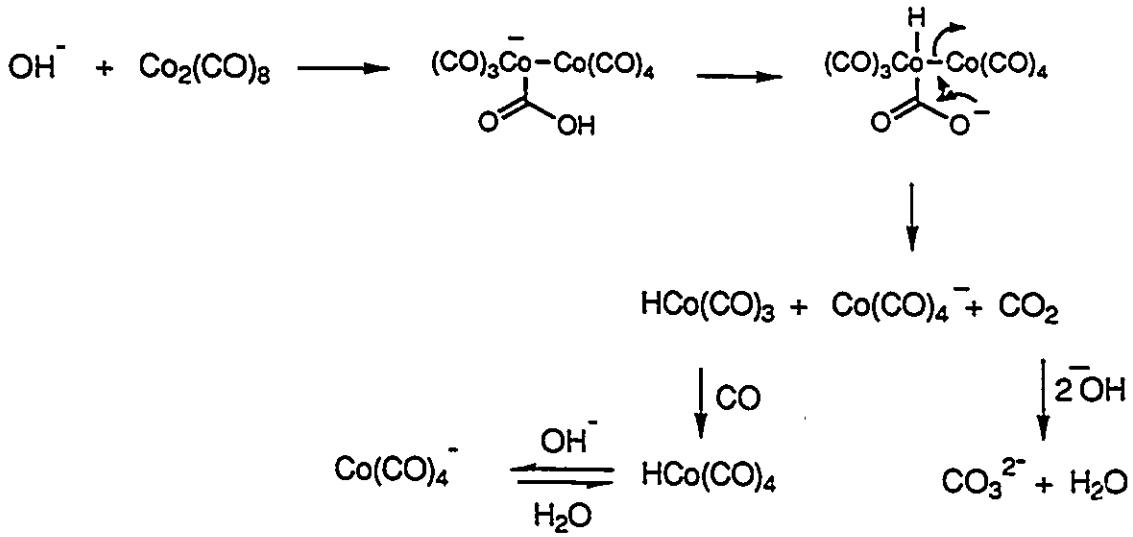
(Scheme 1-11)

The ring expansion process is also applicable to the preparation of five, six and seven membered ring heterocyclic compounds from the corresponding precursors.[41,42]

1-2-4. Phase-Transfer Catalysis in Carbonylation Chemistry[15]

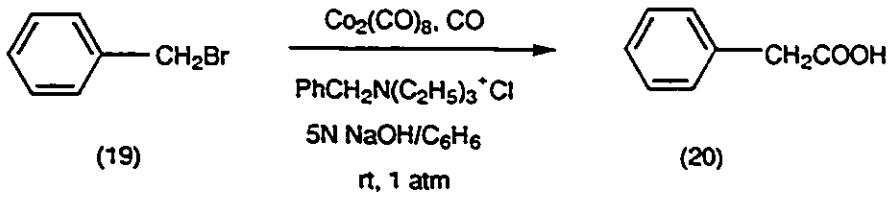
The application of phase transfer catalysis(PTC) in transition-metal-catalyzed reactions (including carbonylation) is an important development in organic synthesis.[43] These reactions are often carried out in an aqueous base-organic two-phase system with ammonium or phosphonium salt or crown ether as the phase-transfer agent. Mild conditions, high reaction rates and simple work up are some of the attractive features of PTC reactions.

The cobalt tetracarbonyl anion, $Co(CO)_4^-$ has been widely used for carbonylation under PTC conditions. Under basic conditions, dicobalt octacarbonyl undergoes disproportionation to give $Co(CO)_4^-$. A possible mechanism for this process, involving initial nucleophilic attack of hydroxide ion on a carbonyl carbon of $Co_2(CO)_8$ is depicted in Scheme 1-12.



Scheme 1-12

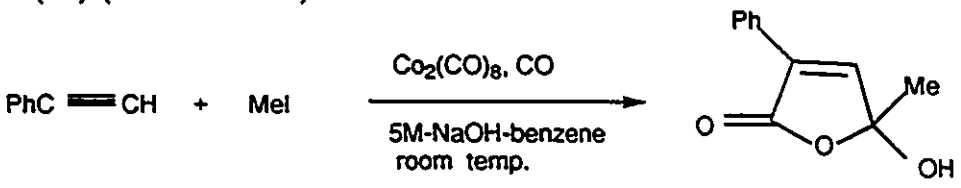
The carbonylation of benzyl halides (19) to the corresponding carboxylic acids (20) catalyzed by cobalt carbonyl is an effective synthetic method. PTC provides mild conditions for effecting conversion in good yield (Scheme 1-13).[44,45]



(19) (20)

Scheme 1-13

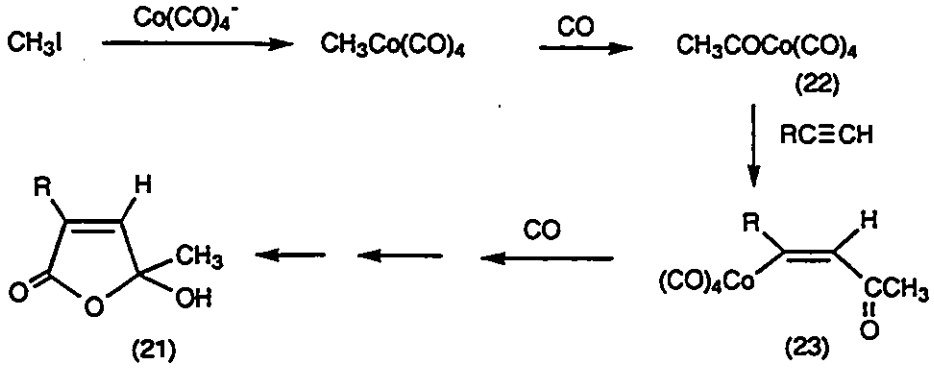
Dicobalt octacarbonyl catalyzes the reaction of alkynes with carbon monoxide in the presence of methyl iodide under PTC conditions to give the pharmacologically important 2-butenolides (21) (Scheme 1-14).[46]



(21)

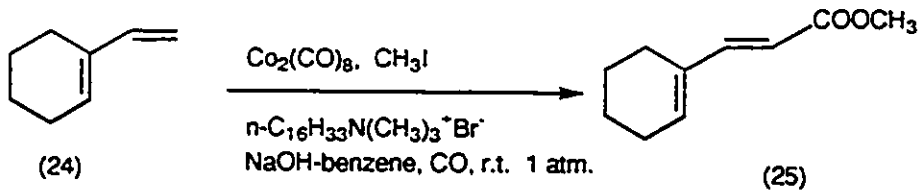
Scheme 1-14

This regiospecific reaction may proceed by addition of the in situ generated acetylcobalt tetracarbonyl(22) to the alkyne giving a vinylcobalt complex(23) which eventually affords the product (21).



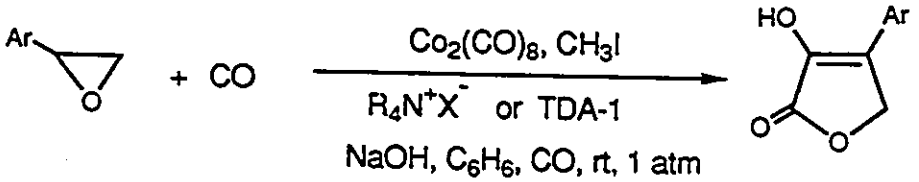
Scheme 1-15

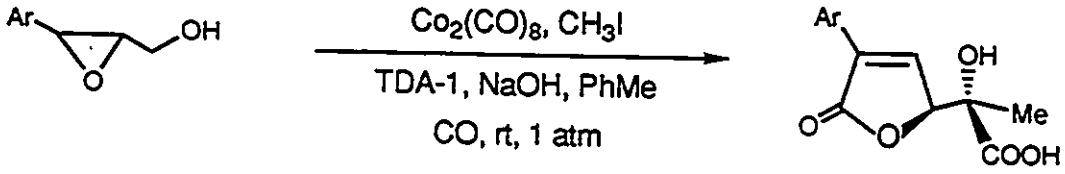
Use of a diene (24) or triene , in place of an alkyne affords (E)-conjugated enones (25) in a highly regiospecific manner (Scheme 1-15).[47]



Scheme 1-16

$Co_2(CO)_8$ catalyzed reactions of oxiranes with CO under PTC conditions in the presence of methyl iodide give rise to double and triple carbonylation products depending on the structure of the starting material (Scheme 1-16).[48,49]





Scheme 1-16

Analysis of the literature shows that the catalytic carbonylation reaction has attracted a great deal of attention among chemists in recent years. The reason is, first of all, that numerous commercially important products or intermediates for their preparation can be obtained via carbonylation. Despite the fact that various catalytic systems based on transition metal complexes have been developed, the search for new, more active and highly regio- and stereoselective catalysts is still under way. This present work is an attempt to contribute to this area of organic catalysis by studying hydroformylation and related reactions such as reductive carbonylation involving various functionally substituted alkenes and alkynes.

1-3. The goals of this research

The project undertaken involves an examination of the regioselective hydroformylation and reductive carbonylation of alkenes, alkynes , allylic esters, alcohols and amines as well as open-chain and cyclic α,β-unsaturated esters. The purpose of this investigation is to extend the current knowledge on the use of cationic, neutral and zwitterionic rhodium(I) complexes in hydroformylation and related reactions. In addition, new methodology for carbonylation has been developed in order to prepare various nitrogen, oxygen and silicon containing compounds, thereby expanding the synthetic utility of these reactions.

Chapter 2

Hydroformylation of Unsaturated Esters and Reductive Carbonylation of Alkenes and Allylic Alcohols

2-1. Introduction

As noted in Chapter 1, hydroformylation is a general term applied to the reaction of an olefin with CO/H_2 to form an aldehyde. Due to the industrial significance, a vast amount of research has been undertaken to develop the hydroformylation process. Statistical data shows that about 5 million tonnes of aldehydes and their derivatives are being produced annually by hydroformylation processes.[4] Currently, attention is focused on regio- and stereospecific hydroformylation and related carbonylation reactions leading to the facile syntheses of sophisticated pharmaceutical, agricultural and other fine chemicals.[50]

In this chapter are presented the results on the investigation of regioselective hydroformylation and reductive carbonylation reactions using zwitterionic, cationic and neutral rhodium (I) complexes as catalysts.

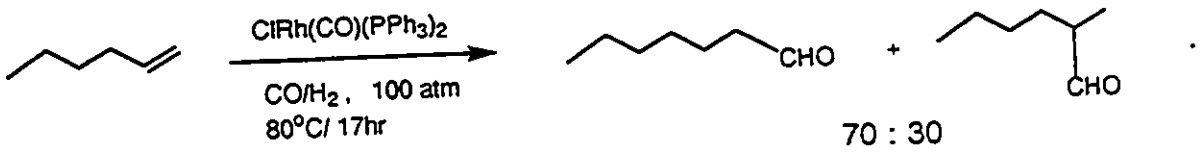
2-2. Regio- and Stereoselective Hydroformylation

Many transition-metal complexes can be employed as catalysts for the hydroformylation reaction. In particular, cobalt and rhodium complexes are the most widely used catalysts. Rhodium complexes are very effective catalysts for the regioselective hydroformylation of olefins under mild conditions (1 atm., r.t.) compared with cobalt catalysts (200-400 atm., 150-200°C).

Recent trends in this field include efforts to seek an efficient catalytic system to obtain regio- or enantioselective products for both laboratory and industrial purposes. The regioselectivity is controlled mainly by two factors: the structure of the alkenes and the ligands of the catalysts.[51]

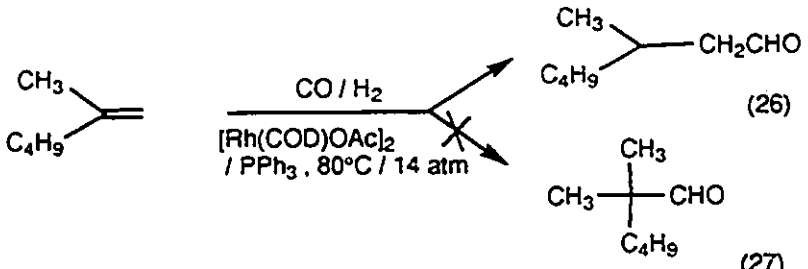
2-2-1. Steric Effect of Substrates

The ratio of regioisomers obtained from the hydroformylation of an alkene is dependent on the steric demands of the substituents attached to the double bond. For example, rhodium(I) complex catalyzed hydroformylation of 1-hexene afforded two isomeric aldehydes where the linear : branched ratio was 70 : 30(Scheme 2-1).[52]



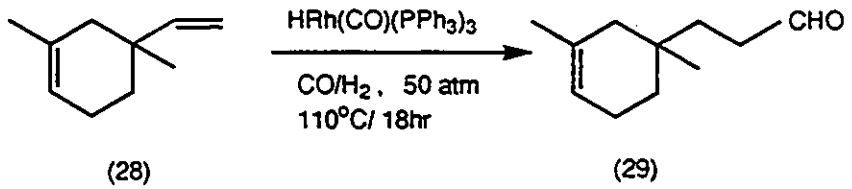
Scheme 2-1

This is in contrast to the hydrofomylation of 2-methyl-1-hexene which gave only the linear aldehyde (26) and not the branched product (27).[53,54]



Scheme 2-2

Similarly, 3-substituted-1-alkenes such as linalool[55] and 1,5-dimethyl-5-vinylcyclohexene(28) gave linear aldehyde(29) only.[56]



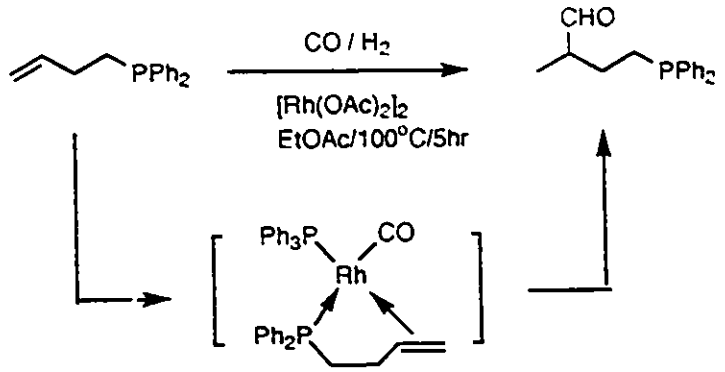
(28) (29)

Scheme 2-3

2-2-2. The Chelation Effect

The regioselectivity can be influenced by chelation of an alkene having a heteroatom like N, O or P as substituents capable of bonding to the metal.[57,58] In the hydroformylation of an alkenyl phosphine, the chelation of the phosphine to the rhodium catalyst directs the selective addition of the formyl group to the double bond via a stable

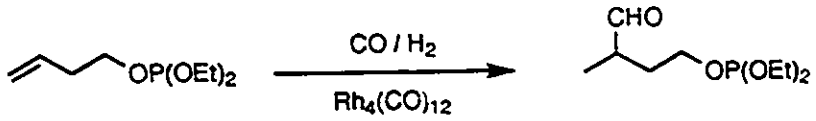
five membered ring chelate(30) (Scheme 2-4).[59,60]



(30)

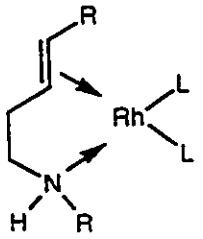
Scheme 2-4

Similarly, in the case of a homoallylphosphite, chelation controls the rhodium-catalyzed hydroformylation (Scheme 2-5).[61]



Scheme 2-5

The reaction of mono- and bis-homoallylic amines with μ-dichlorotetracarbonyldirhodium(I) affords a series of complexes, containing bidentate olefinic ligands. Crystallography revealed that these complexes have a structure (31) which supports the presence of a complex such as (31) as the intermediate in the regioselective hydroformylation reaction[62].

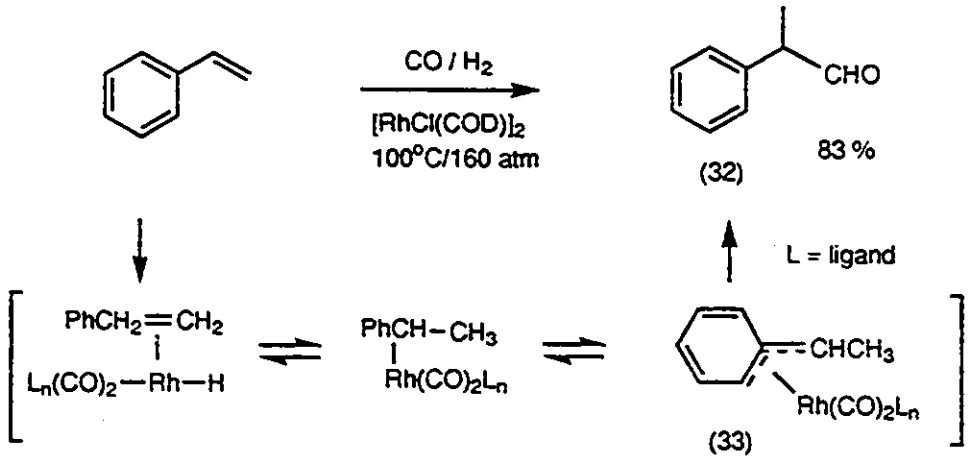


(31)

R -aliphatic group

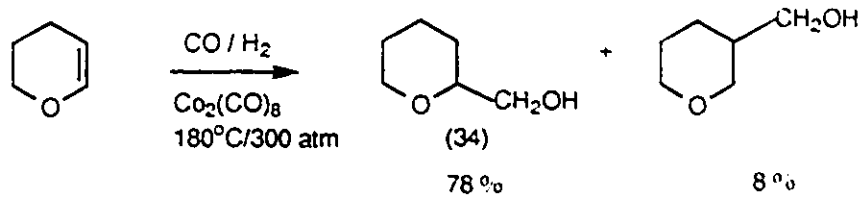
2-2-3. Electronic Effect of Substances

In the rhodium (I) catalyzed hydroformylation of styrene[63] and methyl acrylate,[64] the major product is the branched aldehyde. This result can be attributed to the presence of a substitutent in conjugation with the double bond which can alter the electron density of the double bond. In the case of styrene, the predominance of the branched isomer (32) is believed to be due to the formation of a π-benzyl complex (33)(Scheme 2-6).



Scheme 2-6

The electron-donating substituents conjugated with the double bond(OR, NR_2, Cl) do not inhibit the hydroformylation but favor the addition of the formyl group at the α-position.[65] For example, hydroformylation of 3,4-dihydro-2H-pyran afforded the alcohol(34) as the major product (Scheme 2-7).

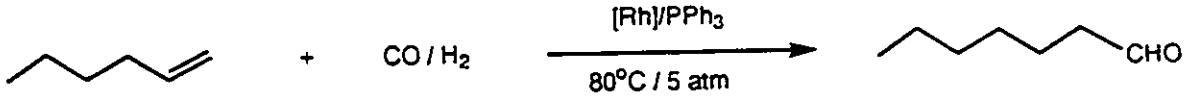


Scheme 2-7

2-2-4. Influence of Ligands

Rhodium complexes modified by ligands such as phosphines generally increase the selectivity of the reaction. In the presence of an excess of triphenylphosphine(40 fold excess relative to the catalyst), the hydroformylation of 1-hexene to heptanal can be achieved under mild conditions with up to 94% selectivity, but the catalytic activity is significantly reduced under such conditions.[66]

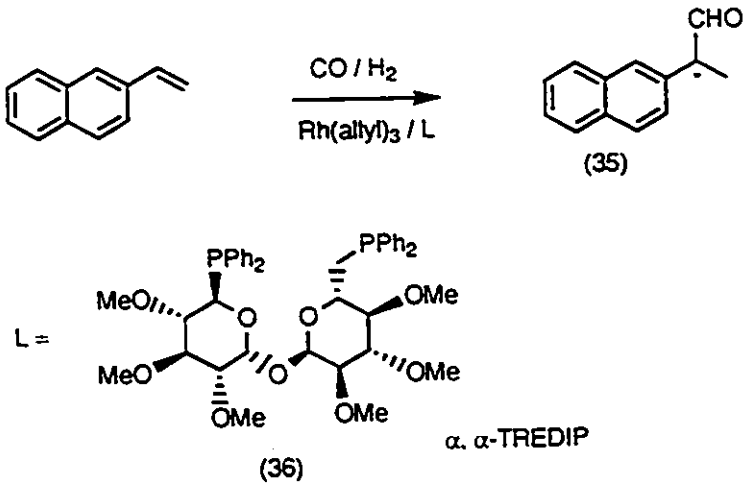
Addition of PPh_3 to the catalytic system consisting of a binuclear rhodium-μ-thiolato complex bearing pendant amino groups offers high selectivity(93%) for the linear aldehyde (Scheme 2-8).[67]



[Rh] = $Rh_2[\mu\text{-}S(CH_2)_3N(CH_3)_2]_2(COD)_2$

Scheme 2-8

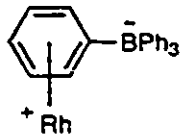
The regioselective hydroformylation of 2-vinylnaphthalene to give the branched aldehyde is a useful reaction, since it leads to the synthesis of 2'-(2-methyl-6-naphthyl) propanal (35), a precursor of the corresponding carboxylic acid, the anti-inflammatory drug, naproxen. Rhodium α,α-TREDIP complexes, formed in situ from $Rh(allyl)_3$ and (36), is an excellent catalytic system for the regioselective formation of the branched isomer(35)(Scheme 2-9).[68]



Scheme 2-9

2-2-5. Regioselective Hydroformylation by a Zwitterionic Rhodium(I) Complex

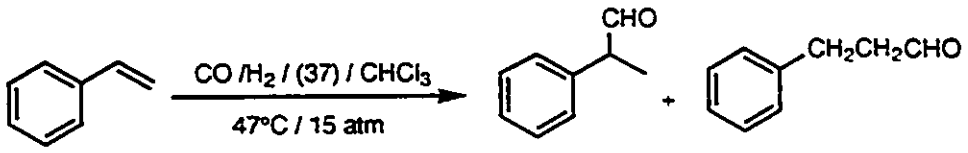
Recently, Alper and co-workers found that the zwitterionic rhodium complex η^6-$C_6H_5BPh_3^-Rh(COD)^+$, (37),[69] is a very efficient and a highly regioselective catalyst for the



(1,5-COD)

(37)

preparation of the branched aldehyde(32) by the hydroformylation of styrene in the absence of any phosphine ligands.[70]

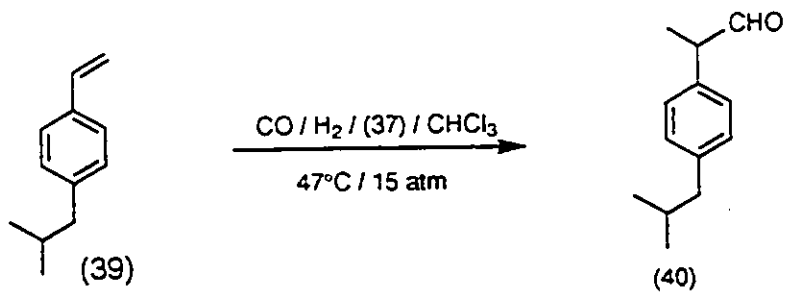


97 : 3

(32) (38)

Scheme 2-10

In this reaction, a 1:2 mixture of carbon monoxide and hydrogen and a catalytic amount of (37) was used together with styrene (styrene/cat.=100:1) at 47°C and 15 atm for 22hr resulting in 89% conversion and a 97.3/2.7 ratio of 2-phenylpropanal(32) to 3-phenylpropanal(38)(Scheme 2-10). These results are superior to those obtained using many other rhodium complexes, including those with a phosphanonorbornadiene ligand which effects low conversion of styrene affording (32)/(38) in a 91/9 ratio.[71] When p-isobutylstyrene (39) was used as the reactant, 2-(4-isobutylphenyl)propanal (40), a precursor to ibuprofen was formed as the exclusive product (Scheme 2-11).



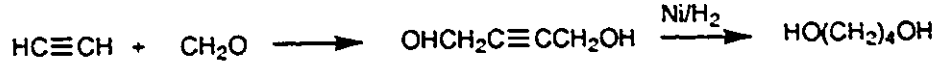
Scheme 2-11

The excellent regioselectivity of the zwitterionic rhodium catalyst for the hydroformylation of styrene and its derivatives prompted us to explore its applications in various carbonylation reactions involving different unsaturated substrates. The results of this study are decribed below.

2-3. The Regioselective Hydroformylation of Allyl Acetates

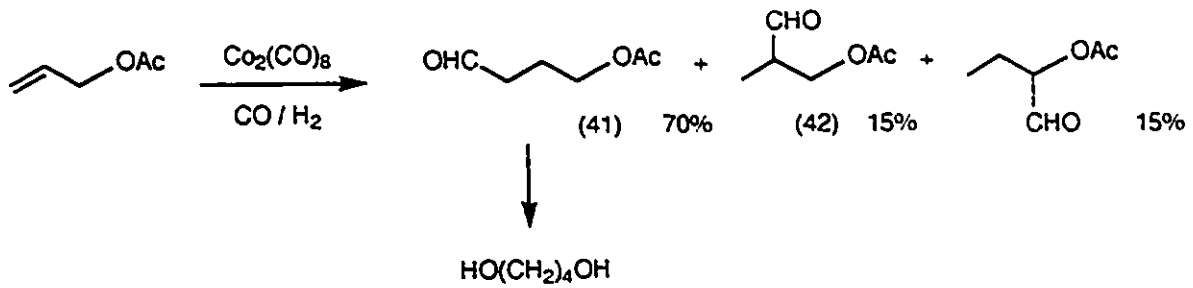
2-3-1. Introduction

1,4-Butanediol, an intermediate in the synthesis of high-performance engineering plastics, is currently manufactured by the Reppe process involving acetylene and paraformaldehyde(Scheme 2-12).[4, 72]



Scheme 2-12

An alternative route which involves $Co_2(CO)_8$ catalyzed hydroformylation of allyl acetate has been pioneered by General Electric (Scheme 2-13).[73]

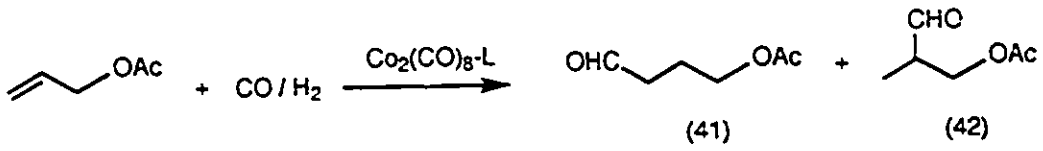


Scheme 2-13

Under typical operating conditions of 125°C and 200 bar for this reaction, 70% of 4-acetoxybutyraldehyde (41) was formed as the major product together with 15% of 3-acetoxy-2-methylpropanaldehyde (42), and 15% of 2-acetoxybutyraldehyde. This route is more attractive because allyl acetate is available by vapor-phase reaction of propene with oxygen and acetic acid in the presence of palladium(II).[74]

It was also discovered that the addition of weakly coordinating ligands enhances the stability and reactivity of cobalt catalysts in the hydroformylation of allyl acetate, but the selectivity for the linear aldehyde was still low (Table 2-1).

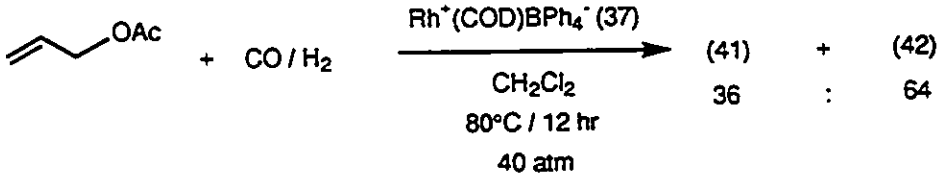
Table 2-1 Hydroformylation of allyl acetate.[74]



(41) (42)

Catalyst-Promoter	Selectivity (%)	
	(41)	(42)
$Co_2(CO)_8$-Ph_3GeH	48	36
$Co_2(CO)_8$-Ph_2S	57	11
$Co_2(CO)_8$-2,2'-dipyridyl	66	14
$Co_2(CO)_8$-succinonitrile	61	19
$Co_2(CO)_8$	65	14

In view of the importance of 1,4-butanediol, the hydroformylation of allyl acetate was carried out to seek regioselectivity for the linear aldehyde. Although the use of the zwitterionic rhodium complex (37) as the catalyst for the hydroformylation of styrene produced mostly branched aldehyde, in the case of allyl acetate, the regioselectivity was poor (Scheme 2-14) when the reaction was effected under conditions similar to those developed by Amer and Alper.[70,75]

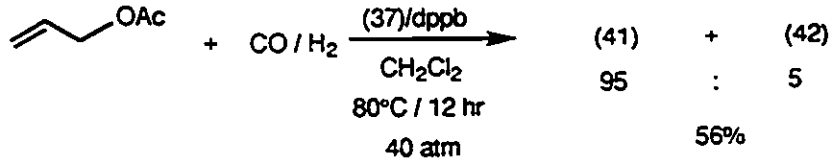


Scheme 2-14

As noted previously, the addition of phosphine ligands to the rhodium systems will increase the formation of linear aldehydes in many cases, hence the hydroformylation of allyl acetate with (37) was undertaken in the presence of phosphines.

2-3-2. Results and discussion

It was gratifying to find that addition of 2 molar equivalents of 1,4-bis(diphenylphosphino)butane (dppb) to the reaction (Scheme 2-15) gave a mixture of aldehydes in 56% yield, the ratio of linear to branched products being 95:5.



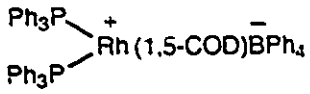
Scheme 2-15

The influence of different phosphine ligands and effect of their concentration are listed in Table 2-2. When triphenylphosphine and tris(4-dimethylaminophenyl)phosphine were employed with the complex (37), a mixture of aldehydes was obtained with low selectivity.

Table 2-2. Hydroformylation of allyl acetate catalyzed by zwitterionic(37) and cationic(43) rhodium(I) complexes

Catalyst	Phosphine	Ratio of Catalyst/ Phosphine	Yield ,% (isolated)	(41) : (42)
(37)	——	——	71	36 : 64
(37)	dppb	1 / 1	76	40 : 60
(37)	dppb	1 / 2	56	95 : 5
(37)	dppb	1 / 4	53	91 : 9
(37)	PPh_3	1 / 1	67	56 : 44
(37)	PPh_3	1 / 4	74	42 : 58
(37)	$P(C_6H_4NMe_2\text{-}p)_3$	1 / 4	63	37 : 63
(43)	——	——	68	20 : 80
(43)	dppb	1 / 2	55	94 : 6

When the cationic rhodium complex, bis(triphenylphosphine)(1,5-cyclooctadiene) rhodium(I) tetraphenylborate(43),[76] was used under similar conditions in the presence of



(43)

two molar equivalents of dppb, the ratio of aldehydes remained the same and in the presence of 1 molar equivalent of dppb, the regioselectivity was poor. Interestingly, in the absence of dppb the ratio of aldehydes (41):(42) was 20:80. These present catalytic systems are superior to those previously reported consisting of rhodium or cobalt complexes (Table 2-3)[77].

Table 2-3. Hydroformylation of Allyl Acetate by $HRh(CO)(PPh_3)_3$ or $Co_2(CO)_8$

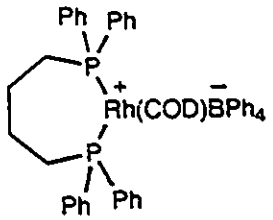
Catalysts	Reaction Conditions	Products
$HRh(CO)(PPh_3)_3 + PPh_3$	30°C, 20 psi, 1 /1 H_2 / CO	No reaction
$HRh(CO)(PPh_3)_3$	120°C, 1800 psi, 1 /1 H_2 / CO	45% 4-Acetoxybutyraldehyde 48% 2-Methylpropionaldehyde
$Co_2(CO)_8$	120°C, 1800 psi, 1 /1 H_2 / CO	52.6% 4-Acetoxybutyraldehyde Seven other products

The key structural difference between rhodium complexes (37) and (43) is that in the zwitterionic rhodium complex (37), one of the benzene rings of the BPh_4 unit is π-coordinated to rhodium, while in (43), BPh^-_4 is present as a counterion and not complexed to the central rhodium atom. It is interesting to observe that essentially the same results for the hydroformylation of allyl acetate were obtained by using the two different catalysts in the presence of dppb (Table 2-4).

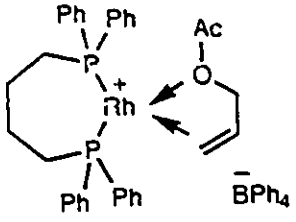
Table 2-4. The effects of the counterion on the hydroformylation of allyl acetate

Catalyst system	Yield, % (isolated)	(41) : (42)
[Rh(dppb)(COD)]$^{+}BF_4^{-}$ (46)	70	30 : 70
(46)/ $NaBPh_4$ (1 : 4)	67	80 : 20
[Rh(COD)Cl]$_2$ (47) / $NaBPh_4$ / DPPB (1 : 4 : 4)	70	96 : 4
(47) / DPPB (1 : 4)	73	56 : 44
(47) / $NaBPh_4$/ (48) 1 : 4 : 4	59	93 : 7

Based on the results summarized in Table 2-4, it is believed that the active catalytic species may be same in both cases with (44) and (45) as possible structures.

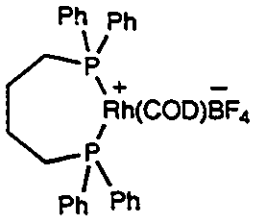


(44)



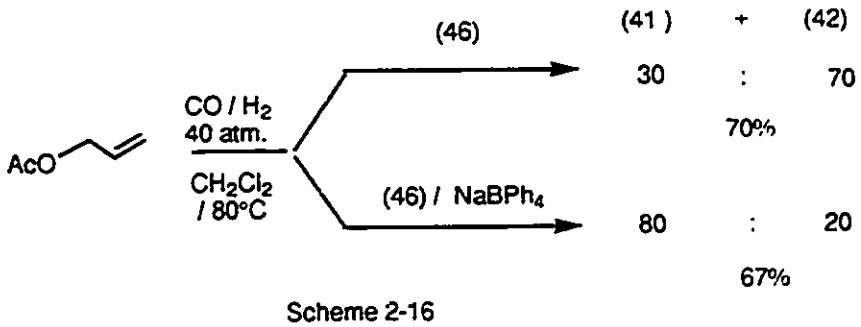
(45)

To test this hypothesis, a related complex, [1,4-bis(diphenylphosphino)butane](1,5-cyclooctadiene)rhodium(I) tetrafluoroborate, (46)[78], which is structurally similar to (44),



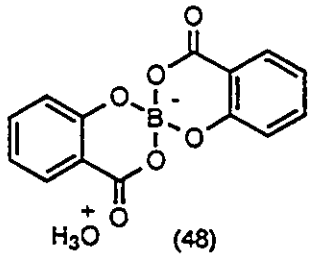
(46)

was used to catalyze the hydroformylation of allyl acetate. The expected result was not observed as the ratio of the linear (41) to the branched aldehyde(42) was 30:70(Scheme 2-16).



Scheme 2-16

However, when a 4-fold excess amount of $NaBPh_4$ with respect to (46) was added in order to replace the BF_4^- anion of (46) by BPh_4^-, the linear aldehyde was obtained in 80% selectivity. This experiment supports the formation of (44) as a key catalytic species, and also indicates that the bulky borate anion plays an important role. Further support for the participation of (44) as the active species comes from the following experiments. A mixture of $[(1,5\text{-cyclooctadiene})RhCl]_2$ (47) (0.02 mmol), dppb(0.08 mmol) and $NaBPh_4$(0.08 mmol) catalyzes the hydroformylation of allyl acetate(4 mmol) to give (41) and (42) in a 96/4 ratio and in 70% isolated yield. When this reaction was performed without $NaBPh_4$, a mixture of (41) and (42) was obtained in 78% overall yield with the selectivity being 56:44. Upon substitution of $NaBPh_4$ by hydronium bis[2-hydroxybenzoato(2-)2-O^1,O^2]borate(1-), (48), in the above reaction, the linear

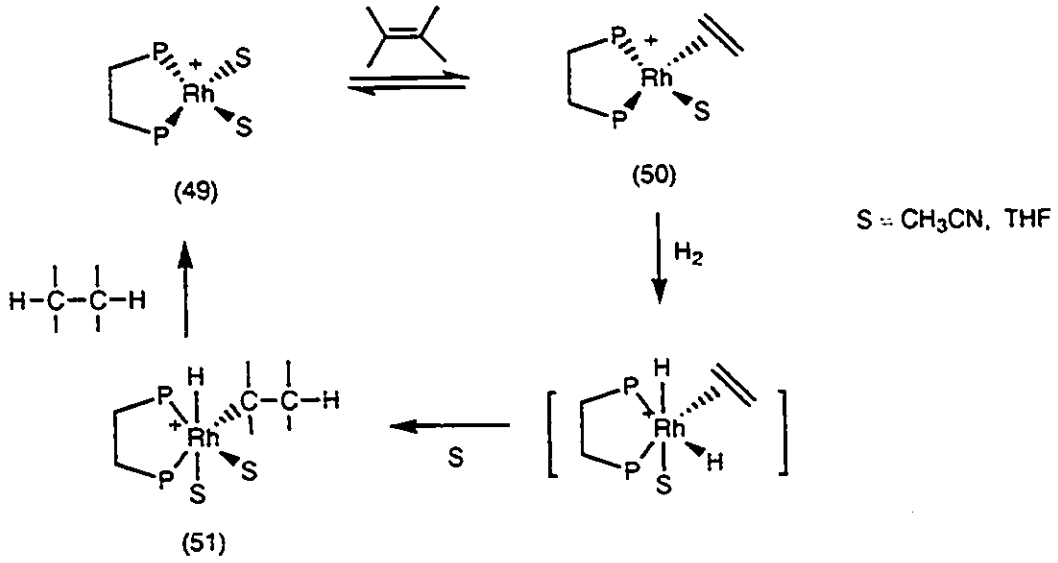


(48)

aldehyde (41) was formed as the major product in 93:7 ratio of (41) : (42)(59 % total yield). The results concerning the effect of counterions are listed in Table 2-4. A suitable counterion is clearly necessary in this process, its role possibly being to stabilize the intermediate(52) (see section 2-3-3, Scheme 2-18).

2-3-3. Mechanism

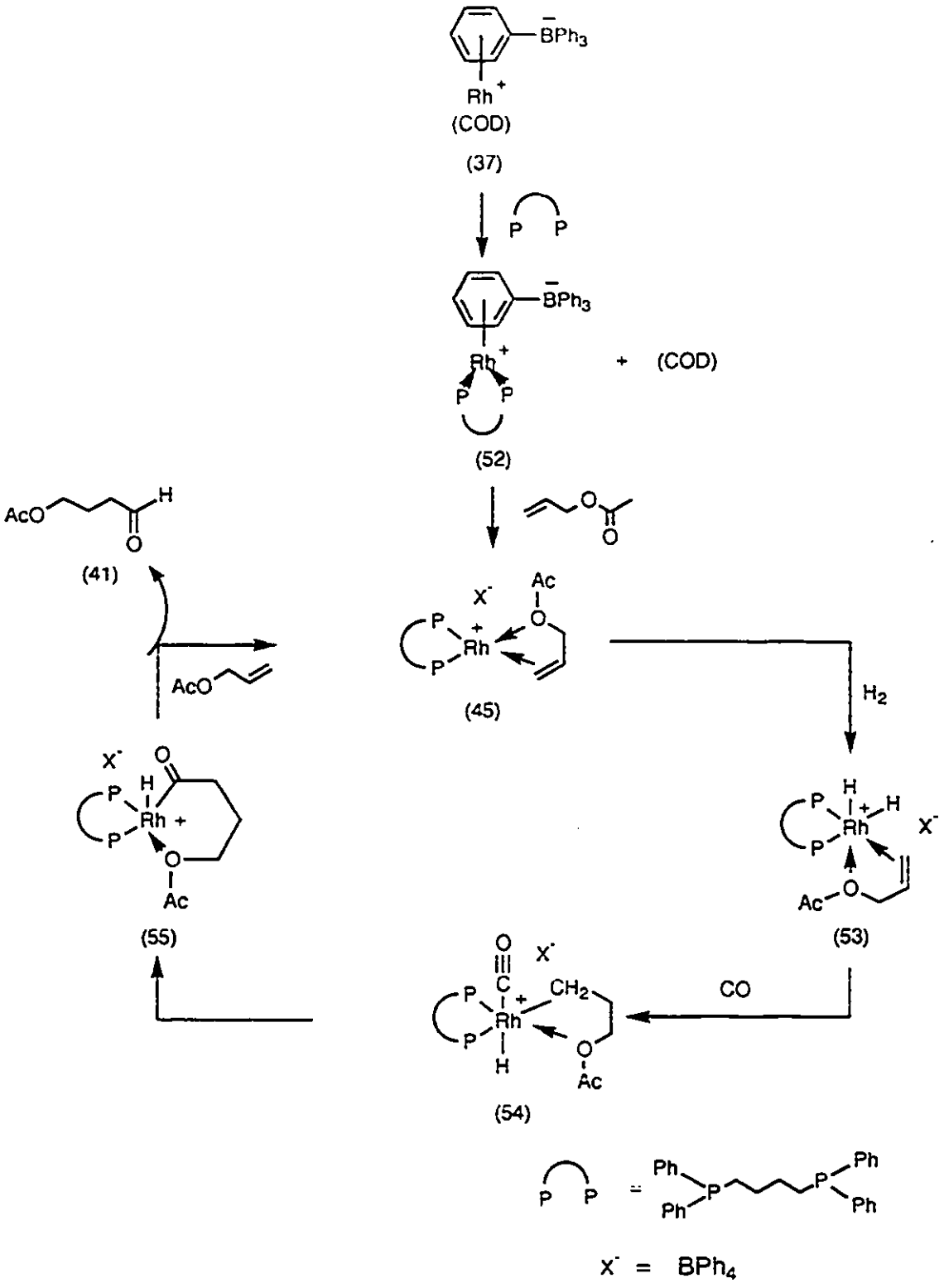
The mechanism of hydrogenation of alkenes catalyzed by the rhodium(I) diphos complex (49) has been investigated by Halpern(Scheme 2-17) amongst others[79,80]



Scheme 2-17

In this catalytic cycle, three complexes (49), (50) and (51) were thoroughly characterized by multinuclear NMR measurements, and two by x-ray diffraction (49 and 50).

Based on the pathways of hydrogenation and hydroformylation of alkenes described in Scheme 1-5 (Section 1-2-1), the following mechanism can be proposed for the hydroformylation of allyl acetate (Scheme 2-18).


BPh3
Rh+
(COD)
(37)
P P
+ (COD)
(52)
AcO
H
O
(41)
X-
Ac
O
Rh+
(45)
H2
AcO
X-
H
Rh +
Ac
(55)
H
Rh+
H
X-
Ac
(53)
CO
O
C
CH2
Rh
H
Ac
(54)
Ph
Ph
Ph
Ph
X- = BPh4

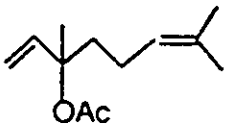
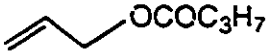
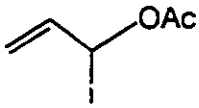
Scheme 2-18

The first step of the hydroformylation probably involves displacement of the COD ligand of (37) by dppb to give (52). Subsequent coordination of allyl acetate would give (45). Addition of hydrogen to (45) may generate the octahedral complex (53). The insertion of coordinated alkene at the Rh-H bond followed by coordination of CO can form complex (54). Subsequent insertion of the coordinated CO at the Rh-C bond affords (55) which reacts with allyl acetate to give the linear aldehyde (41) and regenerates the catalytically active species (45).

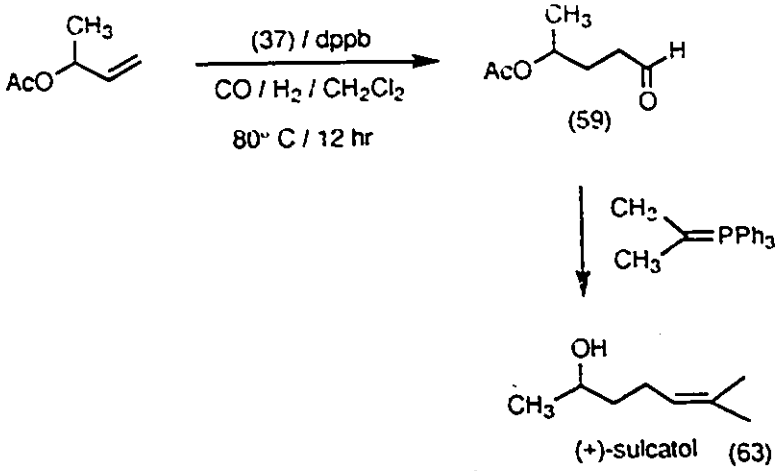
2-3-4. The Hydroformylation of Substituted Allyl Acetates

The results of the hydroformylation of other unsaturated acetates using the zwitterionic Rh(I) complex (37))/dppb catalytic system are shown in Table 2-5. Use of linalyl acetate resulted in regiospecific formation of the linear aldehyde (56) in 29% yield, and allyl butyrate produced 67% of aldehydes in a 96:4 ratio of linear (57) :branched (58) products. 1-Methyl-2-propenyl acetate can be transformed into the linear aldehyde (59) as the predominant product in 69% yield. The latter is an intermediate in the synthesis of (±)-sulcatol (63), an insect pheromone(Scheme 2-19).[81]

Table 2-5. Hydroformylation of Unsaturated Esters Catalyzed by (37) and dppb [a]

Substrate	Yield of Aldehydes %	Product (selectivity)
	29	$OHCCH_2CH_2C(CH_3)(CH_2)_2CH=C(CH_3)_2$ (56) 100 %
	67	$OHC(CH_2)_3OCOC_3H_7$ (57) 91 % $OHCCHCH_2OCOC_3H_7$ (58) 9 %
	69	$OHCCH_2CH_2CHOAc$ (59) 97 % $OHCCH(CH_3)CHOAc$ (60) 3 %
	82[b]	(59):(60) = 83:17
	87	$OHC(CH_2)_4OAc$ (61) 70 % $OHCCH(CH_3)(CH_2)_2OAc$ (62) 30 %
	84[b]	(61):(62) = 50:50

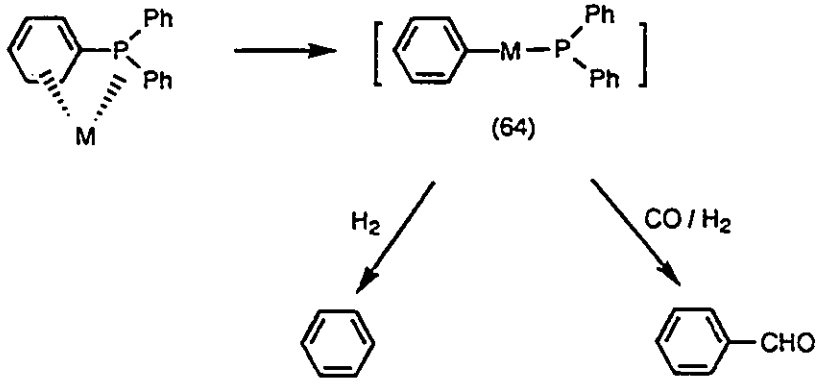
[a] (37): dppb=1:2 [b] (37): dppb=1:0



Scheme 2-19

This convenient route can be used to synthesize (R)-(-) or (S)-(+)sulcatol starting from optically pure 1-methyl-2-propenyl acetate which can be obtained by Sharpless kinetic resolution.[82] It should be mentioned that (37) or (43)/dppb did not catalyze the hydroformylation of allyl acetates having a disubstituted double bond. The homoallylic acetate, CH_2=$CHCH_2CH_2OAc$, does undergo hydroformylation in fair regioselectivity as linear (61) : branched (62) products = 70:30 (in the absence of dppb, the ratio of (61):(62) is 50:50 in 87% yield). The hydroformylation of allyl alcohol under identical conditions yielded a complex mixture. Allyl acetate does not react with CO/H_2 when using (37) in the presence of dppe or cis-1,2-diphenylphosphinoethene. In this case, only a trace amount of benzaldehyde was isolated and starting material was recovered. The formation of benzaldehyde can be explained by the migration of one of the phenyl groups on the phosphine complex to the central rhodium atom followed by carbonylation and hydrogenation. This is another example of phosphorous-carbon bond cleavage.[83] Phosphorus carbon bond cleavage was first noted by Chini and co-workers[84] in 1972.

Arenes or alkanes were produced in $Rh_4(CO)_{12}/PR_3$ (R=aryl, alkyl) catalyzed hydroformylation of olefins. Phosphorus-carbon bond cleavage has been identified as a catalyst deactivation mode for both the Co and Rh systems.[85] The mechanism for the cleavage reaction may involve a P-M-Ph intermediate (64) which could then undergo reaction with either H_2 or CO/H_2 to give the observed products (Scheme 2-20).



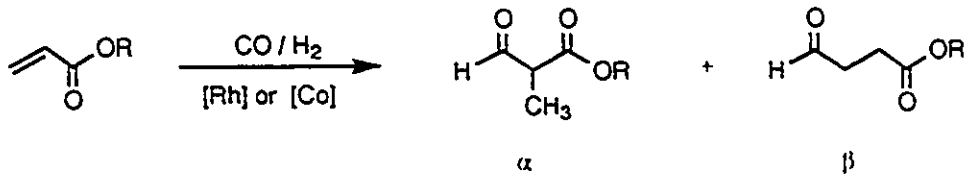
Scheme 2-20

The phosphorus-carbon bond cleavage reaction provides evidence for the coordination of phosphine ligands such as dppb, dppe and cis-1,2-diphenylphosphinoethane with the central metal atom of the zwitterionic rhodium(I) complex (37) [86]. The migration of the phenyl group and the insertion of carbon monoxide results in the formation of benzaldehyde.

2-4. The Regioselective Hydroformylation of α, β-Unsaturated Esters

2-4-1. Introduction

In recent years, the hydroformylation of α,β-unsaturated esters has received much attention. Acrylates and methacrylates have been subjected to considerable investigation. The selective formation of the α and β-isomer results using rhodium and cobalt complexes, respectively, as catalysts (Scheme 2-21).



Scheme 2-21

Falbe and Huppes[88] reported that $Co_2(CO)_8$ catalyzed hydroformylation of ethyl acrylate at 300 atm. and 140°C gave > 90% yield of β-isomer, while the use of rhodium/1,4-bis(diphenylphosphino)butane(dppb), selectively afforded the α-isomer.[14] Both reactions required rather drastic conditions (Co/dppe: 120°C, 50 atm., Rh/dppb: 150°C, 100 atm). The Rh/dppb system displays hydrogenation activity under milder conditions.

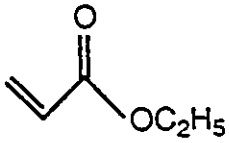
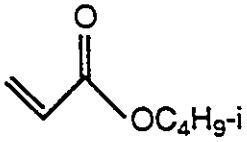
In this section is described the hydroformylation of α,β-unsaturated esters catalyzed by zwitterionic and cationic rhodium complexes with dppb to give the α-isomer (selectivity > 98%) in good yield.

2-4-2. Alkyl Acrylates

The hydroformylation of ethyl acrylate was carried out at 80°C under 40 atm of synthesis gas($CO:H_2$/1:1) using (37)/dppb (1:2) in methylene chloride. The regioselectivity in the absence of dppb was poor with the ratio of α-isomer (65) and β-isomer (66) being 45:55. The selectivity improves substantially by the addition of dppb to the reaction system . Other catalysts such as cationic rhodium(I) complex, $[(Ph_3P)_2Rh(COD)]^+BPh_4^-$ (43), or neutral rhodium(I) complex,$[(COD)RhCl]_2$ (47), in the presence of dppb are also effective for the regioselective hydroformylatiom of α,β-unsaturated esters. Iso-butyl acrylate reacted with synthesis gas in the presence of catalyst (37) under similar conditions to give the branched isomer (67) in 76% isolated yield. The results are listed in Table 2-6.

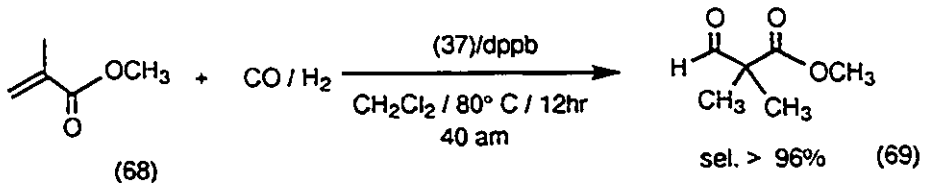
Thus, alkyl acrylates can be hydroformylated almost regiospecifically using Rh(I) zwitterionic complex (37) in the presence of dppb as added ligand.

Table 2-6. Hydroformylation of alkyl acrylates

Substrate	Cat.	Ratio of Cat./dppb	Yield % (isolated)	Ratio of isomers
				α : β (65) (66)
	(37)	1 / 0	52	57 : 43
		1 / 2	78	98 : 2
	(43)	1 / 0	56	85 : 15
		1 / 2	77	98 : 2
	(47)	1 / 0	13.5	45 : 55
		1 / 4	83	99.5 : 0.5
	(37)	1 / 2	76	α (67) : β 100 : 0

2-4-3. Methyl Methacrylate and α-Methylene-γ-butyrolactone

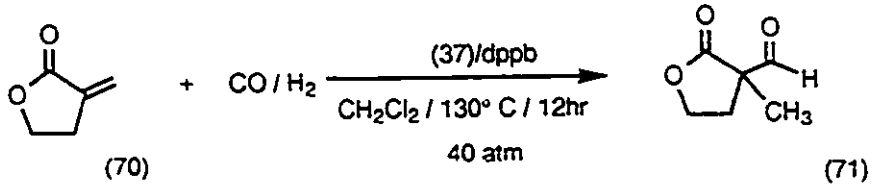
Excellent regioselectivity was found in the reaction of methyl methacrylate(68) or α-methylene-γ-butyrolactone(70) with (37) or (43)/dppb. The reaction of methyl methacrylate gave the α-aldehydic ester(69) containing a quaternary carbon atom attached to the formyl group, a violation of the Keulemans rule[54] (Scheme 2-22).



(68) (69)

Scheme 2-22

α-Methylene-γ-butyrolactone (70) also afforded only α-aldehydic ester(71) (Scheme 2-23). It is possible that electronic effects are dominant in these reactions, particularly when the phosphine-modified rhodium complexes are used as catalysts.[87]



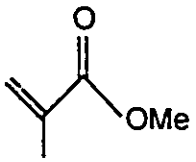
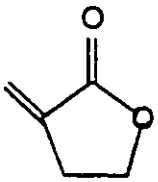
(70) (71)

Scheme 2-23

The hydroformylation of 1,1-disubstituted olefinic esters required higher temperatures than acrylate esters. When the reaction of methyl methacrylate with synthesis gas was carried out at 80°C for 12hr, the yield was low. However, if the reaction

temperature was increased to 130°C , the yield improved to 65% with 96:4 ratio of α to β products. The same ratio was observed by the use of (37) as the catalyst. The hydroformylation of α-methylene-γ-butyrolactone was regiospecific, as only the α-isomer was isolated in 60% yield. The results are listed in Table 2-7.

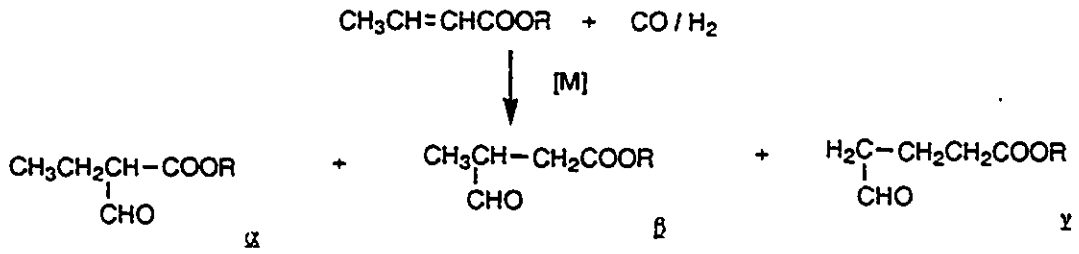
Table 2-7. Hydroformylation of Methyl Methacrylate and α-Methylene-γ-butyrolactone

Reactant	Temp. °C	Cat.	[Rh]/dppb	Yield % (isolated)	Ratio of isomers α (69) : β
 (68)	80	(37)	1 / 2	20	97 : 3
	130	(37)	1 / 2	65	96 : 4
	130	(43)	1 / 2	59	96 : 4
					α (71) : β
 (70)	130	(37)	1 / 2	56	100 : 0
	130	(43)	1 / 2	60	100 : 0

Thus, Rh(I) cationic or zwitterionic complexes readily catalyze the hydroformylation of methyl methacrylate and α-methylene-γ-butyrolactone. In both cases, the reaction occurs with very high regioselectivity for the corresponding α-aldehydic esters.

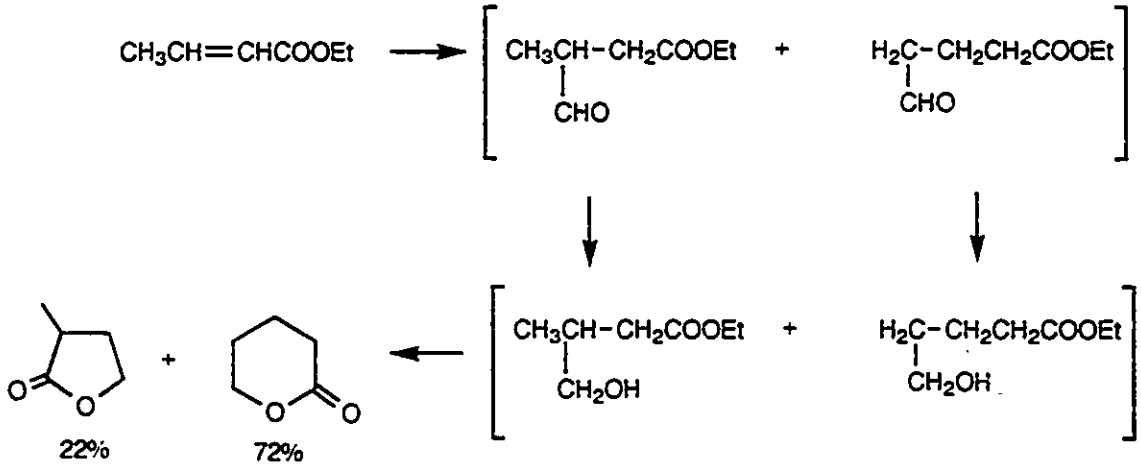
2-4-4. Ethyl Crotonate

In the hydroformylation of crotonate esters, three different aldehydes may be formed, denoted as the α, β or γ-isomers(Scheme 2-24).



Scheme 2-24

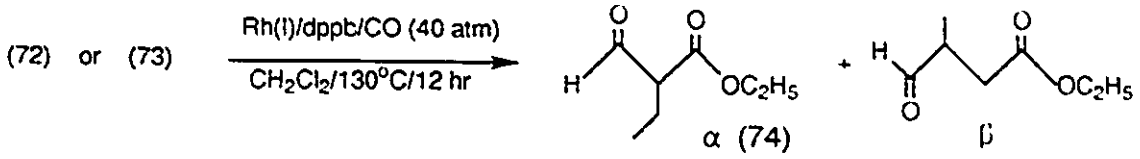
Cobalt catalyzed hydroformylaton of ethyl crotonate led to the isolation of lactones resulting from hydrogenation of the aldehyde and lactonization of the corresponding alcohols at high temperature. The reaction was conducted at 140°C and 300 atm, followed by hydrogenation and cyclization at 200-240°C. The selectivity of the reaction was poor and the final products were a mixture of five and six-membered ring lactones (Scheme 2-25).[89]

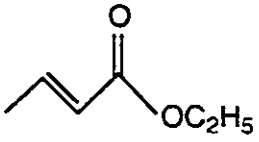
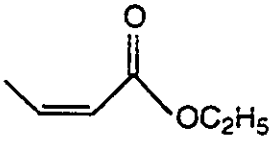


Scheme 2-25

The present experiments show that the hydroformylation of trans (72) or cis (73) ethyl crotonate catalyzed by (37)/dppb, afford the α-isomer(74) in 60-68% yield with excellent regioselectivity irrespective of the stereochemistry of the reactants (Table 2-8).

Table 2-8. Hydroformylation of Ethyl Crotonate



Reactant	Cat.	[Rh]/dppb	Yield,% (Isolated)	α (74) : β
 (72)	37	1 / 2	64	98 : 2
	43	1 / 2	78	98 : 2
 (73)	37	1 / 2	45	98 : 2
	43	1 / 2	68	98 : 2

Only starting materials were recovered in the hydroformylation of methyl tiglate, methyl sorbate and α,β-unsaturated ketones under the above conditions.

As described above, the rhodium(I) complexes (37), (43) or (47)/dppb are very efficient catalysts for the selective hydroformylation of α,β-unsaturated esters. Due to the steric interactions of substrate with the catalyst, the hydroformylation of 1,1-disubstituted and 1,2-disubstituted olefinic esters required higher temperatures compared with that of ethyl acrylate. As expected, 1,1,2-trisubstituted olefinic esters did not undergo hydroformylation even at 130°C.

Of particular note is the recent publication by Neibecker and Reau on the use of rhodium phosphole and phosphanorbornadienes (from $[Rh(CO)_2Cl]_2$ and added ligand) as catalysts[90] for the hydroformylation of ethyl acrylate. Although the reaction was regiospecific, an investigation was not conducted on the scope and limitations using a variety of α,β-unsaturated esters. The work of Neibecker and Reau is derived from the previous study by Tanaka and co-workers[91] who used the same rhodium catalyst but with added bidentate phosphine ligands such as dppb. Furthermore, (37)/dppb compares favorably with the well known $RhH(CO)(PPh_3)_3$ (10)/dppb system (i.e ethyl acrylate with (10)/dppb affords 34% branched and 13% linear aldehydes, together with 53% ethyl propionate).[92]

In conclusion, the Rh(I) zwitterionic complex, in the presence of dppb, catalyzes the hydroformylation of α,β -unsaturated esters to give aldehydic esters in good yields and with high regioselectivity. In some cases, these reactions occur regiospecifically.

2-5. The Regioselective Reductive Carbonylation of Alkenes

2-5-1. Introduction

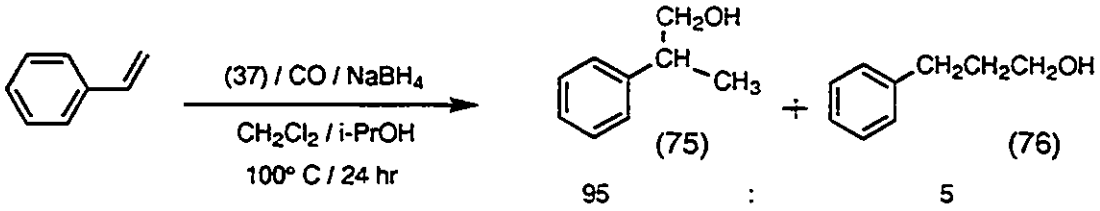
The conversion of olefins to alcohols by reductive carbonylation is another important process in organic chemistry. The resulting alcohols can be used as synthetic intermediates, solvents, detergent materials, flavors and fragrances.

It was mentioned proviously that Amer and Alper[70] reported the use of zwitterionic rhodium complexes as catalysts for the hydroformylation of olefins. Branched-chain aldehydes can be obtained in a very selective manner by reaction of a monosubstituted vinyl arene or vinyl ether with carbon monoxide and hydrogen. Appropriate aliphatic or aromatic 1,1-disubstituted olefins gave linear aldehydes in a regiospecific manner.

Hydrogen sources conventionally used in carbonylation of alkenes are H_2, alcohols, amines, carboxylic acids [10] and silanes[147]. The use of another source of hydrogen viz. $NaBH_4$ and structurally related analogues may modify catalytically active species and provide new reaction pathways. This section describes the use of zwitterionic Rh(I) complex(37) with $CO/NaBH_4$/i-PrOH for achieving the regioselective synthesis of branched or linear alcohols. The results constitute the first examples, to our knowledge, of a borohydride based hydroformylation reaction, as well as the first direct regioselective route to branched chain alcohols from styrene derivatives.

2-5-2. Results and Discussion

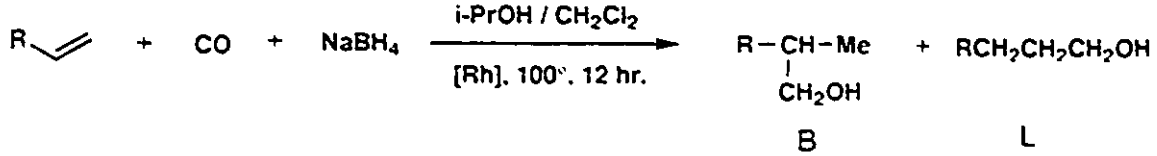
Treatment of styrene with 1.2 equivalents of sodium borohydride, i-PrOH, and (37) in chloroform, for 22 hr at 100°C and 35 atm. of carbon monoxide, gave isomeric alcohols in 83% yield, the ratio of branched (75)/linear (76) products being 95:5(Scheme 2-26).



Scheme 2-26

The ratio of reactant/rhodium catalyst was 100/1. The reductive carbonylation reaction of a variety of substrates are listed in Table 2-9. Styrene, and its para-methyl, methoxyl, and isobutyl derivatives gave similar selectivity in these reactions, while p-chlorostyrene afforded a mixture of branched and linear products in low selectivity(75:25). The reaction of p-bromostyrene yielded a complicated mixture. 3,3-Dimethyl-1-hexene underwent reductive carbonylation leading to the terminal alcohol. High selectivities can also be achieved with substrates such as 2-methyl-1-undecene and limonene. A simple aliphatic monoolefin such as 1-decene displayed little regiochemical control in the reductive carbonylation using (37) as the catalyst, although the product yield was good (Table 2-9).

Table 2-9 Reductive Cabonylation of Alkenes



Alkene	Catalyst	Yield %	B : L
Ph-CH=CH_2	(37)	83	95 : 5
	(10)	90	64 :36
	(43)	92	80 : 20
p-$CH_3C_6H_4$- CH=CH_2	(37)	77	93 : 7
	(10)	95	77 :23
	(43)	90	75 : 25
p-$CH_3OC_6H_4$- CH=CH_2	(37)	91	95 : 5
p-ClC_6H_4- CH=CH_2	(37)	93	75 : 25
p-FC_6H_4- CH=CH_2	(37)	70	90 : 10
p-$(CH_3)_2CHCH_2$-C_6H_4-CH=CH_2	(37)	73	89 : 11
n-C_8H_{17}-CH=CH_2	(37)	90	47 : 53
Cyclohexyl-CH=CH_2	(37)	87	10 : 90
2-Methylundec--1-ene	(37)	75	1 : 99
$C_3H_7C(CH_3)_2$- CH=CH_2	(37)	88	1 : 99
Cyclooctene	(37)	74	
R(+)-limonene	(37)	74	0 : 100

It was instructive to compare the result using a zwitterionic rhodium catalyst with representative cationic and neutral rhodium complexes as well as a cobalt complex. Substitution of (43) for (37) in the reaction of styrene resulted in a 90% yield of alcohols, but the regioselectivity observed was low (B:L = 64:36). The neutral Rh(I) complex, $RhH(CO)(PPh_3)_3$ (10) was also an effective catalyst for the hydroformylation of styrene (92% yield) but again, the regioselectivity (B:L = 80:20) was considerably less than that observed using (37) as the catalyst. The use of cobalt carbonyl under identical conditions gave less than 10% overall yield of alcohol from styrene.

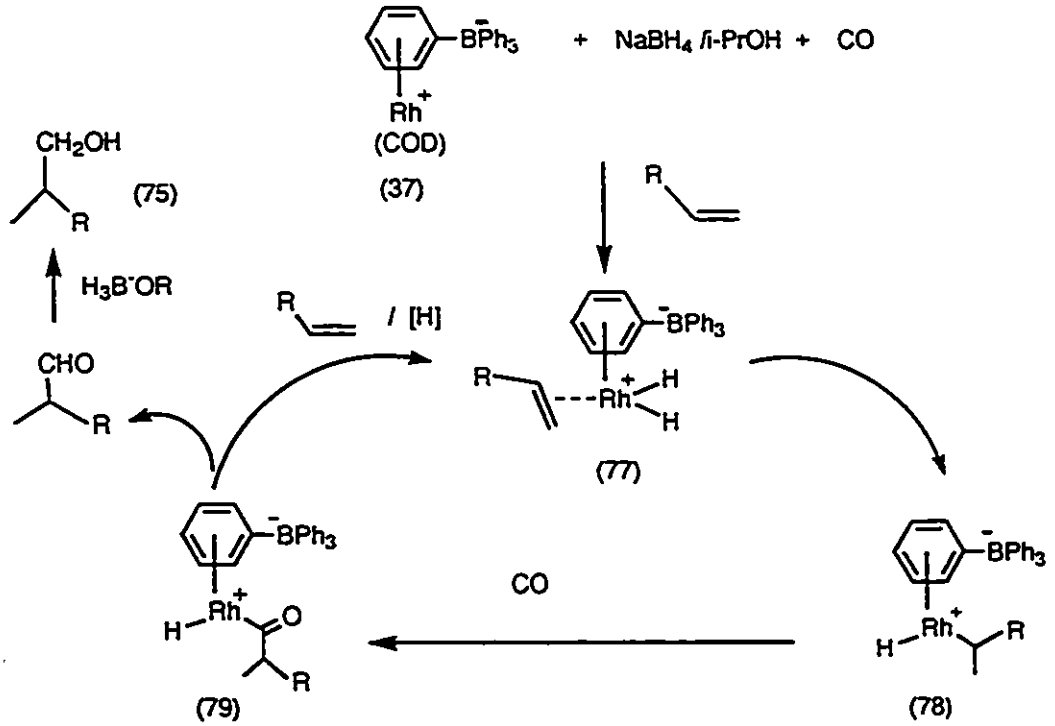
The reductive carbonylation of styrene in solvents such as THF and benzene was unsatisfactory. With the use of THF as the solvent, the yield of alcohol was poor and a mixture of products was obtained. No reaction was observed and only starting material was recovered when benzene was used as the solvent. Sodium triacetoxyborohydride can also be used in place of $NaBH_4$ in these reactions, but the chemo- and regioselectivities are very poor. For instance, styrene reacted with carbon monoxide and $NaBH(OAc)_3$ in the presence of (37), to give a mixture of alcohols (16% yield and B:L = 59/41) and aldehydes (39% yield and B:L= 60/40). It should be noted that no reaction occurs in the absence of either sodium borohydride or isopropanol.

2-5-3. Mechanism

It is conceivable that a positive charge on the rhodium atom of (37) is capable of directing the regiochemistry of the reductive carbonylation, and cationic rhodium hydride

intermediates may be more susceptible to olefin coordination and carbonyl insertion. In addition, the anionic triphenylboron substituent attached to the coordinated arene ring may exert steric and/or electronic effects influencing the stereochemistry.

A mechanism for the reductive carbonylation of alkene is proposed in Scheme 2-27. The reaction of $NaBH_4$ with alcohol to produce alkoxylborohydride has been investigated and monoalkoxyborane species BH_3OR are known.[93] The zwitterionic rhodium(I) complex (37) may possibly react with $NaBH_4$/iso-PrOH and alkene to generate a rhodium hydride species (77) containing π-coordinated alkene. The subsequent intramolecular insertion of the alkene at the Rh-H bond may afford (78) and the insertion of CO into the Rh-C bond may give the intermediate (79) which produces the branched aldehyde and regenerates the catalytically active species (77). The aldehyde is easily reduced by alkoxyborohydride affording the alcohol (Scheme 2-27).

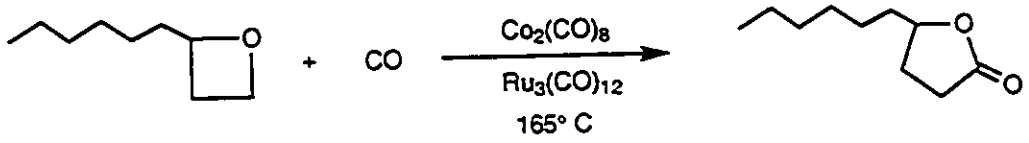


Scheme 2-27

2-6. Lactonization of Allylic Alcohols

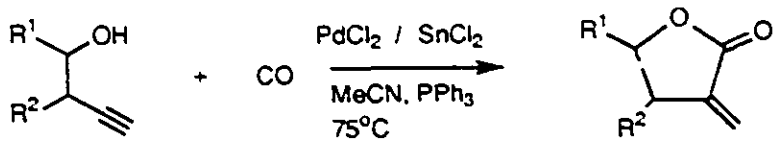
2-6-1. Introduction

Five-membered lactones are an important class of compounds in organic chemistry. One of the simplest routes to synthesize a five-membered lactone is the direct insertion of carbon monoxide into four-membered cyclic ethers (oxetanes). Previous work indicated that this type of reaction could be achieved by using cobalt catalyst under drastic conditions (250 atm., 200°C).[94] Recent investigations have enabled this reaction to be carried out under comparatively mild conditions (Scheme 2-28) and in a regiospecific manner.[38]



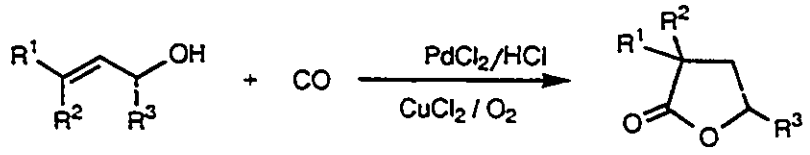
Scheme 2-28

Carbonylation of ethynyl alcohols is an attractive route to α-methylene-γ-butyrolactones,[95,96] although the original methodology involves the use of stoichiometric quantities of a highly toxic nickel tetracarbonyl.[97] A more recent technique employed catalytic amounts of palladium(II) chloride with thiourea.[98] An improved catalyst system consisting of $PdCl_2$ and a tertiary phosphine in the presence of tin(II) chloride gives good yields of α-methylene-γ-butyrolactones (Scheme 2-29).[99]



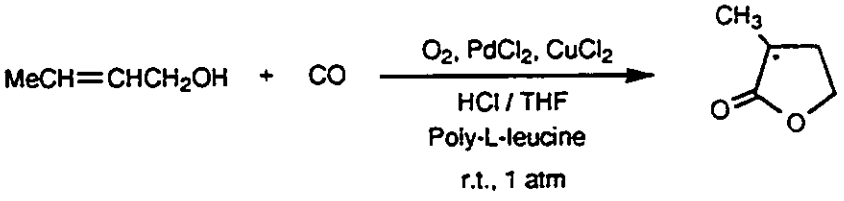
Scheme 2-29

The reaction of primary, secondary and tertiary allylic alcohols with carbon monoxide and oxygen in the presence of catalytic quantities of palladium (II) and copper (II) chlorides gave γ-butyrolactones.[100] The reaction proceeded at room tempe-ature and atmospheric pressure and the yields were in the range of 40%-60% (Scheme 2-30).



Scheme 2-30

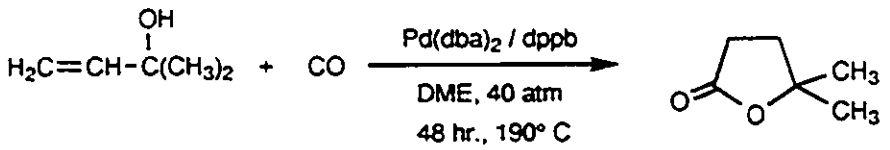
Asymmetric induction can be attained in the cyclocarbonylation of crotyl alcohol, in up to 61% ee, by the use of poly-L-leucine (MW-21,700) as an added chiral ligand (Scheme 2-31).[101]



Scheme 2-31

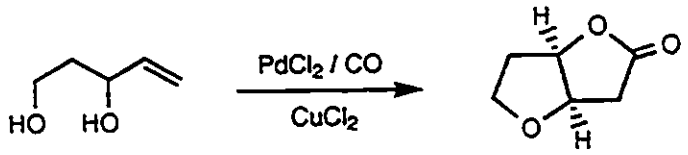
Under neutral conditions, secondary and tertiary allylic alcohols react with carbon monoxide in the presence of catalytic quantities of bis(dibenzylideneacetone)

palladium(0) and 1,4-bis(diphenylphosphino)butane to form lactones in 45-92% isolated yields (Scheme 2-32).[102]



Scheme 2-32

The latter have been also prepared in high yield by intramolecular, palladium-catalyzed oxycarbonylation under mild conditions (25°C, 1 atm) (Scheme 2-33).[103]

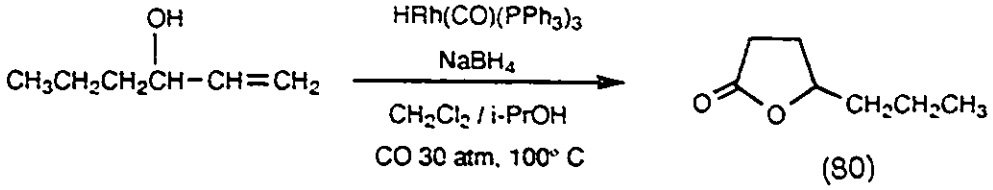


Scheme 2-33

We now describe the use of rhodium(I) complexes, including the zwitterionic rhodium(I) complex (37), for the cyclocarbonylation of allylic alcohols affording γ-butyrolactones.

2-6-2. Results and Discussion

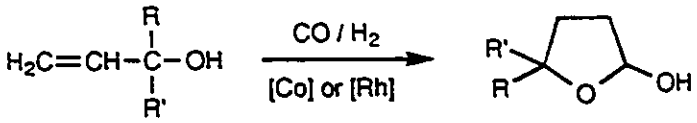
Treatment of a methylene chloride solution of 1-hexen-3-ol with CO, i-PrOH, $NaBH_4$ and $H(CO)Rh(PPh_3)_3$ (10) for 12 hr. at 30 atm. pressure and 100°C gave 4-propyl-γ-butyrolactone(80) in 82% yield(Scheme 2-34).



(80)

Scheme 2-34

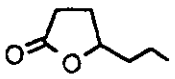
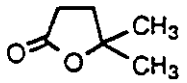
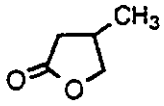
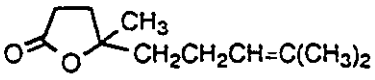
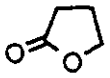
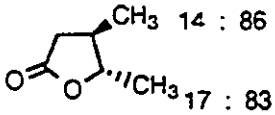
According to previous results (see section 2-5), alkenes gave alcohols under reductive carbonylation conditions.[104] It was therefore surprising to observe the formation of lactones instead of anticipated diols when the analogous catalytic system was applied to an allylic alcohol. The zwitterionic rhodium(I) complex (37) and cationic complex (43), are also effective catalysts for the cyclocarbonylation of allylic alcohols to obtain lactones. Usually, the hydroformylation of allyl alcohols catalyzed by cobalt or rhodium complexes produces 2-hydroxytetrahydrofurans (Scheme 2-35).[105]



Scheme 2-35

The results of the lactonization of allylic alcohols catalyzed by different rhodium (I) complexes with or without i-PrOH are listed in Table 2-10. Notably, 4-propyl-γ-butyrolactone. (80) was obtained in only 10% yield when the reaction was carried out in the absence of i-PrOH. In contrast, the tertiary allylic alcohol, H_2C=CHC(OH)Me_2 and the hydridorhodium(I) complex (10), in the presence of i-PrOH, afforded the corresponding lactone (81) in 21% yield, while the yield increased to 61% in the absence of i-PrOH. 3-Methyl-γ-butyrolactone (82) was isolated by cyclocarbonylation of 2-methyl-2-propen-1-ol in 35% yield in the absence of i-PrOH .

Table 2-10. Reductive cyclocarbonylation of allylic alcohols

Allylic alcohol	Catalyst	i-PrOH	Product	Yield % (isolated)
$H_2C{=}CHCH(OH)C_3H_7$	(10)	yes	 (80)	82
		no		10
	(37)	yes		70
	(43)	yes		59
$H_2C{=}CHCOH(CH_3)_2$	(10)	yes	 (81)	21
		no		61
$H_2C{=}CH(CH_3)CH_2OH$	(10)	yes	 (82)	0
		no		35
Linalool	(37)	yes	 (83)	70
	(37)	no		5
			cis : trans	
$H_2C{=}CH(CH_3)CH(OH)CH_3$	(10)	yes	 14 : 86	50[102]
	(37)	yes	17 : 83 (84)	46

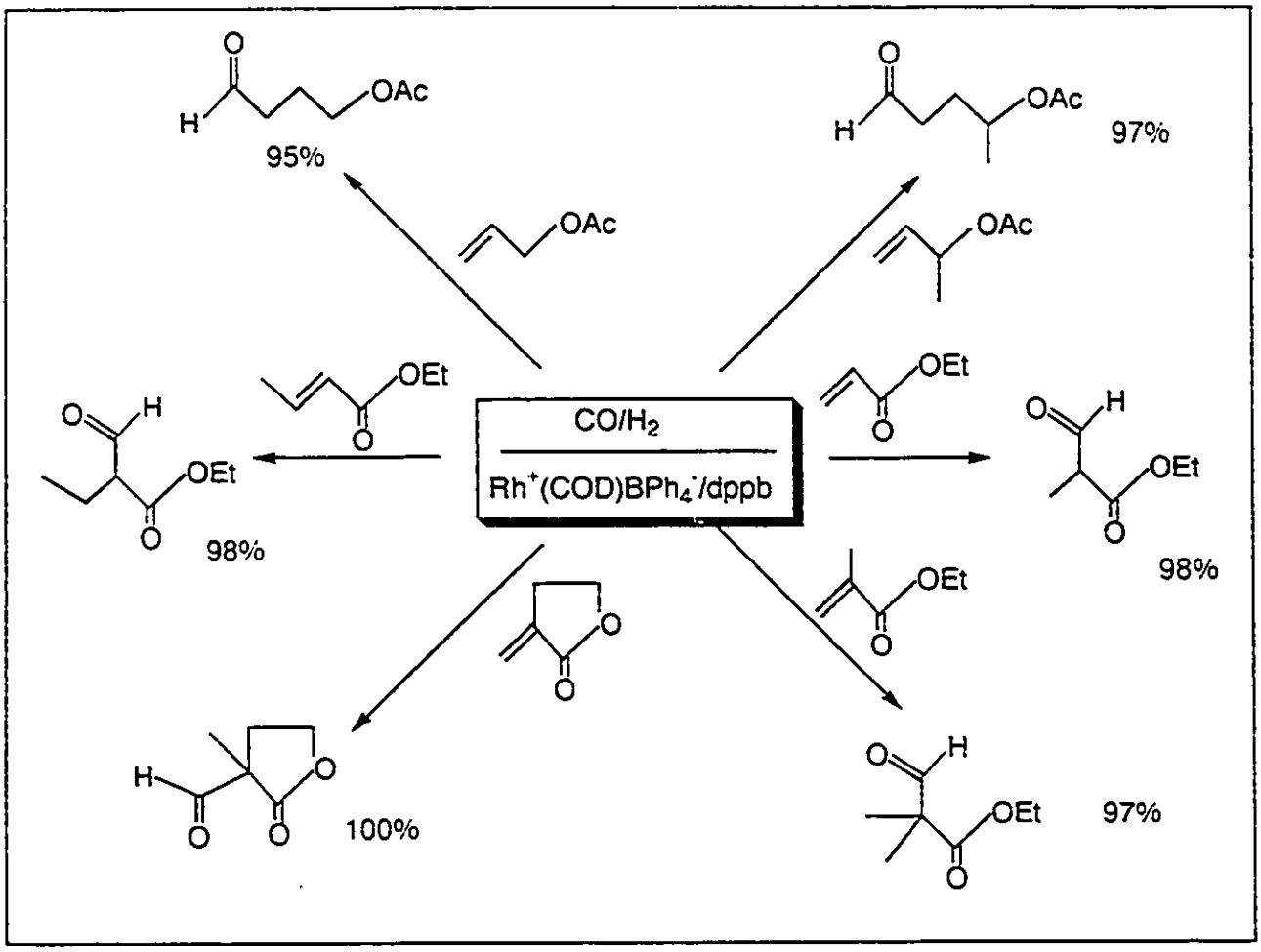
However, no reaction occured in the presence of isopropanol. The cyclocarbonylation of linalool in CH_2Cl_2-i-PrOH using (37)/$NaBH_4$ gave the corresponding lactone (83) in 70% yield (32% yield was obtained in the absence of i-PrOH). 3-Methyl-3-buten-2-ol was converted mainly to the trans-diastereoisomer of (84) in 46-50% yield. 3-Buten-1-ol, under identical carbonylation conditions, affords 2-methylbutyro-γ-lactone in 41% yield.

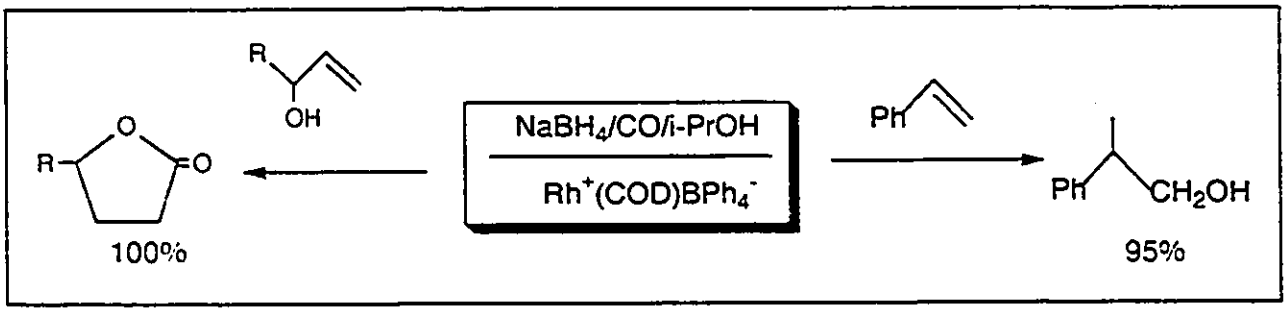
The lactonization of allylic alcohols may begin with the formation of a borate intermediate, H_3B-OCH(R)-CH=CH_2, resulting from the reaction of the alcohol with $NaBH_4$. However, the subsequent steps remain unidentified.

2-7. Conclusion

The study of catalytic hydroformylation and related reactions involving unsaturated esters, alkenes and allylic alcohols has resulted in new, effective, regioselective (or regiospecific) routes to various functionally substituted derivatives. A characteristic feature of these results is the high efficacy of the rhodium(I) zwitterionic complex. The most important highly regioselective transformations catalyzed by this complex are summarized in scheme 2-36.

The selectivities of zwitterionic Rh(I) complex catalyzed carbonylation of alkenes





(Scheme 2-36)

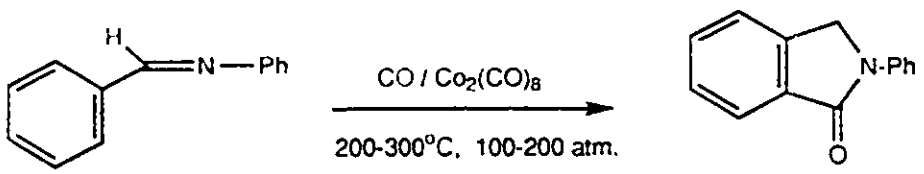
Chapter 3

The Reductive Carbonylation of N-Alkenylamines

3-1. Introduction

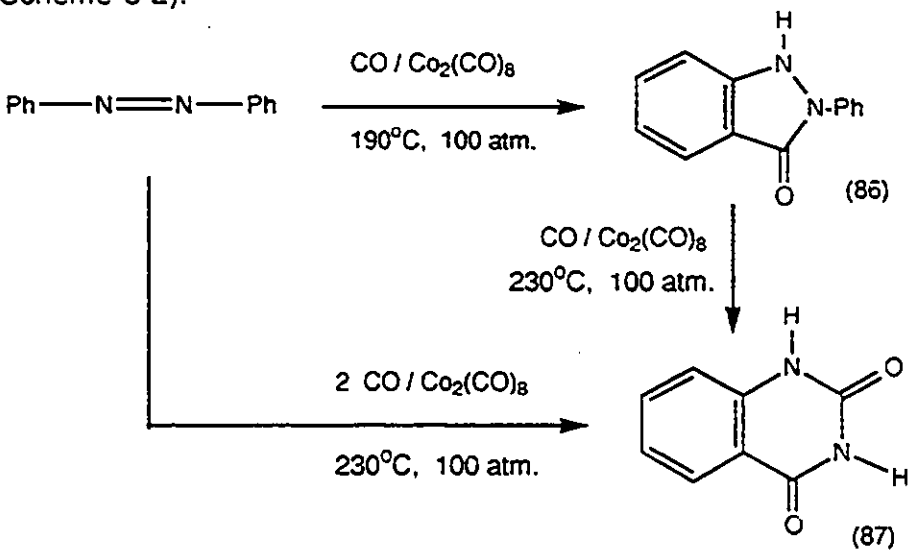
Transition-metal-catalyzed synthesis of heterocyclic compounds is an active research field.[106] Due to the increasing demand for new heterocyclic compounds, particularly for pharmaceutical and crop protection chemicals, the use of transition metal catalysts offers advantages in the synthesis of these chemicals under milder reaction conditions with higher selectivity, or using readily available starting materials.[107-113]

The preparation of nitrogen-containing heterocycles using carbonylation methodology is a useful method in organic synthesis. When Schiff bases were treated with carbon monoxide, excellent yields of substituted phthalimidines were obtained.[114-119] For example, benzaldehyde anil reacts with carbon monoxide (100-200 atm.) at 200-300°C in the presence of dicobalt octacarbonyl in benzene to give N-phenylphthalimidine in 72% yield (Scheme 3-1).



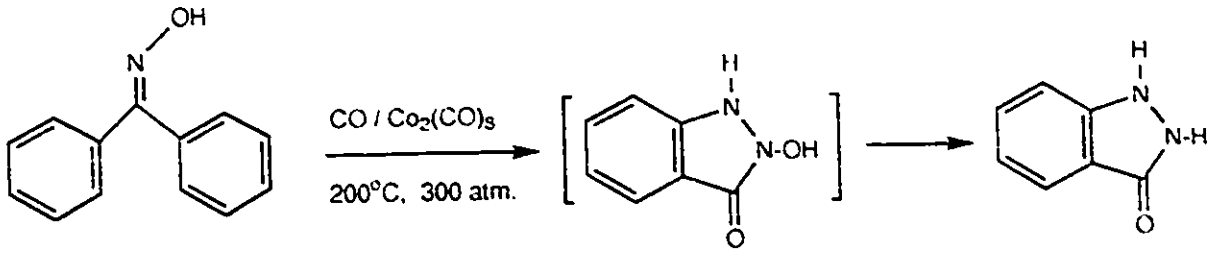
Scheme 3-1

In 1956, Murahashi and Horiie [120] reported that azo compounds reacted similarly to Schiff bases with carbon monoxide and yielded heterocyclic products. Azobenzene reacts with one molecule of CO (100 atm.) at 190°C to give 2-phenylindazolone (86) in 55% yield. At 230°C, azobenzene reacted with two molecules of CO to yield 3-phenyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline (87). The formation of (87) occurs via (86). It was confirmed by the fact that (86) reacted with CO at 230°C to give (87) in quantitative yield (Scheme 3-2).



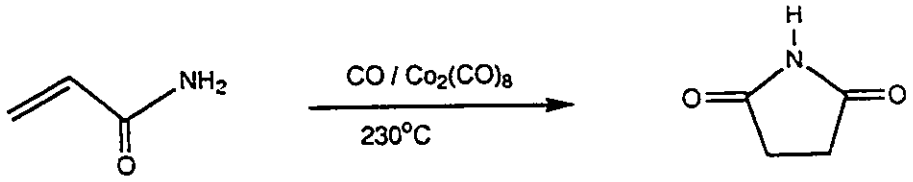
Scheme 3-2

Benzophenone oxime reacted with CO at 300 atm. in the presence of $Co_2(CO)_8$ to produce 3-phenylphthalimidine in 80% yield[121] (Scheme 3-3).



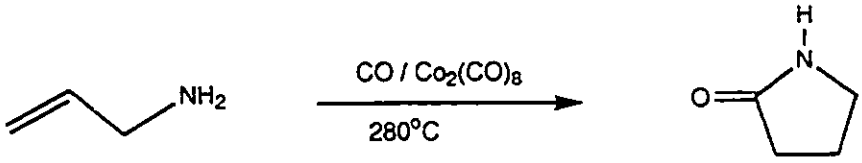
Scheme 3-3

Falbe and Korte [122, 123] found that aliphatic α,β-unsaturated carboxylic acid amides reacted with carbon monoxide (100-300 atm.) at 160-280°C in the presence of dicobalt octacarbonyl to yield succinimides. Acrylamide, under these conditions, gave succinimide in 81% yield (Scheme 3-4).



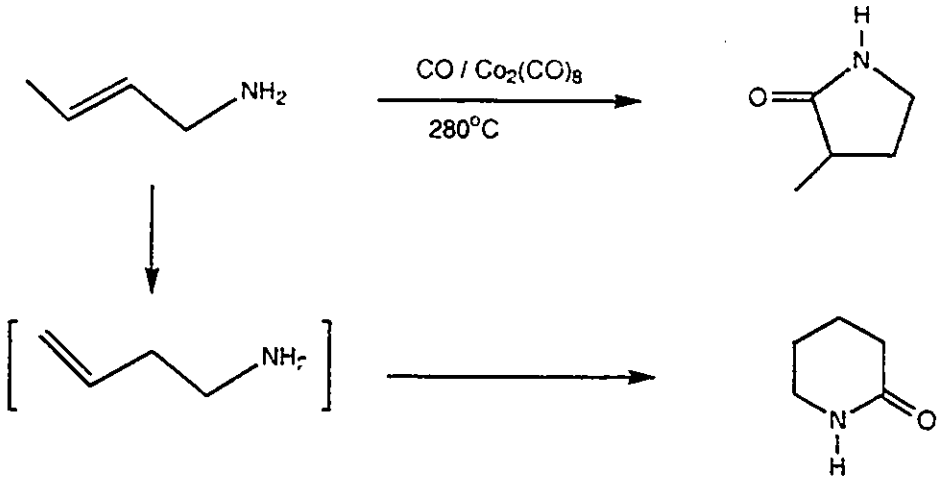
Scheme 3-4

In the presence of dicobalt octacarbonyl, at 280°C, allylamine was converted to 2-pyrrolidone in 60% yield [124] (Scheme 3-5).



Scheme 3-5

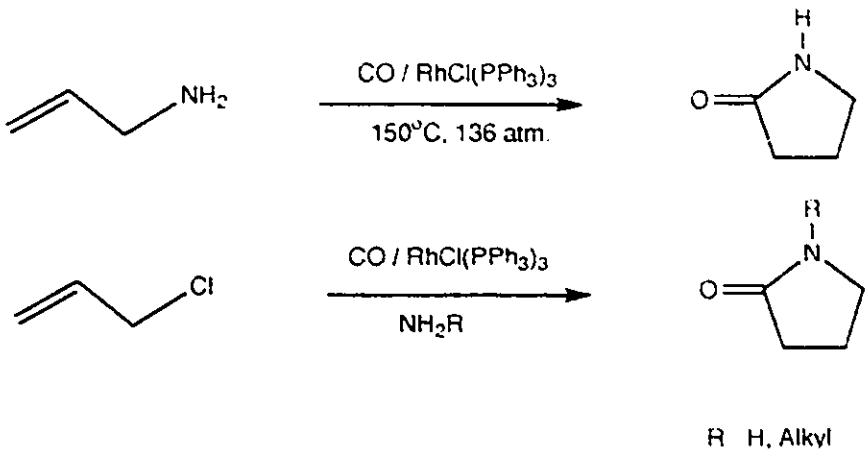
Six-membered heterocycles can also be synthesized from α,β-unsaturated amines capable of isomerization to β,γ-unsaturated amines. Thus, crotylamine was converted into a mixture of 2-piperidone and 3-methyl-2-pyrrolidone (Scheme 3-6).



Scheme 3-6

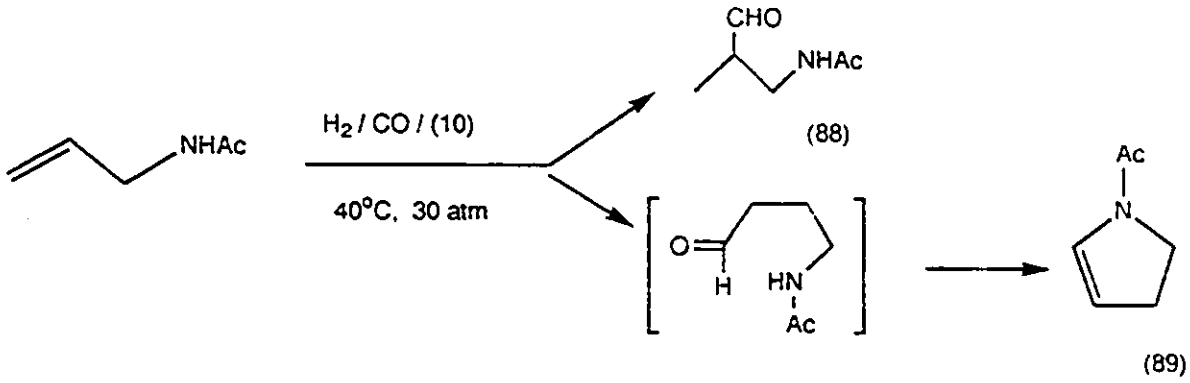
The above reactions using cobalt complexes as catalysts to synthesize heterocyclic compounds require stringent reaction conditions which favor competing isomerization and polymerization.

Rhodium complexes catalyze hydroformylation reactions under considerably milder conditions providing higher selectivity. For example, $RhCl(PPh_3)_3$ catalyzes the transformation of allylamine under CO atmosphere (136 atm.) at 150°C to give γ-butyrolactam in 68% yield. $RhCl(PPh_3)_3$ was also employed for the synthesis of γ-butyrolactam from allyl halides in the presence of CO/NH_3. N-Alkyl-substituted 2-pyrrolidones are formed from allyl halides in the presence of CO and primary alkylamines (Scheme 3-7).[125]



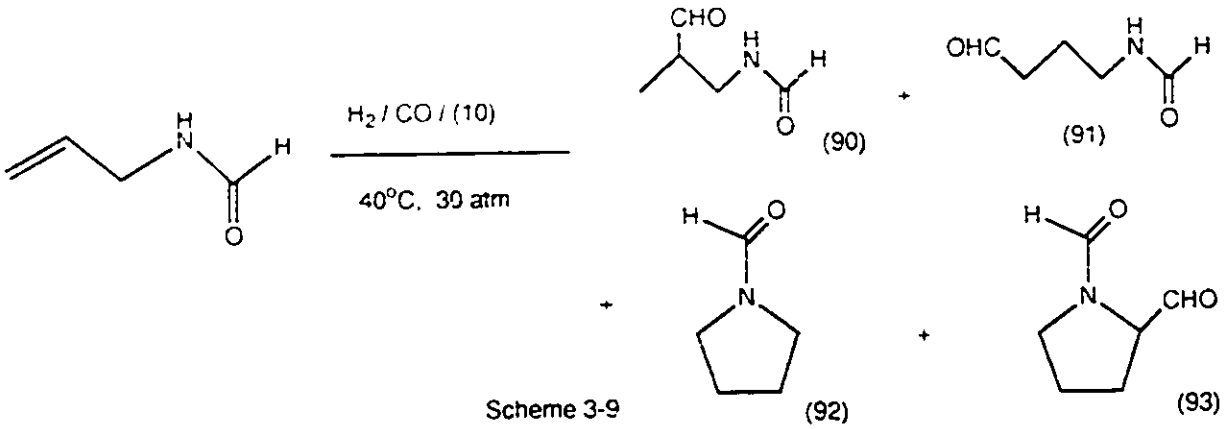
Scheme 3-7

Stille and co-workers reported the hydroformylation of N-allylacetamide catalyzed by $RhH(CO)(PPh_3)_3$ (10) at 40°C and 30 atm. ($CO:H_2$=1:1), which gave the branched aldehyde (88) and N-acetyl-2-pyrroline (89) in a 54:46 ratio (Scheme 3-8).[126]



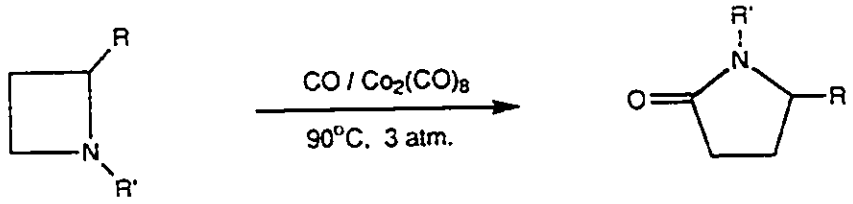
Scheme 3-8

Rhodium catalyzed hydroformylation of N-allylformamide gave a mixture of the branched (90) and linear aldehyde (91), N-formylpyrrolidine (92) and 1,2-diformylpyrrolidine (93) (Scheme 3-9).[127] The selectivity for each of these products depends on the structure of the catalyst. For example, when the neutral complex Rh(I), viz. $RhH(CO)(PPh_3)_3$ (10), is used, the reaction affords (90), (91), (92) and (93) in a 63:11:13:13 ratio in 76% overall yield.



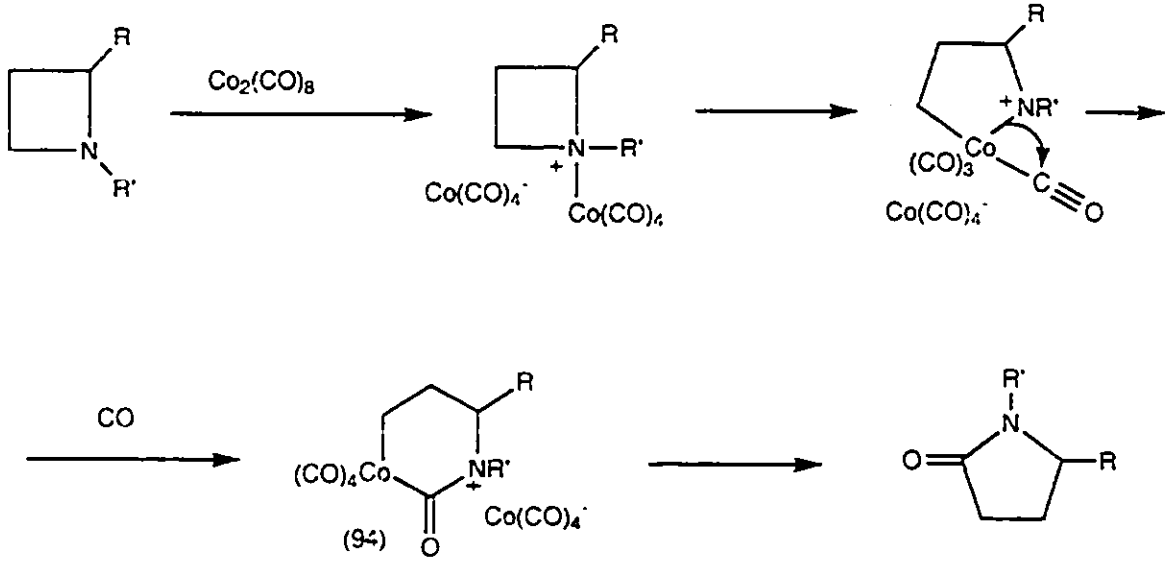
Scheme 3-9

Pyrrolidinones can also be synthesized regioselectively in high yields by dicobalt octacarbonyl catalyzed carbonylation of azetidines (Scheme 3-10)[42].



Scheme 3-10

A possible mechanism of the azetidine ring expansion has been suggested as follows (Scheme 3-11).



Scheme 3-11

The above pathway includes the coordination of the substrate to the metal, the formation of the metallacycle followed by the insertion of CO at the Co-N bond to give the intermediate (94) which affords the product and regenerates the catalytic species.

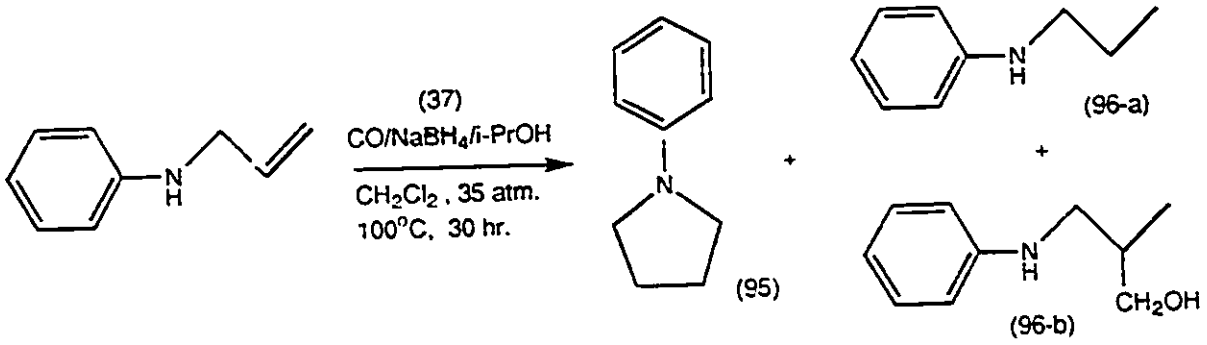
Pyrrolidines, pyrrolidinones and their derivatives are useful as bioactive compounds, solvents and extractants in the petrochemical industry and as monomers for synthetic fibre production.[128] For this reason, the elaboration of simple, one step, catalytic and efficient methods for the preparation of these nitrogen-containing heterocyclic compounds is an important goal.[129] The present chapter describes our results on the catalytic synthesis of N-substituted pyrrolidines and pyrrolidinones via the carbonylation of N-allylamines.[130]

3-2. Synthesis of Pyrrolidines by Reductive Carbonylation of N-Allylanilines

The zwitterionic rhodium complex (37) is an efficient catalyst for the hydroformylation of a variety of simple and functionalized olefins, the process is highly regioselective and even regiospecific in some cases. Also, the Rh(I) complex catalyzes the regioselective preparation of alcohols from olefins using carbon monoxide and sodium borohydride (see Chapter 2, Section 2-5, 2-6). Here, we describe the carbonylation of allylic amine derivatives (Scheme 3-12) catalyzed by (37), under relatively mild conditions,

in the presence of sodium borohydride and 2-propanol.

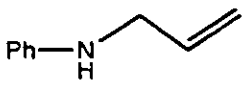
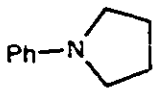
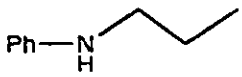
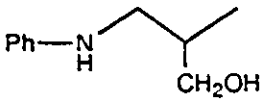
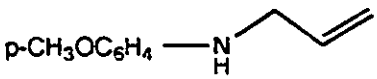
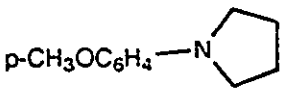
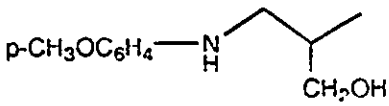
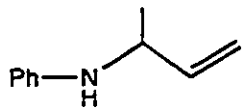
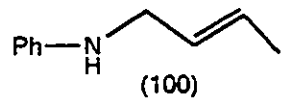
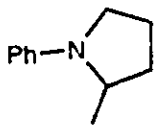
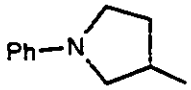
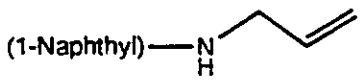
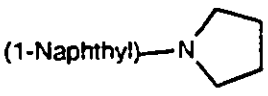
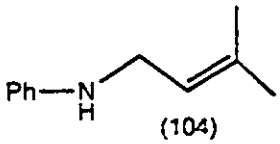
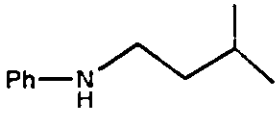
Reaction of allylamine with (37), carbon monoxide (35 atm.), sodium borohydride and 2-propanol in dichloromethane gave numerous products, each of which was formed in low yield. However, the use of N-allylaniline as the reactant afforded 1-phenylpyrrolidine (95) in 31% isolated yield, together with 33 % of the amino alcohol (96-a) and 10% of N-propylaniline (96-b) (Scheme 3-12).



Scheme 3-12

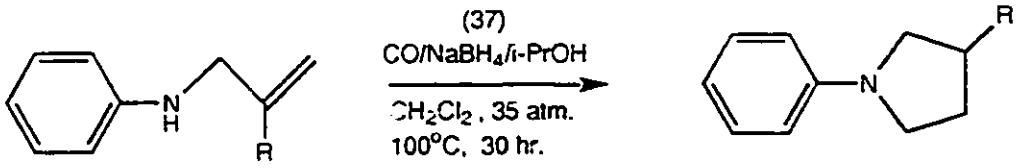
1-(p-Anisyl)-pyrrolidine (97) and the corresponding amino alcohol (98) were isolated in 31 and 32% yield, respectively, when N-allyl-p-anisidine was employed as the reactant. A 65:35 mixture of 1-methylallylaniline (99) and 3-methylallylaniline (100), under identical conditions, gives a 75:25 mixture of the corresponding 1-phenyl-2-methylpyrrolidine (101) and 1-phenyl-3-methylpyrrolidine (102) in 51% overall yield. N-Allyl-N-(1-naphthyl)amine affords N-(1-naphthyl)pyrrolidine (103) in 45% yield. The presence of at least one hydrogen atom at the terminal allylic carbon is essential for the cyclization, as no cyclocarbonylation occurs in the case of N-(3-methyl-2-butenyl)aniline (104) which is converted to the corresponding N-(3-methyl)butylaniline (105) in 48% yield

Table 3-1. Cyclocarbonylation of Allylanilines by $NaBH_4$ /CO/ (37)

Substrate	Product		Yield % (isolated)
		(95)	31
		(96-a)	10
		(96-b)	33
		(97)	31
		(98)	32
 (99)  (100)	 (101)  (102)		51
(99):(100) = 65:35	(101):(102) = 75 :25		
		(103)	45
 (104)		(105)	48

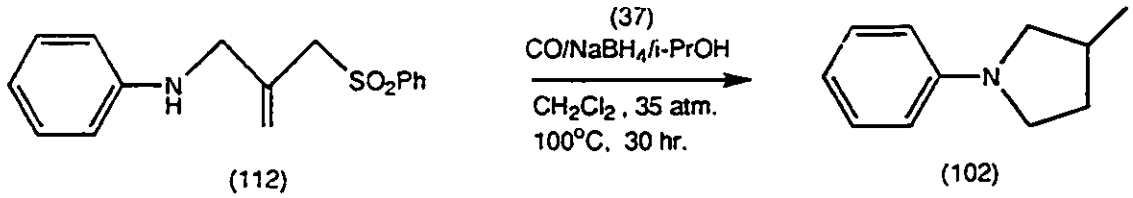
[a] The ratio was determined by ^1H NMR.

3-Substituted pyrrolidines were isolated in good yields when N-(2-substituted)allylanilines were employed as reactants(Scheme 3-13). The results of



Scheme 3-13

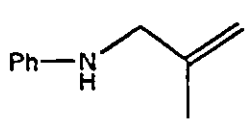
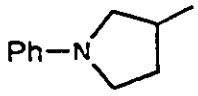
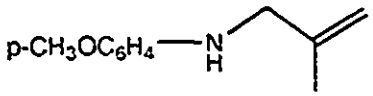
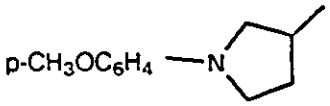
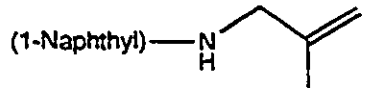
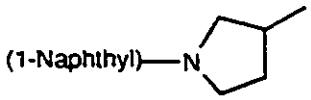
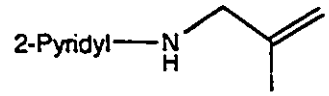
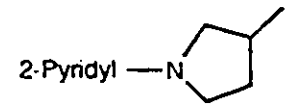
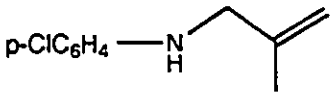
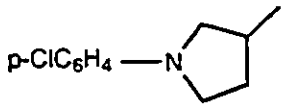
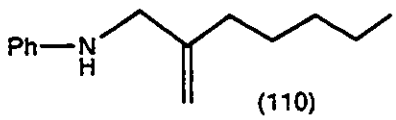
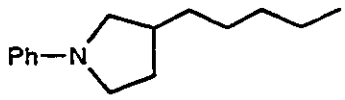
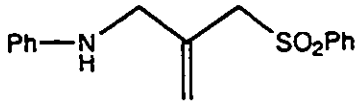
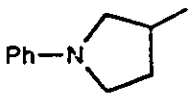
cyclocarbonylation of different substituted allylanilines are listed in Table 3-2. Interestingly, the cyclocarbonylation of N-(2-methylallyl)-N-(2-pyridyl)amine also occurs to give the corresponding N-(2-pyridyl)pyrrolidine (108). It should be noted that the carbonylation of unsaturated phenyl sulfone (112) results in the loss of the phenyl sulfone moiety to generate 3-methyl-N-phenylpyrrolidine (102) (Scheme 3-14).



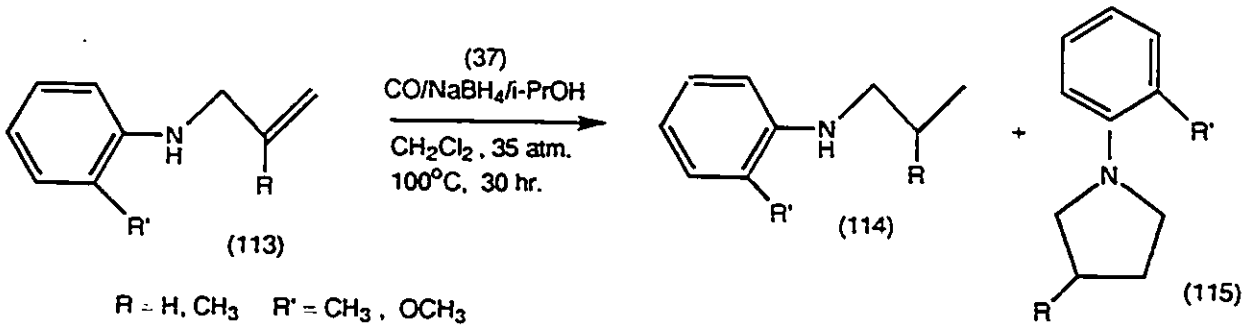
(112) (102)

Scheme 3-14

Table 3-2. Cyclocarbonylation of N-(2-Substituted)-allylanilines by $NaBH_4$ /CO/ (37) System

Substrate	Product	Yield % (isolated)
	 (102)	84
	 (106)	68
	 (107)	57
	 (108)	26
	 (109)	47
 (110)	 (111)	83
 (112)	 (102)	47

Under identical conditions, N-allylanilines (113) bearing a substitutent (CH_3, OCH_3) at the ortho position experienced reduction (Scheme 3-15, Table 3-3).



Scheme 3-15

When R was hydrogen, only hydrogenated products (114) were identified, irrespective of R' being CH_3 or OCH_3. However, in the case of R being CH_3, pyrrolidines (115) were obtained in fair yield. Thus, the reaction is determined by the ortho-effect of the substitutent at the ring and the structure of the allylic fragment.

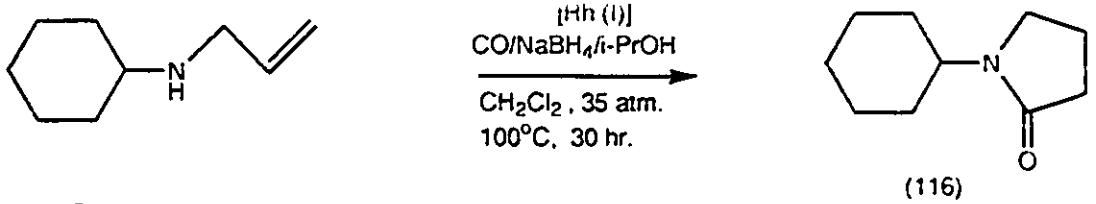
Table 3-3. Reductive Carbonylation of Ortho-substituted Allylaniline

(113)		isolated yield %	
R	R'	(114)	(115)
H	CH_3	72	0
CH_3	CH_3	33	46
H	OCH_3	82	0
CH_3	OCH_3	0	35

For all the above described reactions, a 100:1 ratio of substrate : zwitterionic Rh(I) complex (37) was used with the proportion of allylaniline/$NaBH_4$ being 1:1.2. Isopropanol and sodium borohydride were required since no reaction took place in the absence of either species. The pyrrolidines do not arise from reduction of the corresponding pyrrolidinones, since, for example, 3-methyl-1-phenyl-2-pyrrolidinone was recovered unchanged after its reaction with carbon monoxide, $NaBH_4$/i-PrOH and (37) under identical conditions. Therefore, the cyclocarbonylation of N-allyl substituted anilines to N-arylpyrrolidines does not occur via pyrrolidinone intermediates.

3-3. Syntheses of Pyrrolidinones by Hydroformylation of Aliphatic N-Allylamines

N-Cyclohexylpyrrolidinone (116) was isolated as the only product when N-cyclohexyl-N-allylamine was used as the reactant in rhodium(I) catalyzed carbonylation in a $NaBH_4$/isopropanol system (Scheme 3-16).



Rh(I) = (10), (37) or (43)

(116)

Scheme 3-16

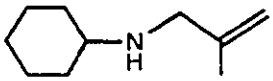
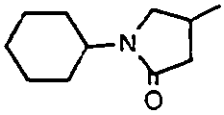
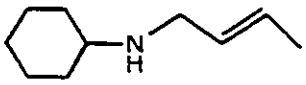
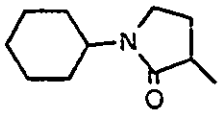
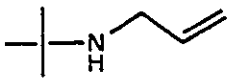
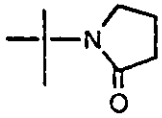
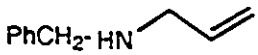
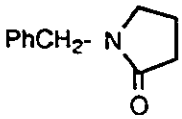
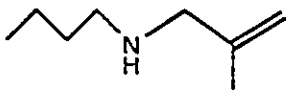
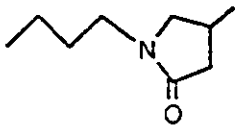
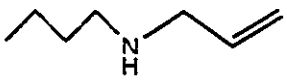
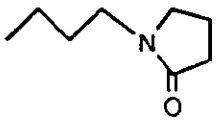
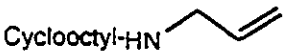
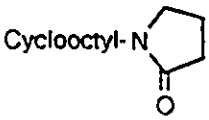
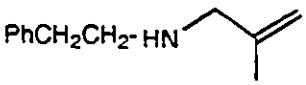
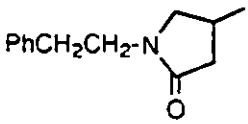
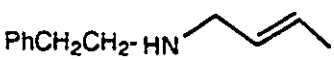
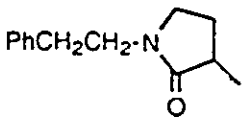
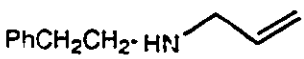
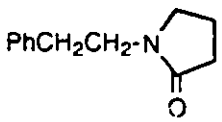
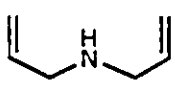
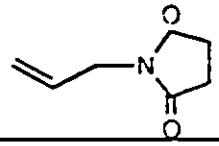
Three different rhodium(I) complexes, (10), (37) and (43), catalyze this reaction, $H(CO)Rh(PPh_3)_3$ (10) being the most active. If $NaBH_4$ is replaced by other borohydrides (e.g. $NaBH_3CN$, $NaBH(OAc)_3$) the yield of the pyrrolidinone (116) decreases appreciably. The effect of the catalyst and borohydride is shown in Table 3-4.

Table 3-4. The Effect of Different Rhodium Catalysts and Boron Hydrides on the Cyclocarbonylation of N-Allyl-N-Cyclohexylamine.

Catalyst	Reductant	isolated yield % (116)
$Rh^+(COD)BPh_4^-$ (37)	$NaBH_4$	48
$[Rh(PPh_3)_2(COD)]^+BPh_4^-$ (43)	$NaBH_4$	61
$RhH(CO)(PPh_3)_3$ (10)	$NaBH_4$	78
	1/2 $NaBH_4$	67
	$NaBH_3CN$	20
	$NaBH(OAc)_3$	traces

Other aliphatic allylamines can also be cyclocarbonylated to obtain the corresponding pyrrolidinones in fair yield. These reactions are smoothly catalyzed by the Rh(I) complex (10) (Table 3-5).

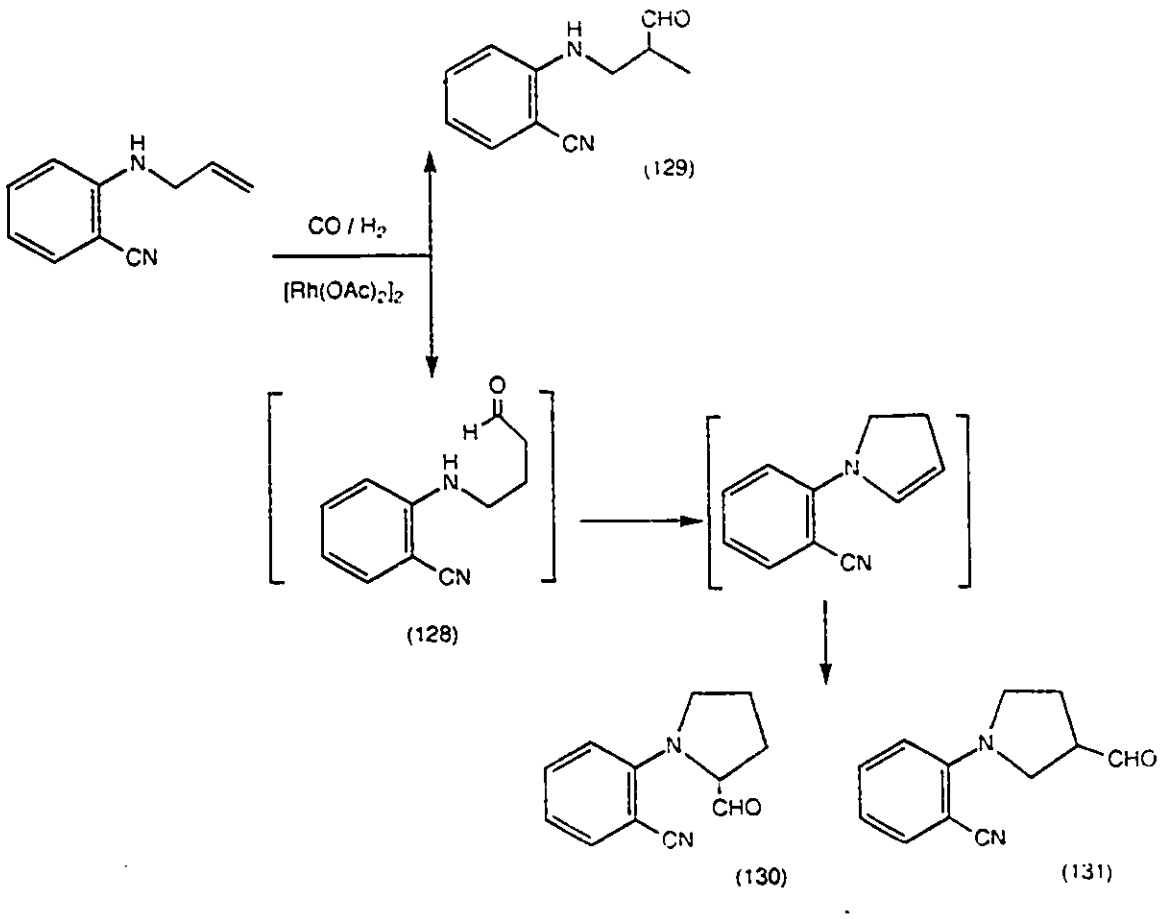
Table 3-5. Cyclocarbonylation of N-Substituted N-allylamines by $NaBH_4$ /CO/ (10) System

Substrate	Product		Yield % (isolated)
		(117)	46
		(118)	28
		(119)	15
		(120)	51
		(121)	28
		(122)	60
		(123)	78
		(124)	67
		(125)	40
		(126)	92
		(127)	20

Thus the reaction of aliphatic allylamines with $CO/NaBH_4$ catalyzed by Rh(I) complexes is a versatile method for the preparation of N-alkyl(cycloalkyl, benzyl)pyrrolidines. All the products were isolated from the reaction mixtures using column chromatography on silica gel. They were identified by ^1H and ^{13}C NMR, IR, and mass spectroscopy. Note that compounds (118), (121) and (123) have been prepared for the first time. See the Experimental Section for spectral data.

3-4. On The Mechanism of Rhodium(I) Catalyzed Synthesis of Pyrrolidines and Pyrrolidinones from Allylamines

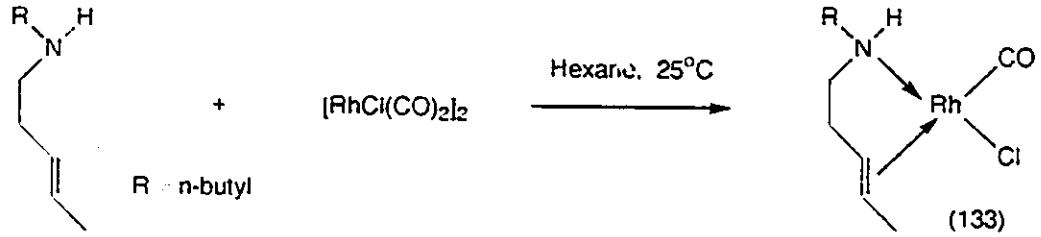
It was mentioned in the previous discussion that different results were obtained from the carbonylation of aromatic allylamines and aliphatic allylamines, i.e. the former gave pyrrolidines and the latter produced pyrrolidinones under the same reaction conditions. Recently, Jackson and coworkers reported[131] that $[Rh(OAc)_2]_2$ catalysed the reaction of o-cyano(N-allyl)aniline with CO/H_2 under relatively mild conditions (30 atm, 80°C, 20 h) to form isomeric N-aryl substituted formylpyrrolidines (130) and (131). The formation of products can be envisaged by the reaction sequence outlined in Scheme 3-17.



Scheme 3-17

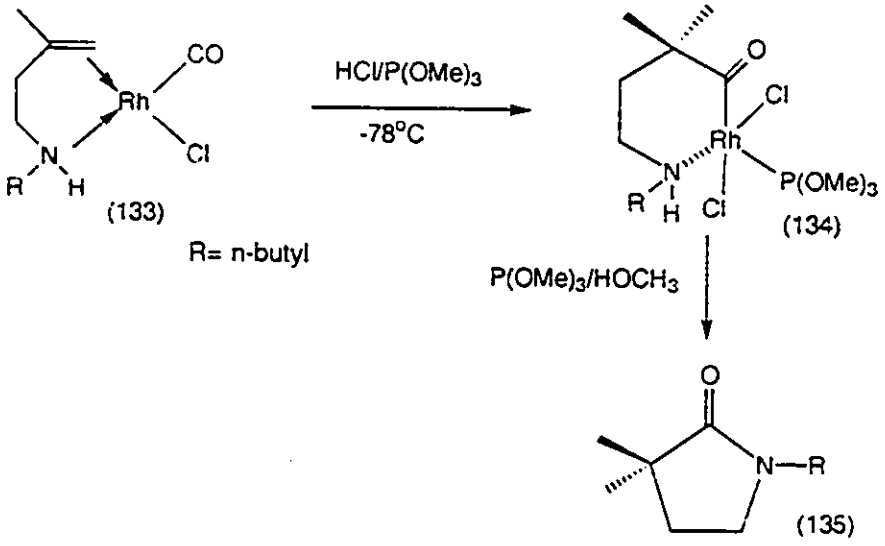
The first step of the reaction gives a mixture of the linear (128) and branched (129) aldehydes. Cyclization of the linear aldehyde produces the enamine and the hydroformylation of the enamine yields a mixture of formyl pyrrolidines (130) and (131). The regioselectivity of this reaction is low. At the same time, hydroformylation of N-allylaniline under the same conditions did not occur at all.[132]

Krafft and Wilson have shown that the reaction of aliphatic unsaturated amines with bis(μ-dichloro)tetracarbonyldirhodium gave rise to stable complexes of structural type (133). The structures of these complexes were confirmed by X-ray diffraction[62] (Scheme



Scheme 3-18

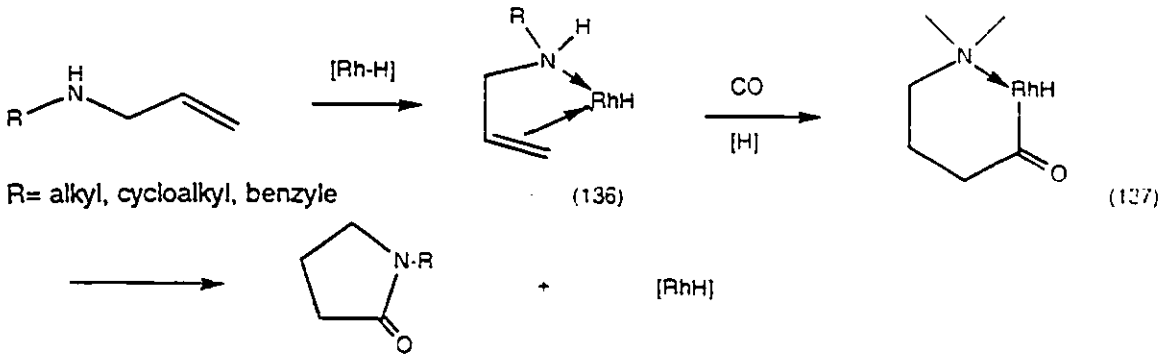
Complex (133) reacts with HCl and trimethylphosphite giving rise to the Rh(III) complex (134). An X-ray crystallographic investigation showed the complex (134) to have a 5-coordinate, square pyramidal geometry. The reaction of (134) with trimethylphosphite in ethanol produced a lactam (135) (Scheme 3-19).[133, 134]



Scheme 3-19

According to the above observations, the pathway proposed for the cyclocarbonylation of aromatic and aliphatic allyl amines catalyzed by the Rh(I) zwitterionic complex in a i-PrOH/$NaBH_4$system is outlined in Scheme 3-20 and 3-21.[135] In the case of N-alkyl-N-allylamines, rhodium hydride species (generated in situ from the catalyst and $NaBH_4$) may give (136). The subsequent reduction of the C=C bond and insertion of CO at the Rh-C bond gives the six-membered metallacycle (137) with a structure similar to that of (134) (see above). The subsequent elimination of rhodium hydride species yields the pyrrolidinone and regenerates the catalyst (Scheme 3-20, Part 1).

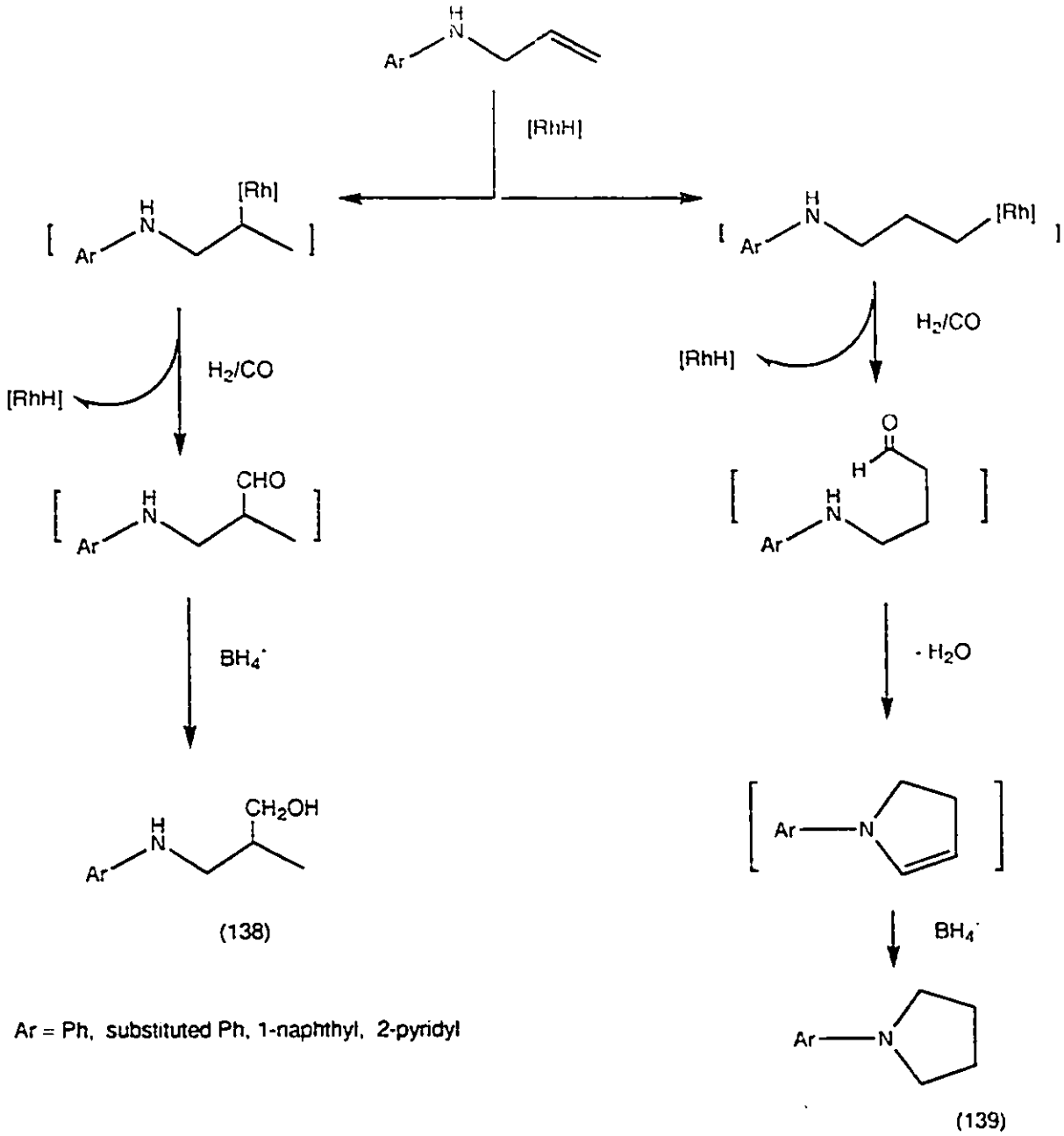
Part 1



Scheme 3-20

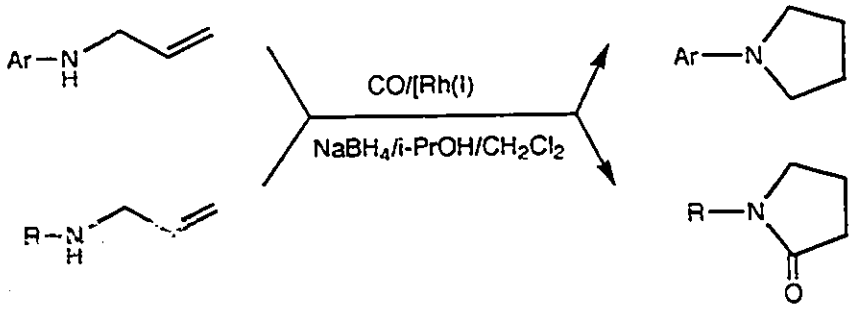
In the case of the much less basic N-allylaniline, the formation of a complex such as (136) probably does not occur. For this reason, this compound probably behaves like a simple alkene and gives a mixture of the branched and linear aldehydes. The reduction of the former with sodium borohydride yields the corresponding amino alcohol (138). The linear aldehyde, under the reaction conditions, may be dehydrated to the intermediate enamine. The reduction of the latter with $NaBH_4$ produces the corresponding pyrrolidine derivative (139) (Scheme 3-21, Part 2).

Part 2



Scheme 3-21

In conclusion, we have found that rhodium(I) catalyzed carbonylation of N-substituted N-allylamines in the presence of $NaBH_4$ and i-PrOH yields N-substituted pyrrolidines or pyrrolidinones depending on the second substituent (aromatic or aliphatic) at the nitrogen atom (Scheme 3-22).



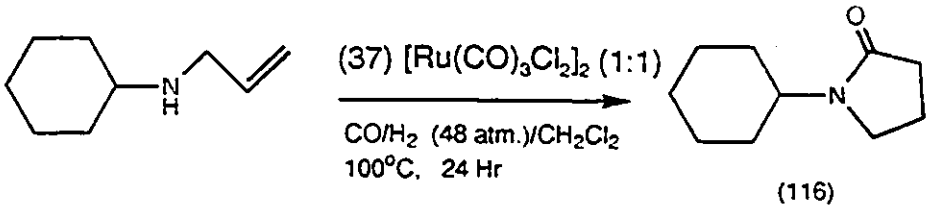
Scheme 3-22

3-5. Synthesis of Pyrrolidinones by the Hydroformylation of Aliphatic Allylamines using a Rhodium-Ruthenium Co-Catalytic System

An alternative transition metal catalyzed synthesis of pyrrolidinones from allylic amines consists of the use of synthesis gas (CO/H_2) instead of $NaBH_4$. Jegorov and coworkers reported that carbonylation of N-allyl-N-alkylamines with CO/H_2 at 65-90 atm.

($CO:H_2$=1:1) using rhodium complexes, containing or lacking phosphine ligands, as catalysts, produced N-alkyl-2-pyrrolidinones and other products in variable yields[136].

We have found that treatment of N-allyl-N-cyclohexylamine with CO/H_2 (1:1) and the zwitterionic rhodium(I) complex (37) in CH_2Cl_2 at 48 atm. and 100° C for 1 day affords the γ-lactam (116) in 15% yield (no reaction occurs when CO is used instead of CO/H_2). However, if the dimeric ruthenium complex, $[Ru(CO)_3Cl_2]_2$, was added as a co-catalyst (Scheme 3-23),



Scheme 3-23

the isolated yield of lactam (116) increases to 59%. No conversion of starting material occured when $[Ru(CO)_3Cl_2]_2$ was used as the only catalyst. While ruthenium carbonyl was as effective a co-catalyst as $[Ru(CO)_3Cl_2]_2$, other metal complexes such as $RuCl_2(PPh_3)_3$, $PdCl_2(PPh_3)_2$, $NiCl_2$(dppb) and $CuCl_2$ were substantially less active co-catalysts. The rhodium hydride complex (10) was also ineffective for this reaction (only 13% yield of (116)), the yield of (116) was low (18%) even in the presence of co-catalyst $[Ru(CO)_3Cl_2]_2$ (Table 3-6).

Table 3-6. The Effect of Co-catalyst on the Cyclocarbonylation of N-Allyl-N-cyclohexylamine

Co-Catalyst	Yield of (116), % (isolated)
$Rh^{+}(COD)BPh_4^{-}$ (37) / —	15
(37) / $Ru_3(CO)_{12}$ (1:1)	59
(37) / $[RuCl_2(CO)_3]_2$ (1:1)	59
(37) / $RuCl_2(PPh_3)_3$ (1:1)	24
(37) / $RuO_2 \cdot H_2O$ (1:1)	48
(37) / $CuCl_2$ (1:1)	0
(37) / $NiCl_2$(dppb) (1:1)	8
(37) / $PdCl_2(PPh_3)_2$ (1:1)	11
$RhH(CO)(PPh_3)_3$ / —	13
$RhH(CO)(PPh_3)_3$ $[RuCl_2(CO)_3]_2$ (1:1)	18

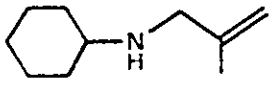
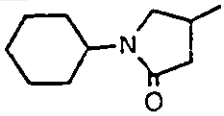
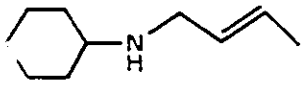
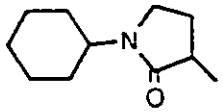
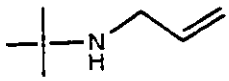
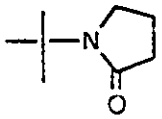
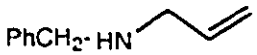
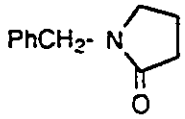
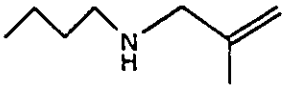
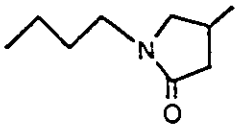
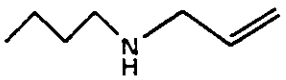
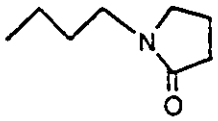
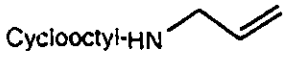
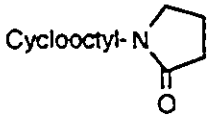
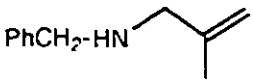
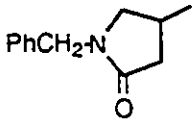
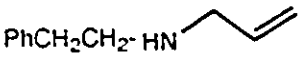
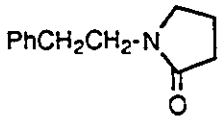
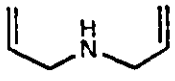
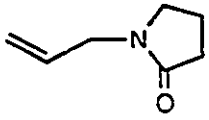
At 100°C, the zwitterionic Rh(I) complex (37)/$[Ru(CO)_3Cl_2]_2$ system exhibits the highest activity for the cyclocarbonylation of N-cyclohexyl-N-allylamine (Table 3-7).

Table 3-7. The Effect of Temperature on the Cyclocarbonylation of N-Allyl-N-cyclohexylamine with CO/H_2 Catalyzed by (37)/$[Ru(CO)_3Cl_2]_2$ (1:1)

Temperature, °C	Yield of (116), % (isolated)
140	18
100	59
70	48

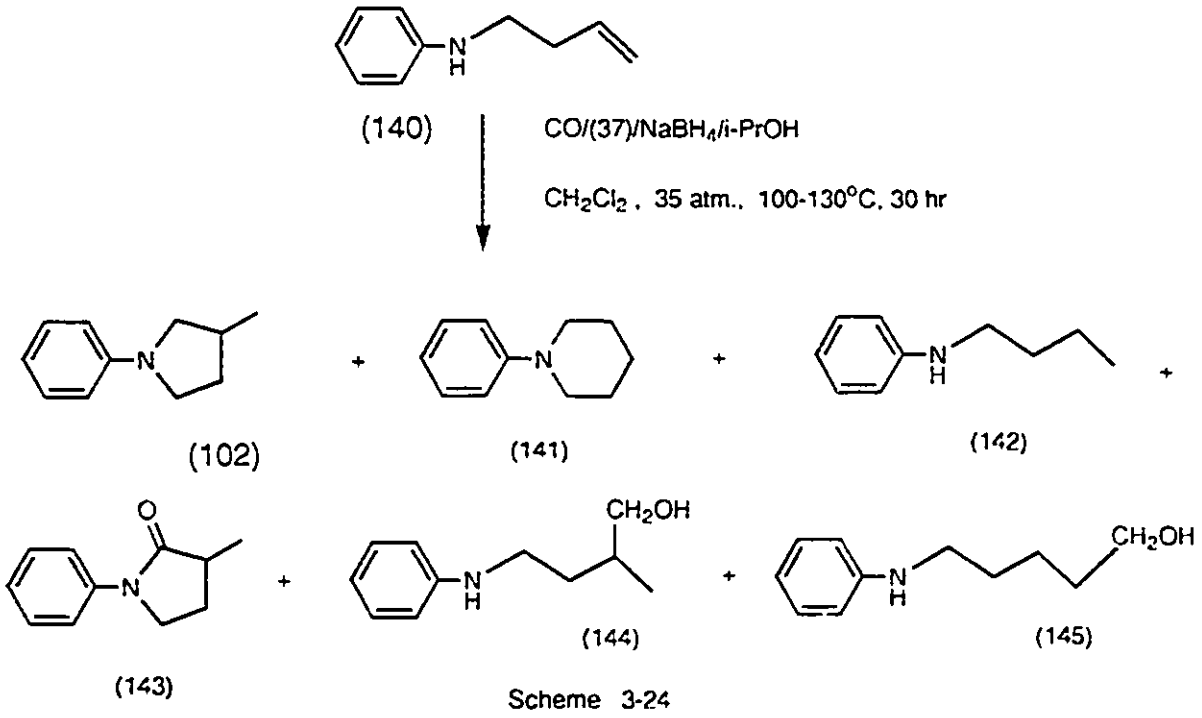
The (37)/$[Ru(CO)_3Cl_2]_2$ catalytic system was applied for the hydroformylation of a variety of aliphatic allylamines, and the results are listed in Table 3-8. N-Alkyl-, N-cycloalkyl- and N-benzyl-N-allylamines are converted to the corresponding N-substituted 2-pyrrolidinones in 7-72% yield. Comparison of these results with those realized using (37)/CO/$NaBH_4$ (Table 3-5) reveals that superior yields are obtained with the borohydride-containing system. However, it must be pointed out that hydrogen is an appreciably less expensive reductant than $NaBH_4$ and that the reaction conditions compare favourably with those reported in the literature.[136] The application of synthesis gas for the reductive carbonylation of N-allylanilines has been shown to be unsuitable since a complex mixture of different products was obtained.

Table 3-8. Cyclocarbonylation of N-Substituted N-allylamines with CO/H_2 Catalyzed by (37)/$[Ru(CO)_3Cl_2]_2$

Substrate	Product		Yield, % (isolated)
		(117)	35
		(118)	14
		(119)	7
		(120)	17
		(121)	39
		(122)	51
		(123)	72
		(124)	39
		(126)	25
		(127)	25

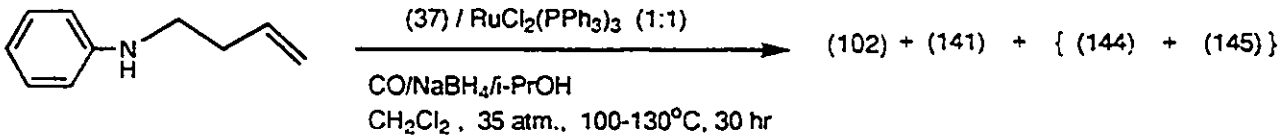
3-6. The Reductive Carbonylation of N-(3-Butenyl)aniline

In section 3-2, we showed that the reductive carbonylation of N-allyl-N-arylamines catalyzed by (37)/i-PrOH/$NaBH_4$ gave N-arylpyrrolidines. This new catalytic system can also be applied to the reductive carbonylation of N-(3-butenyl)aniline. The reaction of N-(3-butenyl)aniline (140) with (37), carbon monoxide, sodium borohydride, and 2-propanol in dichloromethane for 30 h at 100°C and 35 atm of synthesis gas afforded 1-phenyl-3-methylpyrrolidine (102) in 16% isolated yield, together with 19% of 1-phenylpiperidine (141), 8% of 1-phenyl-3-methyl-2-pyrrolidinone (143) and 34% of a mixture of amino alcohols (144 and 145) (Scheme 3-24).



Scheme 3-24

When the reaction was carried out at 130°C, 17% of N-(n-butyl)aniline (142) was isolated together with 13% of (102), 19% of (141) and 33% of a mixture of (144) and (145), but no (143). When $HRh(CO)(PPh_3)_3$ (10) was used instead of (37) at 100°C, 20% of n-butylaniline and 21% of a mixture of (102) and (141) [(102):(141)=46:54] were formed. A complex product mixture resulted when synthesis gas was used instead of $CO/NaBH_4$ for the hydroformylation of N-(3-butenyl)aniline. Since some ruthenium complexes were found to be effective co-catalysts for the synthesis of pyrrolidinones from allylic amines (Section 3-5), this bimetallic catalytic system was also applied for the carbonylation of N-(3-butenyl)aniline. Indeed, addition of a Ru(II) complex improves the selectivity of this process (Scheme 3-25, Table 3-9).



Scheme 3-25

In this reaction, 1,3-disubstituted pyrrolidine (102), 1-phenyl-piperidine (141) and a mixture of (144) and (145) were formed in 20%, 42% and 22% yields respectively. Note that this bimetallic (Rh-Ru) catalytic system does not affect the carbonylation of allylaniline, and the product distribution was almost the same as that obtained when using the rhodium (I) catalyst (37) alone. An increase of the relative amount of the ruthenium(II) complex does not affect the yield of (102) +(141) but decreases the selectivity of the process.

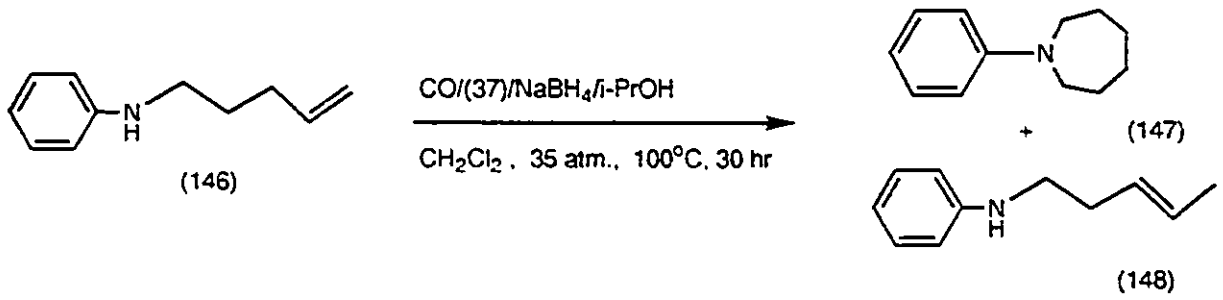
Table 3-9. Reductive Carbonylation of N-(3-Butenyl)aniline

Catalyst/Co-catalyst	Temp., °C	Products (isolated yield, %)				
		(102)	(141)	(142)	(143)	(144) + (145)
$Rh^+(COD)BPh_4^-$ (37) / —	100	16	19	—	8	34
$Rh^+(COD)BPh_4^-$ (37) / —	130	13	19	17	—	33
$RhH(CO)(PPh_3)_3$ (10) / —	100	21 (46:54)[a]		20	—	—
(37)/ $RuCl_2(PPh_3)_3$ (1:1)	100	20	42	—	—	22
(37)/ $RuCl_2(PPh_3)_3$ (1:5)	100	63 (42:58)[a]		—	—	31
(37)/ $RuCl_2(PPh_3)_3$ (1:1)	130	57 (39:61)[a]		20	—	12
(37)/$CoCl_2$ (1:1)	100	21 (33:67)[a]		10	—	—
(37)/$NiCl_2$ (dppb) (1:1)	100	74 (45:55)[a]		—	—	—
$NiCl_2$ (dppb)	100	—	—	26	—	—
(37)/$CeCl_3$ (1:1)	100	32 (42:58)[a]		—	31	5
(37)/$CeCl_3$ (1:10)	100	21 (52:48)[a]		—	35	—
(37)/$PdCl_2(PPh_3)_2$ (1:1)	100	82 (36:64)[a]		—	—	—
$PdCl_2(PPh_3)_2$	100	no reaction				

[a] Yield of (102) + (141) and their ratio.

The reductive carbonylation of N-(3-butenyl)aniline, can also be improved by other co-catalysts such as $NiCl_2(dppp)$, $PdCl_2(PPh_3)_2$, whereas $CoCl_2$ and $CeCl_3$ do not increase the yield of the cyclocarbonylation products. At the same time, the individual Ni(II) and Pd(II) complexes are ineffective.

N-(4-Pentenyl)aniline (146), under the reductive carbonylation conditions gives the seven-membered ring heterocycle, N-phenyloaxepine (147), in 20% yield and 41% of N-(3-pentenyl)aniline, the latter being the result of the isomerization of (146) (Scheme 3-26).

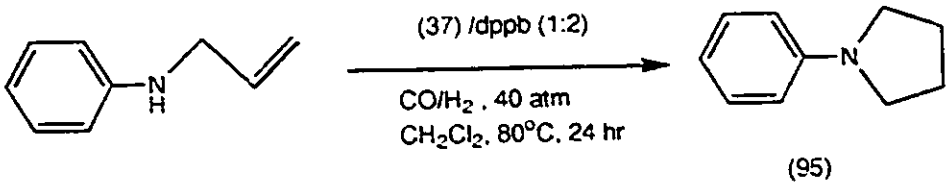


Scheme 3-26

3-7. The Regiospecific Synthesis of Pyrrolidines from N-Allylanilines.

The study of the hydroformylation of allyl acetate and α, β-unsaturated esters has shown that rhodium(I) complexes (zwitterionic, cationic and neutral) in conjunction with

dppb are highly regioselective catalysts for these reactions(see Chapter 2, Section 2-3, 2-4). Bearing this in mind, we examined the hydroformylation of N-allylaniline in the presence of (37) and dppb (Scheme 3-27).

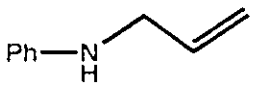
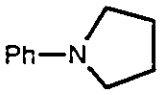
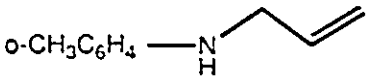
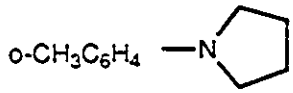
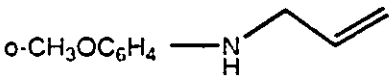
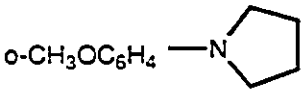
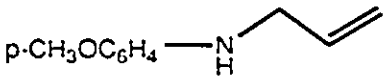
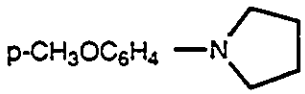
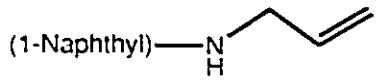
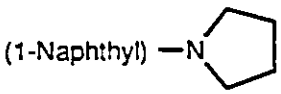
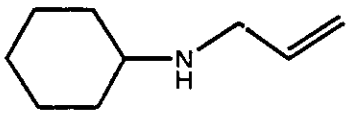


(95)

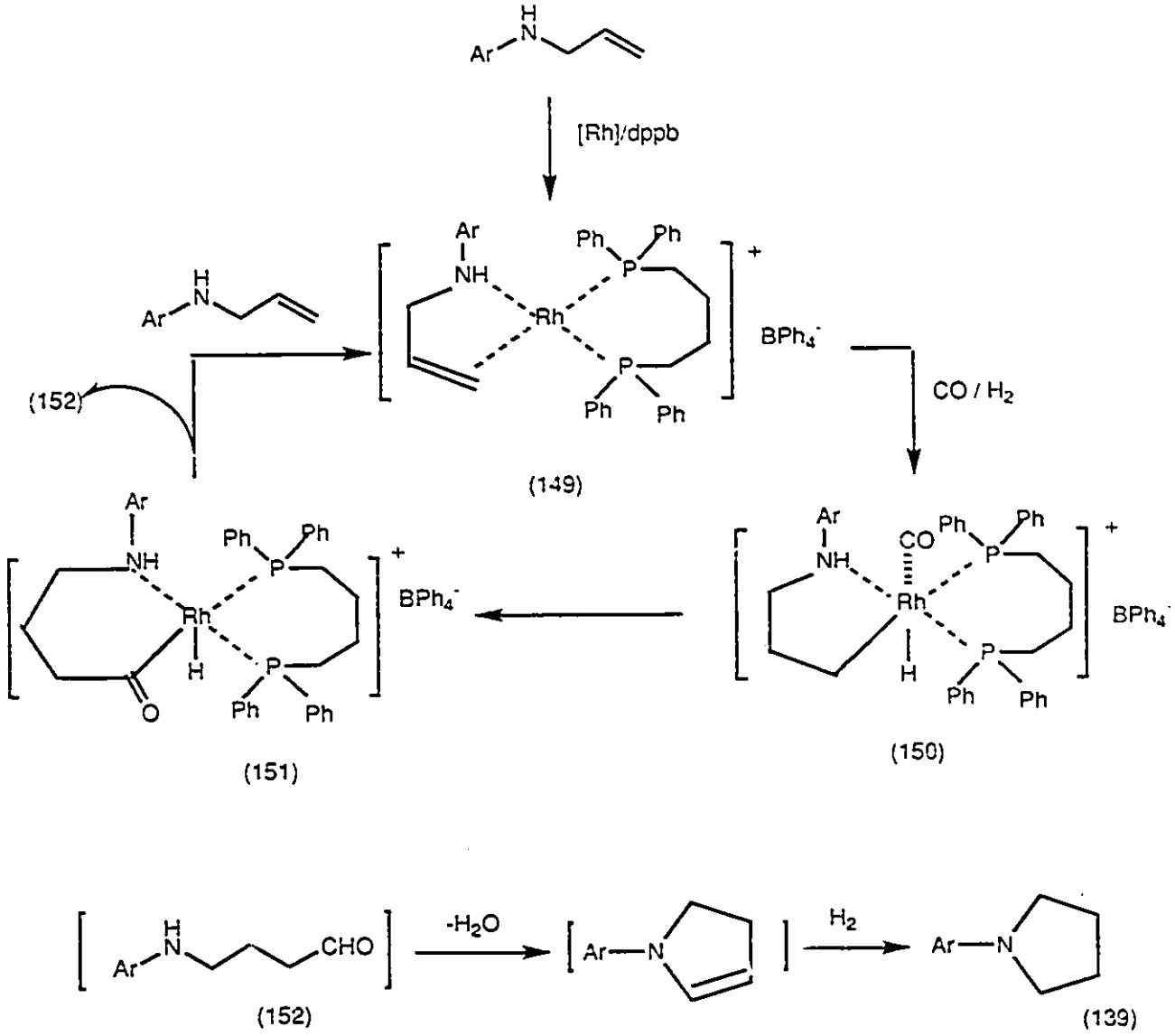
Scheme 3-27

The hydroformylation of N-allylaniline was carried out at 80°C for 24 hr. under 40 atm of CO/H_2 (1:1) using a 1:2 ratio of (37) and dppb. The reaction was specific and only 1-phenylpyrrolidine (95) was obtained in 68% isolated yield. The results of the hydroformylation of various allylanilines are listed in Table 3-10. The cationic rhodium(I) complex, $[Rh(dppb)(COD)]^+BF_4^-$ (46), is somewhat more effective and gives (95) in 75% yield. The system $[Rh(COD)Cl]_2$/dppb also readily catalyses the cyclocarbonylation of N-allylaniline to give (95) in 69% isolated yield. All three specified catalytic systems are superior to the (37)/CO/$NaBH_4$/i-PrOH system for the cyclocarbonylation of N-allylaniline. Moreover, while the latter catalytic system is ineffective for the reductive cyclocarbonylation of N-allyl-N-(o-substituted)arylamines (see Table 3-3), these compounds are readily hydroformylated with CO/H_2 to give the corresponding N-arylpyrrolidines in 55-67% isolated yield (Table 3-10). It should be emphasized that the hydroformylation of N-allylaniline catalyzed by (37) in the absence of dppb affords a complex mixture of products. Therefore, the presence of dppb is essential.

Table 3-10. Cyclocarbonylation of N-Allylanilines with CO/H_2 Catalyzed by (37)/dppb

Substrate	Catalyst	Product	Yield, % (isolated)
	(37)/dppb (1:2)	 (95)	68
	(46) / ------		75
	(47)/dppb (1:4)		69
	(47)/dppb/$NaBPh_4$ (1:4:4)		61
	(37)/dppb (1:2)		67
	(37)/dppb (1:2)		55
	(37)/dppb (1:2)	 (97)	55
	(37)/dppb (1:2)	 (103)	59
	(37)/dppb (1:2)	———	0

Taking into account the experimental findings and the crucial role of the bidentate ligand (dppb), the following possible mechanism for the cyclocarbonylation of N-allylaniline is proposed (Scheme 3-28).[79,80]

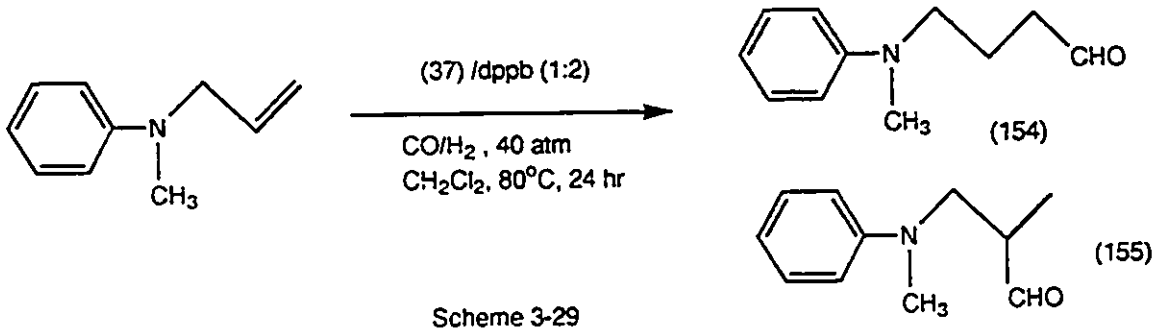


Scheme 3-28

The first step of the process probably involves coordination of the substrate to the dppb-containing rhodium complex such as [Rh(dppb)(COD)]$^+BF_4^-$ (46) (or generated in situ from neutral (47) or the zwitterionic (37) rhodium complex and dppb). Perhaps, the presence of the bidentate diphosphine ligand makes the coordination of N-allylaniline with rhodium easier. The intermediate (149) may add CO and H_2 to give the octahedral complex (150). The subsequent insertion of CO at the Rh-C bond gives (151) which upon reaction with the substrate yields the amino aldehyde, i.e. the product of the regiospecific hydroformylation of the allylic double bond. The amino aldehyde (152) can be dehydrated to the enamine intermediate and the hydrogenation of the latter affords N-arylpyrrolidine (139).

3-8. Hydroformylation of N-allyl-N-methylaniline

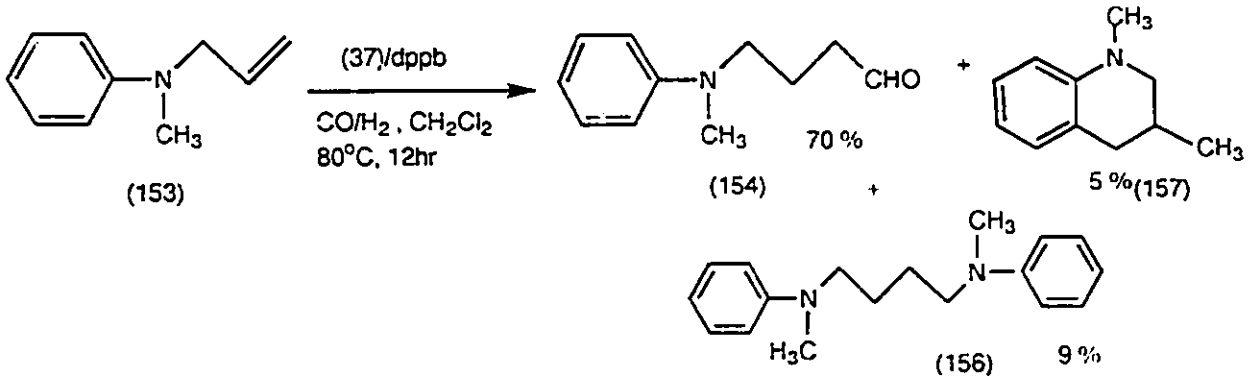
N-Allyl-N-methylaniline (153), a tertiary amine, under typical hydroformylation conditions, gives a mixture of the linear (154) and branched (155) aldehydes (Scheme 3-29).



Scheme 3-29

As anticipated, no cyclization occurs in this case. The reaction is smoothly catalyzed by (37) and produces aldehydes in high overall yield (85%). Unfortunately, the regioselectivity of the process is low [(154):(155)=67:33].

When the hydroformylation of N-allyl-N-methylaniline with CO/H_2 was carried out in the presence of (37)/dppb at 80°C for 12 hr., three compounds were formed: N-(3-formylpropyl)-N-methylaniline (154), 1,4-di(N-methyl-N-phenylamino)butane (156) and 1,3-dimethyl-1,2,3,4-tetrahydroquinoline (157) in 70, 9 and 5% yields, respectively (Scheme 3-30, Table 3-11). N-Allyl-N-methyl-p-toluidine, under the same reaction conditions, gives the corresponding linear hydroformylation product, p-MeC_6H_4-N(Me)$CH_2CH_2CH_2CHO$, in 46% yield. These results differ significantly from those obtained in the absence of dppb (Scheme 3-29). The "chelation-controlled" mechanism (see Scheme 3-28) leading to the linear aldehyde (154) may be operative here. Since the starting material is tertiary amine,



Scheme 3-30

the heterocyclization does not occur in this case. The structure of both unexpected products, the diamine (156) and the heterocycle (157) was confirmed by ^1H and ^{13}C NMR (see Fig. 3-1, 3-2, 3-3 and 3-4) and mass spectra.

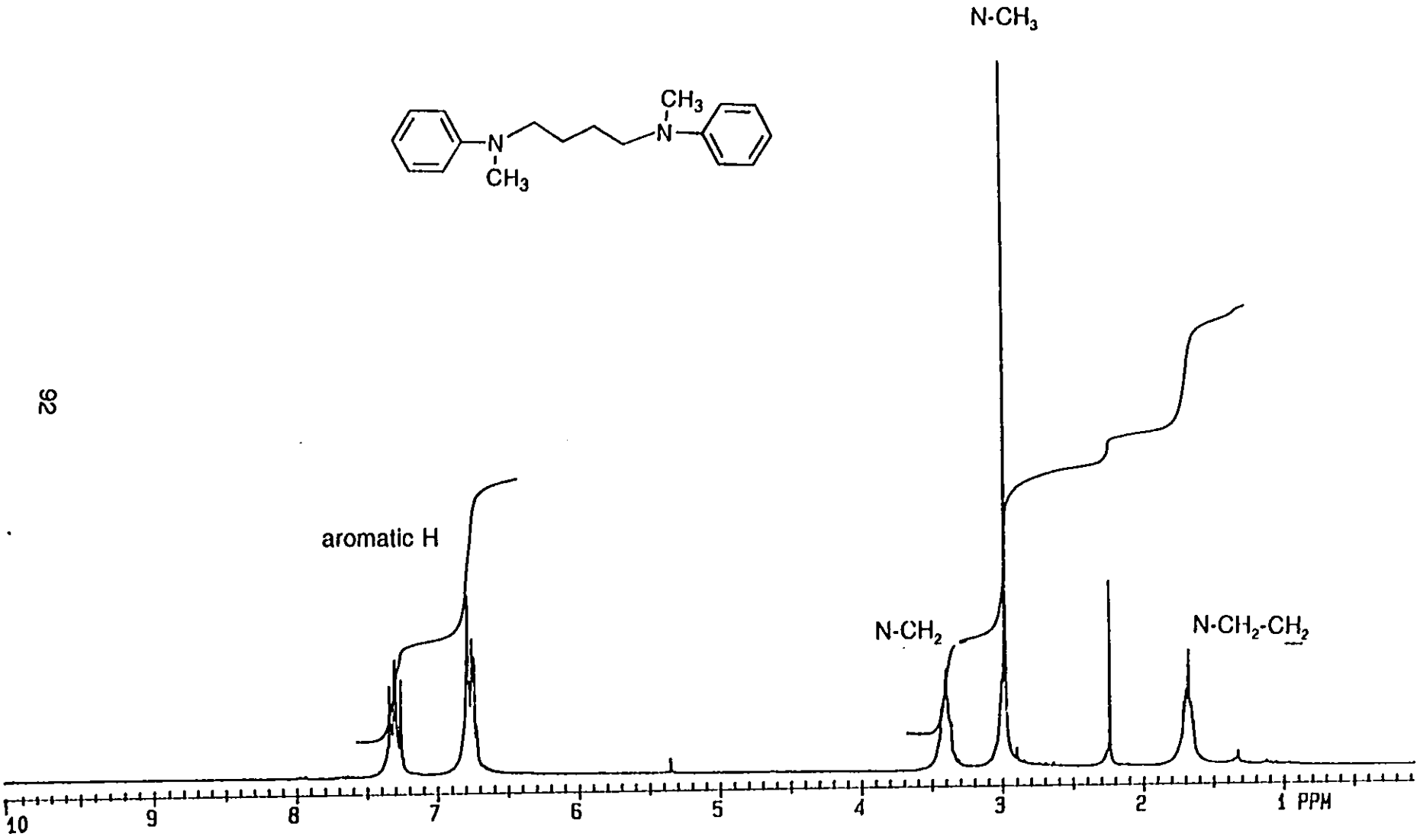
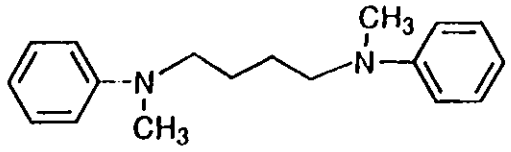


Fig. 3-1. ^{1}H NMR Spectrum of 1,4-di(N-methyl-N-phenyl)aminobutane (156) in $CDCl_3$.

SPECTRAL LINES FOR TH= 10.95
RFL= 810.9 RFP= 0

INDEX	FREQ	PPM	INTENSITY
01	7525.1	149.238	19.768
02	5497.2	109.196	116.335
03	5834.8	115.825	53.857
04	5640.3	112.157	105.731
05	3907.3	77.695	56.596
06	3875.3	77.059	57.184
07	3843.2	76.421	56.290
08	2650.2	52.699	47.269
09	1939.2	38.545	35.757
10	1729.4	34.446	48.127



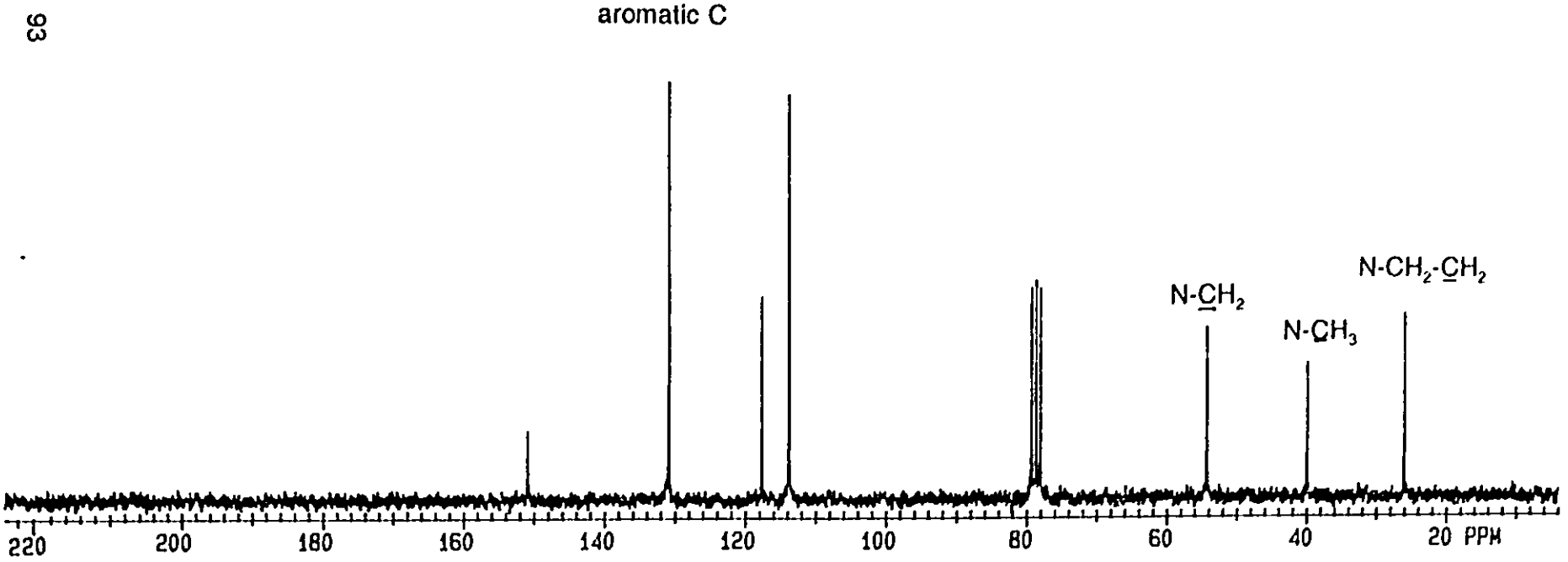


Fig. 3-2. ^{13}H NMR Spectrum of 1,4-di(N-methyl-N-phenyl)aminobutane (156) in $CDCl_3$

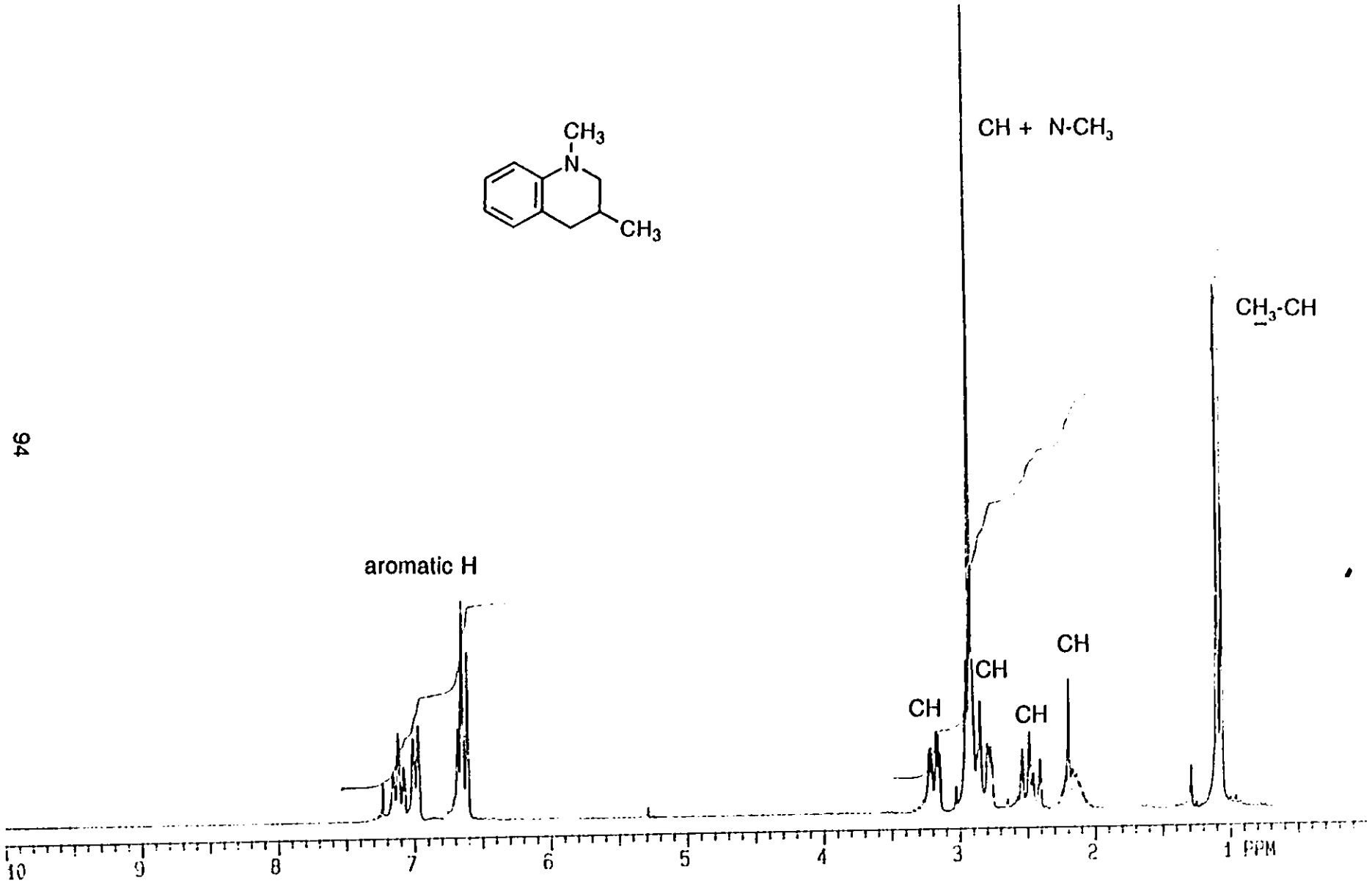


Fig. 3-3. ^1H NMR spectrum of 1,3-dimethyl-1,2,3,4-tetrahydroquinoline (157) in $CDCl_3$.

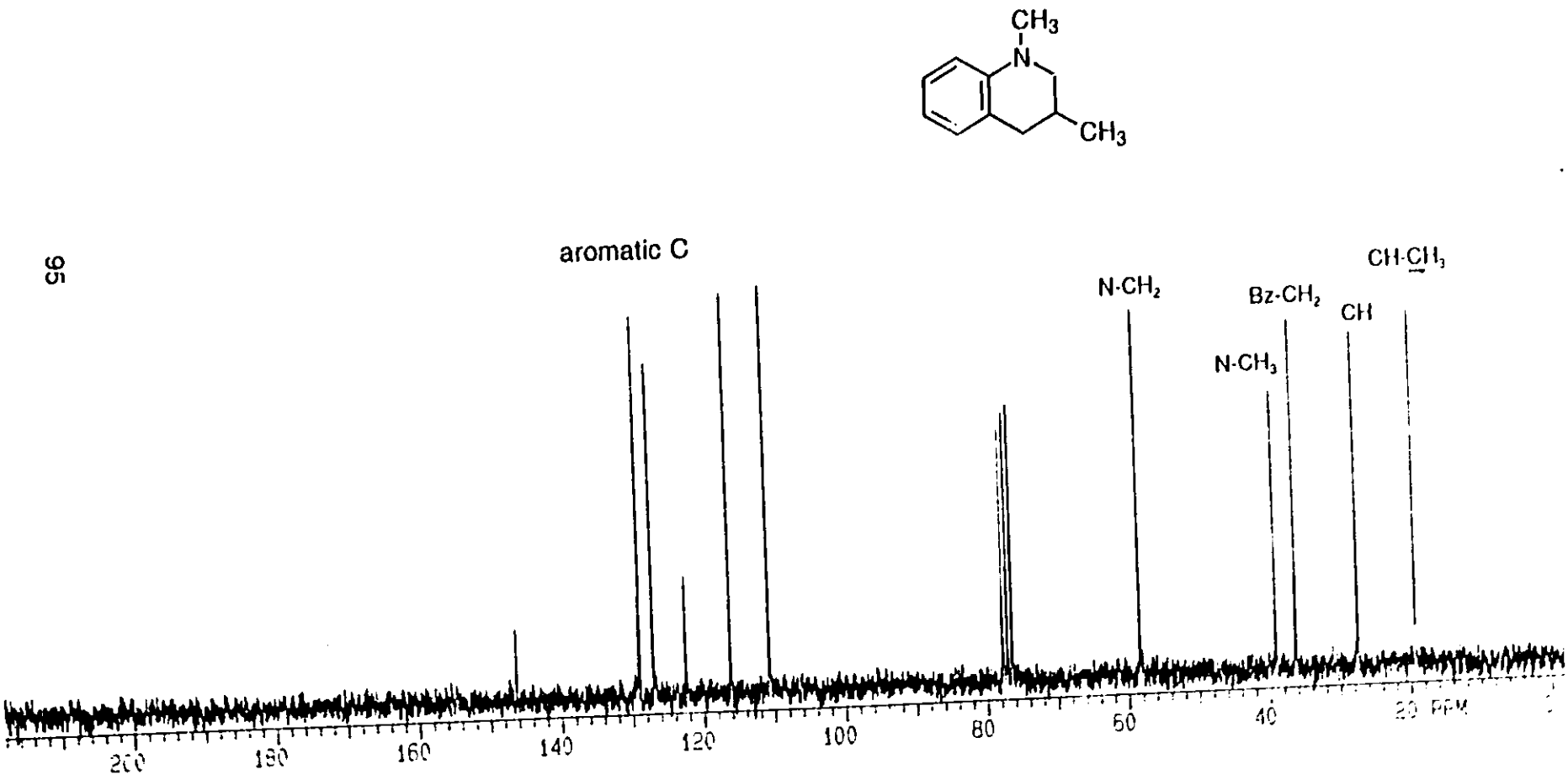
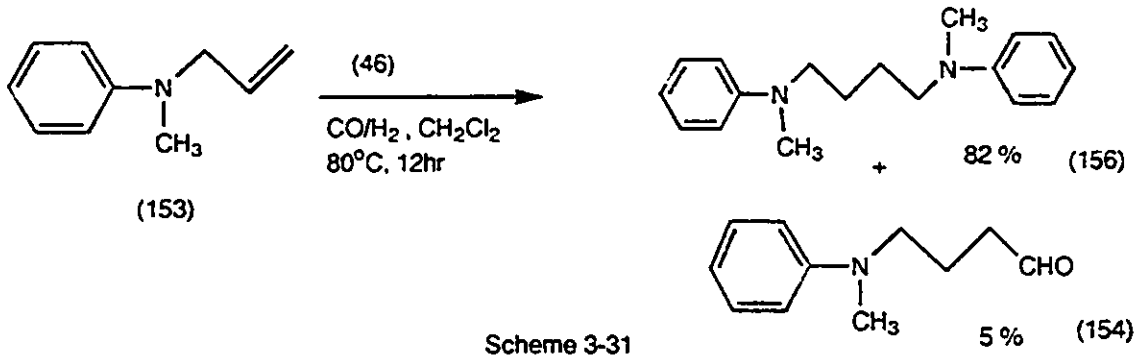


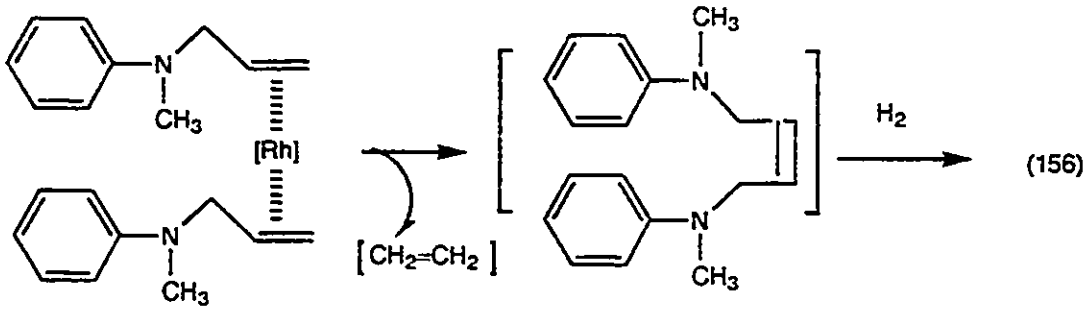
Fig. 3-4. ^{13}C NMR spectrum of 1,3-dimethyl-1,2,3,4-tetrahydroquinoline (157) in $CDCl_3$.

A very interesting result was found when the cationic complex (46) was used instead of (37)/dppb (Scheme 3-31). Under these conditions, the distribution of products was completely different from that observed in the presence of (37)/dppb. The diamine (156) was a major product isolated in 82% yield (Scheme 3-31).



Scheme 3-31

The mechanism of the formation of diamine (156) remains unclear. Presumably, this product may come from a rhodium-catalyzed metathesis type reaction[137-139] involving two molecules of N-allyl-N-methylaniline followed by the hydrogenation of the intermediate alkene (Scheme 3-32).

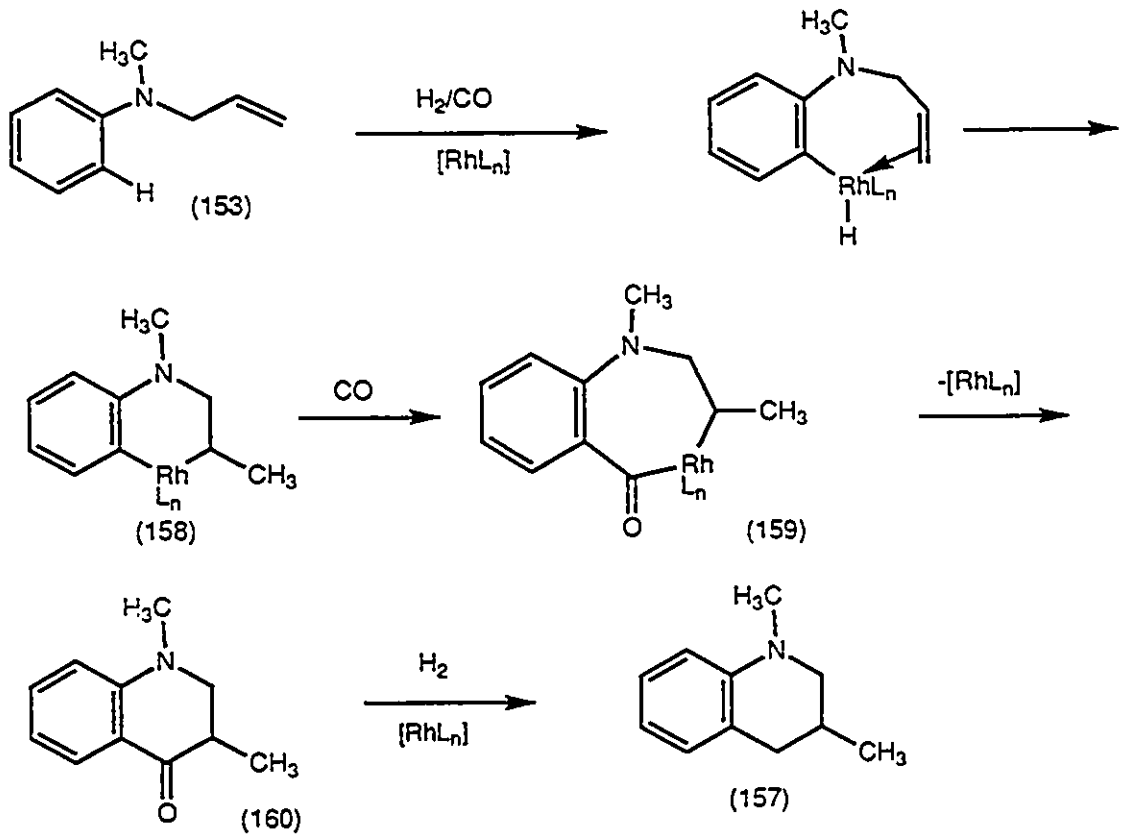


Cheme 3-32

It is well known that olefin metathesis reaction is catalyzed by group VIB metals (W, Mo, Cr).[140, 141] The suggested mechanism involves the in situ formation of a carbene complex. This carbene species adds to the olefin to form a metallacyclobutane

intermediate, which then gives a new alkene and the exchanged carbene complex. To our knowledge, rhodium catalyzed metathesis reactions are not known. Further work needs to be done (for example, the trapping of ethylene or ethane) to support the proposed reaction pathway.

Another unexpected minor product of the Rh(I)-catalyzed hydroformylation of N-allyl-N-methylaniline, viz. 1,3-dimethyl-1,2,3,4-tetrahydroquinoline (157), may arise by the pathway outlined in Scheme 3-33. The proposed mechanism includes the activation of the ortho-proton of the aromatic ring. Examples of such rhodium-catalyzed activation can be found in the literature.[142a]



Scheme 3-33

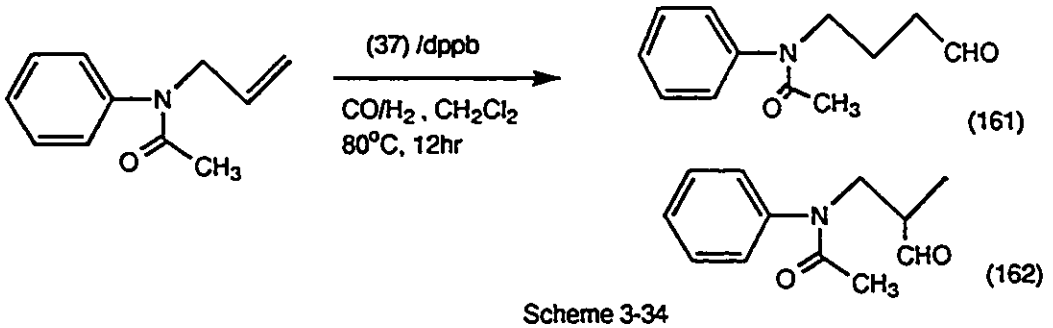
Insertion of the rhodium at the ortho C-H bond of the aniline (153) followed by the intramolecular addition of the Rh-H bond to the allylic double bond may give the metallacycle (158). The latter reacts with CO affording the corresponding seven-membered ring (159) and elimination of the rhodium species from (159) affords (160). Hydrogenation of (160) can lead to the tetrahydroquinoline derivative (157).[142b] Some other ligands and rhodium(I) catalysts have been studied in the hydroformylation of N-allyl-N-methylaniline (Table 3-11). Triphenylphosphine behaves similarly to dppb. Triethylphosphite gives 41% of the linear aldehyde (154) and 33% of the diamine (156). In contrast, triphenylphosphite yields the linear aldehyde (154) as the major product (61%) and 15% of the quinoline derivative (157) while the diamine (156) was formed in trace amounts. The neutral rhodium(I) complex (10) is almost inactive. The cationic complex $[Rh(COD)_2]^+BF_4^-$, in the absence of added dppb, unlike its dppb-containing analogue ($[Rh(COD)(dppb)]^+BF_4^-$), yields the hydrogenated product, N-methyl-N-phenyl-N-propylamine (46%) as a major product. However, the diamine (156) is also formed in appreciable amounts (31%). The addition of dppb (1 equivalent with respect to rhodium) to the above system increases the yield of (156) to 41%. At the same time , the hydrogenation is completely suppressed and the linear aldehyde (154) is obtained in 42% yield. Further, the addition of a two-fold excess of dppb leads to the highly selective formation of the aldehyde (154) in 64% yield.

Table 3-11. Hydroformylation of N-Allyl-N-methylaniline

Catalyst/ Ligand	Product (isolated yield, %)			
	linear aldehyde (154)	branched aldehyde (155)	diamine (156)	quinoline (157)
$Rh(COD)^+BPh_4^-$ (37) / dppb (1:2)	70	—	9	5
(37) / dppb (1:1)	66	—	12	—
(37) / dppb (1:0)		82(67:33)[a]	—	—
(37) / PPh_3 (1:2)	73	—	4	—
(37) / $P(OEt)_3$ (1:2)	41	—	39	—
(37)/1,10-Phenanthroline (1:2)	Starting material was recovered.			
(37) / $P(OPh)_3$ (1:2)	61	—	trace	15
(37) / P(cyclohexyl)$_3$ (1:2)	Complicated mixture			
$[Rh(COD)dppb]^+BF_4^-$ (46)	5	—	82	—
$[Rh(COD)Cl]_2$ (47) /dppb (1:4)	8	—		—
$[Rh(COD)_2]^+BF_4^-$ /dppb (1:2)	64	—	9	—
$[Rh(COD)_2]^+BF_4^-$ /dppb (1:0)	42	—	41	—
$[Rh(COD)_2]^+BF_4^-$ /dppb (1:0)	46 % of N-propyl-N-methylaniline		31	—
$RhCl_3$ /dppb (1:2)	no reaction			

[a] Yield of (154) + (155) and their ratio

It is noteworthy that the (37)/dppb system does not catalyze the hydroformylation of N-crotyl-N-methylaniline and N-(2-methylpropenyl)-N-methylaniline. N-Allyl-N-acetylaniline reacts with CO/H_2 in the presence of (37)/dppb to give a mixture of the linear (161) and branched (162) aldehydes in a 52:48 ratio in 76% yield (Scheme 3-34).

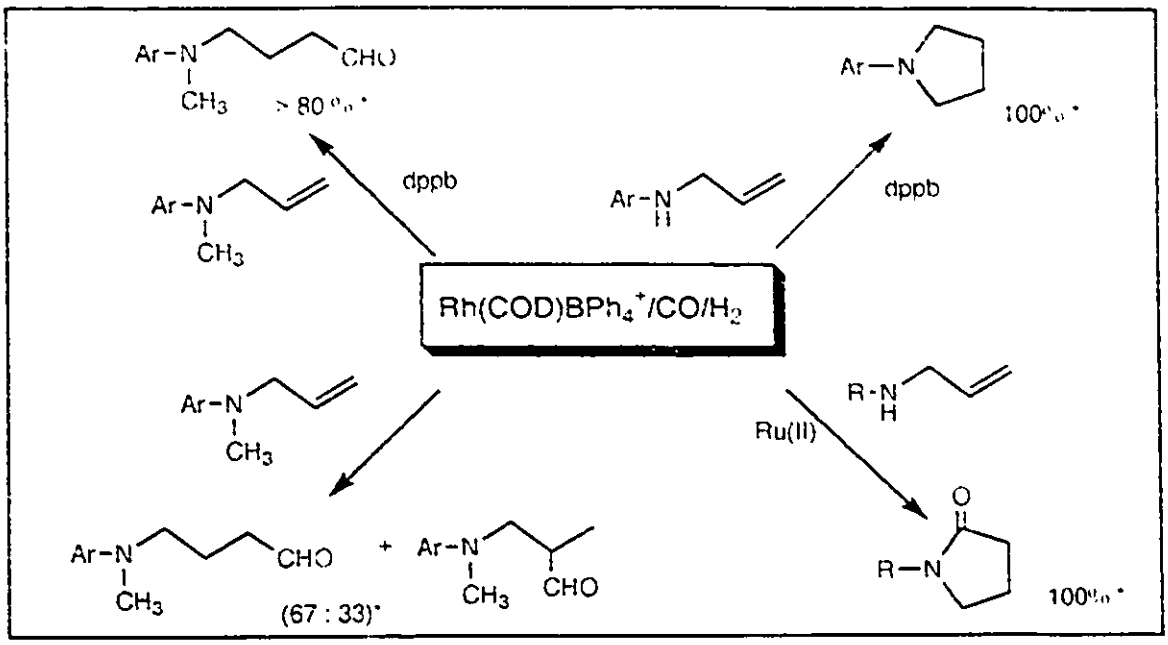


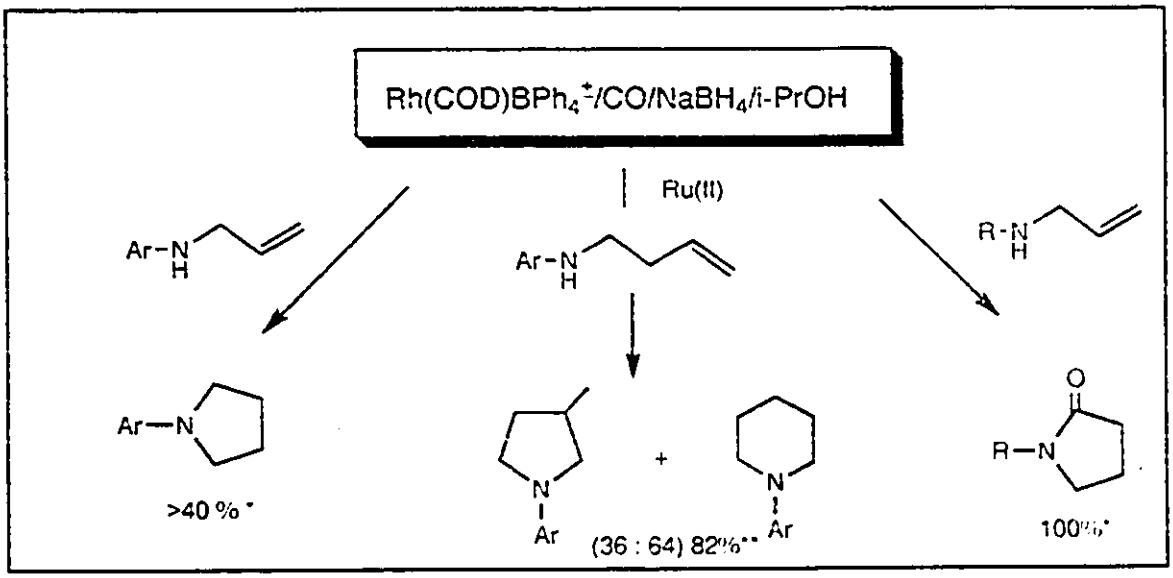
Scheme 3-34

Hydroformylation of N-allyl-N-methyl-p-toluidine affords 4-(N-methyl-N-p-tolyl)amino-butyaldehyde in 46% of isolated yield.

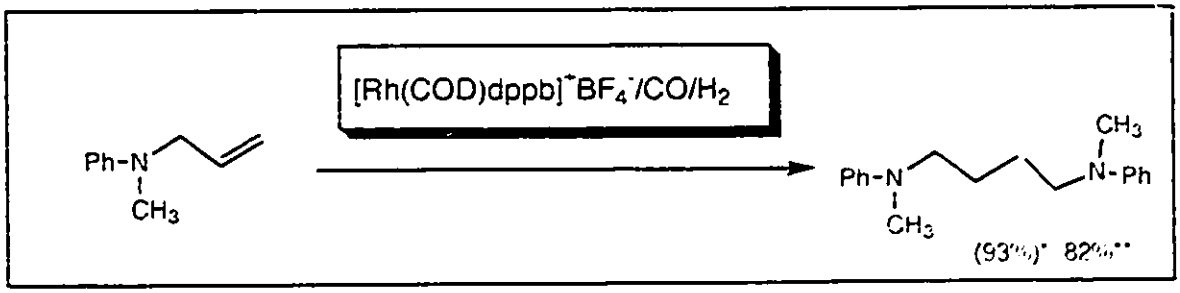
3-9. Conclusion

Several new catalytic systems based on rhodium(I), carbon monoxide, reductant ($NaBH_4$/i-PrOH, or H_2) and (in some cases) co-catalyst or added bidentate phosphine ligand have been developed to carry out various transformations of unsaturated amines. The synthetic applications of these catalytic systems are summarized in Scheme 3-35.





R = Alkyl. Ar =Aryl



* selectivity. ** yield.

Scheme 3-35

Chapter 4

Silylhydroformylation of Alkynes

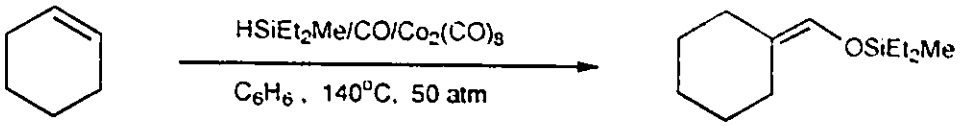
4-1. Introduction

A combination of transition-metal complexes and hydrosilanes is a very useful tool for numerous synthetic transformations of alkenes, alkynes and carbonyl compounds.[143-146] On the other hand, catalytic carbonylation is one of the useful processes for the incorporation of CO into various unsaturated substrates[147] As a consequence, the investigation of hydroformylation reactions in which hydrogen was replaced by a trialkylsilane has been initiated and the reaction of "silylformylation" has been discovered by Murai.[148-150]

4-1-1. Silylformylation of Alkenes, Oxiranes and Aldehydes

The reaction of alkenes with $HSiR_3$/CO in the presence of catalytic amounts of dicobalt octacarbonyl gives silyl enol ethers of the homologous aldehydes as the sole

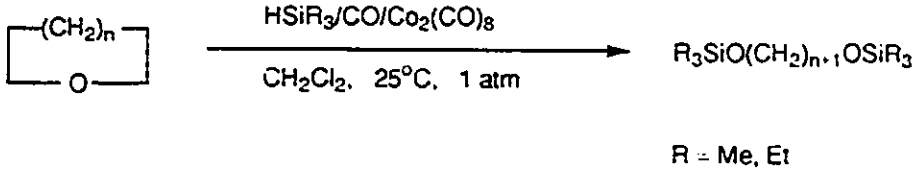
carbonylation products (Scheme 4-1).[148-150]



Scheme 4-1

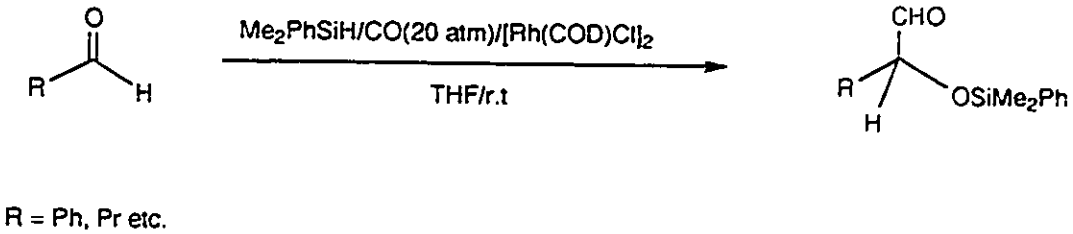
The same outcome has been reported for enamines catalyzed by $[RhCl(CO)_2]_2$ [151] and for terminal alkenes catalyzed by $Rh_4(CO)_{12}$ and $RhCl(PPh_3)_3$.[152]

The silylformylation of unsaturated cyclic ethers such as ethylene oxide, oxetane and tetrahydrofuran with $CO/HSiR_3$ gives α, ω-disiloxyalkanes, and the carbon monoxide is incorporated into the product as a part of siloxymethyl group (Scheme 4-2).[153]



Scheme 4-2

$Co_2(CO)_8$-catalyzed silylformylation of aliphatic aldehydes with Et_2MeSiH/CO in the presence of PPh_3 (100°C, benzene) affords α-siloxyaldehydes in moderate yield.[148,154] Recently, it has been shown that $[Rh(COD)Cl]_2$ is a very effective catalyst for the silylformylation of aldehydes (Scheme 4-3).[155]

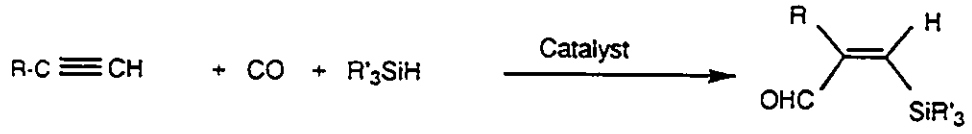


Scheme 4-3

The rhodium(I)-catalyzed silylformylation of aldehydes is very general and affords the α-silyloxyaldehydes in high yields. Also, unlike Murai's procedure, the method[155] does not require the use of excess aldehyde.

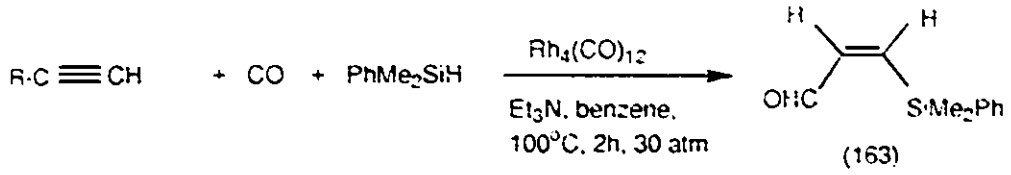
4-1-2. Silylformylation of Alkynes

Addition of the alkyne by both carbon monoxide and trialkylsilane (Scheme 4-4) constitutes an organosilane counterpart to hydroformylation.



Scheme 4-4

In contrast to silylcarbonylations described in section 4-1-1, the reactions involving alkyne, carbon monoxide and hydrosilane give carbon centered silane exclusively. The reaction has been discovered independently by Matsuda[156] and Ojima.[157] They have shown that the silylcarbonylation of alkynes is catalyzed by $Rh_4(CO)_{12}$ or Rh-Co mixed-metal carbonyl clusters.[156,157] These transformations generally occur under mild conditions with a high degree of regiocontrol (Scheme 4-5).[156]

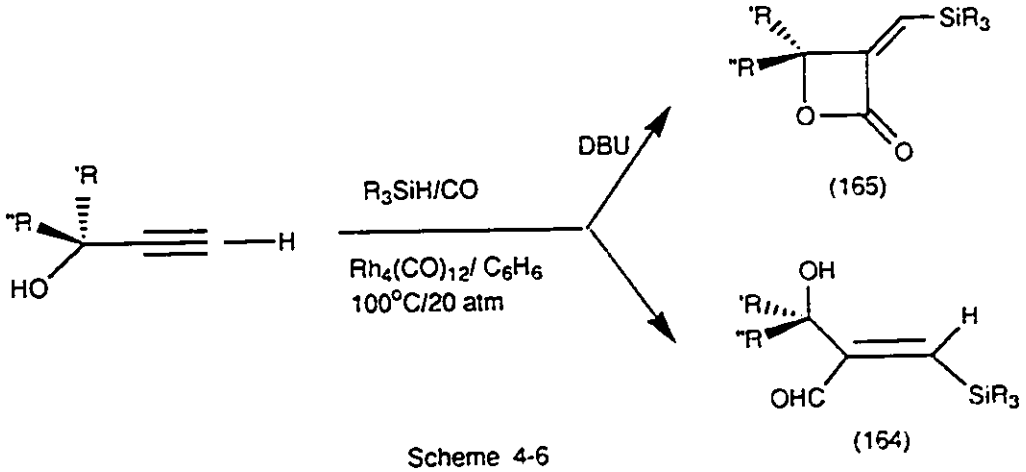


(163)

R	Z/E	Yield of (163), %
Me	80/20	99
Et	100/0	91
C_6H_{11}	100/0	96
Ph	95/5	95

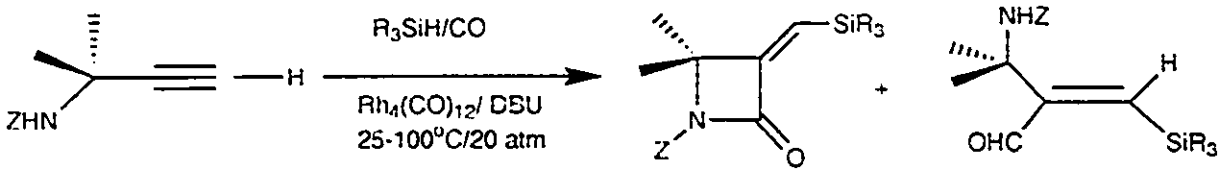
Scheme 4-5

The silylformylation of 1-alkynes to give 3-silyl-2-alkenals (163) represents a useful synthetic approch to these valuable building blocks, due to the ready accessibility of alkynes. Application of this method[156] to propargyl type alcohols also provides a general route to the corresponding 2-hydroxylalkyl-3-silylpropanals (164) in high yields.[158] At the same time, the addition of base constitutes a one-pot cycloaddition to form α-silylmethylene-β-lactones (165) (Scheme 4-6).[158]



Scheme 4-6

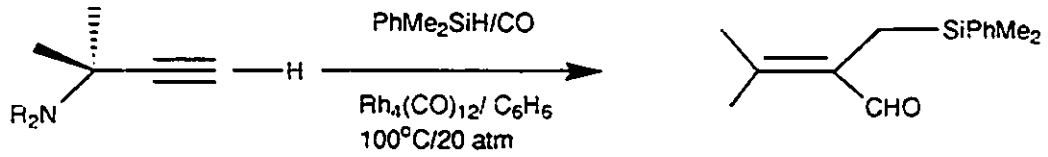
More recently, it has been shown that propargyl amine derivatives, under similar conditions, give α-silylmethylene-β-lactams (166).[159] 3-Silylpropenals (167) are usually formed as well (Scheme 4-7).



(166) (167)

Scheme 4-7

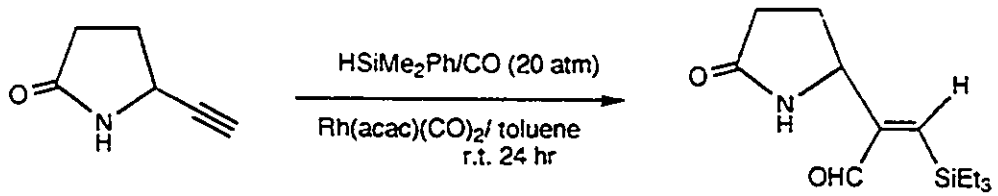
However, when two equivalents of the silane are used, propargyl amines are transformed to 2-silylmethyl-2-propenals (168) (Scheme 4-8).[160] In this case, the presence of a base is not essential (unlike synthesis of (165) or (166)).



(168)

Scheme 4-8

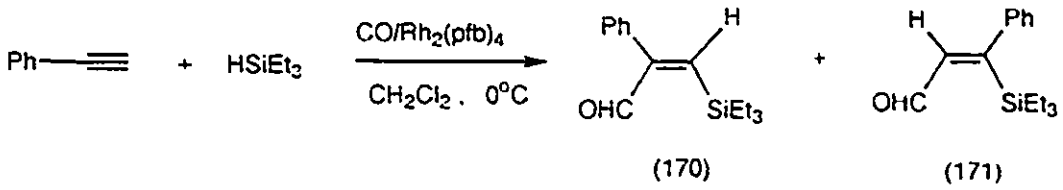
$Co_2Rh_2(CO)_{12}$ or $Rh(acac)(CO)_2$ affords (Z)-[2-(silyl-1-formyl)ethenyl]pyrrolidone (169) as the only products in high yield (Scheme 4-9).[161]



Scheme 4-9 (169)

Compound (169) was used with success in the synthesis of pyrrolizidine alkaloids, (±)-isoretronecanol and (±)-trachelanthamidine.[161]

Rhodium(II) perfluorobutyrate is an effective catalyst for silylcarbonylation of terminal alkynes in reactions performed at atmospheric pressure and at or below room temperature.[162] β-Silylacrylaldehydes are formed with exceptional control for the Z isomer. For example, the reaction of phenylacetylene with Et_3SiH/CO in the presence of $Rh_2(pfb)_4$ gives (Z) and (E)-silylacrylaldehydes (170 and 171) in a 10:1 ratio (82% isolated yield) (Scheme 4-10).



(170) (171)

Scheme 4-10

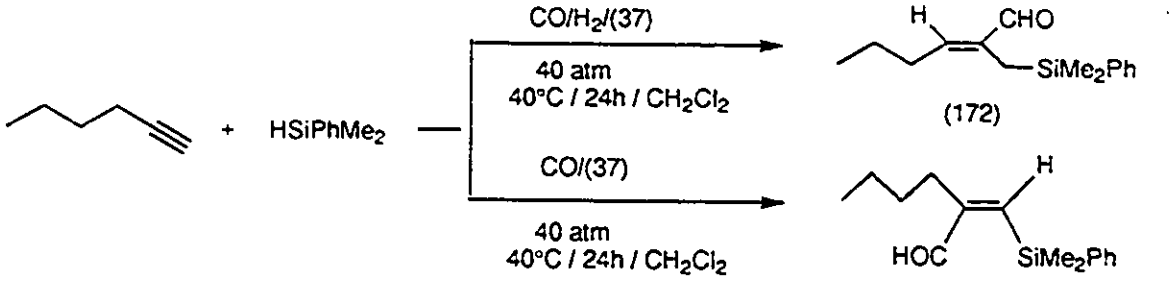
The major competing reaction, viz. hydrosilylation, is almost completely suppressed (< 1%).[162]

We have studied the reactions of a variety of terminal alkynes with hydrosilanes and synthesis gas (CO/H_2) in the presence of the rhodium(I) zwitterionic complex, $Rh^+(COD)BPh_4^-$ (37). To our knowledge, this is the first use of a $HSiR_3/CO/H_2$ mixture as reactant. For this reason, we have applied the term "silylhydroformylation" for these transformations.

4-2. Results and Discussion

4-2-1. Silylhydroformylation of Non-functionalized Terminal Alkynes

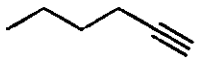
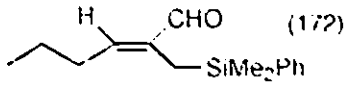
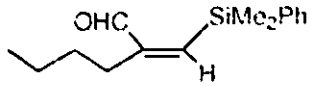
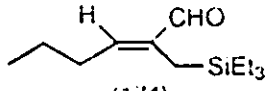
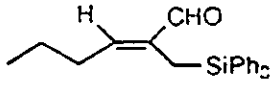
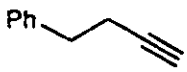
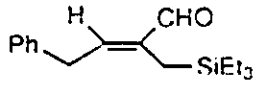
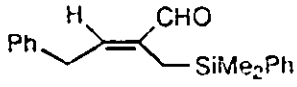
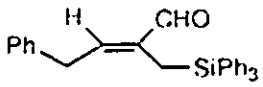
Treatment of 1-hexyne with 1.2 equiv. of dimethylphenylsilane using a catalytic amount of (37) in CH_2Cl_2 solution under CO/H_2 (1:1, 40 atm.) at 40°C for 24 h., gave (E)-1-dimethylphenylsilylmethyl-2-hexen-1-al, (172) in 73% isolated yield. In the absence of hydrogen, 1-hexyne reacts with $HSiMe_2Ph/CO/(37)$ to give 1-(dimethylphenylsilyl)-1-hexen-2-al (173) in 89% yield (Scheme 4-11). The rhodium(I) cationic complex (46) and rhodium carbonyl, $Rh_6(CO)_{16}$, also smoothly catalyze the reaction of 1-hexyne with $HSiMe_2Ph/CO/H_2$, but unlike the zwitterionic complex (37), these catalysts give rise to (173) which is formed stereospecifically and in high yield.



Scheme 4-11

Therefore, catalyst (37) in the system alkyne/$HSiMe_2Ph$/CO behaves similarly to other rhodium catalysts (see Section 4-1-2) while the use of (37) in an alkyne/$HSiR_3$/ CO/H_2 system leads to the opposite stereochemistry. The results of the silylhydroformylation of 1-hexyne and 4-phenyl-1-butyne with different hydrosilanes (R_3SiH) using complex (37) and some other Rh(I) complexes are listed in Table 4-1.

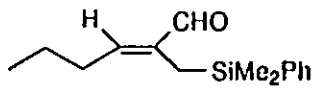
Table 4-1 Silylhydroformylation of Terminal Alkynes Using Rh(I) Complexes

Substrate	Silane	Catalyst[a]	Product	Yield, % (isolated)
	$HSiPhMe_2$	(37)	 (172)	73
	$HSiPhMe_2$	(37)[b]	 (173)	89
	$HSiPhMe_2$	(46)	(173)	87
	$HSiPhMe_2$	$Rh_6(CO)_{16}$	(173)	92
	$HSiEt_3$	(37)	 (174)	78
	$HSiPh_3$	(37)	 (175)	62
	$HSiEt_3$	(37)	 (176)	71
	$HSiPhMe_2$	(37)	 (177)	64
	$HSiPh_3$	(37)	 (178)	54

[a] (37) = $Rh^+(COD)BPh_4^-$, (46) = $[Rh(dppb)(COD)]^+BF_4^-$. [b] Reaction in the absence of hydrogen.

Triethyl- and triphenylsilane react with 1-hexyne under CO/H_2 in the presence of (37) affording the corresponding 1-silylhexen-2-als (174 and 175) in fair yield. It should be noted that the neutral Rh(I) complex, $[Rh(COD)Cl]_2$, unlike its zwitterionic and cationic counterparts, gives a complicated mixture of unidentified products. 4-Phenyl-1-butyne, under the silylhydroformylation conditions, behaves like 1-hexyne and upon Rh(I)-catalyzed reaction with triethyl-, dimethylphenyl- and triphenylsilane, yields (E)-4-phenyl-2-silylmethyl-2-buten-1-als (176-178) in satisfactory yield (Table 4-1). Note that triethoxysilane is an unsuitable reactant for the silylhydroformylation since it affords a complicated mixture of products.

Silylalkenals (172), (174-178) are new compounds. Their structure and purity was established by ^1H and ^{13}C NMR spectra, mass spectra and elemental analyses. A representative ^1H NMR and ^{13}C NMR spectrum of a silylalkenal (172) is shown in Figures 4-1. and 4-2. The trans-configuration was established by ^1H NOE experiments. For example, in the case of (172), the irradiation of H_a leads to a 20% enhancement of the aldehyde proton and no enhancement of H_b is observed (Fig. 4-3-a). Similarly, irradiation of the aldehyde proton induces a 22% enhancement of the H_a proton (Fig. 4-3-b). All the spectral and analytical data for silylalkenals (172)-(178) are given in the Experimental Section.



(172)

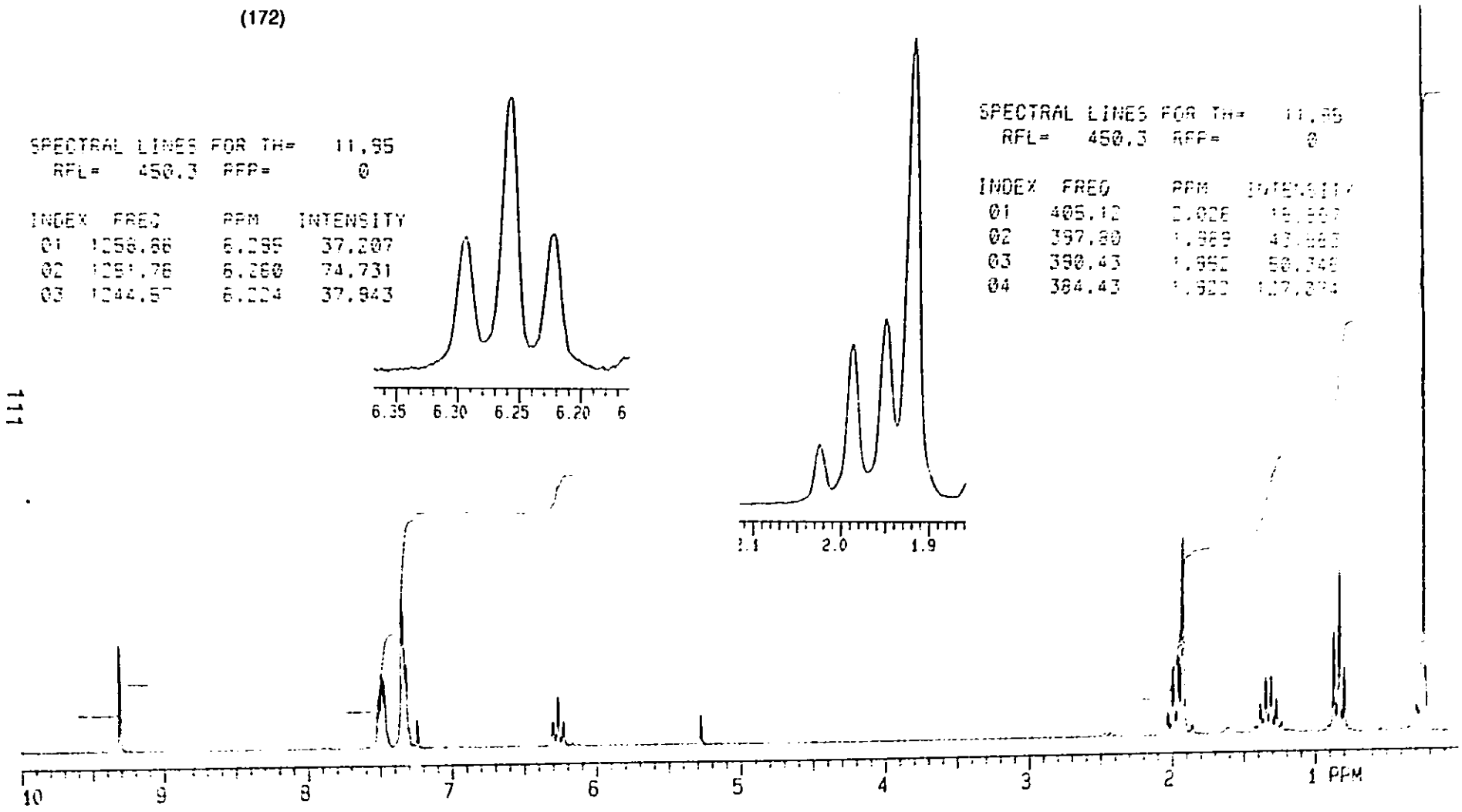
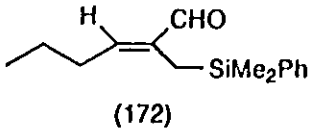


Fig. 4-1. ^1H NMR Spectrum of (E)-2-(Dimethylphenylsilyl)methyl-2-hexen-1-al (172) in $CDCl_3$



(172)

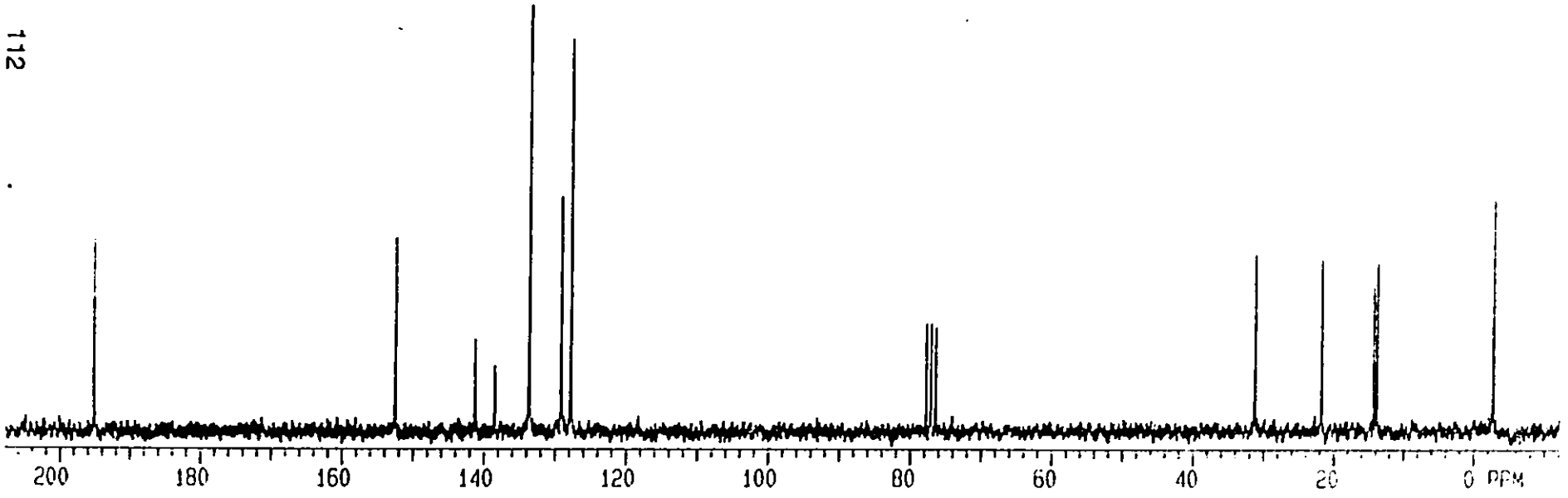
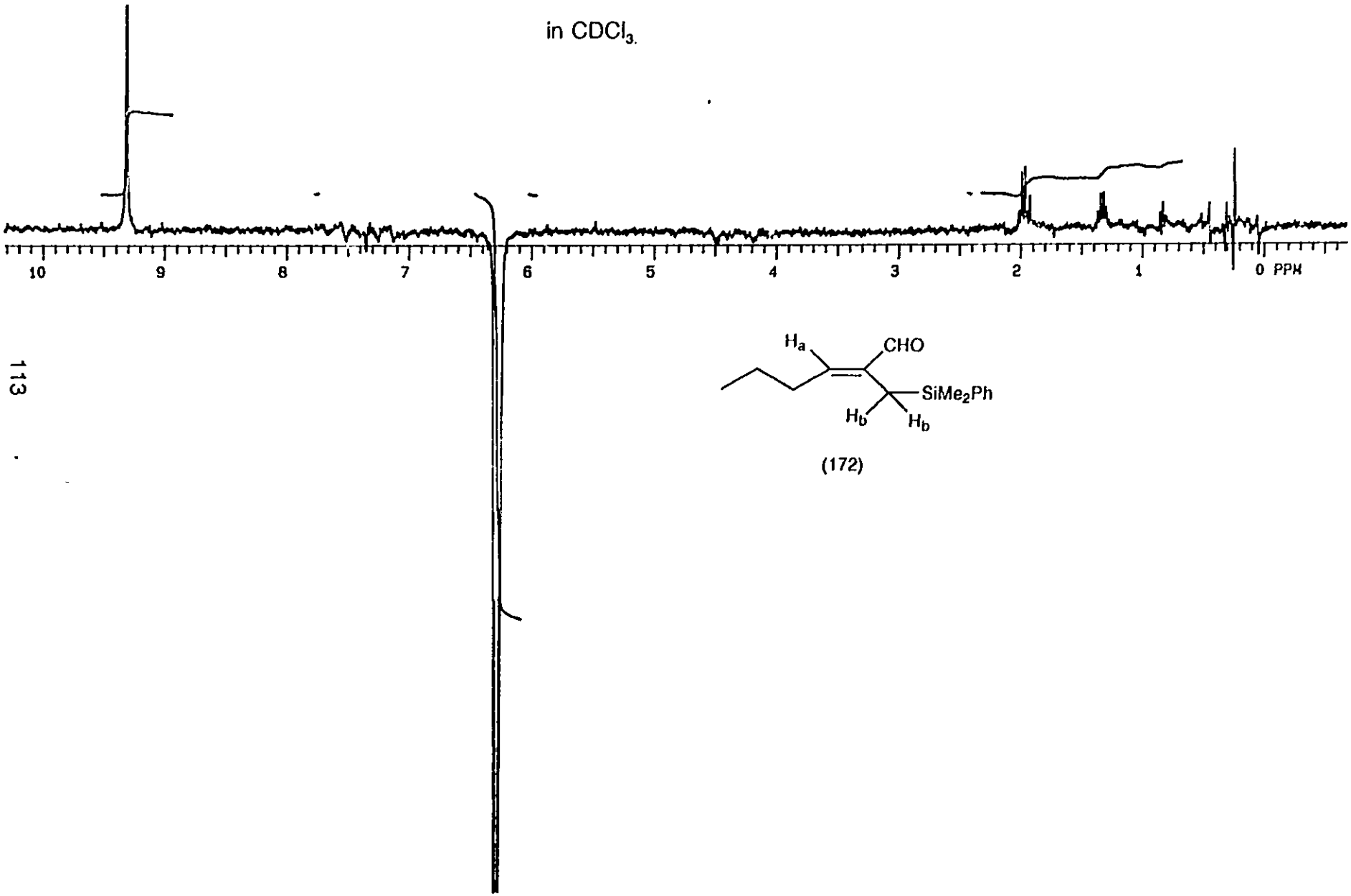


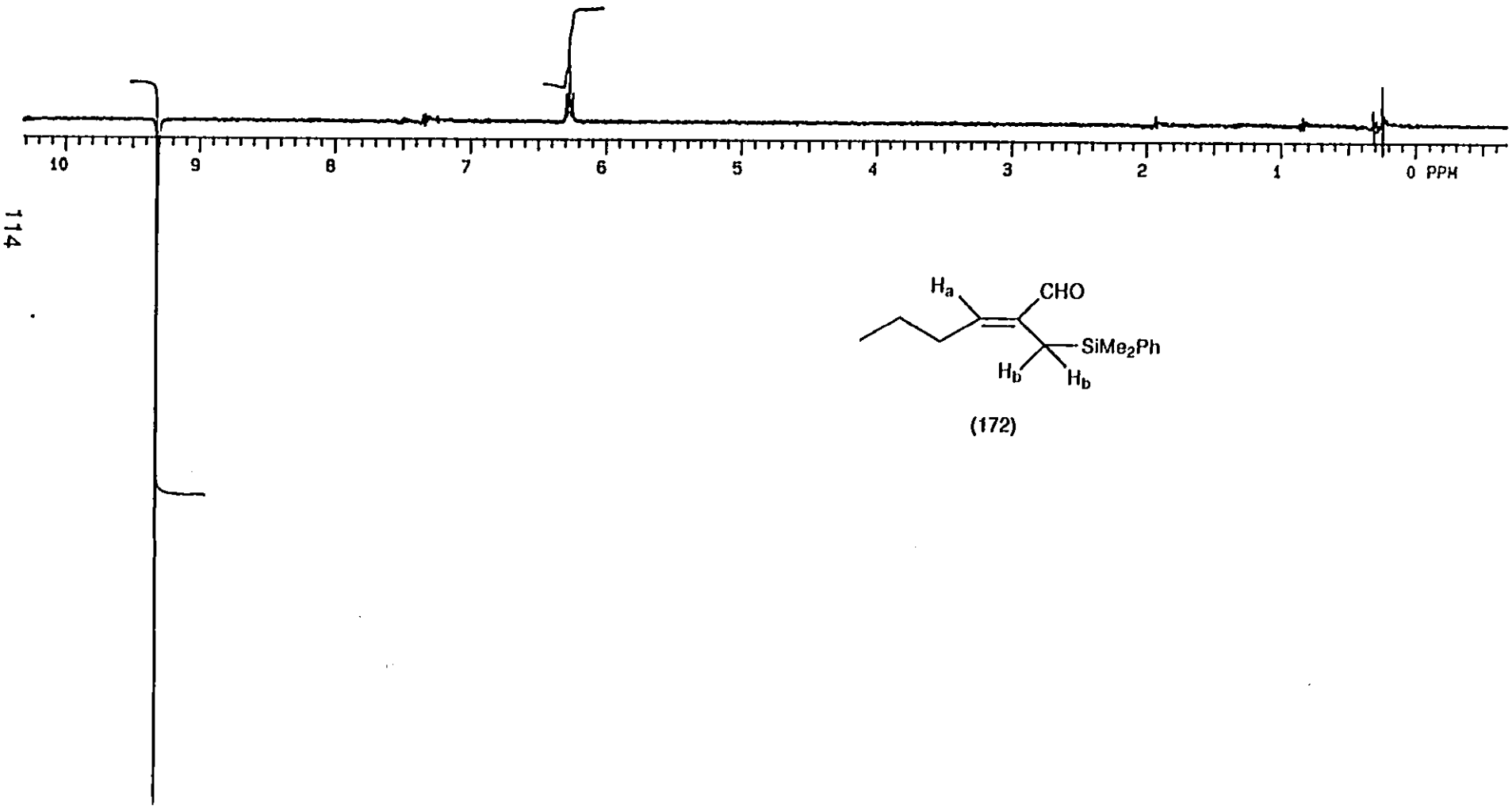
Fig. 4-2. ^{13}C NMR Spectrum of (E)-2-(Dimethylphenylsilyl)methyl-2-hexen-1-al (172) in $CDCl_3$.

Fig. 4-3-a. NOE Experiment for (E)-2-(Dimethylphenylsilyl)methyl-2-hexen-1-al (172) in $CDCl_3$.



(172)

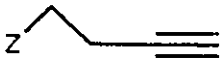
Fig. 4-3-b. NOE Experiment for (E)-2-(Dimethylphenylsilyl)methyl-2-hexen-1-al (172) in $CDCl_3$.



(172)

4-2-2. Silylhydroformylation of Functionally Substituted Terminal Alkynes

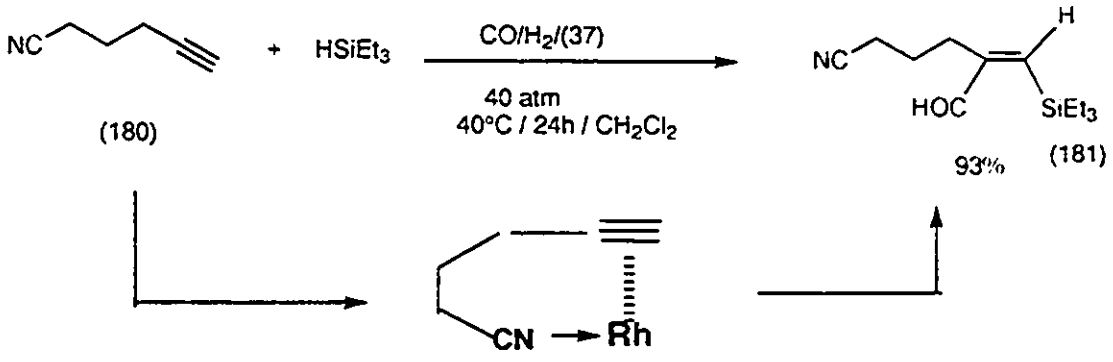
The results obtained in the silylhydroformylation of 1-hexyne and 4-phenyl-1-butyne indicated that similar transformations involving functionally substituted terminal alkynes could give rise to synthetically valuable multifunctionalized derivatives. For this reason, we have studied reactions of acetylenes of general formula (179) with $HSiR_3/CO/H_2$ using (37) as the catalyst.



(179)

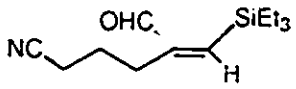
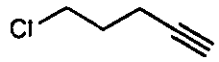
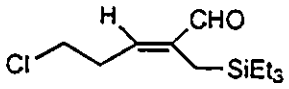
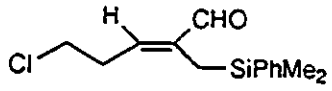
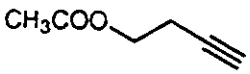
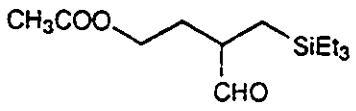
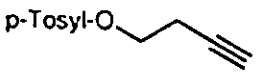
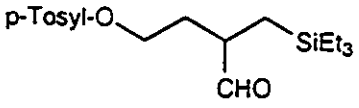
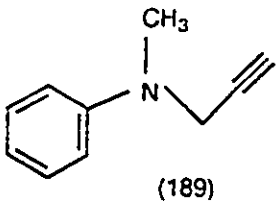
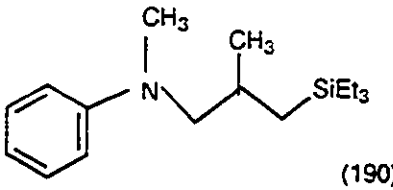
Z = CH_2CN, CH_2Cl, $OCOCH_3$, $OSO_2C_6H_4Me$-p, OH

The results on silylhydroformylation of alkynes (179) are summarized in Table 4-2. 5-Cyano-1-pentyne (180), structurally related to 1-hexyne, reacts with $HSiEt_3$ /CO/H_2 /(37) to give (Z)-5-cyano-1-triethylsilyl-1-penten-2-al (181) in 93% isolated yield (Scheme 4-12). Thus, the presence of the cyano group leads to a significant change in the reaction pathway.

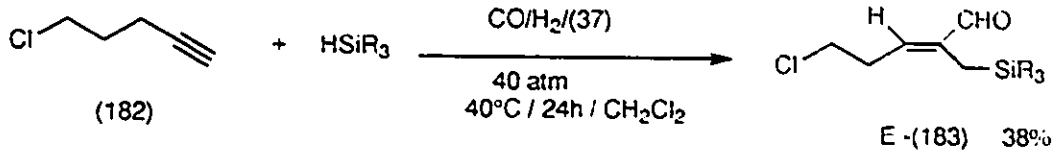


Scheme 4-12

Table 4-2. Silylhydroformylation of Functionally Substituted Terminal Alkynes Catalyzed by (37)

Substrate	Silane	Product	Yield, % (isolated)
 (180)	$HSiEt_3$	 (181)	93
 (182)	$HSiEt_3$	 (183)	38
 (182)	$HSiPhMe_2$	 (184)	62
 (185)	$HSiEt_3$	 (186)	61%
 (187)	$HSiEt_3$	 (188)	54
 (189)	$HSiEt_3$	 (190)	83

It is conceivable that the cyano group interacts with the rhodium catalyst and determines the reaction outcome (Scheme 4-12). In the case of 5-chloro-1-pentyne (182), this intramolecular coordination obviously does not take place and the alkyne (182) behaves similarly to 1-hexyne and affords (E)-5-chloro-1-triethylsilyl-2-penten-2-al (183) in fair yield under the silylhydroformylation conditions (Scheme 4-13, Table 4-2)



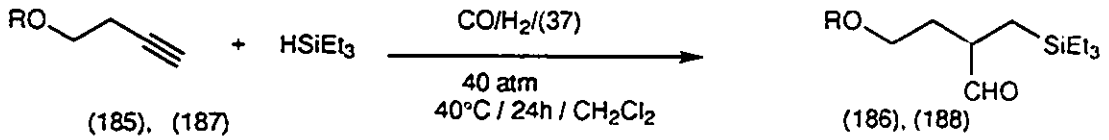
(182)

E -(183) 38%

$HSiR_3$ = $HSiEt_3$ or $HSiMe_2Ph$

Scheme 4-13

Use of 3-butyl-1-ol in reaction with $HSiR_3/CO/H_2$ gives a complicated mixture of unidentified products. When the hydroxy group is protected by an acetyl or p-tosyl group [alkynes (185) and (187)], the reaction yields saturated silylaldehydes, (186) and (188), probably via intermediate silylalkenals of type (181) (Scheme 4-14).



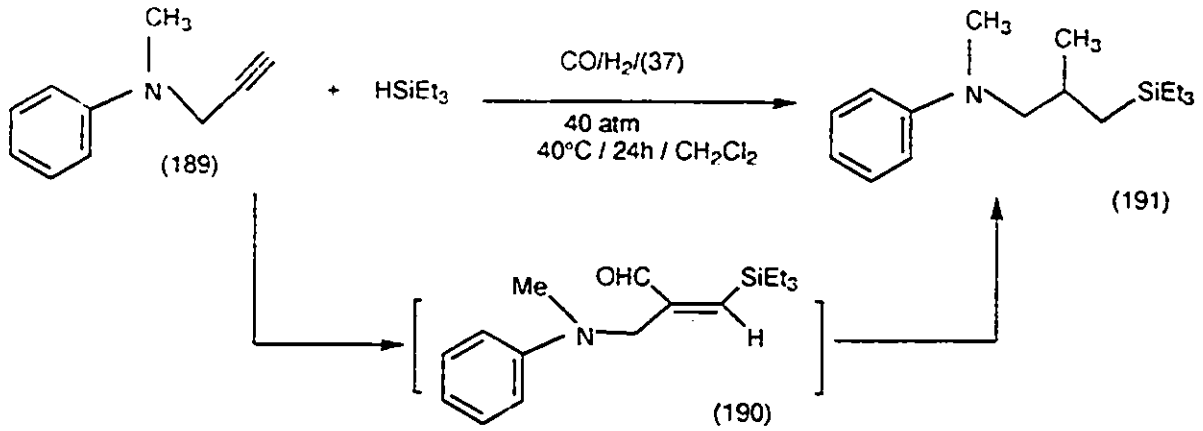
(185), (187)

(186), (188)

R = CH_3CO- , p-Tosyl-

Scheme 4-14

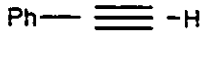
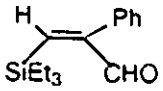
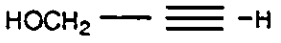
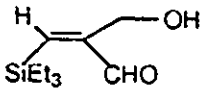
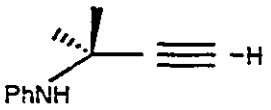
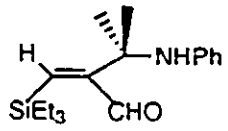
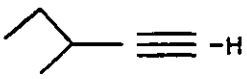
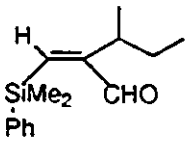
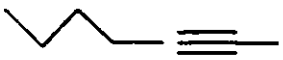
N-Methyl-N-propargylaniline (189), under the same conditions, affords the saturated product (191) in 82% isolated yield (Table 4-2). Presumably, the reaction also occurs via an intermediate silylalkenal (190), followed by the reduction of both the C=C and C=O bonds to give (191) (Scheme 4-15).



Scheme 4-15

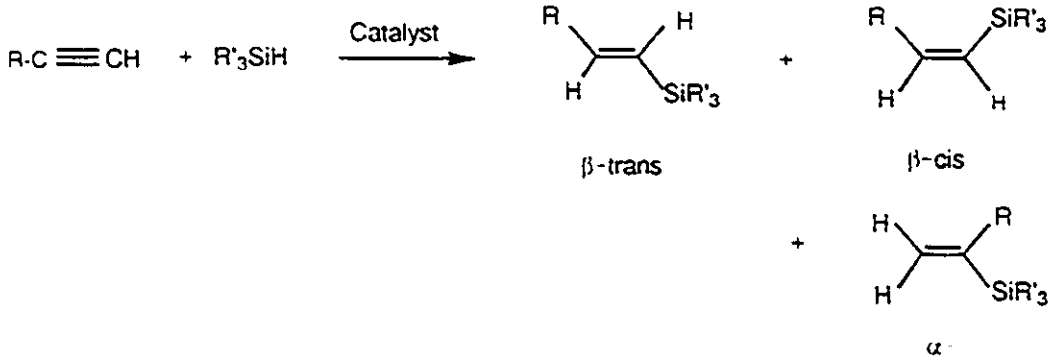
To estimate the scope and limitations of the silylhydroformylation catalyzed by the Rh(I) zwitterionic complex, some other alkynes have also been studied (see Table 4-3). Phenylacetylene (191), propargyl alcohol (192), N-phenyl-3,3-dimethylpropargylamine (193) and 3-methyl-1-pentyne (194) behave similarly, with (Z)-silylalkenals [(170), (197), (198) and (199)] formed regiospecifically and in high yield (Table 4-3). Therefore, the presence of hydrogen does not change the reaction pathway in these cases. The outcome is the same as rhodium carbonyl[156-161] and Rh(II) perflurobutyrate[162] catalyzed silylformylations of alkynes with $HSiR_3$/CO (see Section 4-1-2). It should be noted that an internal alkyne, viz. 2-heptyne (195), does not undergo any transformations under identical conditions.

Table 4-3. Silylhydroformylation of Some Alkynes with $HSiR_3/CO/H_2$ Catalyzed by (37)

Substrate	Silane	Product	Yield, % (isolated)
	$HSiEt_3$		87
 (192)	$HSiEt_3$	 (197)	93
 (193)	$HSiEt_3$	 (198)	91
 (194)	$HSiMe_2Ph$	 (199)	94
 (195)	$HSiMe_2Ph$	no reaction	—

4-2-3. Mechanistic Studies

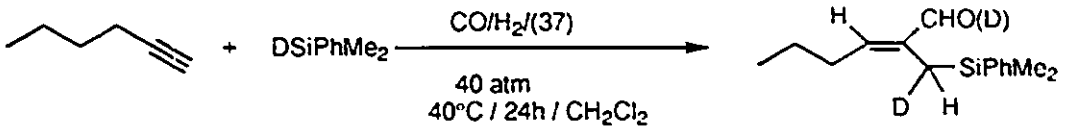
It is conceivable that the mechanism of the silylhydroformylation of alkynes is closely related to the mechanism of hydrosilylation. This well studied transition-metal catalyzed reaction generally can give a mixture of three products (Scheme 4-16)[143-146]



Scheme 4-16

In one the silicon is bound to the α-carbon of the alkyne In the other two, the Si is attached to the β-carbon, but Si-H addition has taken place in either a syn or an anti manner to give trans(E) or cis(Z) products, respectively. The selectivity of the hydrosilylation depends strongly on the catalyst and the structure of the alkyne. Several mechanisms may be considered for the hydrosilylation reaction.[163] A deuterium labeling study, using (deuterio)dimethylphenylsilane as reactant, was carried out to give some insight into the mechanism of the silyihydroformylation reacton.

A mixture of 1-hexyne (4 mmol), $DSiMe_2Ph$ (5.0 mmol), CH_2Cl_2 (10 ml) and zwitterionic rhodium complex (37) (0.04 mmol) was placed in an autoclave under CO/H_2 (1:1, 40 atm). After 24 hr at 40°C, the partially deuterated silylalkenal (174-D) was isolated in 53% yield (Scheme 4-17). The structure of (174-D) was confirmed by ^1H and ^2H NMR spectra, the deuterium percentage was determined by integrating the formyl and alkenyl protons in ^1H NMR spectrum(see Fig. 4-3 and 4-4).

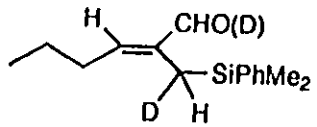


(172-D)

Scheme 4-17

The mechanism of rhodium-catalyzed hydrosilylation of alkynes was proposed independently by Crabtree[163]and Ojima[164] in 1990 to account for the formation of the β-cis adduct. It involves first a silicon shift to the acetylene bond and the carbene type zwitterionic rhodium complex (200) as the key intermediate, which undergoes isomerization from a high energy form (Z complex) to a lower energy form (E complex) (201) followed by reductive elimination to give cis isomer as the kinetic product (Scheme 4-18).[164]

Fig. 4-4. ^{1}H NMR Spectrum of Partially Deuterated (E)-1-(dimethylphenylsilyl)methyl -2-hexen-1-ol in $CDCl_3$



(172-D)

(D) $\overset{O}{\underset{}{=}}\!-D = 100\% - \frac{10.2}{23.0} = 55\%$

(D) $=C\begin{matrix}\diagup DH\text{-}Si \\ \diagdown H\text{-}D\end{matrix} = 100\% - \frac{78.1 - 23\times 3}{23} = 60\%$

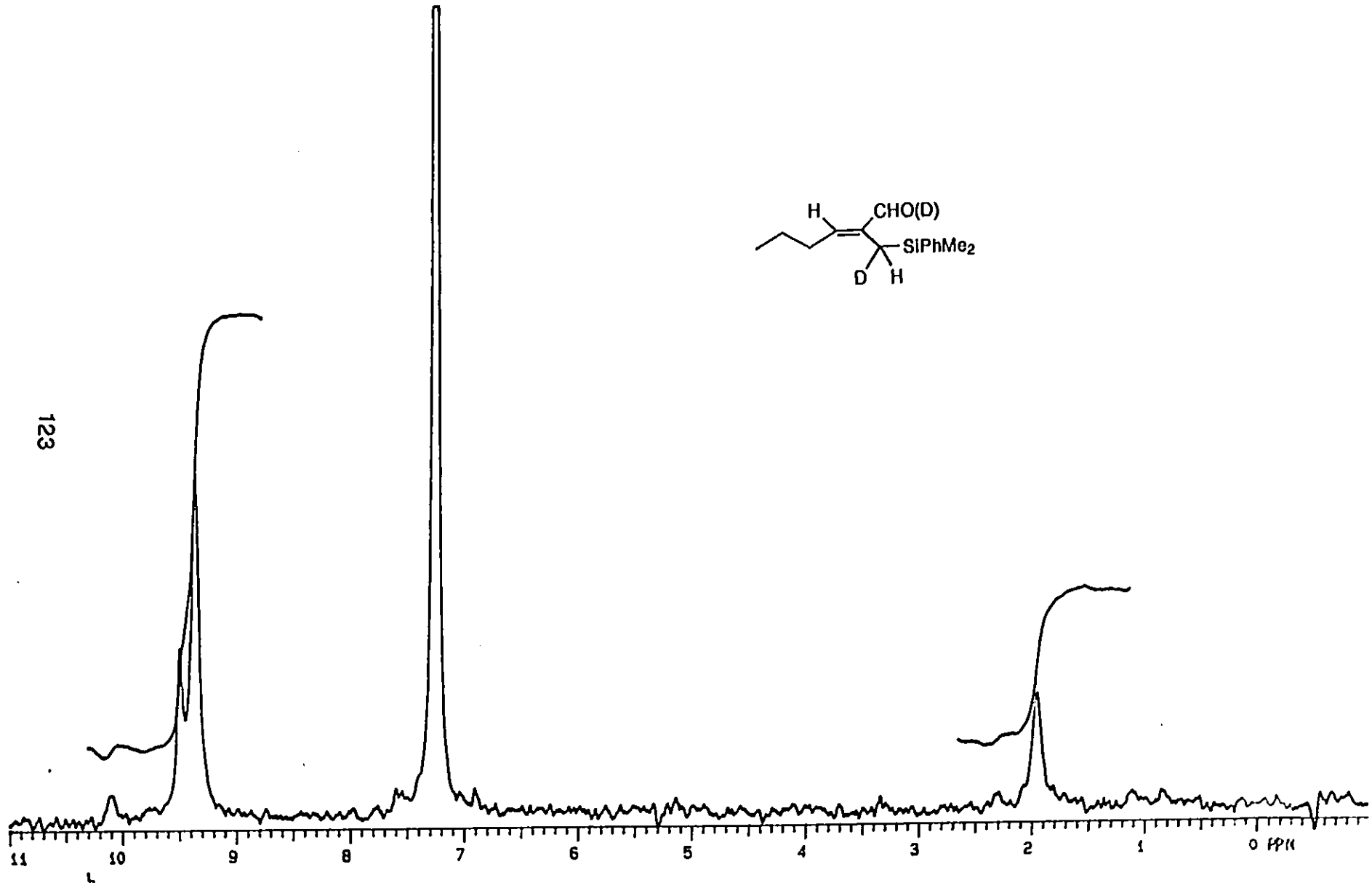
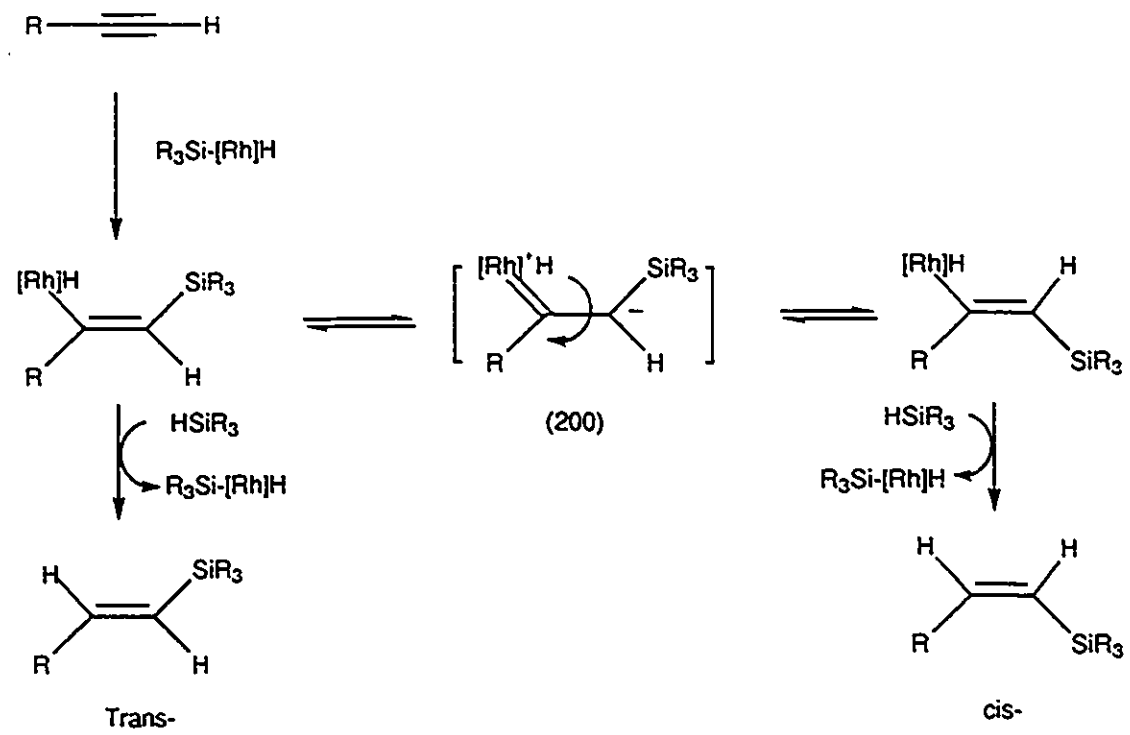
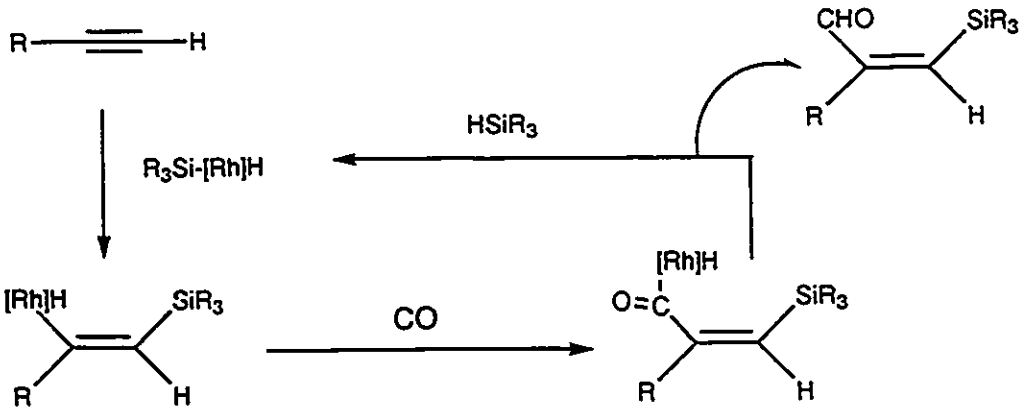


Fig. 4-5. ^{2}H NMR Spectrum of Partially Deuterated (E)-1-(dimethylphenylsilyl)methyl -2-hexen-1-ol in $CDCl_3$



Scheme 4-18

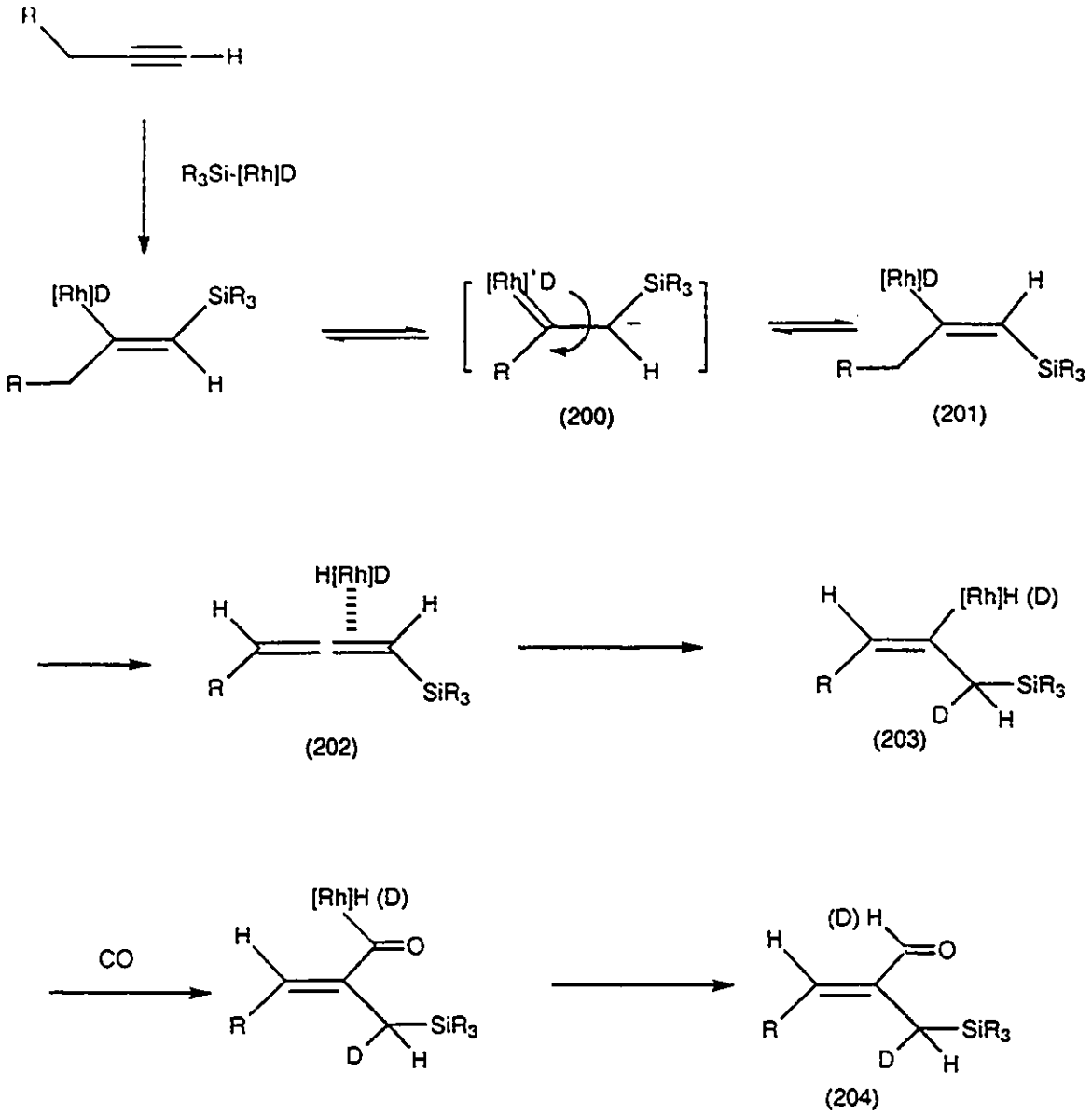
A similar mechanism, including the CO insertion at the rhodium-carbon bond, may operate in the case of the silylformylation (Scheme 4-19).



Scheme 4-19

The mechanism explains the formation of (Z)-silylalkenals when phenylacetylene and some functionally substituted terminal alkynes were used as starting materials (see Section 4-2-2, Table 4-2 and 4-3). Note that in the case of alkynes (185), (187) and (189) (Table 4-3), the corresponding products (186), (188) and (190), mainly result from the consecutive hydrogenation of silylalkenals. Finally, the reaction of 1-hexyne with $HSiEt_3$/CO in the absence of H_2 also gave (Z)-silylalkenenal, i.e. according to Scheme 4-19. However, it remains unclear why the terminal alkynes such as 1-hexyne and 4-phenyl-1-butyne, under silylhydroformylation conditions, give rise to 1-silylmethyl-2-alkene-1-als (see Table 4-1). Taking into account the results of deuterium labeling experiment (Scheme 4-17) as well as the mechanism described above (Scheme 4-19), the following reaction pathway may be proposed (Scheme 4-20).

The first three steps of this mechanism (a silicon shift to the C=C bond, the formation of carben-like Rh complex (200) and its isomerization to (201)) are identical to those show in Scheme 4-18. The key intermediate, presumably responsible for the formation of the (silylmethyl)alkenal, is the rhodium-allenyl π-complex (202) which may afford the π-complex (203). Insertion of CO at the rhodium-carbon bond and reductive elimination yields the 1-(silylmethyl)-2-alkenal (204). It should also be noted that (silylmethyl)alkenals [R_3'$SiCH_2C(CHO)=CHR$] do not result from silylalkenals [$RC(CHO)=CHSiR_3$] and vice versa. This has been shown by reacting each of these compounds with H_2 in the presence of the Rh(I) zwitterionic complex.

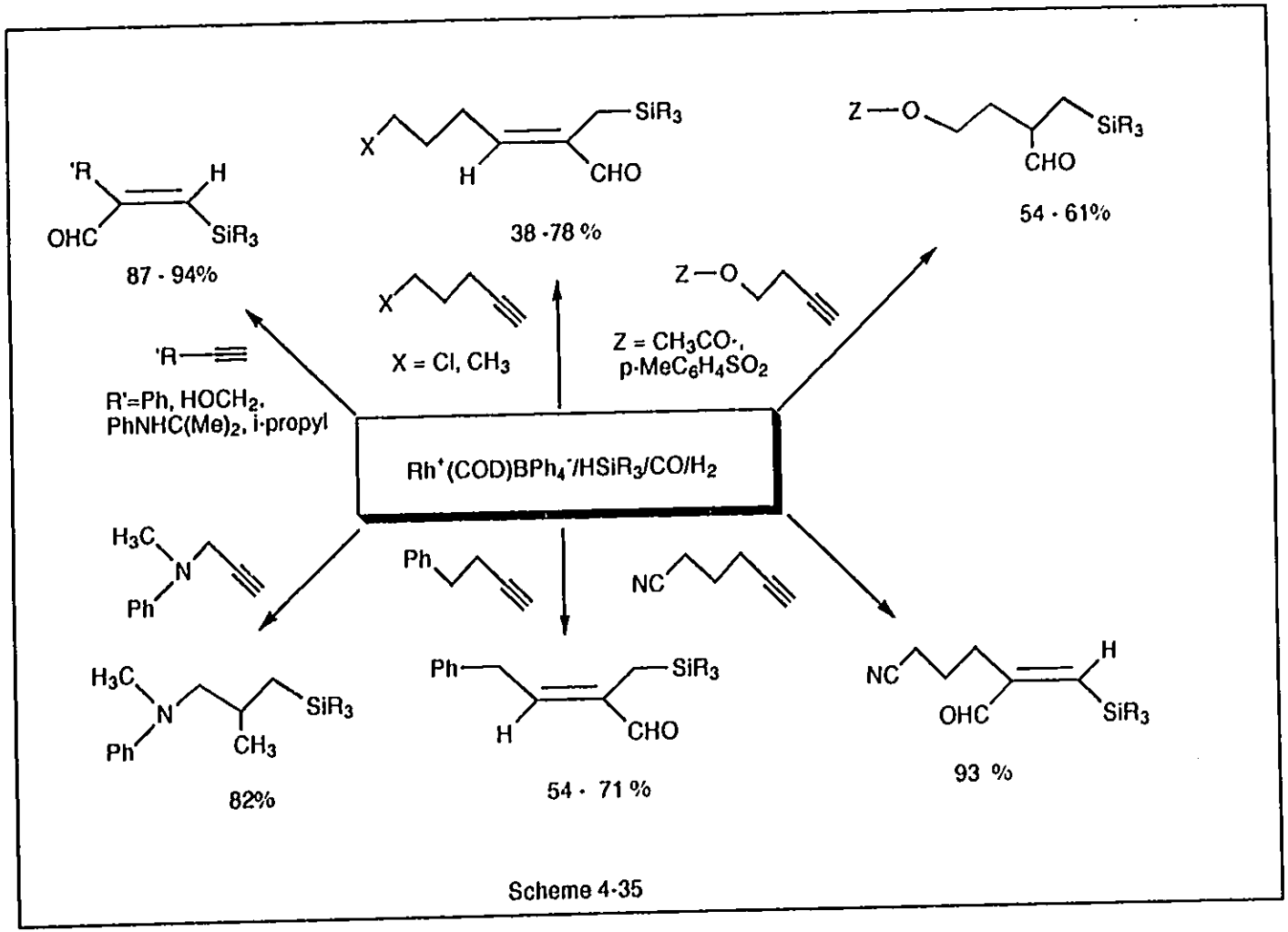

R
H
R3Si-[Rh]D
[Rh]D
SiR3
R
H
[Rh]+D
SiR3
R
H
(200)
[Rh]D
H
R
SiR3
(201)
H[Rh]D
H
H
R
SiR3
(202)
H
[Rh]H (D)
R
SiR3
D
H
(203)
CO
[Rh]H (D)
H
O
R
SiR3
D
H
(D) H
O
H
R
SiR3
D
H
(204)

Scheme 4-20

A more detailed mechanistic study is required to rationalize the catalytic sequence. However, mechanistic aspects aside, the present novel Rh(I)-catalyzed silylhydroformylation reaction of an alkyne, hydrosilane, carbon monoxide and hydrogen is a simple and efficient approach to vinyl, allyl and saturated silylaldehydes which are difficult to prepare, or are inaccessible by other means.

4-3. Conclusion

A new catalytic system consisting of the rhodium(I) zwitterionic complex (37), hydrosilane and synthesis gas has been developed. Using this system for the silylhydroformylation of terminal alkynes, one can obtain various multifunctional products regiospecifically and in high yield. The most interesting synthetic transformations are outlined in Scheme 4-21.


'R
H
OHC
SiR3
87 - 94%
X
SiR3
H
CHO
38 -78 %
Z—O
SiR3
CHO
54 - 61%
X
X = Cl, CH3
Z—O
Z = CH3CO-,
p-MeC6H4SO2
'R
R'=Ph, HOCH2,
PhNHC(Me)2, i-propyl
Rh+(COD)BPh4-/HSiR3/CO/H2
H3C
N
Ph
Ph
NC
H3C
N
Ph
SiR3
CH3
82%
Ph
SiR3
H
CHO
54 - 71 %
NC
H
OHC
SiR3
93 %

Scheme 4-35

Chapter 5

Experimental Section

5-1. General Comments

Infrared spectra were recorded on a Bomem-MB 100 FT-IR Spectrometer. NMR (^{1}H and ^{13}C) spectra were recorded on a Gemini 200 or a Varian XL-300 spectrometer. Chemical shifts are reported relative to TMS. Mass spectra were obtained on a VG 7070 E mass spectrometer. Gas chromatography was performed on a Varian Vista 6000 instrument equipped with a flame ionization detector and a Varian 4270 integrator. The glass columns for gas chromatography are packed with 3% OV-17 or 3% OV-101 on Chromosorb W, HP; The elemental analyses were performed at MHW Laboratories (Phoenix, Arizona).

Organic reactants were prepared by literature methods or were purchased from commercial sources: Aldrich Chemical Co., Fairfield Chemical Co., Lancaster Synthesis Ltd., and Wiley Organics. Rhodium and other metal complexes were either prepared according to literature procedures or purchased from Aldrich or Strem Chemical Co.. Carbon monoxide and hydrogen were supplied by Air Products Co. Thin-layer chromatographic plates (silica gel) were purchased from Terochem Co., or were hand-

made using 60 PF-254 silica gel containing $CaSO_4$ supplied by BDH Inc. Organic solvents were purified by standard methods.

5-2. Preparation of Rhodium Complexes

5-2-1. $RhH(CO)(PPh_3)_3$[165] (10)

$RhCl_3 \cdot 3H_2O$ (0.26 g, 1.0 mmol) in ethanol (20 ml) was added to a refluxing solution of triphenylphosphine (2.64 g, 10 mmol) in ethanol (100 ml), then almost immediately, were added 40% aqueous formaldehyde (10 ml) and hot ethanolic potassium hydroxide (0.8 g, 14 mmol in 20 ml of ethanol). After refluxing for 20 minutes the mixture was allowed to cool to room temperature and filtered to give (10) in 70% yield.

5-2-2. $Rh^+(1,5\text{-COD})(\eta^6\text{-}PhBPh_3)^-$ [60](37)

Sodium tetraphenylborate (1g) was added to $RhCl_3 \cdot 3H_2O$ (0.26 g, 1 mmol) in methanol (25 ml), then 1,5-cyclooctadiene (1 ml) was added and the mixture was stirred overnight at room temperature. After work up, a white-yellow solid product (37) was obtained in 62% yield.

5-2-3. $[(1,5\text{-COD})Rh^+(PPh_3)_2]BPh_4^-$ [76](43)

Triphenylphosphine (0.5 g, 1.9 mmol) was added to a suspension of $[(1,5\text{-COD})RhCl]_2$ (0.5 g, 1 mmol) in methanol (25 ml) and the solution was stirred until complete dissolution. Addition of sodium tetraphenylborate (1.0 g, 2.9 mmol) in methanol (5 ml) resulted in the precipitation of the complex (43) in 52% yield.

5-3. Hydroformylation of Allyl Acetate.

General Procedure

Allyl acetate (4.0 mmol), the Rh(I) catalyst (0.04 mmol) and phosphine (with different ratio to Rh complex) in 10 ml of methylene chloride was stirred at 80°C, under 40 atm. of syngas ($CO:H_2$=1:1) for 12 hr. The reaction was worked up by removal of the solvent followed by a silica gel chromatography using hexane-ethyl acetate (95:5) as an eluant.

5-3-1. Hydroformylation of allyl acetate

5-3-1-1. (37):dppb=1:0

Allyl acetate was hydroformylated according to the general procedure with (37) as the catalyst to afford a mixture of 4-acetoxybutyraldehyde (41) and 3-acetoxy-2-methyl-propanaldehyde (42) [(41):(42)=36:64] in 71% yield.[74]

4-Acetoxybutyraldehyde (41): **MS** (m/e) 87[M^+-43(CH_3CO-)]; **^{1}H NMR** (δ ppm), 9.78(1H, t, CHO), 4.15(2H, t, CH_2), 2.53(2H, t, CH_2), 2.01(3H, s, CH_3), 1.97(2H, m, CH_2).

3-acetoxy-2-methylpropanaldehyde (42): **MS** (m/e) 87[M^+-43(CH_3CO-)]; **^{1}H NMR** (δ ppm), 9.64(1H, d, CHO), 4.27(2H, d, CH_2), 2.68(1H, m, CH), 2.02(3H, s, CH_3), 1.13(3H, d, CH_3).

5-3-1-2. (37):dppb=1:1

Allyl acetate was hydroformylated according to the general procedure with (37) and dppb (1:1) as the catalyst to afford a mixture of (41) and (42) (40:60) in 76% yield.

5-3-1-3. (37):dppb=1:2

Allyl acetate was hydroformylated according to the general procedure with (37) and

dppb (1:2) as the catalyst to afford a mixture of (41) and (42) (95:5) in 56% yield.

5-3-1-4. (37):dppb=1:4

Allyl acetate was hydroformylated according to the general procedure with (37) and dppb (1:4) as catalyst to afford a mixture of (41) and (42) (91:9) in 53% yield.

5-3-1-5. (37):PPh_3=1:1

Allyl acetate was hydroformylated according to the general procedure with (37) and PPh_3 (1:1) as the catalyst to afford a mixture of (41)and (42) (56:44) in 67% yield.

5-3-1-6. (37):PPh_3=1:4

Allyl acetate was hydrcformylated according to the general procedure with (37) and PPh_3 (1:4) as the catalyst to afford a mixture of (41) and (42) (42:58) in 74% yield.

5-3-1-7. (37):$P(C_6H_4NMe_2\text{-}p)_3$=1:4

Allyl acetate was hydroformylated according to the general procedure with (37) and $P(C_6H_4NMe_2\text{-}p)_3$(1:4) as the catalyst, (41) and (42) (37:63) was isolated in 63% yield.

5-3-1-8. (43)

Allyl acetate was hydroformylated according to the general procedure with (43) as the catalyst to afford a mixture of (41) and (42) (20:80) in 68% yield.

5-3-1-9. (43):dppb=1:2

Allyl acetate was hydroformylated according to the general procedure with (43) and dppb(1:2) as the catalyst to afford a mixture of (41) and (42) (94:6) in 55% yield.

5-3-1-10. (46)

Allyl acetate was hydroformylated according to the general procedure in the absence of added phosphine with (46) as the catalyst to afford a mixture of 4-acetoxy-

butyraldehyde and (41) and (42) (30:70) in 70% yield.

5-3-1-11. (46):$NaBPh_4$ (1:4)

Allyl acetate was hydroformylated according to the general procedure with (46) and $NaBPh_4$ as the catalyst to afford a mixture of (41) and (42) (80:20) in 67% yield.

5-3-1-12. (47):dppb

Allyl acetate was hydroformylated according to the general procedure with (47) and dppb (1:4) as the catalyst to afford a mixture of (41) and (42) (56:44) in 73% yield.

5-3-1-13. (47):dppb:$NaBPh_4$ (1:4:4)

Allyl acetate was hydroformylated according to the general procedure with (47), dppb and $NaBPh_4$ as the catalyst to afford a mixture of (41) and (42) (96:4) in 70% yield.

5-3-1-14. (47):dppb:hydronium bis[2-hydroxybenzoato(2-)-O^1,O^2]borate(1-) (48) (1:4:4)

Allyl acetate was hydroformylated according to the general procedure with (47), dppb and bis[2-hydroxybenzoato(2-)-O^1,O^2]borate(1-) (48) (1:4:4) as the catalyst to afford a mixture of (41) and (42) (93:7) in 59% yield.

5-3-2. Hydroformylation of linalyl acetate

Linalyl acetate was hydroformylated according to the general procedure with (37) and dppb (1:2) as the catalyst affording 5,9-dimethyl-5-acetoxy-8-decen-1-al (56) in 29% yield.

5,9-dimethyl-5-acetoxy-8-decen-1-al (56): MS (m/e) 183[M^+-43 (CH_3CO-)]; **^{1}H NMR** (δ ppm) 9.62 (H, t, J=1.2 Hz, CHO), 5.05 (H, m, CH), 2.43 (2H, t, CH_2), 1.58-2.23 (8H, 2(CH_2CH_2)), 1.96 (3H, s, CH_3), 1.65 (3H, s, CH_3), 1.54 (3H, s, CH_3), 1.41 (3H, s, CH_3).

^{13}C NMR (δ ppm) 201.54, 170.02, 131.70, 123.47, 83.21, 39.52, 38.55, 38.00, 30.59, 25.55, 23.39, 22.04, 17.44.

5-3-3. Hydroformylation of allyl butyrate

Allyl butyrate was hydroformylated according to the general procedure with (37) and dppb (1:2) as the catalyst to give a mixture of 4-butyroxybutyraldehyde (57) and 3-butyroxy-2-methylpropanaldehyde (58) (91:9) in 67% yield.

4-Butyroxybutyraldehyde (57): MS (m/e) 87[M^+-71 ($CH_3CH_2CH_2CO$-)]; **^1H NMR** (δ ppm) 9.73(1H, t, J=1.2 Hz, CHO), 4.03(2H, t, CH_2), 0.92-2.53(11H).

3-Butyroxy-2-methylpropanaldehyde (58): MS (m/e) 87[M^+-71 ($CH_3CH_2CH_2CO$-)]. **^1H NMR** (δ ppm) 9.63(1H, d, J=1.2 Hz, CHO), 4.24(2H, d, CH_2), 0.92-2.53(11H).

5-3-4. Hydroformylation of (1-methyl)allyl acetate

5-3-4-1. (37):dppb=1:0

(1-Methyl)allyl acetate was hydroformylated according to the general procedure with (37) in the absence of dppb as catalyst to form a mixture of 4-methyl-4-acetoxy-butyraldehyde (59) and 3-methyl-3-acetoxy-2-methylpropanaldehyde (60) (83:17) in 82% yield.[81]

4-Acetoxy-4-methylbutyraldehyde (59): MS (m/e) 101[M^+-43]; **^1H NMR** (δ ppm) 9.72 (1H, t, CHO), 4.88 (1H, m, CH), 2.43 (2H, t, CH_2), 1.97 (3H, s, CH_3), 1.82 (2H, m, CH_2), 1.15 (3H, d, CH_3).

3-Methyl-3-acetoxy-2-methylpropanaldehyde (60): MS (m/e) 101[M^+-43]; **1H NMR** (δ ppm), 9.67 (1H, d, CHO), 5.17 (1H, m, CH), 2.47 (1H, m, CH), 1.97 (3H, s, CH_3), 1.22 (3H, d, CH_3), 1.05 (3H, d, CH_3).

5-3-4-2. (37):dppb=1:2

(1-Methyl)allyl acetate was hydroformylated according to the general procedure with (37) and dppb (1:2) affording a mixture of (59) and (60) (97:3) in 69% yield.

5-3-5. Hydroformylation of 3-butenyl acetate

5-3-5-1. (37):dppb=1:0

3-Butenyl acetate was hydroformylated according to the general procedure with (37) as the catalyst in the absence of dppb affording a mixture of 5-acetoxypentanaldehyde (61) and 4-acetoxy-2-methylbutyraldehyde (62) (50:50) in 84% yield.[166]

5-Acetoxypentanal (61): **MS** (m/e) 101[M^+-43]; **^{1}H NMR** (δ ppm) 9.73 (1H, t, J=1.2 Hz, CHO), 4.11 (2H, t, CH_2), 2.43 (2H, t, CH_3), 2.05 (3H, s, CH_3), 1.68 (4H, m, CH_2).

4-Acetoxy-2-methylbutyraldehyde (62): **MS** (m/e) 101[M^+-43]; **1H NMR** (δ ppm), 9.60 (1H, d, J=1.2 Hz, CHO), 4.08 (2H, t, CH_2), 2.47 (1H, m, CH), 1.69 (2H, m, CH_2), 1.12 (3H, d, CH_3).

5-3-5-2. (37):dppb=1:2

3-Butenyl acetate was hydroformylated according to the general procedure with (37) and dppb (1:2) as catalyst to afford a mixture of (61) and (62) (70:30) in 84% yield.

5-4. Hydroformylation of α, β-Unsaturated Esters

General Procedure

A mixture of the ester (4.0 mmol), Rh complex (0.04 mmol) and dppb in CH_2Cl_2 (10 ml) was pressurized to 40 atm. of syngas ($CO:H_2$ = 1:1). After stirring for 12-24 h at

80-130°C (see below for details), pure products were obtained by silica gel column chromatography with 7:3 hexane/ethyl acetate as the eluant.

5-4-1. Hydroformylation of ethyl acrylate

5-4-1-1. (37):dppb=1:2

Ethyl acrylate was hydroformylated according to the general procedure with (37) and dppb (1:2) as the catalyst at 80°C for 12 hr producing a mixture of ethyl 2-formyl-propionate (65) and ethyl 3-formylpropionate (66) (98:2) in 78% yield.[91]

Ethyl 2-formylpropionate (65): **MS** (m/e) 130(M^+); **^{1}H NMR** (δ ppm), 9.75 (1H, s, CHO) 4.22 (2H, d, CH_2), 3.37 (1H, q, CH), 1.30 (6H, m, CH_3). **Enol form, ^{1}H NMR** (ppm), 11.43 (1H, d, OH), 6.97(1H, dq, CH_3), 4.22 (2H, d, CH_2), 1.65 (3H, d, CH_3), 1.30(3H, q, CH_3).

5-4-1-2. (37):dppb=1:0

Ethyl acrylate was hydroformylated according to the general procedure with (37) and dppb (1:0) as the catalyst at 80°C for 12 hr affording a mixture of ethyl 2-formyl-propionate (65) and ethyl 3-formylpropionate (66) (57:43) in 52% yield.

5-4-1-3. (43):dppb=1:2

Ethyl acrylate was hydroformylated according to the general procedure with (43) and dppb (1:2) as the catalyst at 80°C for 12 hr affording a mixture of (65) and (66) (98:2) in 77% yield .

5-4-1-4. (43):dppb=1:0

Ethyl acrylate was hydroformylated according to the general procedure with (43) and dppb (1:0) as the catalyst at 80°C for 12 hr giving a mixture of (65) and (66) (85:15)

in 56% yield .

5-4-1-5. (47):dppb=1:4

Ethyl acrylate was hydroformylated according to the general procedure with (47) and dppb (1:4) as the catalyst at 80°C for 12 hr to give a mixture of (65) and (66) (99.5:0:5) in 83% yield (in the absence of dppb, (65):(66)=45:55 in 13.5% yield).

5-4-2. Hydroformylation of i-butyl acrylate

i-Butyl acrylate was hydroformylated according to the general procedure with (37) and dppb (1:2) as the catalyst at 80°C for 12 hr to form i-butyl (2-formyl)propionate (67) in 76% yield.

i-Butyl (2-formyl)propionate (67): MS (m/e) 158(M^+); **^{1}H NMR** (δ ppm), 9.85 (1H, s, CHO), 5.01(H, m, CH), 3.45 (1H, q, CH), 1.30 (8H, m), 0.95(3H, q, CH_3). **Enol form, ^{1}H NMR** (δ ppm), 11.45 (1H, d, OH), 7.05(1H, dq), 5.01 (1H, m, CH), 1.70(3H, d, CH_3), 1.35(5H, m), 0.95(3H, q, CH_3).

5-4-3. Hydroformylation of methyl methacrylate

5-4-3-1. (37):dppb=1:2

Methyl methacrylate was hydroformylated according to the general procedure with (37) and dppb (1:2) as the catalyst at 130°C for 24 hr to afford a mixture of methyl 2-methyl-2-formyl propionate (α-isomer) and methyl 2-methyl-3-formyl propionate (β-isomer) (96:4) in 65% yield[91]. When the reaction was carried out at 80°C, a mixture of the α-isomer and β-isomer (97:3) was obtained in 20% yield.

Methyl 2-methyl-2-formylpropionate (69): MS (m/e) 102[M^+-28]; **^{1}H NMR** (δ ppm), 9.68(1H, s, CHO), 3.82(3H, s, CH_3), 1.40(6H, s, CH_3). **^{13}C NMR** (δ ppm) 199.02, 173.11,

53.79, 52.53, 19.65.

5-4-3-2. (37):dppb=1:2

Methyl methacrylate was hydroformylated according to the general procedure with (37) and dppb(1:2) as the catalyst at 130°C for 24 hr to afford a mixture of the α-isomer and β-isomer (96:4) in 59% yield.

5-4-4. Hydroformylation of α-methylene-γ-butyrolactone

5-4-4-1. (37):dppb=1:2

α-Methylene-γ-butyrolactone was hydroformylated according to the general procedure with (37) and dppb (1:2) as the catalyst at 130°C for 24 hr to form α-methyl-α-formyl-γ-lactone (71) in 56% yield.

α-Methyl-α-formyl-γ-lactone (71): MS (m/e) 100[M^+-28]; **^{1}H NMR** (δ ppm), 1.52 (s, 3H, CH_3)2.17 (m, 1H, CH), 2.83 (m, 1H, CH), 4.33 (m, 2H, CH_2), 9.56 (s, 1H, CHO). The product (71) was also characterized by its reaction with benzylamine to give the corresponding Schiff base, **MS** (m/e) 217 (M^+); **^{1}H NMR** (δ ppm), 1.50 (3H, s, CH), 2.15 (1H, m, CH), 2.91 (1H, m, CH), 4.45 (2H, t, CH_2), 4.69 (2H, s, $PhCH_2$), 7.35 (5H, m, Ph), 7.82 (1H, s, CH=N). ^{13}C NMR (δ ppm), 20.87, 32.63, 48.50, 64.13, 65.57, 127.80, 127.61, 128.50, 138.59, 163.25, 178.37. **Anal.** Calc. for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96. Found: C, 71.60; H, 7.01.

5-4-4-2. (43):dppb=1:2

α-Methylene-γ-butyrolactone was hydroformylated according to the general procedure with (43) and dppb (1:2) as catalyst at 130°C for 24 hr to afford (71) in 60% yield.

5-4-5. Hydroformylation of ethyl crotonate

5-4-5-1. (37):dppb=1:2

trans-Ethyl crotonate (72) was hydroformylated according to the general procedure with (37) and dppb (1:2) as the catalyst at 130°C for 12 hr to afford a mixture of ethyl 2-formylbutyrate (74) and ethyl 3-formylbutyrate (98:2) in 64% yield.[91]

cis-Ethyl crotonate (73) gave a mixture of ethyl 2-formylbutyrate (74) and ethyl 3-formylbutyrate(98:2) in 45% yield .

Ethyl 2-formylbutyrate (74): **MS** (m/e) 144(M^+), **^{1}H NMR** (δ ppm), 9.78 (1H, s, CHO) 4.25 (2H, d, CH_2), 3.18 (1H, d,t, CH), 1.92(2H, m, CH_2) 1.30 (3H, m, CH_3), 1.02(3H, m, CH_3). **Enol form:** **^{1}H NMR** (δ ppm); 11.45 (1H, d, OH), 7.05(1H, d, CH_3), 4.25 (2H, m, CH_2), 2.11(2H, m, CH_2), 1.65 (3H, d, CH_3), 1.30(3H, q, CH_3).

5-4-5-2. (43):dppb=1:2

trans-Ethyl acrylate (72) was hydroformylated according to the general procedure with (43) and dppb (1:2) as the catalyst at 130°C for 12 hr affording a mixture of ethyl 2-formylpropionate (74) and 3-formylpropionate (98:2) in 78% yield.

cis-Ethyl acrylate (73) was hydroformylated according to the general procedure with (43) and dppb (1:2) as the catalyst at 130°C for 12 hr to give a mixture of ethyl 2-formylpropionate (73) and 3-formylpropionate (98:2) in 68% yield.

5-5. Reductive Carbonylation of Alkenes

General Procedure

A mixture of 4.0 mmol of substrate, 0.150 g (4.0 mmol) of $NaBH_4$, 0.5 ml of

propan-2-ol and 0.04 mmol of rhodium(I) complex in 5 ml of CH_2Cl_2 was stirred at 100°C, under 500 psi of carbon monoxide for 22 h when an arylalkene was used and for 30 hr if the reactant was non aromatic. Work-up was effected as follows: Water (10 ml) was added to the cooled mixture, and the layers were separeted. The aqueous layer was extracted with ethyl acetate (20 ml) and the organic solutions were combined. Concentration of the organic phase followed by alumina column chromatography using hexane-ethyl acetate as the eluent afforded pure branched and linear alcohols.

5-5-1. Reductive carbonylation of styrene

5-5-1-1. (37)

Styrene was carbonylated according to the general procedure with (37) as the catalyst affording a mixture of 2-phenylpropanol and 3-phenylpropanol (95:5) in 83% yield.[167]

2-Phenylpropanol: MS (m/e) 136[M^+]; **^{1}H NMR** (δ ppm), 7.25(5H, m, aromatic), 3.68(2H, t, CH_2), 2.93(1H, m, CH), 1.25(3H, d, CH_3).

3-Phenylpropanol: MS (m/e) 136[M^+]; **^{1}H NMR** (δ ppm), 7.15(5H, m, aromatic), 3.64(2H, t, CH_2), 2.70(2H, t, CH_2), 1.85(2H, m, CH_2)

5-5-1-2. (10)

Styrene was carbonylated according to the general procedure with (43) as the catalyst affording a mixture of 2-phenylpropanol and 3-phenylpropanol (64:36) in 90% yield.

5-5-1-3. (43)

Styrene was carbonylated according to the general procedure with (10) as the

catalyst to give a mixture of 2-phenylpropanol and 3-phenylpropanol (80:20) in 92% yield.

5-5-2. Reductive carbonylation of 4-methylstyrene

5-5-2-1. (37)

4-Methylstyrene was carbonylated according to the general procedure, with (10) as the catalyst, affording a mixture of 2-(p-tolyl)propanol and 3-(p-tolyl)propanol (93:7) in 77% yield.[167]

2-(p-Tolyl)propanol: MS (m/e) 150[M^+]; **^{1}H NMR** (δ ppm), 7.15(4H, dd, aromatic), 3.68(2H, t, CH_2), 2.93(1H, m, CH), 2.31(3H, s, CH_3), 1.23(3H, d, CH_3)

3-(p-Tolyl)propanol: MS (m/e) 150[M^+]; **^{1}H NMR** (δ ppm), 7.15(4H, m, aromatic), 3.65(2H, t, CH_2), 2.65(2H, t, CH_2), 2.30(3H, s, CH_3), 1.85(2H, m, CH_2)

5-5-2-2. (10)

4-Methylstyrene was carbonylated according to the general procedure with (10) as the catalyst giving a mixture of 2-(p-tolyl)propanol and 3-(p-tolyl)propanol (77:23) in 95% yield.

5-5-2-3. (43)

4-methylstyrene was carbonylated according to the general procedure with (43) as the catalyst to afford a mixture of 2-(p-tolyl)propanol and 3-(p-tolyl)propanol (75:25) in 90% yield.

5-5-3. Reductive carbonylation of 4-methoxystyrene

5-5-3-1. (37)

4-Methoxystyrene was carbonylated according to the general procedure with (37) as the catalyst to afford a mixture of 2-(p-anisyl)propanol and 3-(p-anisyl)propanol (95:5)

in 91% yield.[167]

2-(p-Anisyl)propanol: MS (m/e) 166[M$^+$]; **^{1}H NMR** (δ ppm), 7.18(2H, d, aromatic), 6.87(2H, d, aromatic), 3.79(3H, s, CH_3), 3.62(2H, t, CH_2), 2.89(1H, m, CH), 1.23(3H, d, CH_3)

3-(p-Anisyl)propanol: MS (m/e) 166[M$^+$]; **^{1}H NMR** (δ ppm), 7.18(2H, d, aromatic), 6.87(2H, d, aromatic), 3.82(3H, s, CH_3), 3.67(2H, t, CH_2), 2.65(2H, t, CH_2), 1.85(2H, m, CH_2).

5-5-4. Reductive carbonylation of 4-chlorostyrene

4-Chlorostyrene was carbonylated according to the general procedure with (37) as the catalyst affording a mixture of 2-(p-chlorophenyl)propanol and 3-(p-chlorophenyl) propanol (75:25) in 93% yield.[167]

2-(p-Chlorophenyl)propanol: MS (m/e) 170[M$^+$]; **^{1}H NMR** (δ ppm) 7.21(4H, dd, aromatic), 3.68(2H, t, CH_2), 2.92(1H, m, CH), 1.25(3H, d, CH_3)

3-(p-Chlorophenyl)propanol: MS (m/e) 170[M$^+$]; **^{1}H NMR** (δ ppm), 7.18(4H, dd, aromatic), 3.65(2H, t, CH_2), 2.65(2H, t, CH_2), 1.85(2H, m, CH_2).

5-5-5. Reductive carbonylation of 4-fluorostyrene

4-Fluorostyrene was carbonylated according to the general procedure with (37) as the catalyst affording a mixture of 2-(p-fluorophenyl)propanol and 3-(p-fluorophenyl) propanol (90:10) in 70% yield.[167]

2-(p-Fluorophenyl)propanol: MS (m/e) 154[M$^+$]; **^{1}H NMR** (δ ppm), 7.05(4H, dd, aromatic), 3.65(2H, t, CH_2), 2.91(1H, m, CH), 1.25(3H, d, CH_3)

3-(p-Fluorophenyl)propanol: MS (m/e) 154[M$^+$]; **^{1}H NMR** (δ ppm), 7.05(4H, dd,

aromatic), 3.64(2H, t, CH_2), 2.65(2H, t, CH_2), 1.85(2H, m, CH_2).

5-5-6. Reductive carbonylation of 4-iso-butylstyrene

When 4-iso-butylstyrene was carbonylated according to the general procedure with (37) as the catalyst a mixture of 2-(p-iso-butylphenyl)propanol and 3-(p-iso-butylphenyl)propanol (89:11) was isolated in 73% yield.[167]

2-(p-iso-Butylphenyl)propanol: MS (m/e) 192[M^+]; **^{1}H NMR** (δ ppm), 7.11(4H, m, aromatic), 3.69(2H, t, CH_2), 2.91(1H, m, CH), 2.41(2H, d, CH_2), 1.85(1H, m, CH), 1.25(3H, d, CH_3), 0.92(6H, d, CH_3).

3-(p-iso-butylphenyl)propanol: MS (m/e) 192[M^+]; **^{1}H NMR** (δ ppm), 7.11(4H, m, aromatic), 3.65(2H, t, CH_2), 2.68(2H, t, CH_2), 2.42(2H, d, CH_2), 1.87(2H, m, CH_2). 0.91(6H, s, CH_3).

5-5-7. Reductive carbonylation of decene-1

Decene-1 was carbonylated according to the general procedure with (37) as the catalyst affording a mixture of 2-methyl-1-decanol and undecanol-1 (47:53) in 90% yield.[168]

2-Methyl-1-decanol: MS (m/e) 152[M^+-18]; **^{1}H NMR** (δ ppm), 3.61(2H, m, CH_2), 1.25-2.11(18H, m), 0.85(3H, t, CH_3).

Undecanol-1: MS (m/e) 152[M^+]; **^{1}H NMR** (δ ppm), 3.45(2H, t, CH_2), 1.25-2.11(18H, m), 0.85(3H, t, CH_3).

5-5-8. Reductive carbonylation of vinylcyclohexane

Vinylcyclohexane was carbonylated according to the general procedure with (37) as the catalyst giving a mixture of 3-cyclohexylpropanol and 2-methyl-2-cyclohexylethanol

(90:10) in 87% yield.[169]

2-Methyl-2-cyclohexylethanol: **MS** (m/e) 140[M$^+$]; **^{1}H NMR** (δ ppm), 3.69(2H, m, CH_2), 1.62-0.93(15H, m).

3-Cyclohexylpropanol: **MS** (m/e) 140[M$^+$]; **^{1}H NMR** (δ ppm), 3.60(2H, t, CH_2), 1.62-0.93(15H, m).

5-5-9. Reductive carbonylation of 2-methylundec-1-ene

2-Methylundec-1-ene was carbonylated according to the general procedure with (37) as the catalyst to afford 3-methyldodecan-1-ol in 75% yield.[170]

3-Methyldodecan-1-ol **MS** (m/e) 182[M$^+$-18]; **^{1}H NMR** (δ ppm), 3.60(2H, t, CH_2), 1.62-0.92(15H m).

5-5-10. Reductive carbonylation of 3,3-dimethylhex-1-ene

When 3,3-dimethylhex-1-ene was carbonylated according to the general procedure, with (37) as the catalyst, 4,4-dimethylheptan-1-ol was obtained in 88% yield.

4,4-Dimethylheptan-1-ol **MS** (m/e) 113[M$^+$-31]; **^{1}H NMR** (δ ppm), 3.49(2H, t, CH_2), 1.62-0.85(17H m).

5-5-11. Reductive carbonylation of cyclooctene

Cyclooctene was carbonylated according to the general procedure with (37) as the catalyst to afford cyclooctylmethanol in 74% yield.[171]

Cyclooctylmethanol: **MS** (m/e) 111[M$^+$-31]; **^{1}H NMR** (δ ppm), 3.45(2H, d, CH_2), 1.52(15H, m). **^{13}C NMR** (δ ppm), 68.74, 40.02, 34.37, 29.05, 27.16, 26.65, 26.19, 25.29, 22.42.

5-5-12. Reductive carbonylation of R(+)-limonene

When R(+)-limonene was carbonylated according to the general procedure with (37) as the catalyst to form 3-methyl-3-(4-methylcyclohex-3-en-1-yl) propanol[172] in 74% yield.

3-Methyl-3-(4-methylcyclohex-3-en-1-yl)propanol: MS (m/e) 168[M$^+$]; **^{1}H NMR** (δ ppm), 5.39(1H, t, CH), 3.65(2H, t, CH_2), 1.92-0.97(16H m).

5-6. Lactonization of Allylic Alcohols

General procedure (A)

A mixture of substrate (4.0 mmol), $NaBH_4$ (4.5 mmol), 2-propanol (0.5ml) and rhodium complex (0.04 mmol, 1%) in CH_2Cl_2 (10 ml) was stirred at 100°C under 30 atm. of carbon monoxide for 12 hr. Water (10 ml) was added to the cocled mixture and the layers were separated. The aqueous layer was extracted with ether, concentration of the organic phase followed by silica gel column chromatography using hexane-ethyl acetate as eluant afforded pure γ-butyrolactone.

General procedure (B)

The reaction procedure was the same as General procedure (A) except no 2-propanol was added.

5-6-1. Lactonization of 1-hexene-3-ol

5-6-1-1. (37) in the presence of i-PrOH

When 1-hexene-3-ol was cyclocarbonylated according to the general procedure (A) with (37) as the catalyst, 4-(n-propyl)butyro-γ-lactone (80) was obtained in 70% yield.[100]

4-(n-Propyl)butyro-γ-lactone (80): MS (m/e) 128[M$^+$]; **^{1}H NMR** (δ ppm), 4.46(1H, m,

CH), 2.25(2H, m, CH_2), 1.85-1.32(6H, m), 0.95(3H, s, CH_3). **^{13}C NMR** (δ ppm), 177.45, 80.70, 37.40, 28.61, 27.75, 18.29, 13.53.

5-6-1-2. (43) In the presence of i-PrOH

1-Hexene-3-ol was cyclocarbonylated according to the general procedure (A) with (43) as the catalyst to afford 4-(n-propyl)butyro-γ-lactone (80) in 59% yield.

5-6-1-3. (10) In the presence of i-PrOH

1-Hexene-3-ol was cyclocarbonylated according to the general procedure (A) with (10) as the catalyst to afford 4-(n-propyl)butyro-γ-lactone (80) in 82% yield.

5-6-1-4. (10) In the absence of i-PrOH

1-Hexene-3-ol was cyclocarbonylated according to the general procedure (B) with (10) as the catalyst to afford 4-(n-propyl)butyro-γ-lactone (80) in 10% yield.

5-6-2. Lactonization of 2-methyl-3-butene-2-ol

5-6-2-1. (10) In the presence of i-PrOH

2-Methyl-3-butene-2-ol was cyclocarbonylated according to the general procedure (A) with (10) as the catalyst to afford 4,4-dimethylbutyro-γ-lactone (81) in 21% yield.[170]

4,4-Dimethylbutyro-γ-lactone (81): MS (m/e) 114[M$^+$]; **^{1}H NMR** (δ ppm), 2.57(2H, m, CH_2), 2.12 (2H, t, CH_2), 1.81(6H, s, CH_3).

5-6-2-2. (10) In the absence of i-PrOH

2-Methyl-3-butene-2-ol was cyclocarbonylated according to the general procedure (B) with (10) as the catalyst to afford 4,4-dimethylbutyro-γ-lactone (81) in 61% yield.

5-6-3. Lactonization of 2-methylpropen-1-ol

5-6-3-1. (10) In the presence of i-PrOH

2-Methylpropen-1-ol was cyclocarbonylated according to the general procedure (A) with (10) as the catalyst. 3-Methylbutyro-γ-lactone (82) was not formed.

5-6-3-2. (10) in the absence of i-PrOH

When 2-Methylpropen-1-ol was cyclocarbonylated according to the general procedure (B) with (10) as the catalyst, 3-methylbutyro-γ-lactone (82) in 35% yield.[101]

3-Methylbutyro-γ-lactone (82): MS (m/e) 100[M$^+$], **^{1}H NMR** (δ ppm), 4.35(1H, dd, CH), 3.82 (1H, dd, CH), 2.61(2H, m,), 2.12(1H, m), 1.11(3H, d, CH_3). **^{13}C NMR** (δ ppm), 177.43, 74.56, 35.90, 30.14, 17.64.

5-6-4. Lactonization of linalool

When linalool was cyclocarbonylated according to the general procedure (A) with (37) as the catalyst, 4-methyl-4-(4-methyl-3-pentenyl)butyro-γ-lactone (83) was obtained in 70% yield.[102]

4-Methyl-4-(4-methyl-3-pentenyl)butyro-γ-lactone (83): MS (m/e) 182[M$^+$]; **^{1}H NMR** (δ ppm), 5.08(1H, t, CH), 2.27(2H, m, CH_2), 2.18 (4H, m), 1.61(8H, m), 1.37(3H, s, CH_3). **^{13}C NMR** (δ ppm), 176.90, 132.34, 123.13, 86.57, 40.67, 32.72, 28.89, 25.39, 25.29, 22.31, 17.37.

5-6-5. Lactonization of allyl alcohol

Allyl alcohol was cyclocarbonylated according to the general procedure (B) with (37) as the catalyst to afford γ-butyrolactone in 5% yield.[173]

γ-Butyrolactone: MS (m/e) 86[M$^+$]; **^{1}H NMR** (δ ppm), 4.15(2H, t, CH_2), 2.32 (2H, t, CH_2), 2.16(2H, m, CH_2).

5-6-6-1. (10)

3-Methyl-3-butene-2-ol was cyclocarbonylated according to the general procedure (A) with (10) as catalyst to afford 3,4-dimethylbutyro-γ-lactone (84) (cis:trans=14:86, determined by ^{1}H NMR) in 50% yield.[102]

5-6-6-2. (37)

When 3-methyl-3-butene-2-ol was cyclocarbonylated according to the general procedure (A) with (37) as the catalyst, 3,4-dimethylbutyro-γ-lactone (84) (cis:trans=17:83, determined by proton NMR) was isolated in 46% yield.

5-6-7. Lactonization of 3-buten-1-ol

3-Buten-1-ol was cyclocarbonylated according to the general procedure (A) with (37) as the catalyst to afford 2-methylbutyro-γ-lactone in 41% yield.[174]

2-Methylbutyro-γ-lactone: MS (m/e) 100[M$^+$]; **^{1}H NMR** (δ ppm) 4.21(2H, m, CH_2), 2.53 (2H, m, CH_2), 1.86(1H, m,), 1.22(3H, d, CH_3). **^{13}C NMR** (δ ppm) 180.36, 66.14 33.90, 30.44, 14.86.

5-7. Synthesis of Pyrrolidines from N-Allyl-N-arylamines Catalyzed by $NaBH_4$/CO/i-PrOH/Rh(I) System

General Procedure

A mixture of 2.0 mmol of the allylic amine substrate, $NaBH_4$ (2.25 mmol), (37) (0.02 mmol, 1%), 2-propanol (0.5 ml) and CH_2Cl_2 (5.0 ml) were placed in a 45 ml autoclave containing a glass liner. The autoclave was pressured to 34.5 atm with carbon monoxide, and the mixture was heated with stirring for 30 h at 100°C. After cooling, water was added to remove unreacted $NaBH_4$. The organic phase was separated and concentrated

and the mixture was heated with stirring for 30 h at 100℃. After cooling, water was added to remove unreacted $NaBH_4$. The organic phase was separated and concentrated by rotary evaporation affording an oil. The products were isolated by silica gel column chromatography using 95:5 hexane/ethyl acetate as the eluant.

5-7-1. N-Allylaniline

N-Allylaniline was carbonylated according to the general procedure to afford N-propyl aniline(96-a) (10%), N-(2-methyl-3-hydroxyl)propylaniline(96-b) (33%) and 1-phenylpyrrolidine(95) (31%).[175]

n-Propylaniline(96-a): **MS** (m/e) 135[M⁺]; **^{1}H NMR**(δ ppm), 7.2 (2H, m, aromatic), 6.57 (3H, m, aromatic), 3.05 (2H, q, CH_2), 3.58 (1H, s, NH), 1.61 (2H, m, CH_2), 0.95 (3H, t, CH_3).

1-Phenylpyrrolidine (95): **MS** (m/e) 147[M⁺]; **^{1}H NMR**(δ ppm) 7.2 (2H, m, aromatic), 6.65 (3H, m, aromatic), 3.25 (4H, t, $2CH_2$), 1.95 (4H, m, CH_2-CH_2). **^{13}C NMR** (δ ppm) 148.06, 129,12, 115.34, 111.61, 47.38, 25.21.

N-(2-Methyl-3-hydroxy)propylaniline (96-b): **MS** (m/e) 165[M⁺]; **^{1}H NMR** (δ ppm), 7.15 (2H, m, aromatic), 6.61 (3H, m, aromatic), 3.62 (2H, m, CH_2), 3.09 (2H, m, CH_2), 2.01 (1H, m, CH), 0.95(3H, d, CH_3).

5-7-2. N-Allyl-p-anisidine

N-Allyl-p-anisidine was carbonylated according to the general procedure to afford N-(2-methyl-3-hydroxy)propyl-p-anisidine(98) (32%) and 1-p-anisylpyrrolidine(97) (31%).[175]

1-p-Anisylpyrrolidine (97): **MS** (m/e) 177[M⁺]; **^{1}H NMR** (δ ppm), 6.85 (2H, dd,

aromatic), 6.65 (2H, dd, aromatic), 3.75(3H, s, CH_3), 3.25 (4H, t, $2CH_2$), 1.95 (4H, m, CH_2-CH_2). **^{13}C NMR** (δ ppm), 150.89, 143.25, 114.93, 112.68, 55.84, 48.14, 25.19.

N-(2-Methyl-3-hydroxyl)propyl-p-anisidine (98): MS (m/e) 195[M$^+$]; **^{1}H NMR** (δ ppm), 6.75 (2H, m, aromatic), 6.61 (2H, m, aromatic), 3.72 (3H, s, CH_3), 3.62 (2H, dd, CH_2), 3.09 (2H, dd, CH_2), 2.01 (1H, m, CH), 0.94 (3H, d, CH_3).

5-7-3. N-(1-Methy)allylaniline and N-crotylaniline

A mixture of N-(1-methyl)allylaniline and N-crotylaniline (65:35) was carbonylated according to the general procedure to afford a mixture of 1-phenyl-2-methylpyrrolidine (102)[177] and 1-phenyl-2-methylpyrrolidine (101)[176](75:25) in 51% overall yield.[173, 176]

1-Phenyl-2-methylpyrrolidine (101): MS (m/e) 161[M$^+$]; **^{1}H NMR** (δ ppm), 7.29 (2H, m, aromatic), 6.68 (3H, m, aromatic), 3.92(1H, m, CH), 3.46(2H, m, CH_2), 2.11 (3H, m, CH, CH_2), 1.70 (1H, m, CH). 1.24(3H, d, CH_3). **^{13}C NMR** (δ ppm), 147.36, 129.26, 115.20, 111.81, 53.50, 48.05, 32.99, 23.16, 19.23.

1-Phenyl-3-methylpyrrolidine (102): MS (m/e) 161[M$^+$]; **^{1}H NMR** (δ ppm), 7.25 (2H, m, aromatic), 6.65 (3H, m, aromatic), 3.51(1H, m, CH), 3.32(2H, m, CH_2), 2.91 (1H, dd, CH), 2.32 (1H, m, CH). 2.11(1H, m, CH), 1.63(1H, m, CH), 1.12(3H, d, CH_3). **^{13}C NMR** (δ ppm), 147.87, 129.04, 115.13, 111.30, 54.86, 47.37, 33.48, 33.20, 18.39.

5-7-4. N-Allyl-N-(1-naphthyl)amine

N-Allyl-N-(1-naphthyl)amine was carbonylated according to the general procedure to afford 1-(1-naphthyl)pyrrolidine(103) in 45% yield.[178]

1-(1-Naphthyl)pyrrolidine(103): MS (m/e) 197[M$^+$]; **^{1}H NMR**(δ ppm), 8.2 (1H, m, aromatic), 7.81(1H, m, aromatic), 7.42(4H, m, aromatic), 6.93 (1H, m, aromatic), 3.51 (4H,

m, $2CH_2$), 2.01 (4H, m, $2CH_2$).

5-7-5. N-(3-Methyl-2-butenyl)aniline

N-(3-Methyl-2-butenyl)aniline was carbonylated according to the general procedure to afford 48% of N-(3-methylbutyl)aniline(105).[179]

N-(3-Methylbutyl)aniline (105): MS (m/e) 163[M$^+$]; **^{1}H NMR** (δ ppm), 7.25 (2H, m, aromatic), 6.71 (3H, m, aromatic), 3.15 (2H, t, CH_2), 1.55 (2H, q, CH_2), 1.75 (1H, m, CH), 1.01 (6H, d, $2CH_3$).

5-7-6. N-Allylaniline

N-Allylaniline was carbonylated according to the general procedure to afford (102) in 84% yield.

5-7-7. N-(2-Methyl)allyl-p-anisidine

N-(2-Methyl)allyl-p-anisidine was carbonylated according to the general procedure to afford 1-p-anisyl-3-methylpyrrolidine (106) in 68% yield.

1-p-Anisyl-3-methylpyrrolidine (106): MS (m/e) 191[M$^+$]; **^{1}H NMR**(δ ppm), 6.81 (2H, dd, aromatic), 6.45 (2H, dd, aromatic), 3.72 (3H, s, CH_3), 3.34 (1H, dd, CH), 3.23 (2H, m, CH_2), 2.78 (1H, dd, CH), 2.35 (1H, m, CH), 2.07 (1H, m, CH), 1.55 (1H, m, CH), 1.03 (3H, d, CH_3). **^{13}C NMR** (δ ppm), 150.71, 143.22, 115.03, 112.22, 55.87, 55.40, 47.04, 33.43, 33.12, 18.45. **Anal.** Calcd. for **$C_{12}H_{17}NO$**: C, 75.35; H, 8.95; N, 7.32. Found: C, 75.55; H, 8.59; N, 7.30.

5-7-8. N-(2-Methyl)allyl-N-(1-naphthyl)amine

N-(2-Methyl)allyl-N-(1-naphthy)amine was carbonylated according to the general procedure to form 1-(1-naphthyl)-3-methylpyrrolidine (107) in 57% yield.

1-(1-Naphthyl)-3-methylpyrrolidine (107): **MS** (m/e) 211[M$^+$]; **^{1}H NMR**(δ ppm), 8.2 (1H, m, aromatic), 7.81(1H, m, aromatic), 7.35(4H, m, aromatic), 6.91 (1H, m, aromatic), 3.51 (2H, m, CH_2), 3.35(1H, m, CH), 3.07(1H, dd, CH), 2.45(1H, m, CH), 2.15(1H, m, CH), 1.60(1H, m, CH), 1.15(3H, d, CH_3). **^{13}C NMR** (δ ppm), 147.87, 135.08, 128.26, 127.81, 125.93, 125.47, 124.01, 124.07, 120.75, 110.71, 60.20, 52.39, 33.28, 32.73, 18.92. **Anal.** Cald. for $C_{15}H_{17}N$: C, 85.30, H, 8.05, N, 6.63. Found: C, 85.15, H, 8.02, N, 6.65.

5-7-9. N-(2-Methyl)allyl-N-(2-pyridyl)amine

N-(2-Methyl)allyl-N-(2-pyridyl)amine was carbonylated according to the general procedure to give 1-(2-pyridyl)-3-methylpyrrolidine (108) in 26% yield.

1-(2-Pyridyl)-3-methylpyrrolidine (108): **MS** (m/e) 162[M$^+$]; **^{1}H NMR**(δ ppm), 8.1 (1H, m, aromatic), 7.40 (1H, m, aromatic), 6.51 (1H, m, aromatic), 6.3 (1H, m, aromatic), 3.5 (3H, m, CH, CH_2), 2.95 (1H, dd, CH), 2.40 (1H, m, CH), 2.10 (1H, m, CH), 1.60(1H, m, CH), 1.12(3H, d, CH_3).

5-7-10. N-(2-Methyl)allyl-N-(p-chlorophenyl)amine

N-(2-Methyl)allyl-N-(p-chlorophenyl)amine was carbonylated according to the general procedure to form 1-(p-chlorophenyl)-3-methylpyrrolidine (109) in 47% yield.

1-(p-Chlorophenyl)-3-methylpyrrolidine (109): **MS** (m/e) 197[M$^+$]; **^{1}H NMR**(δ ppm), 7.15 (2H, dd, aromatic), 6.45 (2H, dd, aromatic), 3.31 (3H, m, CH_2CH), 2.82(1H, dd, CH), 2.40 (1H, m, CH), 2.11 (1H, m, CH), 1.63 (1H, m, CH), 1.12 (3H, d, CH_3).

5-7-11. N-(2-Pentyl)allylaniline

N-(2-Pentyl)allylaniline was carbonylated according to the general procedure to

afford 1-phenyl-3-pentylpyrrolidine (111) in 83% yield.

1-Phenyl-3-pentanylpyrrolidine (111) **MS** (m/e) 217[M$^+$]; **^{1}H NMR**(δ ppm), 7.23 (2H, m, aromatic), 6.61 (3H, m, aromatic), 3.45 (1H, dd, CH), 3.35 (2H, m), 2.90 (1H, dd), 2.20 (2H, m), 1.40(8H, m), 0.92 (4H, m). **^{13}C NMR** (δ ppm), 147.98, 129.13, 115.17, 111.37, 53.34, 47.26, 38.72, 33.70, 31.82, 31.60, 27.87, 22.4328, 18.8526.

5-7-12. N-(2-Benzensulfonylmethyl)allylaniline

N-(2-Benzensulfonylmethyl)allylaniline was carbonylated according to the general procedure to afford 1-phenyl-2-methylpyrrolidine (102) in 47% yield.

5-7-13. N-Allyl-o-toluidine

N-Allyl-o-toluidine was carbonylated according to the general procedure to afford N-(n-propyl)-o-toluidine in 72% yield.[180]

N-(n-Propyl)-o-toluidine: MS (m/e) 149[M$^+$]; **^{1}H NMR** (δ ppm), 7.15 (2H, m, aromatic), 6.68 (2H, m, aromatic), 3.18 (2H, t, CH_2), 2.17 (3H, s, CH_3), 1.73 (2H, m, CH_2), 1.05 (3H, t, CH_3).

5-7-14. N-(2-Methyl)allyl-o-toluidine

N-(2-Methyl)allyl-o-toluidine was carbonylated according to the general procedure to afford 33% of N-(i-butyl)-o-toluidine[181] and 46% of 1-o-tolyl-3-methylpyrrolidine.

N-(i-Butyl)-o-toluidine: MS (m/e) 163[M$^+$]; **^{1}H NMR** (δ ppm), 7.11 (2H, m, aromatic), 6.65 (2H, m, aromatic), 3.57(1H, s, NH), 3.01 (2H, d, CH_2), 2.15 (3H, s, CH_3), 1.97 (1H, m, CH), 1.02 (3H, t, CH_3).

1-(o-Tolyl)-3-methylpyrrolidine: MS (m/e) 175 [M$^+$]; **^{1}H NMR** (δ ppm), 7.15 (2H, m, aromatic), 6.85 (2H, m, aromatic), 3.25 (3H, m, CH, CH_2), 2.91 (1H, dd, CH), 2.45 (1H,

m, CH), 2.10 (1H, m, CH), 1.55 (1H, m, CH), 2.35 (3H, s, CH_3), 1.15 (3H, d, CH_3). **Anal.** Calcd. for $C_{12}H_{17}N$: C, 82.23, H, 9.77, N, 8.00. Found: C, 82.34, H, 9.67, N, 7.61.

5-7-15. N-(2-Methyl)allyl-o-anisidine

N-(2-Methyl)allyl-o-anisidine was carbonylated according to the general procedure to afford 1-(o-anisyl)-2-methylpyrrolidine in 35% yield.

1-(o-Anisyl)-2-methylpyrrolidine: MS (m/e) 191[M^+]; **^{1}H NMR** (δ ppm), 6.75 (4H, m, aromatic), 3.83 (3H, s, CH_3), 3.46 (2H, m, CH_2), 3.23 (1H, m, CH), 2.92 (1H, dd, CH), 2.32 (1H, m, CH), 2.08 (1H, m, CH), 1.51 (1H, m, CH), 1.10 (3H, d, CH_3). **^{13}C NMR** (δ ppm), 150.19, 140.09, 121.17, 119.12, 114.90, 111.79, 58.08, 55.47, 50.35, 33.16, 32.58, 18.63. **Anal.** Cald. for $C_{12}H_{17}NO$: C, 75.35; H, 8.95; N, 7.32. Found: C, 75.31; H, 8.83; N, 7.42.

5-7-16. N-Allyl-o-anisidine

N-Allyl-o-anisidine was carbonylated according to the general procedure to afford N-(n-propyl)-o-anisidine in 82% yield.[182]

N-(n-Propyl)-o-anisidine: MS (m/e) 165[M^+], ^{1}H NMR (δ ppm) 6.7 (4H, m, aromatic), 3.83 (3H, s, CH_3), 3.06 (2H, t, CH_2), 1.65 (2H, m, CH_2), 0.95 (3H, t, CH_3).

5-8. Synthesis of Pyrrolidinones from N-Allyl-N-alkylamines Catalyzed by $NaBH_4$/CO/i-PrOH/Rh(I) System

General Procedure

A mixture of 2.0 mmol of the allylic amine, $NaBH_4$ (2.25 mmol), $RhH(CO)(PPh_3)_3$ (10) (0.02 mmol,1%), 2-propanol (0.5 ml) and CH_2Cl_2 (5.0 ml) were placed in a 45 ml

autoclave containing a glass liner. The autoclave was pressurized to 34.5 atm with carbon monoxide, and the mixture was heated with stirring for 30 h at 100°C. After cooling, water was added to remove unreacted $NaBH_4$. The organic phase was concentrated by rotary evaporation affording an oil. The products were isolated by a silica gel column using a 95:5 hexane/ethyl acetate as the eluant.

5-8-1. N-Allyl-N-cyclohexylamine

5-8-1-1. (10)

When N-allyl-N-cyclohexylamine was carbonylated according to the general procedure using (10) as the catalyst, 1-cyclohexyl-2-pyrrolidinone (116) was obtained in 78% yield.[136]

1-Cyclohexyl-2-pyrrolidinone (116): MS (m/e) 161[M^+]; **^{1}H NMR** (δ ppm), 3.87(1H, m, CH), 3.25 (2H, m, CH_2), 2.31(2H, m, CH_2), 1.92(2H, m, CH_2), 1.71(6H, m), 1.35(4H, m). **^{13}C NMR** (ppm), 174.32, 50.26, 42.64, 31.40, 30.02, 25.20, 17.87.

5-8-1-2. (10)/$NaBH(OAc)_3$

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure using $NaBH(OAc)_3$ instead of $NaBH_4$ to afford trace amount of (116).

5-8-1-3. (10)/$NaBH_3CN$

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure using $NaBH_3CN$ instead of $NaBH_4$ forming (116) in 20% yield.

5-8-1-4. (37)

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (37) as catalyst to afford (116) in 48% yield.

5-8-1-5. (43)

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (43) as catalyst to afford (116) in 61% yield.

5-8-2. N-(2-Methylallyl)-N-cyclohexylamine

N-(2-Methylallyl)-N-cyclohexylamine was carbonylated according to the general procedure to afford 1-cyclohexyl-4-methyl-2-pyrrolidinone (117) in 46% yield.[183]

1-Cyclohexyl-4-methyl-2-pyrrolidinone (117): **MS** (m/e) 161[M$^+$]; **^{1}H NMR** (δ ppm) 3.89(1H, m, CH), 3.40(1H, dd, J=8.4 Hz, J=7.9 Hz CH), 2.84(1H, dd, J=8.4 Hz, J=7.6 Hz CH), 2.51(1H, dd, CH), 2.34(1H, m, CH), 1.98(1H, dd, J=16.4 Hz, J=7.5 Hz, CH), 1.75(6H, m), 1.35(4H, m) 1.12(3H, d, CH_3). **^{13}C NMR** (δ ppm), 173.87, 50.00, 39.79, 30.07, 29.94, 26.35, 25.21, 25.15, 19.51.

5-8-3. N-Crotyl-N-cyclohexylamine

N-Crotyl-N-cyclohexylamine was carbonylated according to the general procedure to afford 1-cyclohexyl-3-methyl-2-pyrrolidinone (118) in 28% yield.

1-Cyclohexyl-3-methyl-2-pyrrolidinone (118): **MS** (m/e) 181[M$^+$]; **IR** 1663 cm^{-1}; **^{1}H NMR** (δ ppm), 3.85(1H, m, CH), 3.21(2H, m, CH_2), 2.44(1H, m, CH), 2.16(1H, m, CH), 1.60(7H, m), 1.23(4H, m), 1.12(3H, d, CH_3). **^{13}C NMR** (δ ppm), 176.90, 50.41, 40.75, 37.14, 30.03, 29.97, 27.11, 25.22, 16.10.

5-8-4. N-(t-Butyl)-N-allylamine

When N-(t-butyl)-N-allylamine was carbonylated according to the general procedure, 1-(t-butyl)-2-pyrrolidinone (119) was isolated in 15% yield.[184]

1-(t-Butyl)-2-pyrrolidinone (119): **MS** (m/e) 141[M$^+$], **^{1}H NMR (δ ppm)**, 3.45(2H, t,

CH_2), 2.32(2H, t, CH_2), 1.89(2H, m, CH_2), 1.36(9H, s, CH_3), **^{13}C NMR** (δ ppm) 175.70, 53.71, 45.77, 32.98, 27.47, 17.68.

5-8-5. N-Benzyl-N-allylamine

N-Benzyl-N-ailylamine was carbonylated according to the general procedure affording 1-benzyl-2-pyrrolidinone (120) in 51% yield.[183]

1-Benzyl-2-pyrrolidinone (120): **MS** (m/e) 175[M$^+$]; **^{1}H NMR (δ ppm)**, 7.25(5H, m, aromatic), 4.34(2H, s, CH_2), 3.16(2H, t, CH_2), 2.36(2H, t, CH_2), 1.92(2H, m, CH_2), **^{13}C NMR** (δ ppm) 175.13, 136.51, 128.65, 128.07, 127.53, 46.41, 46.34, 30.70, 17.42.

5-8-6. N-(n-Butyl)-N-(2-methylallyl)amine

N-(n-Butyl)-N-(2-methylallyl)amine was carbonylated according to the general procedure to afford 1-(n-butyl)-4-methyl-2-pyrrolidinone (121) in 28% yield.

1-n-Butyl-4-methyl-2-pyrrolidinone (121): **MS** (m/e) 155[M$^+$]; **^{1}H NMR** (δ ppm), 3.44(1H, dd, CH), 3.22(2H, t, CH_2), 2.91(1H, dd, CH), 2.45(2H, m, CH_2), 1.98(1H, dd, CH), 1.54-1.23(4H, m), 1.09(3H, d, CH_3) 0.88(3H, t, CH_3). **^{13}C NMR** (δ ppm), 174.59, 54.29, 41.93, 39.34, 29.10, 26.14, 19.77, 19.65, 13.51. **Anal.** Cald. for **$C_9H_{17}NO$**: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.51; H, 10.91; N, 8.88.

5-8-7. N-(n-Butyl)-N-allylamine

N-(n-Butyl)-N-allylamine was carbonylated according to the general procedure forming 1-(n-butyl)-2-pyrrolidinone (122) in 60% yield.[185]

1-(n-Butyl)-2-pyrrolidinone (122): **MS** (m/e) 155[M$^+$]; **^{1}H NMR** (δ ppm) 3.32(2H, t, CH_2), 3.22(2H, t, CH_2), 2.31(2H, m, CH_2), 1.95(2H, m, CH_2) 1.43(2H, m, CH_2), 1.24(2H, m, CH_2), 0.91(3H, t, CH_3), **^{13}C NMR** (δ ppm), 176.02, 47.97, 43.56, 31.86, 29.22, 21.15,

18.79, 14.57.

5-8-8. N-Cyclooctyl-N-allylamine

N-Cyclooctyl-N-allylamine was carbonylated according to the general procedure affording 1-cyclooctyl-2-pyrrolidinone (123) in 78% yield.

1-Cyclooctyl-2-pyrrolidinone (123): IR (C=O) 1669 cm^{-1}; **MS** (m/e) 195[M^+]; **^{1}H NMR** (δ ppm) 4.31(1H, m, CH), 3.37(2H, t, CH_2), 2.36(2H, t, CH_2), 1.96(2H, m, CH_2), 1.61(14H, m). **^{13}C NMR** (δ ppm), 173.84, 50.96, 42.86, 31.26, 30.69, 26.41, 25.44, 24.38, 17.99. **Anal.** Cald. for $C_{12}H_{21}NO$: C, 73.84; H, 10.84. Found C, 73.98; H, 10.74.

5-8-9. N-Benzyl-N-(2-methyl)allylamine

N-Benzyl-N-(2-methyl)allylamine was carbonylated according to the general procedure forming 1-benzyl-4-methyl-2-pyrrolidinone (124) in 67% yield.[174]

1-Benzyl-4-methyl-2-pyrrolidinone (124): MS (m/e) 189[M^+]; **^{1}H NMR** (δ ppm), 7.25(5H, m, aromatic), 4.39(2H, s, CH_2), 3.31(1H, dd, CH), 2.79(1H, dd, CH), 2.52(1H, m, CH), 2.34(1H, m, CH), 2.05(1H, m CH), 1.02(3H, d, CH_3). **^{13}C NMR** (δ ppm), 174.74, 136.51, 128.68, 128.09, 127.55, 53.74, 46.28, 39.19, 26.08, 19.53.

5-8-10. N-Benzyl-N-crotylamine

When N-benzyl-N-crotylamine was carbonylated according to the general procedure, 1-benzyl-3-methyl-2-pyrrolidinone (125) resulted in 40% yield.

1-Benzyl-3-methyl-2-pyrrolidinone (125): MS (m/e) 189[M^+]; **^{1}H NMR** (δ ppm), 7.24(5H, m, aromatic), 4.41(2H, s, CH_2), 3.44(2H, dd, CH_2), 2.47(1H, m, CH), 2.14(1H, m, CH), 1.57(1H, m, CH), 1.21(3H, d, CH_3) **^{13}C NMR** (δ ppm) 177.53, 136.63, 128.64, 128.02, 127.48, 46.51, 44.46, 36.53, 26.78, 16.15.

5-8-11. N-(2-Phenyl)ethyl-N-allylamine

N-(2-Phenyl)ethyl-N-allylamine was carbonylated according to the general procedure to afford 1-(2-phenyl)ethyl-2-pyrrolidinone (126) in 92% yield.[186]

1-(2-phenyl)ethyl-2-pyrrolidinone (126): **MS** (m/e) 180[M$^+$]; **^{1}H NMR** (δ ppm), 7.18(5H, m, aromatic), 3.44(2H, t, CH_2), 3.19(2H, t, CH_2), 2.77(2H, t, CH_2), 2.27(2H, t, CH_2), 1.85(2H, m, CH_2). **^{13}C NMR** (δ ppm), 175.10, 138.82, 128.66, 128.51, 126.42, 47.51, 43.87, 33.59, 30.78, 17.72.

5-8-12. N,N-Diallylamine

N,N-Diallylamine was carbonylated according to the general procedure to afford 1-allyl-2-pyrrolidinone (127) in 20% yield.[187]

1-Allyl-2-pyrrolidinone (127): **MS** (m/e) 125[M$^+$]; **^{1}H NMR** (δ ppm), 5.67(1H, m, CH), 5.14(2H, m, CH_2), 3.84(2H, d, CH_2), 3.33(2H, t, CH_2), 2.44(2H, t, CH_2), 1.97(2H, m, CH_2). **^{13}C NMR** (δ ppm), 174.92, 132.46, 117.76, 46.56, 45.01, 30.77, 17.53.

5-9. Synthesis of Pyrrolidinones from N-Allyl-N-alkylamines Catalyzed by Rh/Ru Co-Catalyst System under Syngas Atmosphere

General Procedure

A mixture of 2.0 mmol of the allylic amine, the Rh catalyst (0.02 mmol)/co-cayalyst (O.O2 mmol), and CH_2Cl_2 (5.0 ml) were placed in a 45 ml autoclave containing a glass liner. The autoclave was pressurized to 40 atm with syngas (CO/H_2, 1:1) and the mixture was heated with stirring for 24 h at 100°C. The products were isolated by a silica gel column using a 95:5 hexane/ethyl acetate as the eluant.

5-9-1. Carbonylation of N-Allyl-N-cyclohexylamine

5-9-1-1. (37)/–

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (37) in the absence of co-catalyst to form (116) in 15% yield.

5-9-1-2. (37)/$Ru_3(CO)_{12}$ (1:1)

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (37)/$Ru_3(CO)_{12}$ (1:1) as the catalyst affording (16) in 59% yield.

5-9-1-3. (37)/$[RuCl_2(CO)_3]_2$ (1:1)

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalyst to afford (116) in 59% yield.

5-9-1-4. (37)/$RuCl_2(PPh_3)_3$ (1:1)

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (37)/$RuCl_2(PPh_3)_3$ (1:1) as the catalyst to afford (116) in 24% yield.

5-9-1-5. (37)/RuO_2 H_2O (1:1)

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (37)/RuO_2 H_2O (1:1) as the catalyst to give (116) in 48% yield.

5-9-1-6. (37)/$NiCl_2$(dppb) (1:1)

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (37)/$NiCl_2$(dppb) (1:1) as the catalyst to afford (116) in 8% yield.

5-9-1-7. (37)/$PdCl_2(PPh_3)_2$ (1:1)

N-Allyl-N-cyclohexyiamine was carbonylated according to the general procedure with (37)/$PdCl_2(PPh_3)_2$ (1:1) as catalyst to afford (116) in 11% yield.

5-9-1-8. (10)

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (10), in the absence of a co-catalyst, to afford (116) in 13% yield.

5-9-1-9. (10)/$[RuCl_2(CO)_3]_2$ (1:1)

N-Allyl-N-cyclohexylamine was carbonylated according to the general procedure with (10)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalyst giving (116) in 18% yield.

5-9-2. Carbonylation of N-cyclohexyl-N-(2-methylallyl)amine

N-Cyclohexyl-N-(2-methylallyl)amine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalysts producing 1-cyclohexyl-4-methyl-2-pyrrolidinone (117) in 35% yield.

5-9-3. Carbonylation of N-crotyl-N-cyclohexylamine

N-Crotyl-N-cyclohexylamine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalysts affording 1-cyclohexyl-3-methyl-2-pyrrolidinone (118) in 14% yield.

5-9-4. Carbonylation of N-allyl-N-(t-butyl)amine

N-Allyl-N-(t-butyl)amine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalysts forming 1-(t-butyl)-2-pyrrolidinone (119) in 7% yield.

5-9-5. Carbonylation of N-allyl-N-benzylamine

N-Allyl-N-benzylamine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalysts to form 1-benzyl-2-pyrrolidinone (120) in 17% yield.

5-9-6. Carbonylation of N-(n-butyl)-N-(2-methyl)allylamine

N-(n-Butyl)-N-allylamine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalysts to afford 1-(n-butyl)-4-methyl-2-pyrrolidinone (121) in 39% yield.

5-9-7. N-Allyl-N-(n-butyl)amine

N-Allyl-N-(n-butyl)amine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalyst to form 1-(n-butyl)-2-pyrrolidinone (122) in 51% yield.

5-9-8. N-Allyl-N-cyclooctylamine

N-Allyl-N-cyclooctylamine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalyst to afford 1-cyclooctyl-2-pyrrolidinone (123) in 72% yield.

5-9-9. N-Benzyl-N-(2-methyl)allylamine

N-Benzyl-N-(2-methyl)allylamine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalysts to afford 1-benzyl-4-methyl-2-pyrrolidinone (124) in 39% yield.

5-9-10. N-Allyl-N-(2-Phenyl)ethylamine

N-Allyl-N-(2-Phenyl)ethylamine was carbonylated according to the general procedure with (37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalysts to afford 1-(2-phenyl)ethyl-2-pyrrolidinone (126) in 25% yield.

5-9-11. N,N-Diallylamine

N,N-Diallylamine was carbonylated according to the general procedure with

(37)/$[RuCl_2(CO)_3]_2$ (1:1) as the catalysts producing 1-allyl-2-pyrrolidinone (127) in 25% yield.

5-10. Reductive Carbonylation of N-(3-Butenyl)aniline

General Procedure

A mixture of 2.0 mmol of the N-(3-butenyl)aniline, $NaBH_4$ (2.25 mmol), Rh catalyst (0.02 mmol)/co-catalyst (0.02 mmol, 1%), 2-propanol (0.5 ml) and CH_2Cl_2 (5.0 ml) were placed in a 45 ml autoclave containing a glass liner. The autoclave was pressurized to 34.5 atm with carbon monoxide, and the mixture was heated with stirring for 30 hr at 100°C. The products were isolated by a silica gel column using a 95:5 hexane/ethyl acetate as the eluant.

5.10.1. (37)

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (37) in the absence of a co-catalyst to give 16% of 1-phenyl-3-methylpyrrolidine (102), 19% of 1-phenylpiperidine (141)[188], 8% of 1-phenyl-3-methyl-2-pyrrolidinone (143)[189] and 34% of a mixture of amino alcohols [(144)+(145)].

1-Phenylpiperidine (141): MS (m/e), 161(M⁺); **^{1}H NMR** (δ ppm), 7.23 (2H, m, aromatic), 6.89 (3H, m, aromatic), 3.12 (4H, t, 2 CH_2), 1.65 (4H, m, 2 CH_2), 1.54 (4H, m, 2CH_2). **^{13}C NMR** (δ ppm), 152.48, 129.13, 119.28, 116.64, 50.65, 25.80, 24.26.

1-Phenyl-3-methyl-2-pyrrolidinone (143): IR (C=O) 1690 cm^{-1}, **MS** (m/e), 175(M⁺), **^{1}H NMR** (δ ppm), 7.61 (2H, m, aromatic), 7.32 (2H, m, aromatic), 7.08 (1H, m, aromatic), 3.73(2H, m, CH_2), 2.64(1H, m, CH), 2.30(1H, m, CH), 1.72(1H, m, CH), 1.25(3H, d, CH_3).

^{13}C NMR (δ ppm), 176.73, 139.74, 128.77, 124.27, 119.74, 46.35, 38.10, 26.79, 15.94.

Amino alchols (144) and (145): MS (m/e), 179(M^+).

5-10-2. (37) at 130°C

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (37) in the absence of a co-catalyst at 130°C affording 13% of 1-phenyl-3-methylpyrrolidine (102), 19% of 1-phenylpiperidine (141), 17% of N-(n-butyl)aniline (142) and 33% of a mixture of aminoalcohols [(144)+(145)].

N-(n-Butyl)aniline (142): MS (m/e), 149(M^+).

5-10-3. (10)

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (10) in the absence of a co-catalyst to afford 21% of a mixture of (102) and (141) (46:54) and 20% of (142).

5-10-4. (37)/$RuCl_2(PPh_3)_3$ (1:1)

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (37)/$RuCl_2(PPh_3)_3$ (1:1) as the catalysts to afford 20% of (102), 42% of (141) and 22% of [(144) + (145)].

5-10-5. (37)/$RuCl_2(PPh_3)_3$ (1:5)

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (37)/$RuCl_2(PPh_3)_3$ (1:5) as the catalysts to afford 63% of a mixture of (102) and (141) (42:58) and 31% of [(144) + (145)].

5-10-6. (37)/$RuCl_2(PPh_3)_3$ (1:1), at 130°C

N-(3-Butenyl)aniline was carbonylated according to the general procedure with

(37)/$RuCl_2(PPh_3)_3$ (1:1) as the catalysts at 130°C to afford 57% of a mixture of (102) and (141) (39:61), 20% of (142) and 12% of [(144) + (145)].

5-10-7. (37)/$CoCl_2$ (1:1)

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (37)/$CoCl_2$ (1:1) as the catalyst system giving 21% of a mixture of (102) and (141) (33:67) and 10% of (142).

5-10-8. (37)/$NiCl_2$(dppb) (1:1)

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (37)/$NiCl_2$(dppb) (1:1) as the catalysts forming 74% of a mixture of (102) and (141) (45:55).

5-10-9. $NiCl_2$(dppb)

N-(3-Butenyl)aniline was carbonylated according to the general procedure in the absence of (37) with $NiCl_2$(dppb) as the catalysts to afford (142) selectively in 26% yield.

5-10-10. (37)/$CeCl_3$ (1:1)

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (37)/$CeCl_3$ (1:1) as the catalysts affording 32% of a mixture of (102) and (141) (42:58), 31% of (143) and 5% of [(144)+(145)].

5-10-11. (37)/$CeCl_3$ (1:10)

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (37)/$CeCl_3$ (1:10) as the catalysts to afford 21% of a mixture of (102) and (141) (52:48) and 35% of (143).

5-10-12. (37)/$PdCl_2(PPh_3)_2$ (1:1)

N-(3-Butenyl)aniline was carbonylated according to the general procedure with (37)/$PdCl_2(PPh_3)_2$ (1:1) as the catalysts to afford 82% of a mixture of (102) and (141) (36:64).

5-11. Hydroformylation of N-Allyl-N-arylamines

General Procedure

N-Allyl-N-arylamine(4.0 mmol), the Rh catalyst(0.04 mmol) and dppb (Rh:dppb= 1:2) in 10 ml of dichloromethane were stirred at 80°C, under 40 atm. of syngas for 12 hr. The reaction was worked up by removal of the solvent followed by a silica gel chromatography using hexane-ethyl acetate (95:5) as the eluant.

5-11-1. Hydroformylation of N-allylaniline

5-11-1-1. (37):dppb

N-Allylaniline was hydroformylated according to the general procedure with (37)/dppb(1:2) as the catalyst to afford 1-phenylpyrrolidine (95) in 68% yield. In the absence of dppb, a complicated mixture of products was formed.

5-11-1-2. (46)

N-Allylaniline was hydroformylated according to the general procedure with (46) as the catalyst to afford (95) in 75% yield.

5-11-1-3. (47):dppb

N-Allylaniline was hydroformylated according to the general procedure with (47)/dppb(1:4) as the catalyst affording (95) in 69% yield.

5-11-1-4. (47):dppb:$NaBPh_4$

N-Allylaniline was hydroformylated according to the general procedure with (47)/dppb/$NaBPh_4$(1:4:4) as the catalyst to afford (95) in 61% yield.

5-11-2. Hydroformylation of N-allyl-o-toluidine

N-Allyl-o-toluidine was hydroformylated according to the general procedure with (37)/dppb (1:2) as the catalyst to afford 1-(o-tolyl)-pyrrolidine in 67% yield.[178,179]

5-11-3. Hydroformylation of N-allyl-o-anisidine

N-Allyl-o-anisidine was hydroformylated according to the general procedure with (37)/dppb (1:2) as the catalyst to afford 1-(o-anisyl)pyrrolidine in 55% yield.[178,179]

5-11-4. Hydroformylation of N-allyl-p-anisidine

N-Allyl-p-anisidine was hydroformylated according to the general procedure with (37)/dppb (1:2) as the catalyst to afford 1-(p-anisyl)pyrrolidine (97) in 55% yield.

5-11-5. Hydroformylation of N-allyl-N-(1-naphthyl)amine

N-Allyl-N-(1-naphthyl)amine was hydroformylated according to the general procedure with (37)/dppb (1:2) as the catalyst to give 1-(1-naphthyl)pyrrolidine (103) in 59% yield.

5-12. Hydroformylation of N,N-Disubstituted anilines

General Procedure

A mixture of N,N-disubstituted aniline (4.0 mmol), the Rh catalyst (0.04 mmol) and phosphine (with different ratio to Rh complex) in 10 ml of methylene chloride were stirred at 80°C, under 40 atm. of syngas for 12 hr. The reaction was worked up by removal of the scivent followed by a silica gel chromatography using hexane-ethyl acetate (95:5) as

the eluant.

5-12-1. Hydroformylation of N-allyl-N-methylaniline

5-12-1-1. (37):dppb=1:2

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (37):dppb=1:2 as catalyst to afford 70% of 4-(N-methyl-N-phenyl)aminobutyraldehyde (154)[70], 9% of 1,4-di(N-methyl-N-phenyl)aminobutane (156)[190] and 5% yield of 1,3-dimethyl-2,4-dihydroquinoline (157).

4-(N-Methyl-N-phenyl)aminobutyraldehyde (154): MS (m/e), 177[M$^+$]; **^{1}H NMR** (δ ppm), 9.73(1H, t, CHO), 7.22(2H, m, aromatic), 6.71(3H, m, aromatic), 3.34(2H, t, CH_2), 2.92(3H, s, CH_3) 2.48(2H, t, CH_2), 1.92(2H, m, CH_2)2. **^{13}C NMR** (δ ppm), 201.88, 149.23, 129.27, 116.51, 112.43, 51.92, 41.26, 38.41, 19.70.

1,4-Di(N-methyl-N-phenyl)aminobutane (156): MS (m/e) 268[M$^+$]; **^{1}H NMR** (δ ppm), 7.25(4H, m, aromatic), 6.67(6H, m, aromatic), 3.34(4H, m, $2CH_2$), 2.91(6H, s, $2CH_3$). 1.63(4H, m, $2CH_2$) ^{13}C NMR (δ ppm) 149.24, 129.20, 116.03, 112.16, 52.67, 38.35, 24.45.

1,3-Dimethyl-2,4-dihydroquinoline (157): MS (m/e) 161[M$^+$]; **^{1}H NMR** (δ ppm), 7.02(2H, m, aromatic), 6.62(2H, m, aromatic), 3.19(1H, m, CH), 2.91(3H, s, CH_3), 2.85(1H, m, CH). 2.46(1H, m, CH), 2.12(1H, m, CH), 1.08(3H, d, CH_3) ^{13}C NMR (δ ppm), 146.03, 128.67, 126.72, 121.85, 115.80, 111.34, 58.08, 38.78, 36.05, 27.47, 18.88.

5-12-1-2. (37):dppb=1:1

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (37):dppb=1:1 as the catalyst to afford 66% of (154), 12% of (156).

5-12-1-3. (37):dppb=1:0

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (37):dppb=1:0 as the catalyst to afford 82% yield of a mixture of the linear and branched aldehyde in the ratio 67:33[70].

5-12-1-4. (37):PPh_3=1:2

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (37):PPh_3=1:2 as the catalyst to afford 73% of (154), 4% of (156).

5-12-1-5. (37):$P(OEt)_3$=1:2

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (37):PPh_3=1:2 as the catalyst to afford 41% of (154), 39% of (156).

5-12-1-6. (37):1,10-Phenanthroline=1:2

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (37):1,10-phenanthroline=1:2 as the catalyst. The starting material was recovered after work-up.

5-12-1-7. (37):$P(OPh)_3$=1:2

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (37):$P(OPh)_3$=1:2 as the catalyst to afford 61% of (154), 4% of (156) and 15% of (157).

5-12-1-8. (37):$P(cyclohexyl)_3$=1:2

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (37):$P(cyclohexyl)_3$=1:2 as the catalyst to afford a complicated mixture of products.

5-12-1-9. (46)

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (46) as the catalyst to form 5% of (154), and 82% of (156).

5-12-1-10. (47):dppb=1:4

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with (47):dppb=1:4 as the catalyst to afford (154) in 8% yield..

5-12-1-11. $[Rh^{+}(COD)_2]BF_4^{-}$:dppb=1:2

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with $[Rh^{+}(COD)_2]BF_4^{-}$:dppb=1:2 as the catalyst to afford 64% of (154) and 9% of (156).

5-12-1-12. $[Rh^{+}(COD)_2]BF_4^{-}$:dppb=1:1

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with $[Rh^{+}(COD)_2]BF_4^{-}$:dppb=1:1 as the catalyst to afford 42% of (154) and 41 of (156).

5-12-1-13. $[Rh^{+}(COD)_2]BF_4^{-}$:dppb=1:0

N-Allyl-N-methylaniline was hydroformylated according to the general procedure with $[Rh^{+}(COD)_2]BF_4^{-}$:dppb=1:0 as the catalyst to afford 46% of N-propyl-N-methylaniline and 31% of (156).

5-12-2. Hydroformylation of N-acetyl-N-allylaniline

N-Acetyl-N-allylaniline was hydroformylated according to the general procedure with (37):dppb=1:2 as the catalyst to afford linear (161) and branched aldehyde (162) in 76% yield in the ratio of 52:48.

(161): MS (m/e), 205[M^{+}]; **^{1}H NMR** (δ ppm), 9.52(1H, d, CHO), 7.25(5H, m, aromatic), 4.17(1H, dd, CH), 3.25(1H, dd, CH), 2.53(1H, m, CH), 1.78(3H, d, CH_3), 1.02(3H, d, CH_3).

(162): **MS** (m/e), 205[M$^+$]; **^{1}H NMR** (δ ppm), 9.71(1H, t, CHO), 7.52(5H, m, aromatic), 3.67(2H, t, CH_2), 2.45(2H, t, CH_2), 1.78(3H, s, CH_3), 1.76(2H, m, CH_2).

5-12-3. Hydroformylation of N-allyl-N-methyl-p-toluidine

When N-methyl-N-allyl-toluidine was hydroformylated according to the general procedure with (37):dppb=1:2 as the catalyst, 4-[N-methyl-N-(p-tolyl)]aminobutyraldehyde was obtained in 46% yield.

4-(N-Methyl-N-p-tolyl)aminobutyraldehyde MS (m/e) 191[M$^+$]; **^{1}H NMR** (δ ppm), 9.71(1H, t, CHO), 7.02(2H, d, aromatic), 6.61(2H, d, aromatic), 3.34(2H, t, CH_2), 2.92(3H, s, CH_3). 2.45(2H, t, CH_2), 2.24(3H, s, CH_2), 1.90(2H, m, CH_2). **^{13}C NMR** (δ ppm), 201.88, 147.37, 129.83, 125.89, 112.97, 52.36, 41.42, 38.69, 20.35, 19.83.

5-13. Silylhydroformylation of Alkynes

General procedure

A mixture of alkyne (4 mmol), silane (4.5 mmol) and Rh(I) catalyst (37) (0.04 mmol) in 10 ml of CH_2Cl_2 was placed in a 45 ml autoclave and the reactor was pressured to 40 atm with CO:H_2 (1:1). The reaction mixture was stirred at 40°C for 24 hr and then cooled to room termperature. Purification was achieved by silica gel chromatography using hexane/ethyl acetate (95:5) as the developer.

5-13-1. Silylhydroformylation of 1-hexyne

5-13-1-1. $HSiMe_2Ph$/(37)

1-Hexyne was siylhydroformylated with $HSiMe_2Ph$ according to the general procedure to afford (172) in 73% yield.

(E)-2-dimethylphenylsilylmethyl-2-hexen-1-al (172): MS (m/e) 246(M^+); **^{1}H NMR** (δ ppm), 9.30(s, 1H, CHO), 7.49(m, 2H, aromatic protons), 7.32(m, 3H, aromatic protons), 6.27(t, 1H, CH, J=7.4 Hz), 1.97(q, 2H, CH_2, J=7.4 Hz), 1.97(s, 2H, CH_2), 1.32(m, 2H, CH_2), 0.83(t, 3H, CH_3, J=7.4 Hz), 0.23(s, 6H, CH_3). **^{13}C NMR** (δ ppm) 195.57, 152.47, 141.24, 138.48, 133.68, 129.12, 127.75, 31.28, 21.80, 14.35, 13.88, -2.70. **Anal.** Calcd for **$C_{15}H_{22}SiO$**: C, 73.17; H, 8.90. Found:C, 73.38; H, 8.67.

5-13-1-2. $HSiMe_2Ph$/(37) in the absence of H_2

Compound (173)[156] was isolated in 89% yield when 1-hexyne was silylhydroformylated with $HSiMe_2Ph$ in the absence of H_2 (CO 40 atm).

(Z)-1-Dimethylphenylsilyl-2-formyl-1-hexene (173): MS (m/e) 246(M^+); **^{1}H NMR** (δ ppm), 9.75(1H, s, CHO), 7.52(2H, m, aromatic), 7.34(3H, m, aromatic), 6.91(1H, s, CH), 2.26(2H, t, CH_2), 1.34(4H, m, $2CH_2$), 0.89(3H, t, CH_3), 0.51(6H, s, $2CH_3$).

5-13-1-3. $HSiMe_2Ph$/(46)

1-Hexyne was silylhydroformylated with $HSiMe_2Ph$ and (46) [instead of (37)] as the catalyst to afford (173) in 87% yield.

5-13-1-4. $HSiMe_2Ph/Rh_6(CO)_{16}$

1-Hexyne was silylhydroformylated with $HSiMe_2Ph$ and $Rh_6(CO)_{16}$ [instead of (37)] as the catalyst to form (173) in 92% yield.

5-13-1-5. $HSi(Et)_3$

1-Hexyne was silylhydroformylated with triethylsilane according to the general procedure to afford (174) in 78% yield.

(E)-2-triethylsilylmethyl-2-hexen-1-al (174): MS (m/e) 226(M^+), **^{1}H NMR** (δ ppm),

9.28(s, 1H, CHO), 6.22(t, 1H, CH, J=7.4 Hz), 2.23(q, 2H, CH_2, J=7.4 Hz), 1.65(s, 2H, CH_2), 1.49(m, 2H, CH_2), 0.88(m, 12H, CH_3), 0.46(q, 6H, CH_2, J=7.3 Hz). **^{13}C NMR** (δ, ppm) 195.08, 151.31, 142.24, 31.32, 21.91, 13.88, 9.91, 7.24, 3.70. **Anal.** Calcd for **$C_{13}H_{26}SiO$:** C, 69.00; H, 11.50. Found: C, 68.66; H, 11.21.

5-13-1-6. $HSiPh_3$

1-Hexyne was silylhydroformylated with $HSiPh_3$ according to the general procedure to afford (175) in 62% yield.

(E)-2-triphenylsilylmethyl-2-hexen-1-al (175): MS (m/e), 370(M^+); **^{1}H NMR** (δ ppm) 9.13(s, 1H, CHO), 7.52(m, 6H, aromatic protons), 7.37(m, 9H, aromatic protons), 6.25(t, 1H, CH, J=7.4 Hz), 2.59(s, 2H, CH_2), 1.82(q, 2H, CH_2, J=7.4 Hz), 1.21(m, 2H, CH_2), 0.73(t, 3H, CH_3, J=7.4 Hz). **^{13}C NMR** (δ ppm), 194.24, 152.90, 140.63, 135.92, 134.14, 129.60, 127.74, 31.36, 21.65, 13.82, 11.77. **Anal.** Calcd. for **$C_{25}H_{26}SiO$:** C, 81.08; H, 7.03. Found: C, 81.00; H, 7.32.

5-13-2. Silylhydroformylation of 4-phenyl-1-butyne

5-13-2-1. $HSi(Et)_3$

4-Phenyl-1-butyne was silylhydroformylated with $HSiEt_3$ according to the general procedure to afford (176) in 71% yield.

(E)-4-Phenyl-2-triethylsilylmethyl-2-buten-1-al (176): MS (m/e) 274(M^+); **^{1}H NMR** (δ ppm), 9.36(s, 1H, CHO), 7.26(m, 5H, aromatic protons), 6.43(t, 1H, CH, J=7.5 Hz), 3.62(d, 2H, CH_2, J=7.5 Hz), 1.83(s, 2H, CH_2), 0.95(t, 9H, CH_3, J=7.3 Hz), 0.53(q, 6H, CH_2, J=7.3 Hz). **^{13}C NMR** (δ ppm) 194.89, 149.01, 142.37, 139.05, 129.43, 129.21, 126.35, 37.89, 10.74, 7.98, 4.11. **Anal.** Calcd for **$C_{17}H_{26}SiO$:** C, 74.45; H, 9.49. Found:

C, 74.81; H, 9.01.

5-13-2-2. $HSiMe_2Ph$

When 4-phenyl-1-butyne was silylhydroformylated with $HSiMe_2Ph$, (177) was obtained in 64% yield.

(E)-4-Phenyl-2-dimethylphenylsilylmethyl-2-buten-1-al (177): MS (m/e) 294(M^+); **^1H NMR** (δ ppm), 9.32(s, 1H, CHO), 7.32(m, 10H, aromatic protons), 6.41(t, 1H, CH, J=7.5 Hz), 3.23(d, 2H, CH_2, J=7.5 Hz), 2.05(s, 2H, CH_2), 0.32(s, 6H, CH_3). **^{13}C NMR** (δ ppm) 194.78, 150.01, 141.59, 138.61, 138.29, 133.66, 129.28, 128.69, 128.39, 127.89, 126.57, 35.12, 14.64, -2.68. **Anal.** Calcd for **$C_{19}H_{22}SiO$**: C, 77.55; H, 7.48. Found: C, 77.54; H, 7.60.

5-13-2-3. $HSiPh_3$

When 4-phenyl-1-butyne was silylhydroformylated with $HSiPh_3$ (178) was obtained in 54% yield.

(E)-4-Phenyl-2-triphenylsilylmethyl-2-buten-1-al (178): MS (m/e) 418(M^+); **^1H NMR** (δ ppm) 9.18(s, 1H, CHO), 7.62-6.91 (m, 20H, aromatic protons), 6.42(t, 1H, CH, J=7.5 Hz), 3.12(d, 2H, CH_2, J=7.5 Hz), 2.73(s, 2H, CH_2). **^{13}C NMR** (δ ppm), 194.01, 150.54, 126.56, 35.35, 12.10.

5-13-3. Silylhydroformylation of 5-cyano-1-pentyne (180)

5-Cyano-1-pentyne (180) was silylhydroformylated with $HSiEt_3$, according to the general procedure, to afford (181) in 93% yield. When this reaction was carried out at 90°C, the yield of (181) was 84%.

(Z)-5-Cyano-1-triethylsilyl-1-penten-2-al (181): MS (m/e) 237(M^+); **^1H NMR** (δ ppm),

9.18(s, 1H, CHO), 6.81(s, 1H, CH), 2.43(t, 2H, CH_2, J=7.4 Hz), 1.76(m, 2H, CH_2), 0.97(t, 9H, CH_3, J=7.3 Hz), 0.68(q, 6H, CH_2, J=7.3 Hz). **^{13}C NMR** (δ ppm) 192.98, 154.96, 151.32, 119.25, 31.35, 24.29, 16.62, 7.35, 5.26. MS(m/e) 237(M^+). **Anal.** Calcd for **$C_{13}H_{23}SiON$**: C, 65.82; H, 9.70. Found: C, 66.07; H, 9.83.

5-13-4. Silylhydroformylation of 5-chloro-1-pentyne (182)

5-13-4-1. $HSi(Et)_3$

When 5-chloro-1-pentyne (182) was silylhydroformylated with $HSiEt_3$ (183) was isolated in 38% yield.

(E)-5-Chloro-1-triethylsilyl-2-penten-2-al (183): MS (m/e) 231(M^+-15), **^{1}H NMR** (δ ppm), 9.34(s, 1H, CHO), 6.29(t, 1H, CH, J=7.3 Hz), 3.62(t, 2H, CH_2, J=7.3 Hz), 2.74(q, 2H, CH_2, J=7.3 Hz), 1.69(s, 2H, CH_2), 0.87(t, 9H, CH_3, J=7.35 Hz), 0.48(q, 6H, CH_2, J=7.35 Hz). **^{13}C NMR** (δ ppm), 194.66, 145.07, 42.75, 32.18, 10.46, 7.27, 3.75. **Anal.** Calcd for **$C_{12}H_{23}SiOCl$**: C, 58.53; H, 9.30. Found: C, 58.82; H, 9.34.

5-13-4-2. $HSiMe_2Ph$

5-Chloro-1-pentyne (182) was silylhydroformylated with $HSiMe_2Ph$, according to the general procedure, to form (184) in 62% yield.

(E)-5-Chloro-1-dimethylphenylsilyl-2-penten-2-al (184): MS (m/e) 243(M^+-15); **^{1}H NMR** (δ ppm), 9.33(s, 1H, CHO), 7.45(m, 2H, aromatic) , 7.32(m, 3H, aromatic), 6.27(t, 1H, CH, J=7.3 Hz), 3.31(t, 2H, CH_2, J=7.3 Hz), 2.34(q, 2H, CH_2, J=7.3 Hz), 1.92(s, 2H, CH_2), 0.25(t, 6H, CH_3). **^{13}C NMR** (δ ppm) 194.41, 146.07, 142.94, 137.90, 133.49, 129.22, 127.76, 42.49, 31.87, 14.83, -2.93. **Anal.** Calcd for **$C_{14}H_{19}SiOCl$**: C, 63.15; H, 7.14. Found: C, 63.48; H, 7.18.

5-13-5. Silylhydroformylation of 3-butynyl acetate (185)

3-Butynyl acetate (185) was silylhydroformylated with $HSiEt_3$ according to the general procedure to afford (186) in 61% yield.

3-Formyl-4-(triethylsilyl)butyl acetate (186): **^{1}H NMR** (δ ppm), 9.51(d, 1H, CHO, J=2.1 Hz), 4.07(m, 2H, CH_2), 2.42(m, 1H, CH), 2.01(m, 1H, CH), 1.98(s, 3H, CH_3), 1.73(m, 1H, CH), 0.92(m, 10H, CH, CH_2), 0.55(m, 7H, CH, CH_2). **^{13}C NMR** (δ ppm), 203.30, 170.74, 61.96, 44.92, 30.63, 20.74, 10.53, 7.24, 3.67. **Anal.** Calcd for **$C_{13}H_{26}O_3Si$**: C, 60.46; H, 10.07. Found: C, 60.81; H, 10.19.

5-13-6. Silylhydroformylation of 3-butynyl tosylate (187)

3-Butynyl tosylate (187) was siylhydroformylated with $HSiEt_3$ according to the general procedure to afford (188) in 54% yield.

3-Formyl-4-(triethylsilyl)butyl tosylate (188): **^{1}H NMR** (δ ppm), 9.45(d, 1H, CHO, J=2.1 Hz), 7.74(d, 2H, aromatic protons), 7.32(d, 2H, aromatic protons), 4.04(m, 2H, CH_2), 2.43(m, 4H, CH + CH_3), 1.98(m, 1H, CH), 1.75(m, 1H, CH), 0.89(t, 9H, $3CH_3$, J=7.6 Hz), 0.79(dd, 1H, CH, J=15.1 Hz), J=7.0 Hz), 0.50(q, 6H, $3CH_2$, J=7.6 Hz), 0.47(dd, 1H, CH, J=15.1 Hz, J=7.6 Hz). **^{13}C NMR** (δ ppm) 202.82, 144.88, 132.78, 129.85, 128.01, 127.87, 67.95, 44.03, 30.62, 10.70, 7.30, 3.71.

5-13-7. Silylhydroformylation of N-methyl-N-propargylaniline (189)

When N-methyl-N-propargylaniline (189) was silylhydroformylated with $HSiEt_3$, (190) was obtained in 83% yield.

3-(N-Methyl-N-phenyl)amino-2-(triethylsilylmethyl)propane (190): **MS** (m/e) 277[M^+]; **^{1}H NMR** (δ ppm), 7.21(2H, m, aromatic protons), 6.69(3H, m, aromatic protons), 3.17(1H,

dd, J=6.0 Hz, CH), 2.97(1H, dd, J=8.9 Hz, J=14.5 Hz, CH), 2.93(3H, s, CH_3), 2.04(1H, m, CH) 0.93(3H, d, J=7.5 Hz, CH_3), 0.92(9H, t, J=7.7 Hz, $3CH_3$), 0.64(1H, dd, J=3.3 Hz, J=7.5 Hz, CH_3), 0.57(6H, q, J=7.5 Hz, $3CH_2$), 0.35(1H, dd, J=10.5 Hz, J=14.9 Hz, CH). **^{13}C NMR** (δ ppm), 149.76, 123.01, 115.61, 111.85, 62.91, 39.29, 28.62, 20.80, 16.80, 7.47, 4.05.

5-13-8. Silylhydroformylation of phenylacetylene

When phenylacetylene was silylhydroformylated with $HSiEt_3$, (196) was obtained in 87% yield.[156]

(Z)-α-Formyl-β-triethylsilylstyrene (196): MS (m/e) 231 (M^+-15); **^{1}H NMR** (δ ppm), 10.02(1H, s, CHO), 7.38(5H, m, aromatic), 7.12 (1H, s, CH), 1.05(9H, t, $3CH_3$), 0.82 (6H, q, $3CH_2$). **^{13}C NMR** (δ ppm), 192.20, 155.22, 152.19, 137.33, 128.13, 127.99, 127.93, 7.35, 5.11.

5-13-9. Silylhydroformylation of propargyl alcohol

Propargyl alcohol was silylhydroformylated with $HSiEt_3$, according to the general procedure, affording (197) in 93% yield.[158]

(Z)-2-Formyl-1-triethylsilyl-1-propen-3-ol (197): MS (m/e) 165 (M^+-15); **^{1}H NMR** (δ ppm), 9.73(s, 1H, CHO), 6.98(1H, t, J=1.4 Hz, CH), 4.28(2H, d, J=1.4 Hz, CH_2), 0.95(9H, t, $3CH_3$), 0.56(6H, q, $3CH_2$). **^{13}C NMR** (δ ppm), 193.62, 155.01, 146.62, 62.20, 7.31, 5.15.

5-13-10. Silylhydroformylation of N-(1,1-dimethyl)propargylaniline (193)

N-(1,1-Dimethyl)propargylaniline (193) was silylhydroformylated with $HSiEt_3$, according to the general procedure, to afford (198) in 91% yield.

(Z)-2-Formyl-3-methyl-3-(N-phenyl)amino-1-triethylsilyl-1-butene (198): MS (m/e) 303

(M⁺); **^{1}H NMR** (δ ppm), 9.98(1H, s, CHO), 7.09(2H, m, aromatic), 7.12 6.92(1H, s, CH), 6.67(1H, m, aromatic), 6.54(2H, m, aromatic), 4.05(1H, s, NH), 1.56(6H, s, $2CH_3$), 0.91(9H, t, $3CH_3$), 0.68(6H, q, $3CH_2$). **^{13}C NMR** (δ ppm), 193.46, 160.05, 148.44, 146.14, 128.68, 117.89, 116.13, 57.08, 28.61, 7.49, 5.17. **Anal.** Cald. for **$C_{18}H_{29}NO$**: C,71.29; H,9.57; N,4.62. Found: C, 72.02; H, 9.63; N, 4.85.

5-13-11. Silylhydroformylation of 3-methyl-1-pentyne

3-Methyl-1-pentyne was silylhydroformylated with $HSiMe_2Ph$, according to the general procedure, forming (199) in 94% yield.

(Z)-1-Dimethylphenylsilyl-2-formyl-3-methyl-1-pentene (199): MS (m/e) 231 (M^+-15); **^{1}H NMR** (δ ppm), 9.78(s, 1H, CHO), 7.56(m, 2H, aromatic protons), 7.34(m, 3H, aromatic protons), 6.87(s, 1H, CH), 2.72(m, 1H, CH), 1.38(m, 2H, CH_2), 1.02(d, 3H, CH_3, J=7.3 Hz), 0.84(t, 3H, CH_3, J=7.3 Hz), 0.52(s, 6H, CH_3). **^{13}C NMR** (δ ppm), 193.32, 162.09, 146.89, 138.16, 133.51, 129.43, 128.16, 34.86, 28.87, 19.52, 11.75, 0.01. **Anal.** Calcd for **$C_{15}H_{22}SiO$**: C, 73.17; H, 8.9. Found: C, 72.78; H, 8.51.

5-13-12. Silylhydroformylation of 1-hexyne with $DSiMe_2Ph$

The deuterated silane was prepared by reduction of $ClSiMe_2Ph$ with $LiAlH_4$ in ether as described in the literature.[191] A mixture of 1-hexyne (328 mg, 4 mmol), $DSiMe_2Ph$ (685 mg, 5.0 mmol) and the Rh(I) complex (37) (24 mg, 0.04 mmol) in 10 ml of CH_2Cl_2 were placed in an autoclave under CO/H_2 (1:1, 40 atm). The mixture was stirred at 40°C for 24 hr. The partially deuterated silylalkene (172-d) was isolated in 53% yield by column chromatography on silica gel using a 95:5 hexane-ethyl acetate as eluent. For ^{1}H and ^{2}H NMR data, see Fig. 4-4 and 4-5 (Section 4-2-3).

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Claims to Original Research

1. Highly regioselective (95-100%) hydroformylation of allyl acetates to γ-formylpropyl acetates and α,β-unsaturated esters to β-aldehydoesters, respectively, catalyzed by the zwitterionic rhodium(1,5-cyclooctadiene)tetraphenylborate complex, $Rh^{+}(COD)BPh_4^{-}$, in the presence of the bidentate ligand, 1,4bis(diphenylphosphino)-butane (dppb).

2. Regiospecific reductive carbonylation of allyl alcohols with carbon monoxide/sodium borohydride/2-propanol system to γ-butyrolactones.

3. Highly regioselective (>90%) reductive carbonylation of vinylarenes with $Rh^{+}(COD)BPh_4^{-}/NaBH_4$ /CO/i-PrOH to α-(hydroxymethyl)ethylarenes.

4. Regiospecific reductive cyclocarbonylation of N-allylanilines with synthesis gas to N-arylpyrrolidines catalyzed by $Rh^{+}(COD)BPh_4^{-}$/dppb.

5. Regiospecific preparation of N-alkylpyrrolidones by cyclocarbonylation of N-allyl-N-alkylamines with CO/H_2 or $CO/NaBH_4$ /i-PrOH catalyzed by $Rh^{+}(COD)BPh_4^{-}$ /$[Ru(CO)_3Cl_2]$ or $Rh^{+}(COD)BPh_4^{-}$.

6. Highly regioselective (>80%) catalytic synthesis of 3-(N-aryl-N-methyl)aminobutyraldehyde by reductive carbonylation of N-allyl-N-methylaniline with synthesis gas in the presence of $Rh^{+}(COD)BPh_4^{-}$/dppb.

7. Chemoselective (82%) synthesis of 1,4-di(N-methyl-N-phenyl)aminobutane from N-allyl-N-methylaniline under hydroformylation conditions in the presence of the rhodium (I) cationic complex, $[Rh^{+}(COD)dppb]BF_4^{-}$.

8. Stereospecific synthesis of (E)-β-silylalkenals (including functionally substituted derivatives) using newly discovered reaction of silylhydroformylation of terminal alkynes with hydrosilane/carbon monoxide/hydrogen catalyzed by $Rh^{+}(COD)BPh_4$. Highly chemoselective preparation of functionally substituted saturated β-silylaldehydes by the catalytic silylhydroformylation of O-protected 3-butyn-1-ols. Synthesis of N-silylalkyl derivative of aniline by silylhydroformylation of N-propargyl-aniline catalyzed by the Rh(I)zwitterionic complex.