INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Bell & Howell Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®

Université d'Ottawa · University of Ottawa

0-612-48183-2

بسم الله الرحمن الرحيم

وَقُل رَّبِّ زِدْنِي عِلْمًا

Dedicated To
My Wonderful
Mother

ACKNOWLEDGMENTS

I wish to express my gratitude to my supervisor, Dr. Howard Alper, for his guidance, patience, understanding and encouragement.

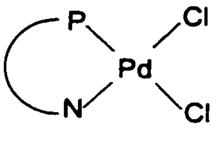
Thanks are owed to Dr. Glenn Yap for the X-ray analysis, Dr. Glenn Facey and Mr. Raj Capoor for NMR experiments, Dr. Clem Kazakoff for mass spectra and to all the staff members of the department for their continuous help.

I wish to gratefully acknowledge Chitchamai Larksarp and Vladmir Kuznetsov for their help and encouragement throughout the years.

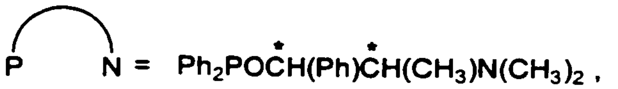
Special thanks to my best friends "Eyad" and "Faiza" and to my family, my brothers (Mohammad and Youssef), my sisters (Soussan and Sara), my brother-in-law (Husni), most amazing nephews (Fadel and Mohammad), and last but not least, my wonderful fiancé (Ibrahim Mortada) for his love and affection. Finally, I can't begin to express my gratitude to my amazing mother, *Amira Dakroub*, for her unconditional love, understanding, and constant encouragement and advice.

ABSTRACT

The chiral (P,N)-ligated dichloropalladium (II) complexes, cis-dichloro[(+)*O*-diphenylphosphino-N-methylephedrine] palladium dichloride (**2.15a**), cis-dichloro[(*S*)-Prophos] palladium dichloride (**2.15b**), and cis-dichloro[(*S*)-1-methyl-2-(diphenylphosphinomethyl)pyrrolidine] palladium dichloride (**2.15c**) complexes, have been synthesized and completely characterized in the solid state. The synthetic procedure involves a simple one pot reaction of equivalent amounts of $(CH_3CN)_2PdCl_2$ and the corresponding ligand. These complexes are active precatalysts for the cycloaddition reactions of aziridines and heterocumulenes, yielding imidazolidinimines (**2.34**, X=NAr) for the case of carbodiimides. The cycloaddition reactions of aziridines and isocyanates are dependent on the catalyst used. When **2.15b** is the catalyst, one product (imidazolidinones **2.34**, X=O) is formed. However, when either **2.15(a,c)** are used, two products (imidazolidinones **2.34**, X=O and oxazolidinimines **2.35**, X=O) are formed. Catalysts **2.15(a-c)** failed to provide stereoselectivity. The one pot reaction of $(CH_3CN)_2PdCl_2$ and two equivalents of the chiral aminophosphinite ligand L*, [L*= (+)*O*-diphenylphosphino-N-methylephedrine (**2.2**), (*S*)-1-methyl-2-(diphenylphosphinomethyl) pyrrolidine (**2.8**)] resulted in the formation of $[Ph_2P(O)PdL^*Cl]$ **2.18(a,c)**. A mechanism was proposed explaining the formation of the phosphine oxide moiety $[Ph_2P(O)]$ in these complexes. The structure of **2.18a** was confirmed by an X-Ray crystal structure determination. The geometry of the compound is square planar with a slight distortion caused by the "trans-influence" of the phosphorus groups, causing them to be cis to each other.

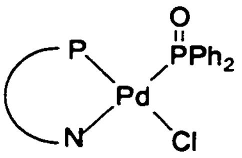


2.15

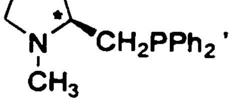


$= Ph_2PO\overset{*}{C}H(Ph)\overset{*}{C}H(CH_3)N(CH_3)_2$,

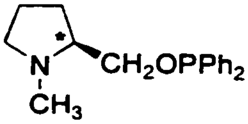
2.2
a



2.18



2.7
b



2.8
c

ABBREVIATIONS

Anal	analytical
atm	atmosphere
BOC	*tert*-butyoxycarbonyl
br	broad
t-Bu	*tert*-butyl
calcd	calculated
d	doublet
dba	dibenzylideneacetone
dd	doublet of doublets
dppb	diphenylphosphinebutane
dppp	diphenylphosphinepropane
ee	enantiomeric excess
Et	ethyl group
FT-IR	Fourier-transform infrared
g	grams
GC	gas chromatography
H	hours
Hz	Hertz
J	coupling constant, in Hz
L	ligand
M	metal center
Me	methyl group
Min	minutes
ml	milliliters
mmol	millimols
mp	melting points
MS	mass spectrometry
NMR	Nuclear Magnetic Resonance

Ph	phenyl group
ppm	parts per million
PPN	(triphenylphosphine)iminium
psi	pounds per square inch
q	quartet
rt	room temperature
s	singlet
t	triplet
T	Temperature
THF	tetrahydrofuran
TLC	thin layer chromatography

TABLE OF CONTENTS

List of Tables

List of Figures

1. INTRODUCTION

The development of catalytic methods for a range of synthetically useful transformations is one of the most intensely studied areas in contemporary organic synthesis because it offers many advantages, such as the economic benefits arising from the reduced use of expensive materials, and the environmental benefits of reduced waste. This is particularly true in the development of approaches to enantiomerically pure compounds where enantioselective catalysis compares favourably to the conventional methods of asymmetric synthesis which require enantiopure reagents or auxiliaries. This is particularly useful commercially in the pharmaceutical industry, where the benefits of producing enantiopure drugs rather than racemates is clearly recognized, which provides much of the impetus for the development of efficient enantioselective catalysts. At the forefront of this development is the application of "man-made" chiral organometallic complexes in homogeneous catalysis.

During the past few decades, the importance of asymmetric synthesis in organic chemistry has increased because of the increasing availability of optically pure, chiral organic compounds. The availability of these compounds eliminates the use of expensive optically active starting materials in asymmetric synthesis. Asymmetric catalysts are an intensely studied class of chemical substances due to their important use in catalysis, which is generally the most efficient way of performing some chemical reactions. Heterogeneous asymmetric catalysts seem to be of a limited value,[1] and heterogeneous catalysis generally leads to moderate optical yields. As a result, important progress in the field of asymmetric synthesis was made possible by the discovery of homogeneous asymmetric catalysts.[2] These catalysts are complexes of transition metals with various chiral ligands, and are soluble in organic solvents. Their achiral precursors were introduced into laboratory practice more than 30 years ago by Wilkinson and Osborn.[3] These catalysts turned out to be far more reactive than any of the previous heterogeneous catalysts. Soon after, such catalysts were successfully used for asymmetric hydrogenation,[4] hydrosilylation,[4(c,f),5] cross-coupling,[4c,6] alkylation,[4c,7] cyclization,[8] and intramolecular cyclization[9] reactions.

The catalyst used in such reactions must possess a chirality carrier. In principle, the central transition metal atom could carry out this property, but one or more chiral ligands were assumed to be more convenient. A number of catalysts with various chiral ligands were thus synthesized during the past decade.[10] Rational steric modification of the chiral ligands were performed to markedly improve the optical yields. On the other hand, chemical modifications of the ligands extended the use of these catalysts to a larger selection of substrates. The objective was to synthesize new various chiral ligands to improve the optical yields of the products in asymmetric synthesis reactions. A large variety of chiral ligands were synthesized for this purpose.[10a]

In view of the extensive literature on the synthesis and use of chiral ligands,[10a,11] this section will be limited to chiral ligands containing both phosphorus and nitrogen atoms. Some of these chiral aminophosphine and aminophosphinite (P,N) ligands are shown in Fig.1.

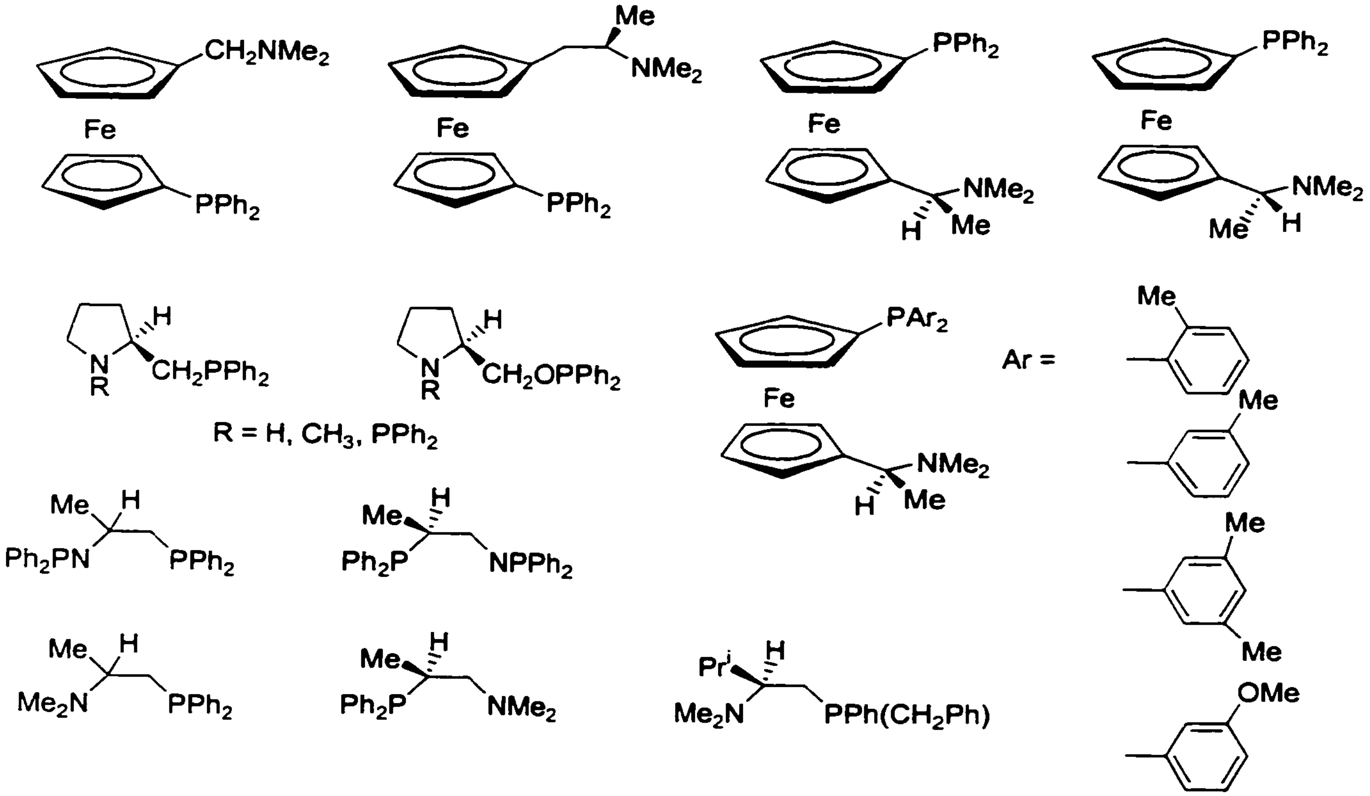


Fig.1: Some chiral aminophosphine and aminophosphinite ligands used in asymmetric synthesis reactions

1.1 *Synthesis of Ligands*

During the past two decades, enantioselective homogeneous catalytic synthesis did not have ready applications in chemical industry for two reasons:[10c]

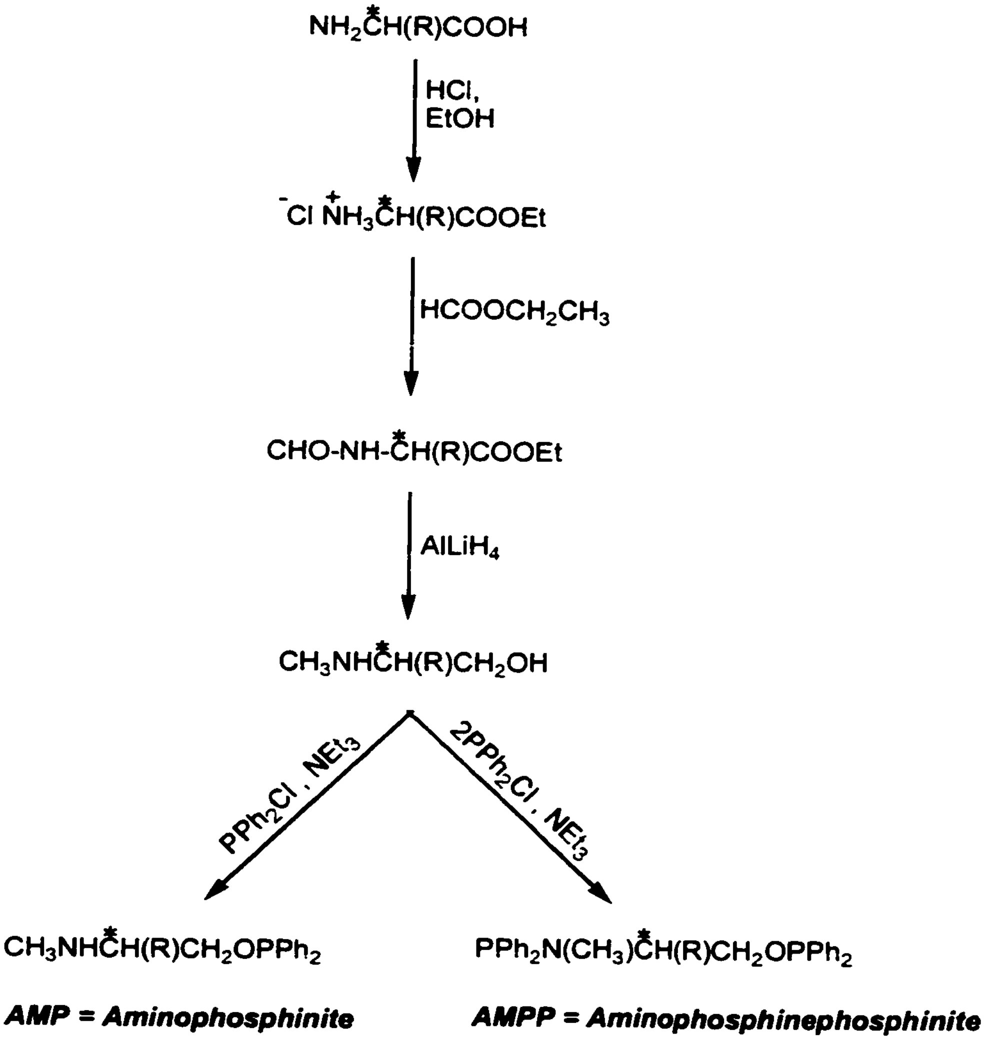
- The transition metal used was generally an expensive noble metal and because of the homogeneous character of the reaction, it was not easy to recover the catalyst at the end of the reaction.
- The ligands available from the chemical producers were as expensive as the metal itself.

It was for these reasons that many research groups have concentrated their efforts on the synthesis of new and cheap chiral ligands and, as well, to enhance the substrate/catalyst ratio in order to minimize the metal cost. To reach the first of these objectives, it seemed essential to have a great variety of ligand precursors, cheap and available on a large scale: natural aminoacids and aminoalcohols have such characteristics. P,N-ligands, such as aminophosphine phosphinites, aminophosphinites, and aminophosphines; have been extensively used in asymmetric hydrogenation,[4c,12] hydrosilylation,[13,14] Grignard cross-coupling,[7d,15,16] and allylic alkylation.[17] Results obtained for the asymmetric cross coupling using various kinds of modified ferrocenylphosphine ligands have proved that the amino group on the phosphine ligand is the first requisite for high stereoselectivity and that the surroundings around the nitrogen exert a strong effect on the stereoselectivity.[15] For this reason, many research groups have focussed mainly on the synthesis of various P,N-chiral ligands.[10a,11] Three major classes of ligands are most commonly used in asymmetric synthesis: linear bidentate, cyclic bidentate, and polydentate ligands.

1.1.1 *Linear Bidentate*

1.1.1.1 From Aminoacids

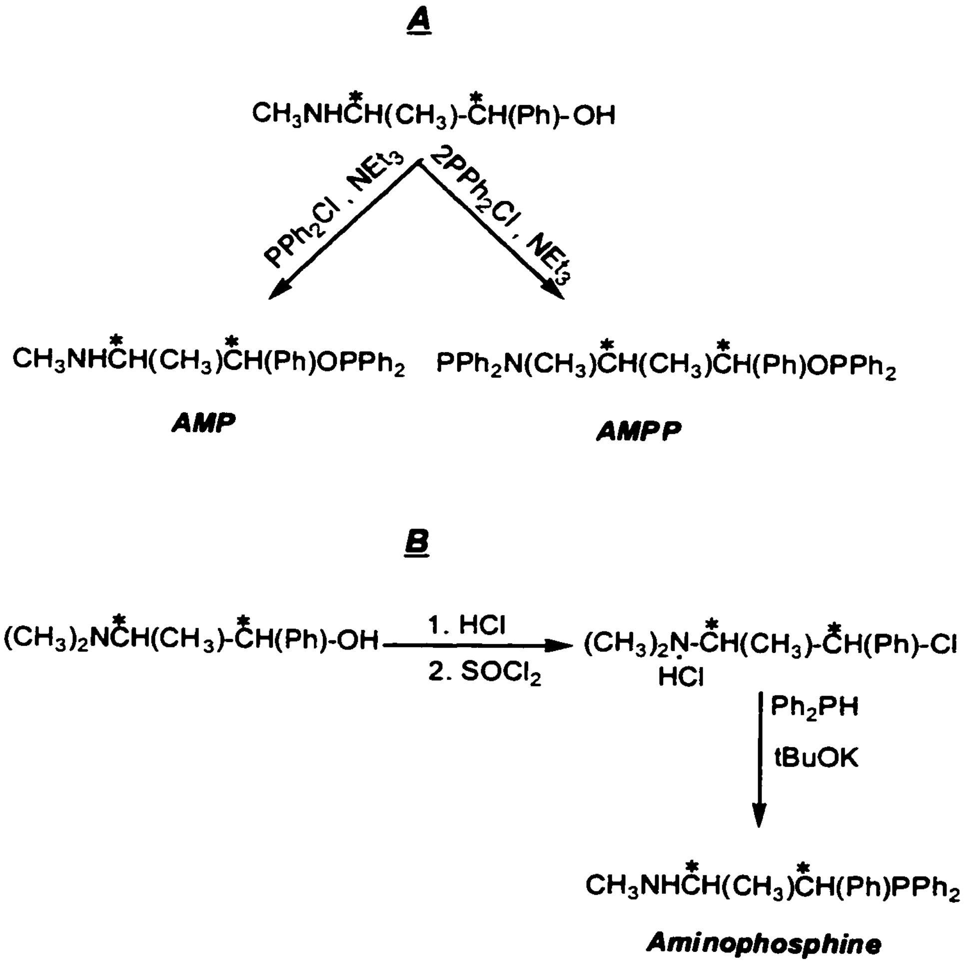
Natural aminoacids provide a large variety of precursors. The preparation of the ligands from aminoacids precursors have been described in several publications.[11] Scheme 1 summarizes the four-step synthesis used to obtain aminophosphine-phosphinites & aminophosphinites. Numerous ligands were so prepared, with variations of the R substituent according to the starting aminoacid. The use of aminoacids as optically active starting compounds is convenient because aminoacids with various substituents are readily available in an optically pure form.



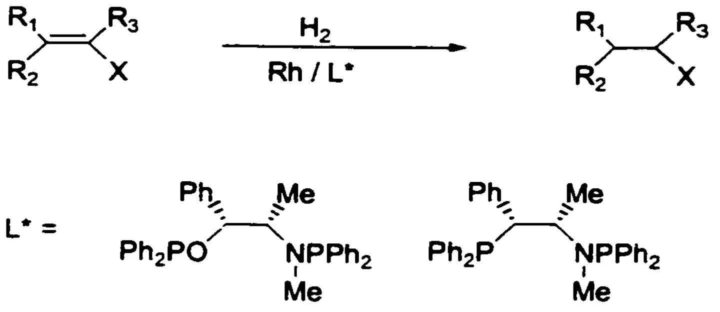
Scheme 1: Preparation of aminophosphine-phosphinite and aminophosphinite ligands

1.1.1.2 From Aminoalcohols

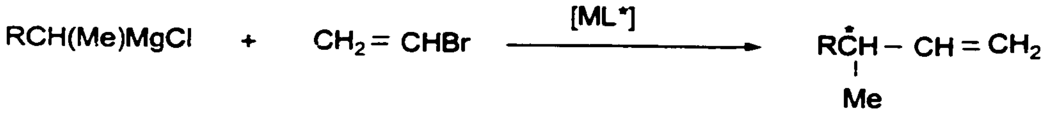
Natural ephedrines have been the subject of thorough investigations as a source of chiral ligands bearing two asymmetric centers, one linked to the aminophosphinite group and the other to the aminophosphine (for the aminophosphinephosphinite ligands), or to the amine (for the aminophosphinite ligands), Scheme 2. Ligands of that type were prepared simultaneously by several research groups[11(b,c),14,18] and successfully tested as ligands for control of enantioselectivity in metal complex-catalyzed asymmetric reactions.[19] They are extensively used in asymmetric hydrogenation[4c,12] (eq 1) and Grignard cross-coupling[7d,20] (eq 2) reactions.



Scheme 2: Preparation of chiral ligands bearing two asymmetric centers from ephedrines

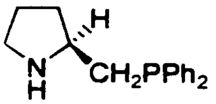


(1)



(2)

$L^* = (CH_3)_2N\overset{*}{C}H(R')CH_2PPh_2$,



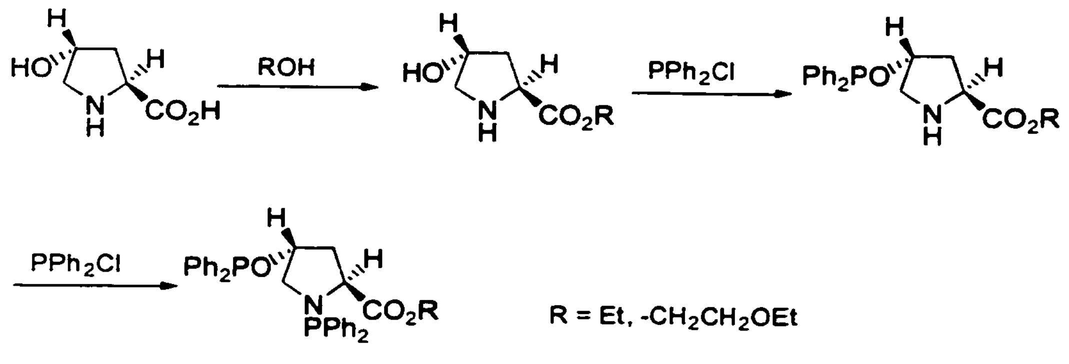
$R' = Me, tBu, CH_2Ph, iPr$
$M = Pd, Ni$

R = Ph, P-tolyl, n-hexyl, 2-naphthyl

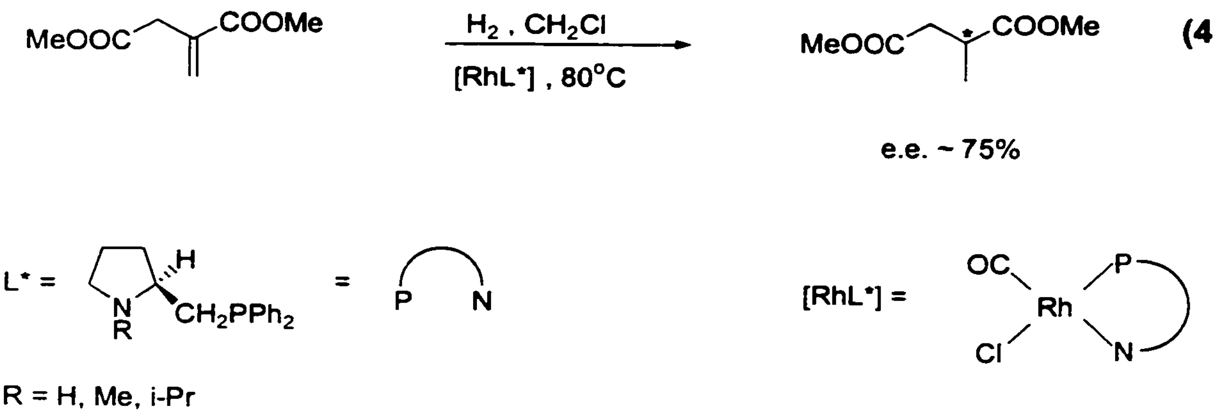
up to e.e. 94%

1.1.2 *Cyclic Bidentate*

Another class of chiral ligands can also be considered, in which a more rigid framework could give rise to stereoinduction. This is the case for ligands prepared from proline and hydroxyproline, which contains two asymmetric carbon atoms. These aminoacids have already been considered as precursors for diphenylphosphine ligands either as mono or bidentates (PM, BPM, BPPM and PPPM) prepared by Achiwa[21] and CAP by Ojima.[22] Aminophosphinephosphinite ligands have been also prepared from these starting materials,[23] (eq 3). Cyclic bidentate chiral ligands have been commonly used in asymmetric hydrogenation[10c,24] (eq 4) and Grignard cross-coupling (eq 2) reactions.



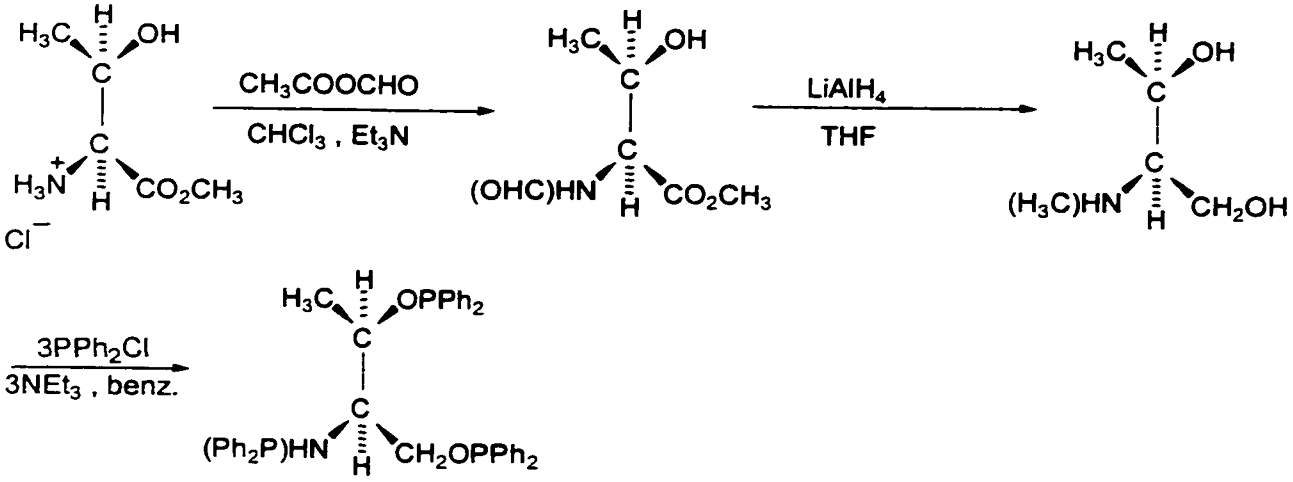
(3)



(4)

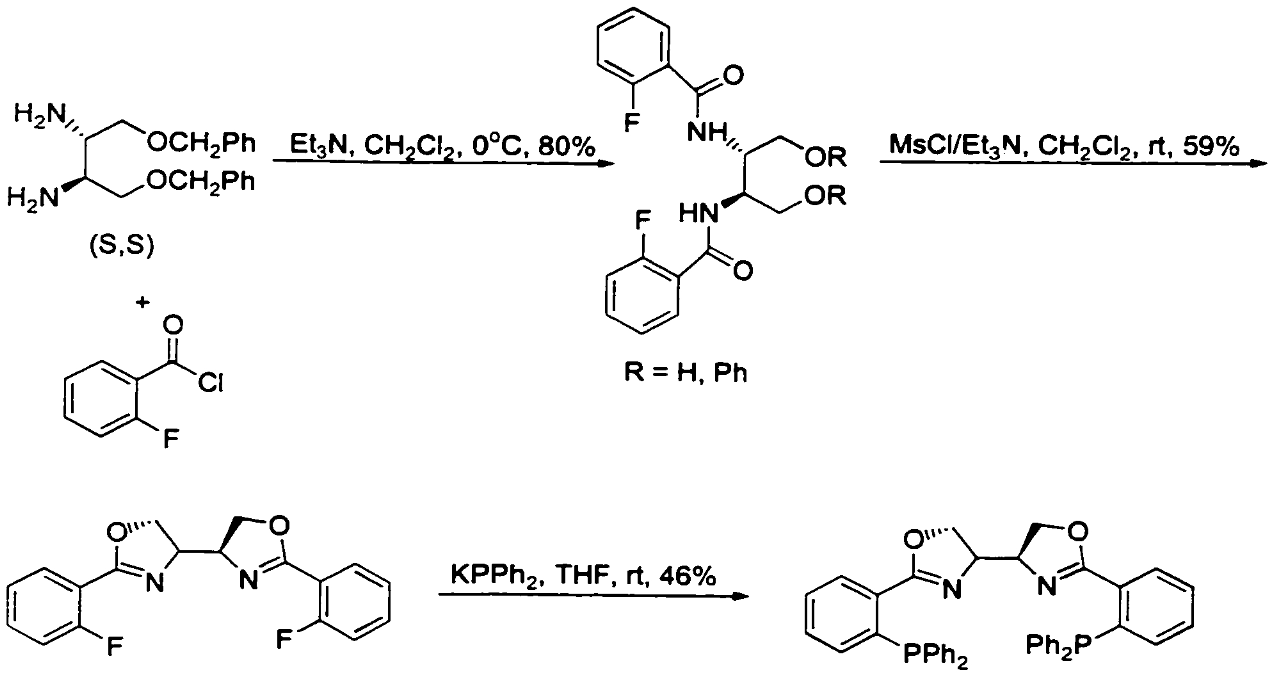
1.1.3 *Polydentate*

A third series of chiral ligands consists in potentially polydentate systems. Preparation of the tridentate class of chiral ligands[24] is illustrated in eq 5. The use of such ligands in asymmetric synthesis has been limited due to the low stereoselectivity obtained in asymmetric hydrogenation reactions (9-32%e.e.).[10c,25] The preparation of tetradentate chiral ligands is more complicated than that of the tridentate analogs as can be seen in eq 6. The chiral compounds (P_2N_2 ligands) commonly have two soft phosphorus atoms and two hard nitrogen atoms. Chiral tetradentate ligands were shown to give better stereoselectivity in asymmetric hydrogenation reactions of ketones (up to 97% e.e.) and were successfully used recently in enantioselective allylic alkylation reactions (94-97% e.e.).[18b]



(5)

Aminophosphinephosphinite
(Threophos)



(6)

P_2N_2

1.2 *Asymmetric Cycloaddition Reactions*

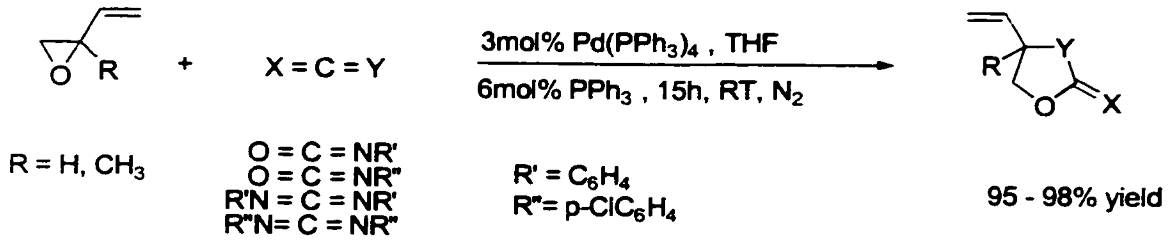
The discovery and development of new chemical reactions is the focus of research activity in organic chemistry. The availability of natural chemical compounds has opened a vast array of new methods and creative strategies of chemical sythesis.[26a] The reactions and classes of reactions that have found the broadest applicability in organic chemistry are those that address the issues of stereo- and enantio- control and are compatible with a variety of functional groups. Of the many classes of reactions discovered over the past 75 years, cycloaddition reactions hold a prominent place in the synthetic methods currently available to organic chemists.[26b] In general, cycloaddition reactions of unactivated olefins, dienes, and acetylenes are notoriously poor and extreme conditions or special methods are necessary to achieve good yields of the cycloadducts.

Metal catalysts provide new opportunities for highly selective cycloaddition reactions since complexation of the metal to an olefin, diene, or acetylene has improved reactivity and novel chemistry. Complexation temporarily activates unreactive species and, therefore; enhances the rate of cycloaddition. The presence of the metal catalyst also helps to achieve enantioselective transformations by adding chiral ligands, which is considered to be one of the most attractive features of the strategy.

A wide variety of cycloaddition reactions have been classified and discussed in a recent review.[26c] The focus will be directed to the cycloaddition and ring expansion reactions of three-membered ring heterocycles with heterocumulenes to form five-membered ring products.

1.2.1 *Asymmetric Cycloaddition Reaction of Vinyl Oxiranes and Heterocumulenes*

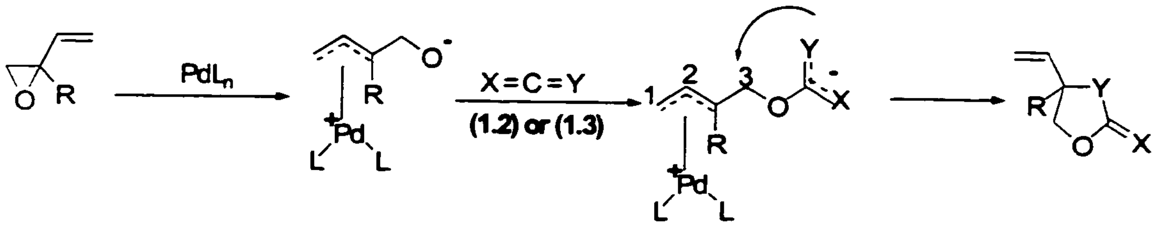
Asymmetric synthesis is an important strategy for the preparation of enantiomerically pure or enriched compounds.[26d,e] The cycloaddition reactions of three-membered ring heterocycles such as aziridines[26f,g] and oxiranes[26h] with heterocumulenes, (e.g. eq 7), have been widely studied and used in the past several years as an effective method to prepare five-membered ring products. Palladium complexes are the best catalysts for cycloaddition reactions.[26i]



(7)

(1.1) (1.2) or (1.3) (1.4,1.5)

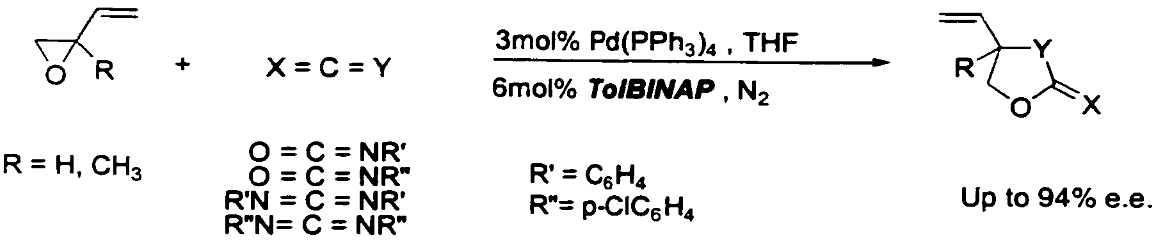
The cycloaddition reaction proceeds via zwitterionic (π-allyl) palladium intermediates generated by oxidative addition of vinyloxirane **1.1** to a palladium (0) species[26j] followed by reaction with the heterocumulene **1.2, 1.3**. Intramolecular attack of the nitrogen at the C-3 carbon of intermediate **1.6** generates the five-membered heterocyclic product as can be seen in eq 8.



(8)

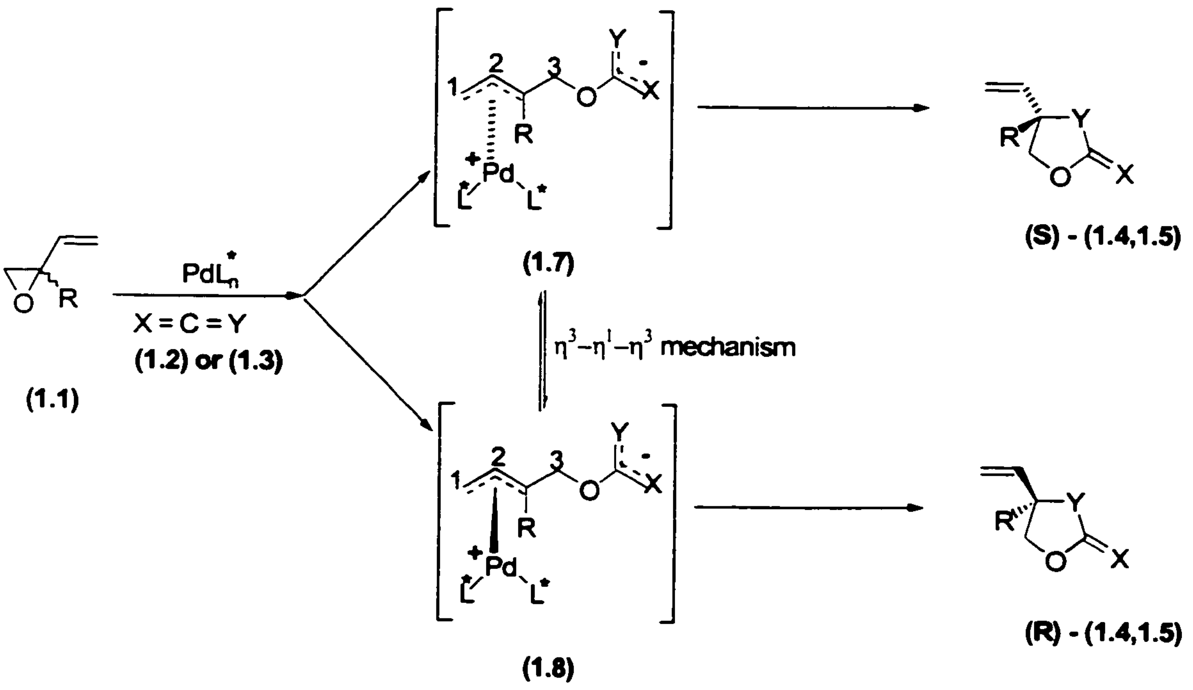
(1.1) (1.6) (1.4,1.5)

Asymmetric induction in the cycloaddition reaction of vinyloxiranes and heterocumulenes, specifically carbodiimides, can be easily achieved depending on the appropriate combination of metal and chiral ligand, as well as reaction conditions and substrates,[26c,k] (eq 9). The pathway outlined in Scheme 3 explains the high degree of asymmetric induction found in the cycloaddition reaction. Oxidative addition of the chiral phosphine-palladium complex to racemic vinyloxirane **1.1** followed by heterocumulene interception afforded the diastereomeric π-allyl palladium complexes **1.7** and **1.8**. Intramolecular attack of the nitrogen nucleophile (X=Y=NR) at the C-3 carbon of **1.7** and **1.8** gives the corresponding *(S)*- and *(R)*- oxazolidine derivatives, respectively.[26g] Palladium (0) [$Pd_2(dba)_3$•$CHCl_3$] is the most effective and suitable catalyst for this system when used with chiral (P,P) ligands such as (-)- DIOP[26l] (20% e.e.), (-)- MeDUPHOS[26m] (45% e.e.), (R,R)-NORPHOS[26n] (6% e.e.) and (R)-PROPHOS[26o] (3% e.e.) which are less effective in terms of asymmetric induction, whereas (R)- BINAP[26p] (94% e.e.) gives the same e.e. as that obtained by using (S)-TolBINAP.[26q]



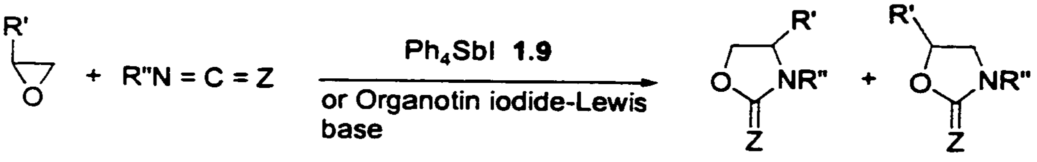
(9)

(1.1) **(1.2) or (1.3)** **(1.4,1.5)**



Scheme 3: Mechanistic pathway to highly enantioselective vinyloxazolidines

The selectivity for product formation is influenced by the change of the reaction catalyst. The use of a catalytic amount of tetraphenylstibonium iodide **1.9** promotes unusual cycloaddition reactions of oxiranes with isocyanates or carbodiimides,[26r] forming 3,4 & 3,5-disubstituted oxazolidin-2-ones **1.10**,**1.11** or 3,4-disubstituted oxazolidin-2-imines **1.12** under very mild conditions, respectively. In particular, carbodiimides give **1.12** exclusively, (eq 10).



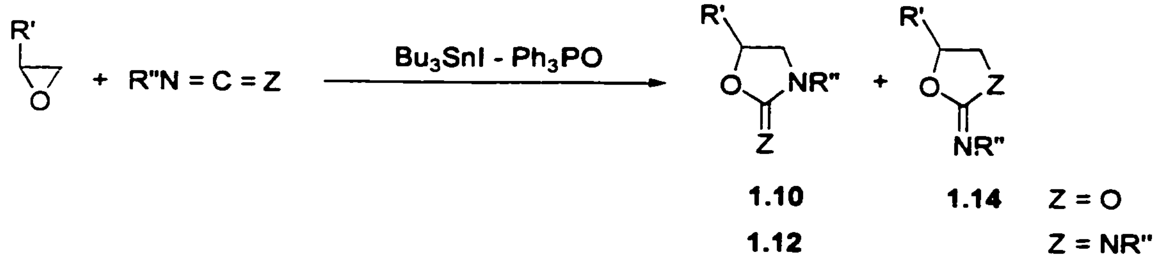
(10)

1.10 **1.11** Z = O

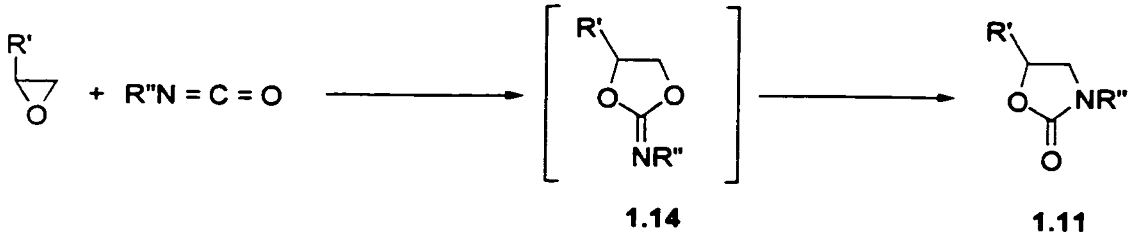
1.12 **1.13** Z = NR"

Many organotin reagents have become widely used in organic synthesis.[27a] Organotin halides with Lewis bases are considered to be excellent catalysts for the cycloaddition reaction of heterocumulenes with oxiranes.[18b] The cycloaddition reaction occurs under mild conditions in the presence of a catalytic amount of an organotin halide-Lewis base complex such as (Bu_3SnI-Ph_3PO). Reactions of the oxiranes proceeded via the regioselective cleavage at the unsubstituted carbon-oxygen bond of the oxirane (β-cleavage), (eq 11). For isocyanates, 2-dioxolanimine **1.14** is the major product while 2-oxazolidinones **1.10** is the minor. 2-Dioxolanimines **1.14** have not been isolated in the reactions activated by previous catalysts,[27b] although they are considered as precursors for the formation of 2-oxazolidinones **1.11**,[27c,d] (eq 12). In the catalytic cycloaddition reaction, N-alkyl-2-dioxolanimine **1.14** is formed first and then N-alkyl-2-oxazolidinone **1.10** arises by the isomerization of **1.14**. Addition of a Lewis-base significantly accelerates this reaction by lowering the proportion of **1.14**. The cycloaddition of carbodiimides with oxiranes gave 2-oxazolidinimines **1.12**. From earlier observations, 2-imidazolidinone **1.15** is the major product under severe conditions using several catalysts,[27e] and it is considered to be formed by isomerization of 2-oxazolidinimine

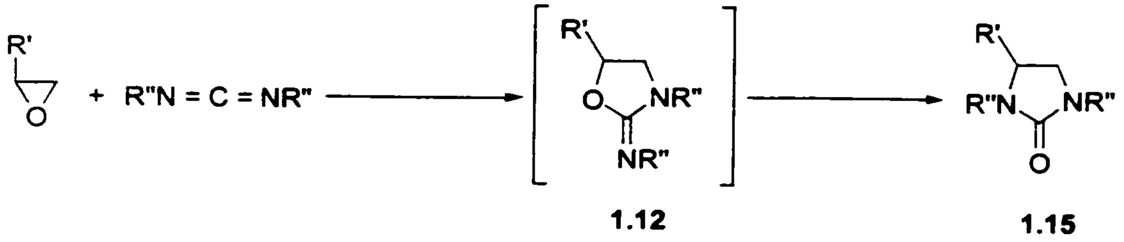
(**1.12**),[27f] (eq 13). These results indicate that under severe reaction conditions (170°C), isomerization of the intermediate [2-oxazolidinimine (**1.12**)] to give imidazolidinone **1.15** occurs, while under mild reaction conditions (40°C), the intermediate can be trapped quantitatively without isomerization.[27g,f]



(11)



(12)

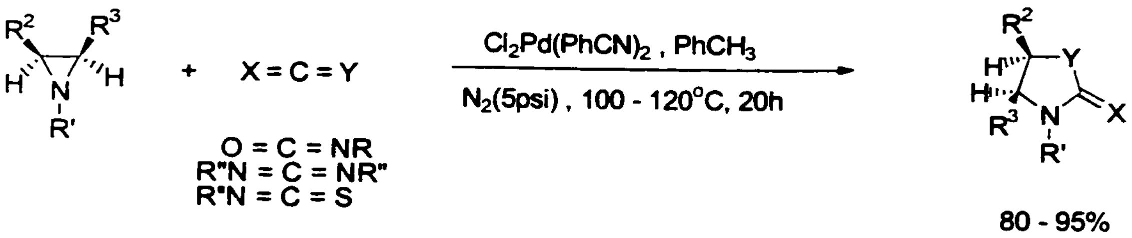


(13)

Oxazolidine derivatives have been given some synthetic uses in the past. For example, oxazolidin-2-ones are used to enhance the stereoselectivity of the aldol reaction.[27h] Moreover, oxazolidin-2-one rings can be regarded as "masked" β-aminoalcohols, which are found in a substantial number of bioactive compounds,[27i] being finally converted into the corresponding β-aminoalcohols by hydrolysis.[27j] The oxazolidin-2-imines cycloadducts can also be readily hydrolyzed into the corresponding oxazolidin-2-ones or β-aminoalcohols.

1.2.2 *Cycloaddition Reaction of Aziridines and Heterocumulenes*

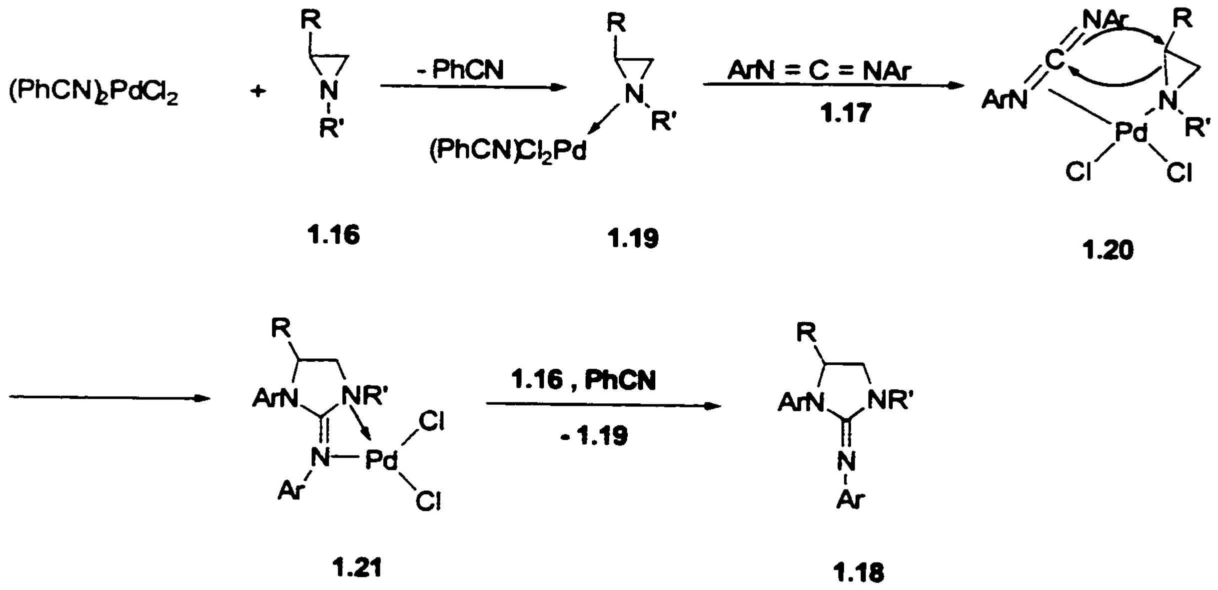
Cycloaddition reactions of three-membered ring heterocycles with heterocumulenes have been extensively studied because of the potential biological activity of the products.[28(a-l)] The cycloaddition reactions of stereochemically defined aziridines and azetidines (including chiral, optically active derivatives) with heterocumulenes (carbodiimides, isocyanates, and isothiocyanates) in the presence of a Pd(II) catalyst have been investigated recently,[26g,28(m-p)] (eq 14).



(14)

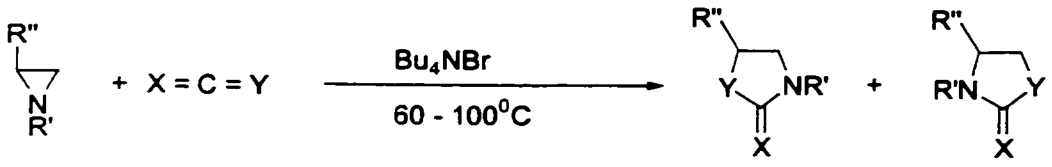
The metal-catalyzed reaction of aziridines **1.16** with carbodiimides **1.17**, a process which does not occur in the absence of a metal catalyst; results in the regiospecific formation of imidazolidinimines **1.18** in excellent yields.[28n] The reaction is believed to proceed via the mechanism outlined in Scheme 4. Interaction of $(PhCN)_2PdCl_2$ with the aziridines may afford the N-donor ligand complex **1.19**. Reaction of the latter with the carbodiimide can form complex **1.20** in which there is π-complexation of one of the carbon-nitrogen double bonds to palladium. Then, cycloaddition of the aziridine to the uncomplexed double bond of the carbodiimide ligand occurs to give complex **1.21**. This cycle then repeats itself with the additional aziridine present in the reaction mixture to afford imidazolidinimine **1.18** and regenerate complex **1.19**. Bis(benzonitrile) palladium (II) dichloride is an effective catalyst for such systems. The process is a regioselective one since it involves the cleavage of the more substituted ring carbon-nitrogen bond.

To our knowledge, no methods exist for the stereoselective synthesis of imidazolidinimines from aziridines and heterocumulenes using chiral palladium (II) catalysts. It is necessary to experiment with various chiral ligands to find a suitable substrate/ligand match to achieve high asymmetric induction.



Scheme 4: Possible mechanism for the palladium-catalyzed cycloaddition reaction of aziridines and carbodiimides

It is well known that the direction of ring opening of activated aziridines (**1.16**, R'= acyl or sulfonyl, etc.) is influenced by the nucleophiles employed and/or the reaction media. Thus, two types of products, resulting from ring cleavage across the less substituted C-N[29] and the more substituted C-N bonds,[30] can be separately synthesized. On the other hand, reactions of the less activated aziridines (**1.16**, R' = alkyl or aryl,etc.) with nucleophiles generally gave type **1.24** products by ring cleavage across the N-CH_2 bond, although contaminated by significant amounts of type **1.23** by-products,[31] (eq 15). The direction of the latter ring cleavage dominates when R" is the aryl or aroyl, since these groups stabilize the charge generated at the ring carbon during the reaction.[31f]

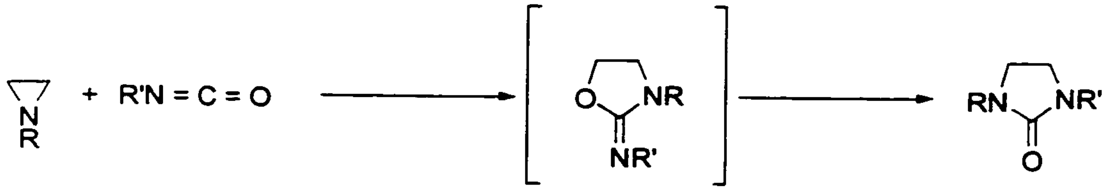


(15)

1.16 1.22 1.23 1.24

X = Y = O
X = NPh, Y = S

When lithium-halide is used as the catalyst for the cycloaddition reaction of aziridines with heterocumulenes, 1,3-disubstituted 2-imidazolidinone **1.28** is formed.[32] The reaction is believed to proceed via formation of 2-imino-oxazolidine **1.27** as the intermediate, which then rearranges under high reaction temperature (170°C) to give 1,3-disubstituted 2-imidazolidinone **1.28**, (eq 16). Although intermediate **1.27** has not been isolated directly from this reaction, it has been shown to be involved in the reaction of oxiranes with carbodiimides,[27f] (eq 13).



(16)

1.25 1.26 1.27 1.28

1.3 *Reaction of Palladium (II) with Bidentate P,N-Chelating Ligands*

1.3.1 *One Ligand*

The synthesis of polydentate and/or asymmetric ligands containing mixed sets of donor atoms is a subject of considerable current interest, in particular with respect to the development of new homogeneous catalysts containing phosphorus ligands. However, the synthesis of such ligands and the complexes thereof often require multistep manipulations with sometimes low yields and/or special reaction conditions.[33a] Many chiral ligands used in palladium- or nickel- catalyzed asymmetric cross-coupling reactions contain both a phosphorus and a nitrogen donor atom.[33b] Due to the relevance of such structures to catalysis, studies of the reactions of isolated organopalladium complexes possessing (P,N)- bidentate ligands would be very interesting, but surprisingly, little work seems to have been carried out in this area.

In the catalytic systems based on preformed complexes, the palladium compounds always bear at least one molecule of the chelating ligand in the coordination sphere. The other two coordination sites can be occupied either by anionic or neutral ligands (some examples are shown in Fig.2).[33b-e] Such catalysts have been widely used in a variety of asymmetric reactions. The structure of (P,N)$PdCl_2$ catalyst, (P,N) being a chiral aminophosphine ligand, is the subject of many publications.[33f-i] The palladium atom is in the center of the approximately square-planar coordination of (P,N) and the two chlorine atoms. The chlorine atoms are cis as required by the geometry of the bidentate chelate ligand. The two Pd-Cl bond distances differ significantly from each other. The longer bond of Pd-Cl reflects the larger trans-influence of phosphorus over nitrogen.[33j] The greater length of Pd-Cl (trans to Pd-P) than Pd-Cl (trans to Pd-N) is consistent with the observation that the Pd-Cl bond length decreases as the electronegativity of the trans atom increases.[164] The divalent palladium is a “soft” metal center and that the presence of good “soft” σ- donor ligand, such as a tertiary phosphine, is necessary for the stabilization of the organometallic complexes. Organometallic complexes of palladium with bidentate ligands having both phosphorus and nitrogen donor sites are readily accessible, and the five-membered Pd-N-C-C-P chelating ring of the complexes in Fig.2

is very stable.[33g] Similar behaviour has been observed for dihaloplatinum complexes containing P,N bidentate ligands.[33k]

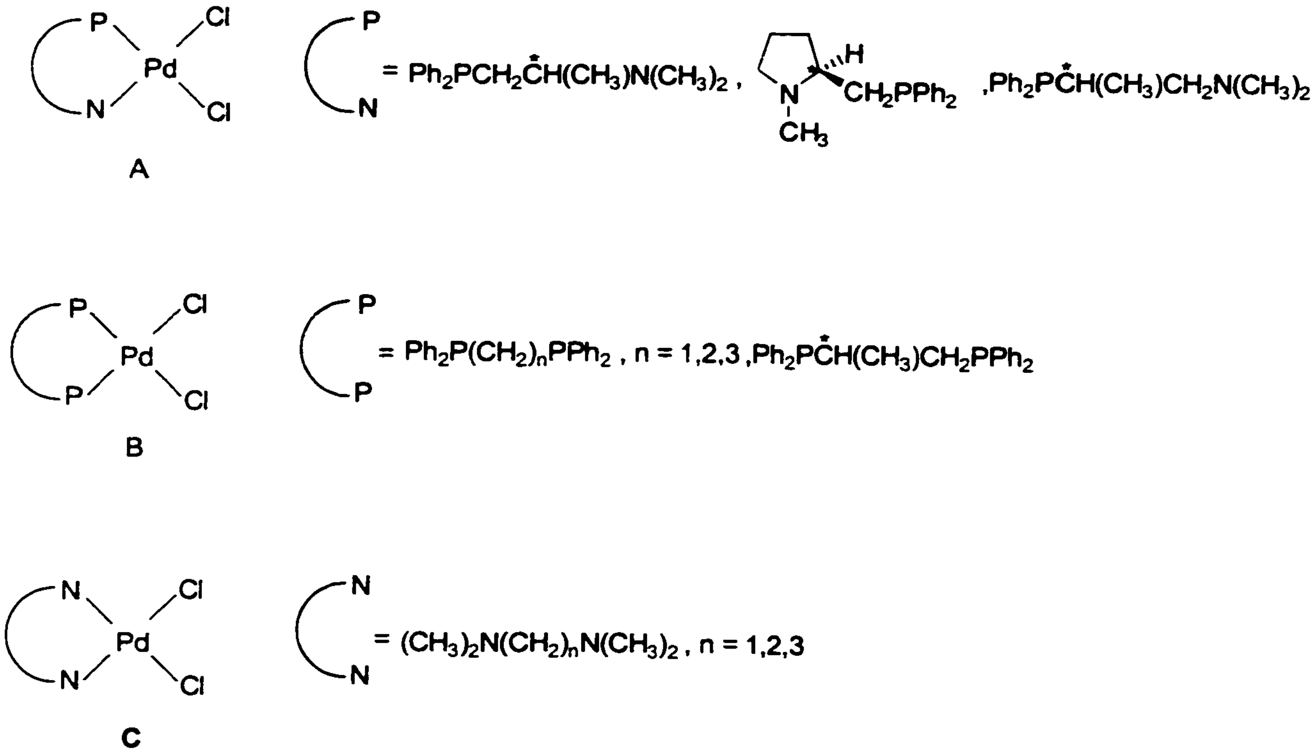
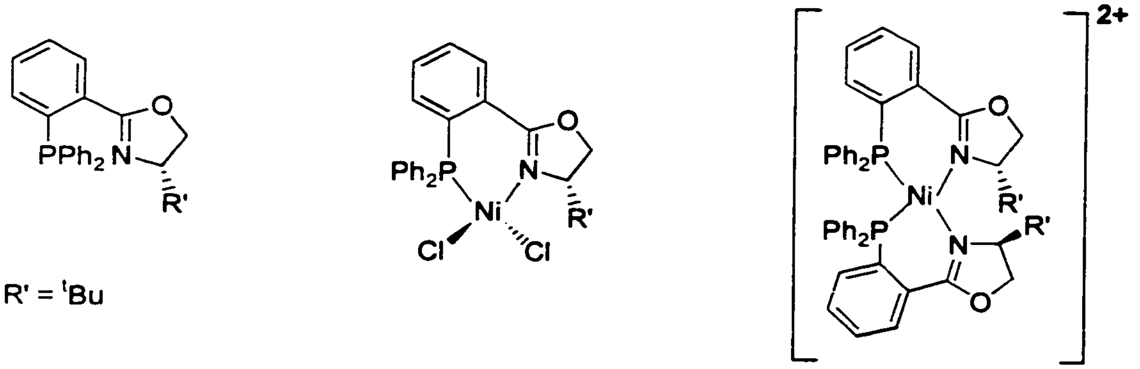


Fig. 2: Some examples of palladium(II) complexes bearing different chelating ligands, (P,N), (P,P) and (N,N).

In the coordination chemistry of P,N-bidentate ligands, the nature of the Pd-N bond will be strongly influenced by the oxidation state of palladium. When the palladium center is zerovalent, the coordination of nitrogen to palladium is not favourable; this is reflected in the molecular structure of $Pd[N(CH_2CH_2PPh_2)_3]$, reported by Orlandi et al.[33l] In palladium (II) complexes, Pd-N coordination is well documented,[33m] but the smaller trans effect of nitrogen relative to phosphorus implies that Pd-N coordination should be weaker than Pd-P coordination.[33j] Another aspect of (P,N)-bidentate ligands is that the hard amine site should help stabilize higher oxidation states, and so their use might facilitate reactions proceeding via organopalladium (IV) intermediates and, under suitable circumstances, may lead to isolable organopalladium (IV) species.

1.3.2 *Two Ligands*

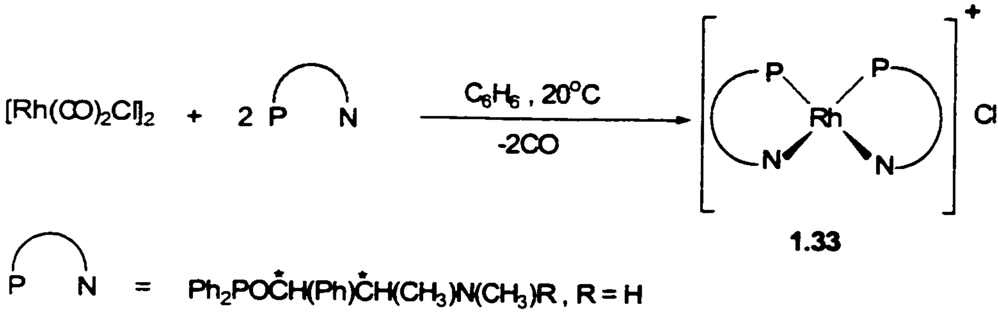
Chiral ligand self-recognition phenomena have been reported for transition metal complexes of the type $[(P,P)_2M(L)_n]$ where "P,P" is a bidentate diphosphine ligand.[34] Only recently there has been a report of such a phenomena using (P,N) ligands, specifically using phosphinoaryl oxazolines **1.29** (Fig. 3).[35] Complexes of **1.29**, which can function as highly enantioselective catalysts, all show remarkable similarity in ligand conformation which therefore appears to be independent of the other ligands at the transition metal center as well as the metal geometry itself.[36] Reaction of Ni (II) with one equivalent of the ligand gives **1.30**. Addition of another molecule of the ligand to this complex affords **1.31**. Two arrangements of the (P,N) chiral ligand allow for a square planar geometry; either having the phosphorus atoms cis or trans to each other. The arrangement where P-atoms are cis to each other is preferred since the π-accepting P centers are trans to the σ-donating N centers. The homochirality of this complex is believed to allow the near-perfect complemantarity in the fitting of the two ligands about the Ni (II) center.



1.29 **1.30** **1.31**

Fig. 3: Phosphinoaryl oxazoline ligands **1.29** and Ni(II) complexes **1.30** and **1.31**

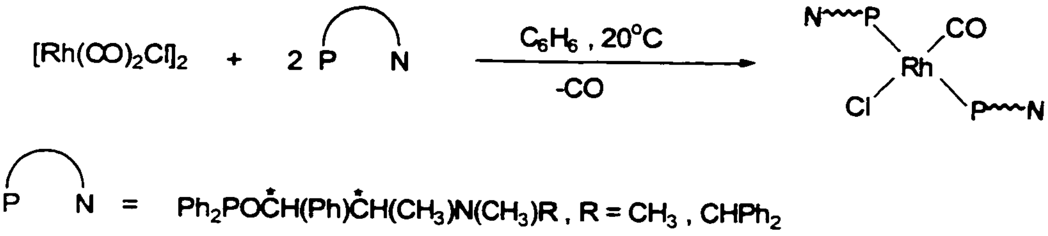
Recent findings by Alper et al.[37] using chiral (P,N)-chelating ligands with rhodium have revealed interesting results. The one pot reaction of the chloro(dicarbonyl)rhodium (I) dimer with two molecules of ligand **1.32** gave complex **1.33** (eq 17). This result is similar to using Ni(II). However, upon changing the R group on ligand **1.32** into a CH_3 or $CHPh_2$, it becomes difficult for the amine groups of the ligand to coordinate to the metal site, affording a complex with free amines and coordinated to phosphorus groups only (eq 18).



1.33

1.32

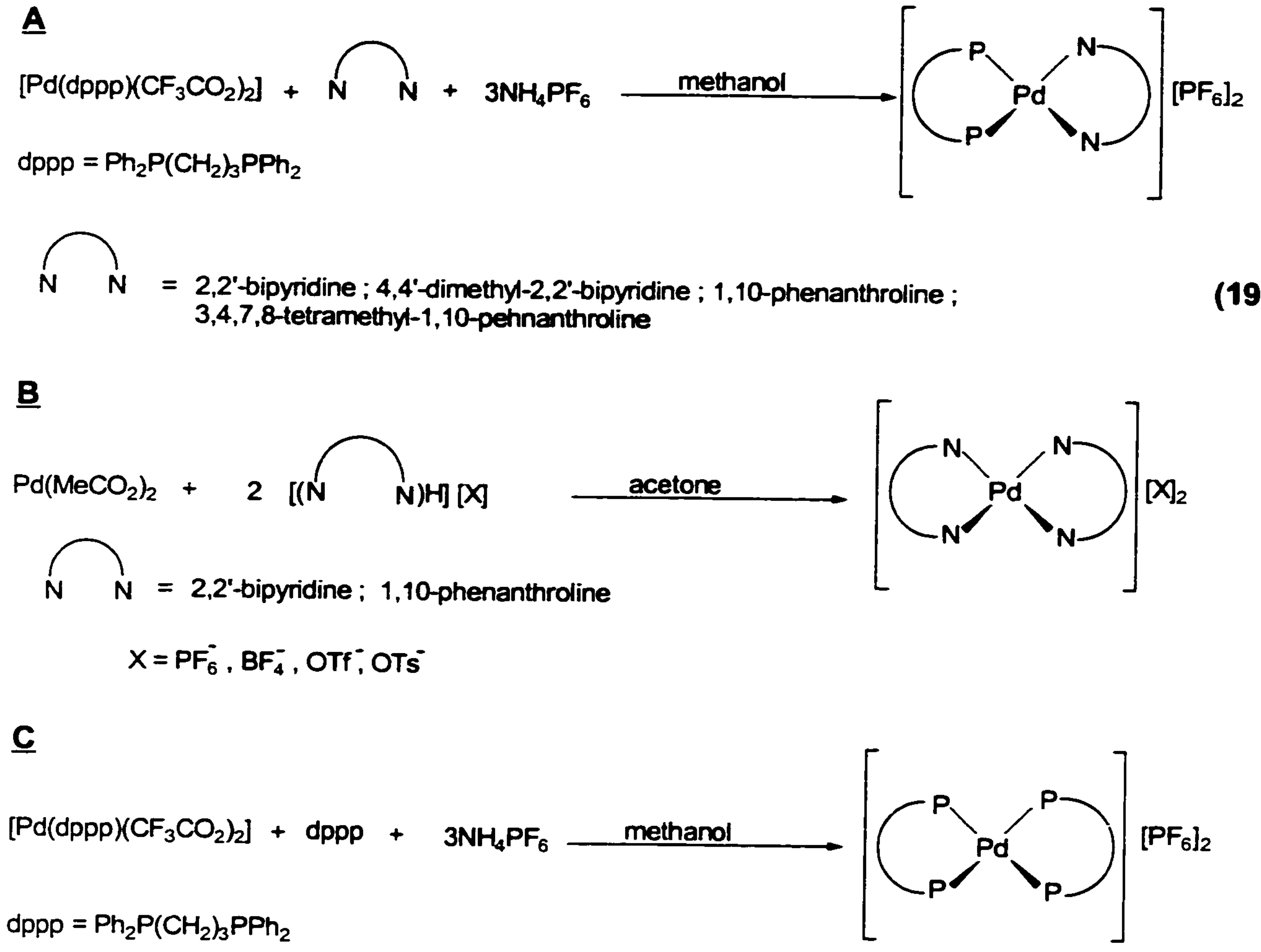
(17)



(18)

It is safe to conclude that the presence of bulky R groups on the nitrogen (of the ligand) blocks its coordination to rhodium. The presence of the oxygen in the phosphinito moiety of the ligand [-O-P-] does not seem to affect the nature of the products. These catalysts have been tested in hydrogenation reactions but failed to give any enantiomeric excess.[24]

Bis-chelated palladium (II) complexes with a diphosphine and dinitrogen[34b] $[Pd(P,P)(N,N)][X]_2$, and nitrogen-donor[38] $[Pd(N,N)_2][X]_2$, chelating ligands have recently been found to be efficient catalyst precursors for the co- and ter- polymerization of CO and olefins;[38,29] compared to those with diphosphine chelating ligands,[34b] $[Pd(P,P)_2][X]_2$. The structure and synthesis of these complexes are illustrated in eq 19.



(19)

Preliminary results on the CO/ethylene copolymerization catalyzed by $[Pd(N,N)(N',N')][PF_6]_2$, [(N,N) = 2,2'-bipyridine, 1,10-phenanthroline] with (N,N) either equal or different to (N',N') complexes helped to recognize some important features of the catalytic system:[34b,38,40] (i) the anion should be non-coordinating; (ii) the nitrogen ligand is labile and can dissociate to give the monochelated active species; (iii) the phosphorus chelating ligand is the ancillary ligand that helps to stabilize the catalyst (Fig 4).

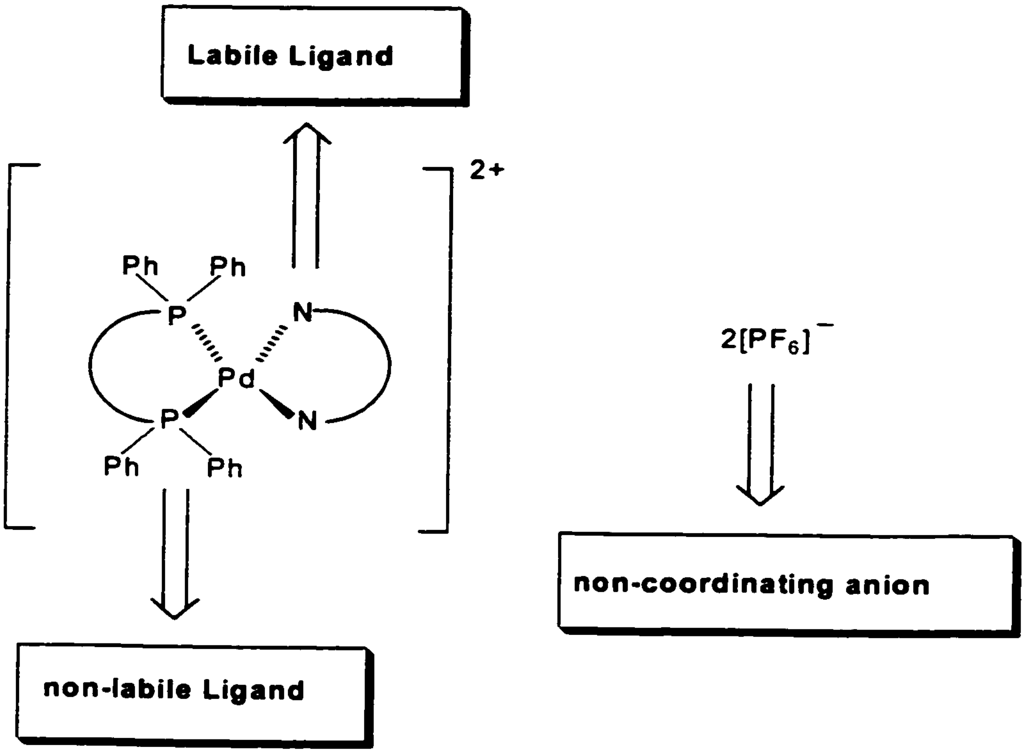


Fig.4:Schematic drawing of the different components of the catalyst precursor

Based on these considerations and the strong trans-influence of the phosphine ligands,[41] the bis-chelated palladium (II) complexes with a diphosphine & a dinitrogen ligand, and complexes with nitrogen-donor chelating ligands, give higher productivity than the corresponding bis-chelated diphosphine complexes,[34b] since the active species is formed by dissociation of the nitrogen-donor chelating ligand. Moreover, optically active co- and ter- polymers may be obtained by using a chiral dinitrogen $[Pd(N,N)_2][X]_2$ or diphosphine & dinitrogen $[Pd(P,P)(N,N)][X]_2$ as the ancillary ligand.

1.4 *Aims of Research*

The purpose of this research was to explore the organic and inorganic aspects of chiral bidentate aminophosphinite ligands. Organically, the purpose was to test the effectiveness of such ligands on the enantioselectivity of asymmetric cycloaddition reactions of aziridine based heterocycles with heterocumulenes using palladium as the metal catalyst. In an inorganic perspective, the purpose was to examine the coordination behaviour of the ligand to the metal center, using one molecule and two molecules of the ligand relative to the metal; and study the behaviour of such complexes in solution. The reaction of palladium (II) with two equivalents of the ligand gave a surprising result that was not predicted based on the literature findings.

2 RESULTS AND DISCUSSION

2.1 SYNTHESIS OF STARTING MATERIALS

2.1.1 Synthesis of Chiral Bidentate Aminophosphine/ Aminophosphinite Ligands

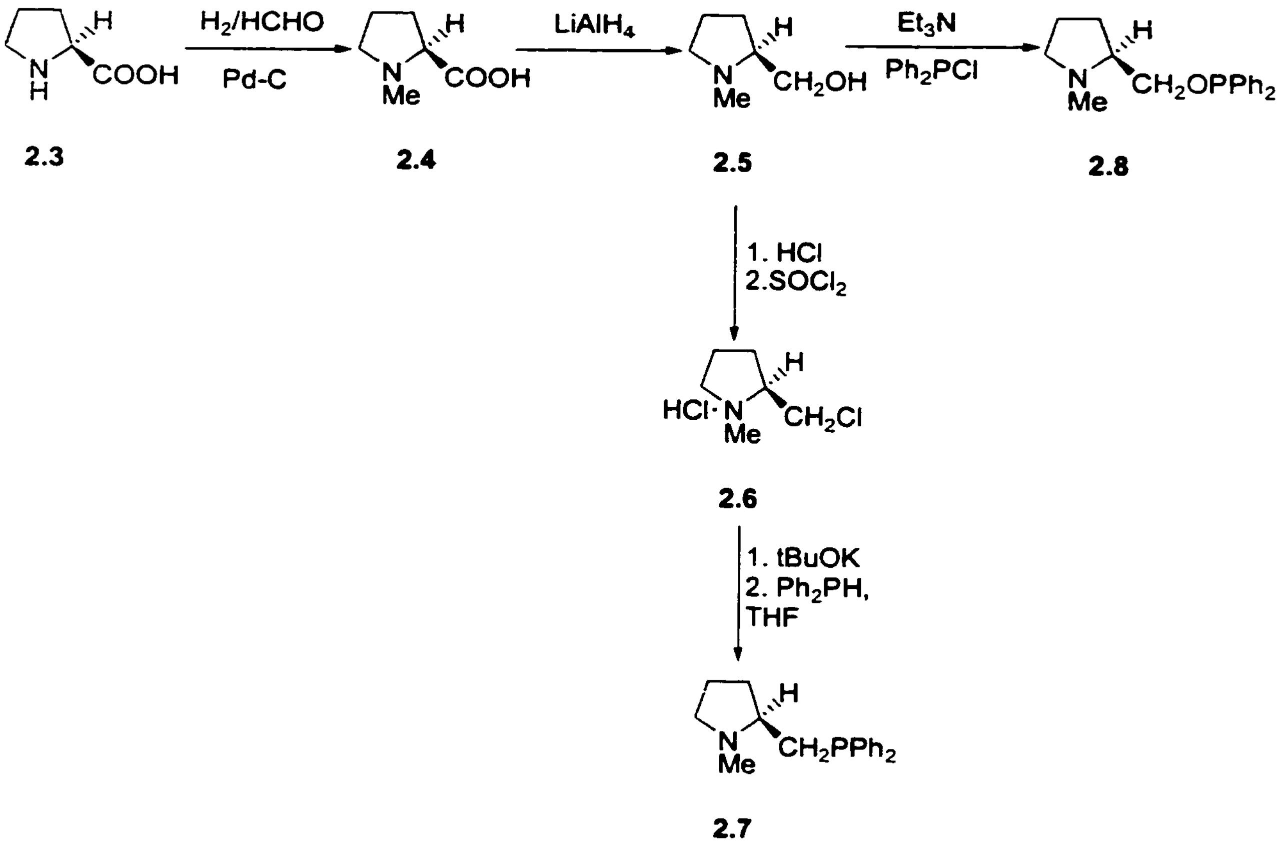
The linear bidentate aminophosphinite ligand, (+) O-diphenylphosphino-N-methylephedrine **2.2** possessing two chiral centers was prepared by treatment of the N-substituted ephedrine **2.1** with Ph_2PCl in the presence of Et_3N at room temperature, (eq 20). The ligand was isolated as an air stable colorless oil (81%) and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy.[14]

$$\underset{\textbf{2.1}}{\mathrm{HO\overset{*}{C}H(Ph)\overset{*}{C}H(CH_3)N(CH_3)_2}} + \mathrm{Ph_2PCl} \xrightarrow[\mathrm{-Et_3N\cdot HCl}]{\mathrm{Et_3N}} \underset{\textbf{2.2}}{\mathrm{Ph_2PO\overset{*}{C}H(Ph)\overset{*}{C}H(CH_3)N(CH_3)_2}} \quad \textbf{(20)}$$

Monitoring the reaction by ^{31}P NMR showed clean conversion of the starting material to the product. The reaction was fast since the reaction was complete within 5 minutes at room temperature. The ligand was stored and used under nitrogen at all times.

The cyclic bidentate aminophosphine **2.7** and aminophosphinite **2.8** ligands possessing one chiral center were both prepared from (*S*)-proline.[16a] The (β-aminoalkyl)phosphines **2.7** and **2.8** were prepared stepwise as shown in eq 21, starting with the amino acid (*S*)-proline **2.3**. N-methylation of **2.3** by reductive condensation with formaldehyde and hydrogenation in the presence of Pd/C[42] gave N-methylproline **2.4** which was converted by reduction with lithium aluminum hydride in THF[43] to (*S*)-1-methyl-2-(hydroxymethyl)pyrrolidine **2.5**. The alcohol was then converted to (*S*)-1-methyl-2-(chloromethyl)pyrrolidine hydrochloride **2.6** by treatment with hydrochloric acid and thionyl chloride in chloroform. According to the procedure by Whitesides,[44] **2.6** was then treated with diphenylphosphine and potassium tert-butoxide in THF to give the chiral phosphine with the pyrrolidine five-membered ring, (*S*)-Prophos **2.7**, in 80% yield.

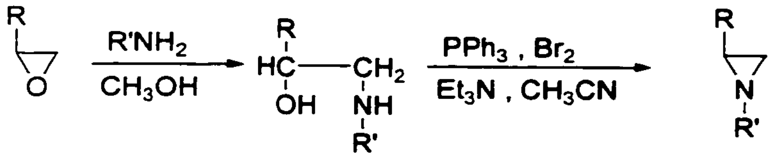
Using the procedure outlined earlier for the synthesis of ligand **2.2**, treatment of **2.5** with Ph_2PCl in the presence of Et_3N afforded (*S*)-1-methyl-2-(diphenylphosphinomethyl) pyrrolidine **2.8** (78%).



(21)

2.1.2 Synthesis of An Aziridine

The 1-alkyl-2-arylaziridine **2.11** was prepared by the cyclization of the corresponding amino alcohol **2.10**. The latter was readily available from the reaction of 2-substituted oxiranes **2.9** with primary amines, as shown in eq 22.[45] Dehydration of **2.10** by using Ph_3PBr_2 in the presence of Et_3N resulted in the formation of the 2-substituted aziridine **2.11** in good yield. The known aziridine obtained was characterized by ^1H and ^{13}C NMR spectra as well as by mass spectroscopy.

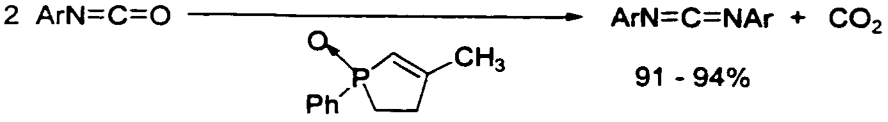


$R = Ph$, $R' = C(CH_3)_3$ **(22)**

2.9 **2.10** **2.11**

2.1.3 Synthesis of Heterocumulenes

Aryl isocyanates **2.12** were commercially available. Diaryl carbodiimides **2.14** were prepared from the corresponding aryl isocyanates **2.12** in the presence of a catalytic amount of 3-methyl-1-phenylphospholene-1-oxide **2.13** (eq 23).[46]



(23)

2.12 **2.13** **2.14**

(Ar = Ph , p-ClC_6H_4)

2.2 REACTION OF PALLADIUM (II) WITH CHIRAL BIDENTATE AMINOPHOSPHINE/ AMINOPHOSPHINITE LIGANDS

2.2.1 Using One Equivalent of the Ligand

Several research groups during the 1970's were interested in the synthesis of organopalladium (II) complexes of the formula [$LPdCl_2$], where L is either a chiral or achiral (P,N)-bidentate ligand.[23,33h,i] In all palladium (II) complexes with L as the bidentate ligand, a well-defined 1/1 palladium/ligand ratio was found, and the spectroscopic and crystallographic results showed that these ligands form "slightly distorted" square-planar d^8 species with bidentate P-N chelate coordination. Similar (P,N)-bonding was found for the d^8 coordination complexes, $PdCl_2$ [o-butylphenylphosphino-α-methyl-N,N-dimethylbenzylamine], $PdCl_2$[(*R*)-(*S*)-PPFA],[33f,h] and [Rh(cyclooctadiene){(*R*)-(*S*) PPFA}]PF_6,[47] (PPFA= diphenylphosphinoferrocenyl ethylamine). The "slight-distortion" in the square-planar geometry was due to the "trans-influence" of the phosphorus atom on the Pd-Cl bond trans to it. Pidcock defined the "trans-influence" of a ligand in a metal complex in 1966 as the extent to which that ligand weakens the bond trans to itself in the equilibrium state of that complex.[48] From the studies of organopalladium (II) complexes having (P,P)-bidentate ligands, it was reported that the Pd-Cl bond was shortest when Cl or N were the trans atoms while the longest Pd-Cl bond was found when P or σ-bonded C ligands were the trans group. In general, the Pd-Cl bond length decreases as the electronegativity of the trans atom increases, as has been observed for dihaloorganopalladium (II) complexes containing a (P,N)-bidentate ligand.[23,33c,h] Figure 5 clearly illustrates the effect of the "trans-influence" on bond lengths and angles of a dichloro [N,N-dimethyl-α-methyl-o-(butylphenylphosphino)benzylamine] palladium (II) complex. The two Pd-Cl bond distances differ significantly from each other. The greater length of Pd-Cl(1) (trans to Pd-P) than Pd-Cl(2) (trans to Pd-N) is consistent with the observation that the Pd-Cl bond length decreases as the electronegativity of the trans atom increases. The Pd-Cl(1) distance, 2.386 A°, is in the range expected for a Pd-Cl bond trans to Pd-P. On the other hand, the Pd-Cl(2) distance, 2.285 A°, is shorter and the Pd-N, 2.134 A°, is longer than those found so far in Cl-Pd-N systems.

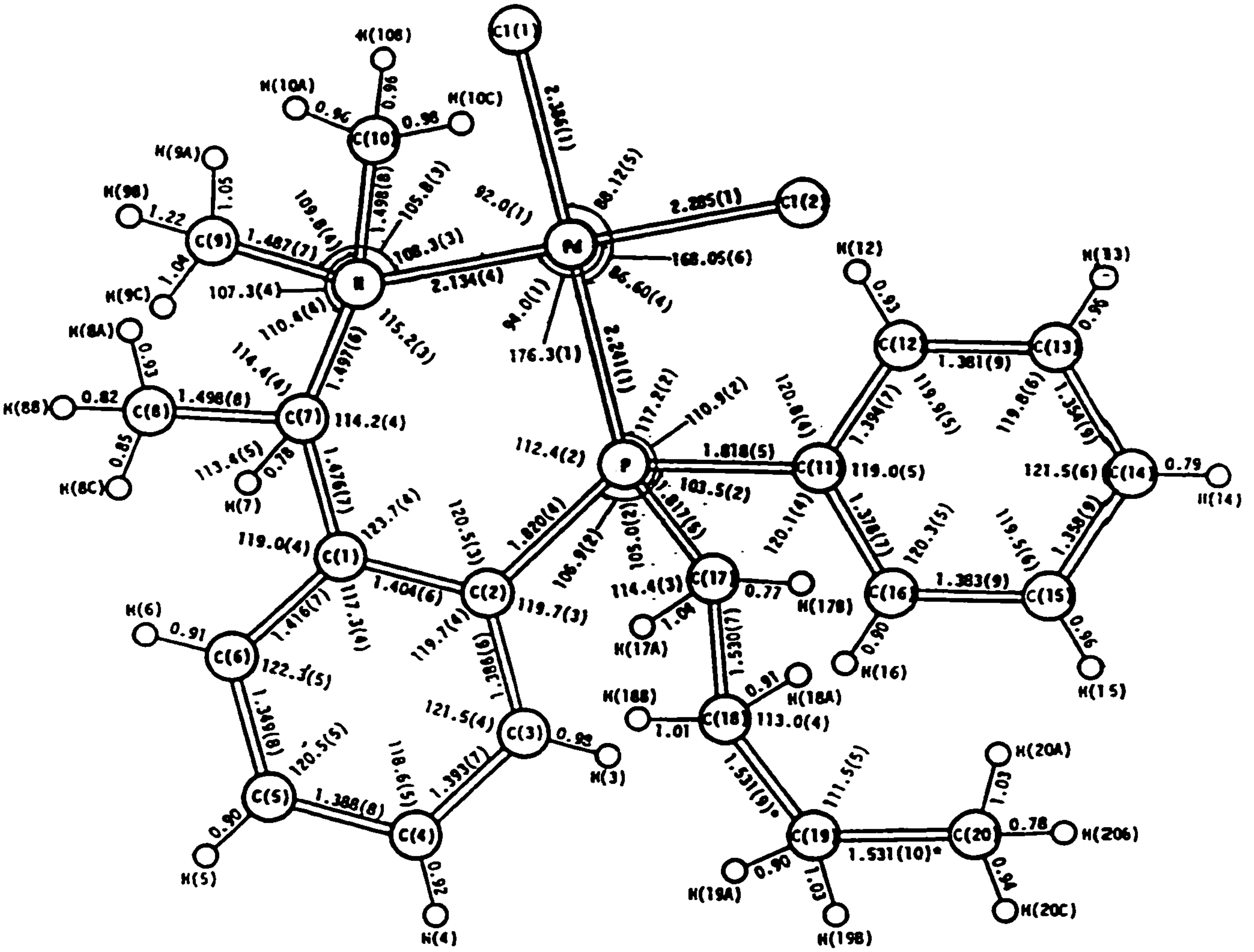


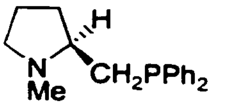
Fig. 5: The effect of the "*trans-influence*" on bond lengths and angles of a dichloro [N,N-dimethyl-α-methyl-o-(butylphenylphosphino)benzylamine] palladium (II) complex.

Bidentate (P,N) ligands possessing two chiral centers, such as ligand **2.2**; have rarely been used in asymmetric synthesis, although they were found to be very active in the linear dimerization of butadiene when used with Ni(0)[49] and recently in asymmetric hydrogenation with Rh(I), which gave moderate results.[24] Organopalladium (II) complexes of such ligands, to our knowledge, are unknown.

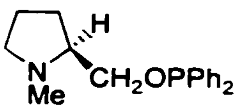
Three different (P,N)-bidentate chiral ligands were synthesized for the purpose of complexation to Pd(II). Ligand **2.2** possesses two chiral centers at the carbons, while ligands **2.7** and **2.8** each possess only one chiral center at a carbon. Ligands **2.2** and **2.8** each contain an aminophosphinite (N-R-O-P) moiety while ligand **2.7** has an aminophosphine (N-R-P) moiety. We investigated the complexation of these ligands to palladium (II) and their effect on the asymmetric induction in the palladium catalyzed cycloaddition reaction of aziridines with heterocumulenes.

$Ph_2PO\overset{*}{C}H(Ph)\overset{*}{C}H(CH_3)N(CH_3)_2$

2.2



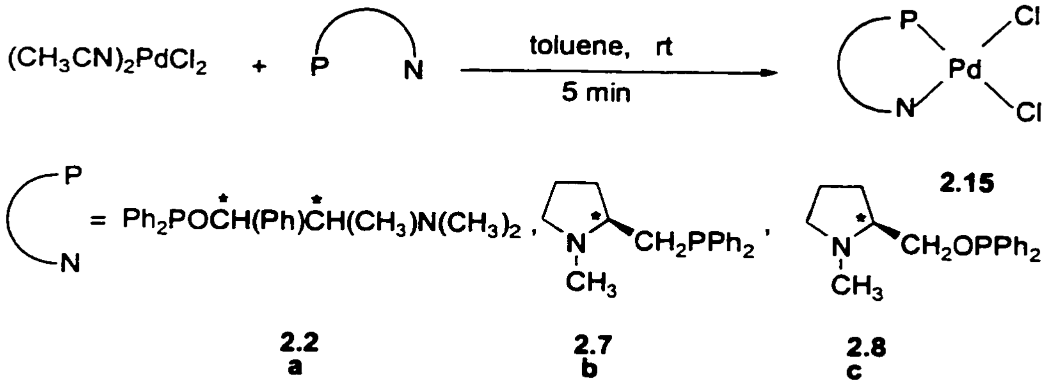
2.7



2.8

2.2.1.1 Synthesis of Chiral (P,N)-Ligated Dichloropalladium (II) Complexes

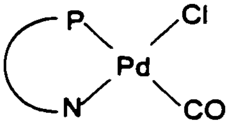
(P,N)-Ligated dichloropalladium (II) complexes **2.15 (a-c)** were easily synthesized by the one pot reaction of bis(acetonitrile) palladium dichloride $(CH_3CN)_2PdCl_2$ with an equivalent amount of the ligand (**2.2**, **2.7**, **2.8**), in toluene (eq 24). The reaction mixture was then stirred for 5 minutes at room temperature. The consumption of the ligand was monitored by ^{31}P NMR spectroscopy-indicated by the disappearance of the signal of P in the free ligand [δ= 111.9 ppm for **2.2**, δ= -20.6 ppm for **2.7**, δ= 115.2 ppm for **2.8**] and the appearance of new peaks for P in the complex, 102.8 (**2.15a**), 47.3 (**2.15b**) and 102.9 (**2.15c**). Complexes **2.15 (a-c)** were isolated by filtration. The resulting light yellow solid was then washed with toluene and dried under vacuum. The isolated yields of **2.15a**, **2.15b** and **2.15c** were 81, 87 and 91% respectively.



(24)

Toluene was found to be the best solvent for this reaction since the products **2.15 (a-c)** were insoluble and precipitated from the reaction mixture. This made it easier to isolate the products in a pure form and the need for purification was eliminated. However, when methylene chloride was used as the solvent, the products were soluble and the isolation was more difficult. Purification and recrystallization were necessary for the latter to obtain pure products. A slow decomposition of the products into palladium black occurred, when they were left in the reaction mixture for a few hours. However, the products, which were isolated from toluene, then re-dissolved in methylene chloride, were stable for a few days in solution before decomposing into palladium black.

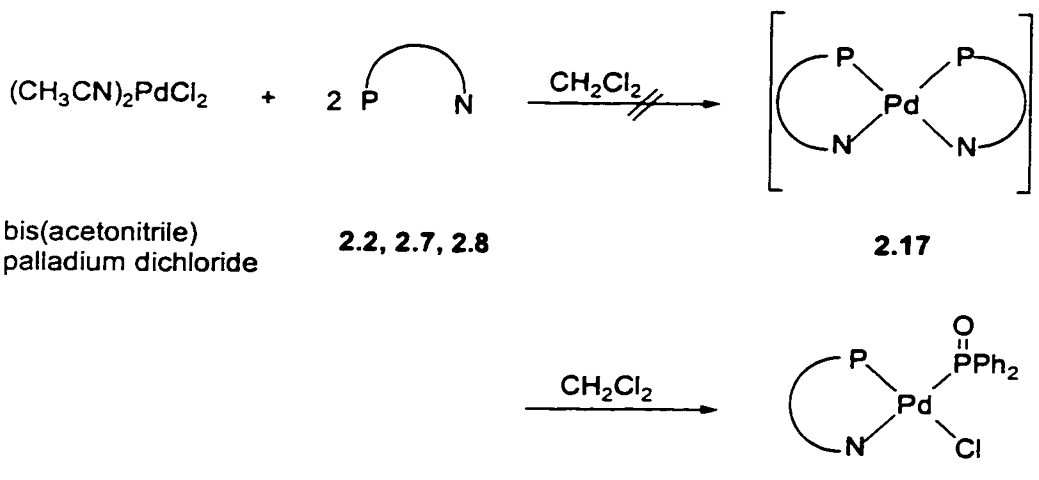
Complexes **2.15 (a-c)** were found to survive heating up to 120°C without change. In contrast, upon bubbling CO gas into a solution of **2.15** in methylene chloride in an attempt to synthesize complex **2.16**, the solution turned darker in color followed by a very slow decomposition into palladium black. A series of ^{31}P NMR spectra of this reaction over a period of 5 hours showed very slow decomposition of complex **2.15**. Despite this slow decomposition, most of complex **2.15** remained stable for over 5 hours. This behaviour was observed for all complexes **2.15 (a-c)**. An attempt to reduce these complexes with lithium aluminum hydride resulted in the decomposition of the complexes.



2.16

2.2.2 Using Two Equivalents of the Ligand

In section 1.3.2 was briefly discussed the synthesis of bis(chelated) palladium (II) complexes with a chelating diphosphine ligand, $(P,P)_2PdX_2$, a nitrogen-donor chelating ligand, $(N,N)_2PdX_2$, and a diphosphine and dinitrogen chelating ligand $(P,P)(N,N)PdX_2$, eq 19, as well as the successful attempt to synthesize bis-chelated rhodium (I) complexes of the formula $(P,N)_2RhCl$. To our knowledge, palladium (II) complexes of the general formula $(P,N)_2PdX_2$ have not been synthesized as reported. According to the successful synthesis of palladium (II) complexes of the formula $(P,P)(N,N)PdX_2$, $(N,N)_2PdX_2$ and $(P,P)_2PdX_2$ and their efficient use as catalyst precursors in polymerization reactions, it was expected that the reaction of $(CH_3CN)_2PdCl_2$ with two equivalents of ligand **2.2**, **2.7** or **2.8** would result in the formation of complex **2.17**, eq 25, which could then be used as a catalyst for asymmetric synthesis reactions.



(25)

bis(acetonitrile) palladium dichloride

2.2, 2.7, 2.8

2.17

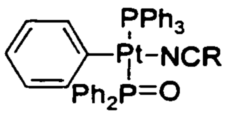
2.18

The reaction of complexes **2.15 (a,c)** with an equivalent amount of the corresponding ligand or the one pot addition of two equivalents of the ligand (**2.2**, **2.8**) to a suspension of bis(acetonitrile) palladium dichloride in methylene chloride afforded a light yellow homogeneous solution which was then concentrated, followed by dilution with ether. The solution was left standing overnight to afford colorless crystals. A ^{31}P NMR spectrum showed the presence of two sets of doublets, which implied the presence of two non-equivalent phosphorus atoms in the complex coupling to each other. If the resulting complex was of the form **2.17**, the ^{31}P NMR should exhibit only one set of doublets, i.e. two equivalent phosphorus atoms present in the complex. ^{1}H and ^{13}C NMR spectra confirmed the presence of only one type of P,N-ligand, the integration of the proton spectrum revealed the presence of extra phenyl groups, and the ^{13}C NMR spectrum showed the presence of extra phenyl carbons. An ^{15}N NMR spectrum also showed two sets of doublets, which also eliminated the presence of product **2.17**. X-ray crystallography of the colorless crystals obtained showed a unique type of complex, **2.18 (a,c)**, whose structure supported the spectroscopic data obtained. An ORTEP drawing is presented in Figure 6.

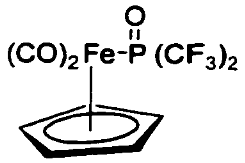
A few examples in the literature reported a phosphine oxide moiety [O=PPh$_2$] being complexed to a metal. Amido-bridged diplatinum complexes such as **2.19** have structures similar to that of **2.18**. This complex was synthesized by the reaction of the chelate (dppm)PtCl$_2$ with NaOH in liquid ammonia.[50] Complexes **2.20**,[51] **2.21**[52] and **2.22**[53] are some other complexes reported in the literature which possess a phosphine oxide moiety. This moiety was generally obtained by the addition of a base such as NaOH and Na$_2$CO$_3$[50,53] or of an oxide such as nitrile oxide[52,54] to the reaction mixture.

trans **cis**

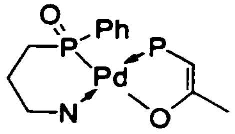
2.19



2.20



2.21



2.22

*2.2.2.1 Using Ligand **2.7***

The case was different when ligand **2.7** was used instead of ligands **2.2** and **2.8**. The lack of the phosphinite moiety [-O-PPh$_2$] from ligand **2.7** would prevent the formation of complex **2.18** and might proceed to form complex **2.17** as the only possible product. The reaction of $(CH_3CN)_2PdCl_2$ with ligand **2.7** was monitored using ^{31}P NMR spectroscopy. When two equivalents of the ligand **2.7** were added to a suspension of $(CH_3CN)_2PdCl_2$ in methylene chloride, the solution became light clear yellow. The ^{31}P NMR spectrum exhibited the sharp signal of complex **2.15b** and a broad signal at 35.5ppm with a ratio of 1:10, respectively (Fig 7a). When the reaction was stirred for an additional 4 hours, neither the spectrum nor the ratio changed.

A temperature-variation ^{31}P NMR experiment was performed in order to resolve this broad signal. Decreasing the temperature from (-10°C) to (-95°C), resulted in multiple broad signals (Fig 7b). The ^{1}H and ^{13}C NMR spectra of the isolated solid were not informative enough to identify the structure of the complex, due to the high degree of impurity present.

*2.2.2.2 X-Ray Analysis of **2.18a***

The ORTEP of **2.18a** as illustrated in Fig 6 shows that the two phosphorus atoms are cis to each other as required by the trans-influence. This influence is slightly greater for the phosphorus ligand than that of the phosphine oxide moiety, which causes the Pd-Cl bond to be slightly longer than that of Pd-N. The bond angles are also affected by this influence, causing a slight distortion in the square-planar geometry of the complex, which is also partly due to the effect of the bond lengths.

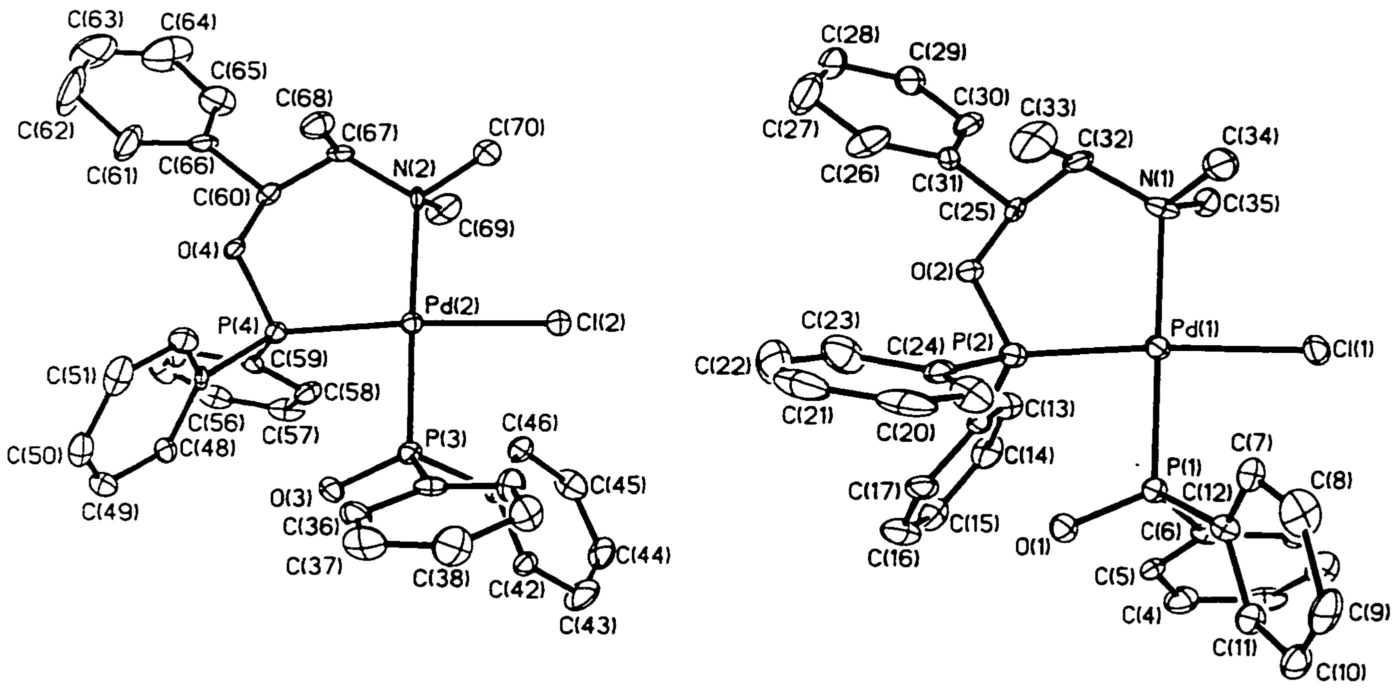


Fig. 6: View of **2.18a**, showing the atomic numbering and thermal ellipsoids.

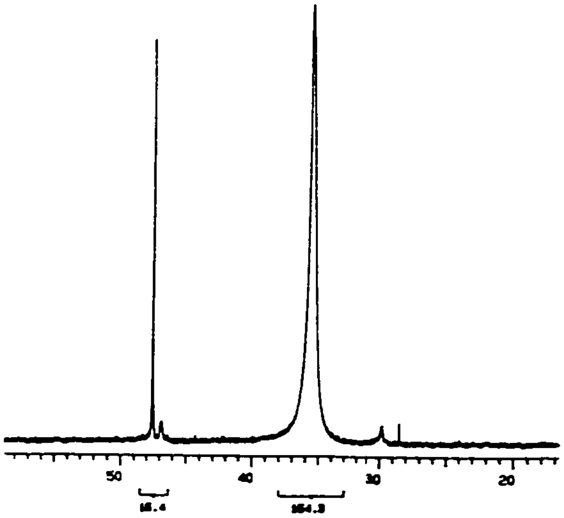


Fig. 7a: The reaction of bis(acetonitrile)palladium dichloride with two equivalents of ligand **2.7**.

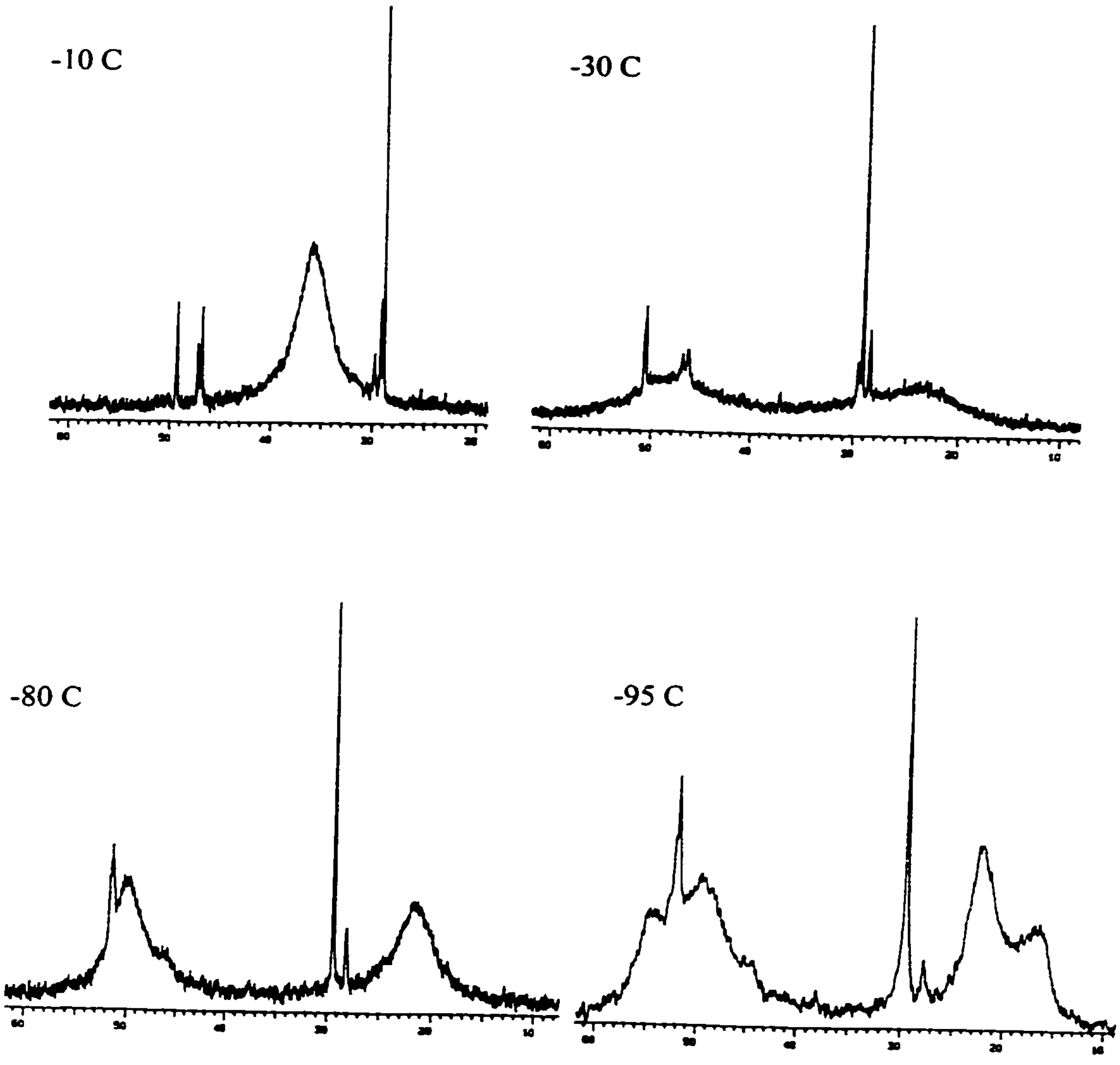
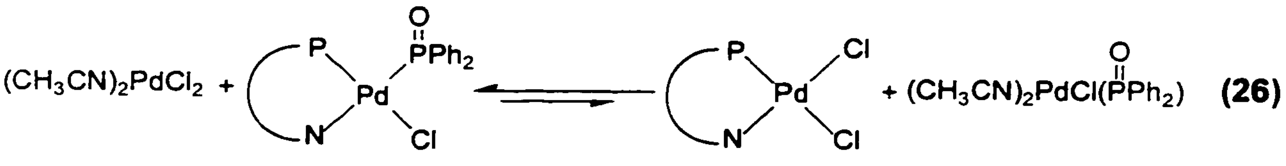


Fig. 7b: A Temperature-Variation ^{31}P-NMR spectra, showing more broadening of the signal from Fig. 7a.

2.2.2.3 Reversibility

As mentioned earlier, complexes **2.18 (a,c)** could be synthesized from the reaction of **2.15 (a,c)** with an equivalent amount of the corresponding ligand. It was found that complexes **2.15 (a,c)** could also be synthesized from **2.18 (a,c)** by adding $(CH_3CN)_2PdCl_2$ to a solution of **2.18** in methylene chloride. This reversible reaction was slow and the conversion was incomplete. The formation of complexes **2.18 (a,c)** was preferred over that of **2.15 (a,c)**, i.e. the equilibrium lay towards the formation of complexes **2.18 (a,c)** (eq 26). This might be due to the strong Pd-P bond of the phosphine oxide moiety, trans to the Pd-N bond, which would make it harder to cleave, and replace it by a chlorine atom.



(26)

2.18 (a,c) **2.15 (a,c)**

*2.2.2.4 Behavior of **2.18 (a,c)** in Solution*

It was found that the phosphorus atoms in complex **2.18a**, as well as in **2.18c**, not only couple but also exchange with each other while in solution. The coupling was confirmed by a COSY-^{31}P experiment (Fig 8) while the exchange was confirmed by a NOESY-^{31}P spectrum (Fig 9). This exchange could be explained by the proposed mechanism outlined in Scheme 5. The reaction of $(CH_3CN)_2PdCl_2$ with one equivalent of the ligand (**2.2**, **2.8**), simply gives complex **2.15 (a,c)**. Upon addition of a second equivalent of the ligand, intermediate **2.23** may be formed. A possible interaction between the phosphorus atom and one of the chlorine atoms causes the Pd-Cl to weaken and dissociate, followed by the formation of a P-Cl bond and a Pd(I) intermediate, **2.24**. The free amine from the ligand forms an organic halide **2.25** and dissociates from the phosphinite moiety of the ligand to form complex **2.18**. The presence of the amino-halide **2.25** in the mother solution causes this exchange between the phosphorus atoms. This has been confirmed by carrying a NOESY experiment of complex **2.18**, which has been isolated and crystallized from the organic halide **2.25**. Figure 10 shows the COSY experiment performed on the isolated complex **2.18** which clearly illustrates the coupling between the two phosphorus atoms in the complex, and figure 11 shows the NOESY experiment performed on the same isolated complex which clearly illustrates that the phosphorus atoms no longer exchange with each other. These results support the proposed mechanism of the behaviour of complex **2.18** in the mother solution.

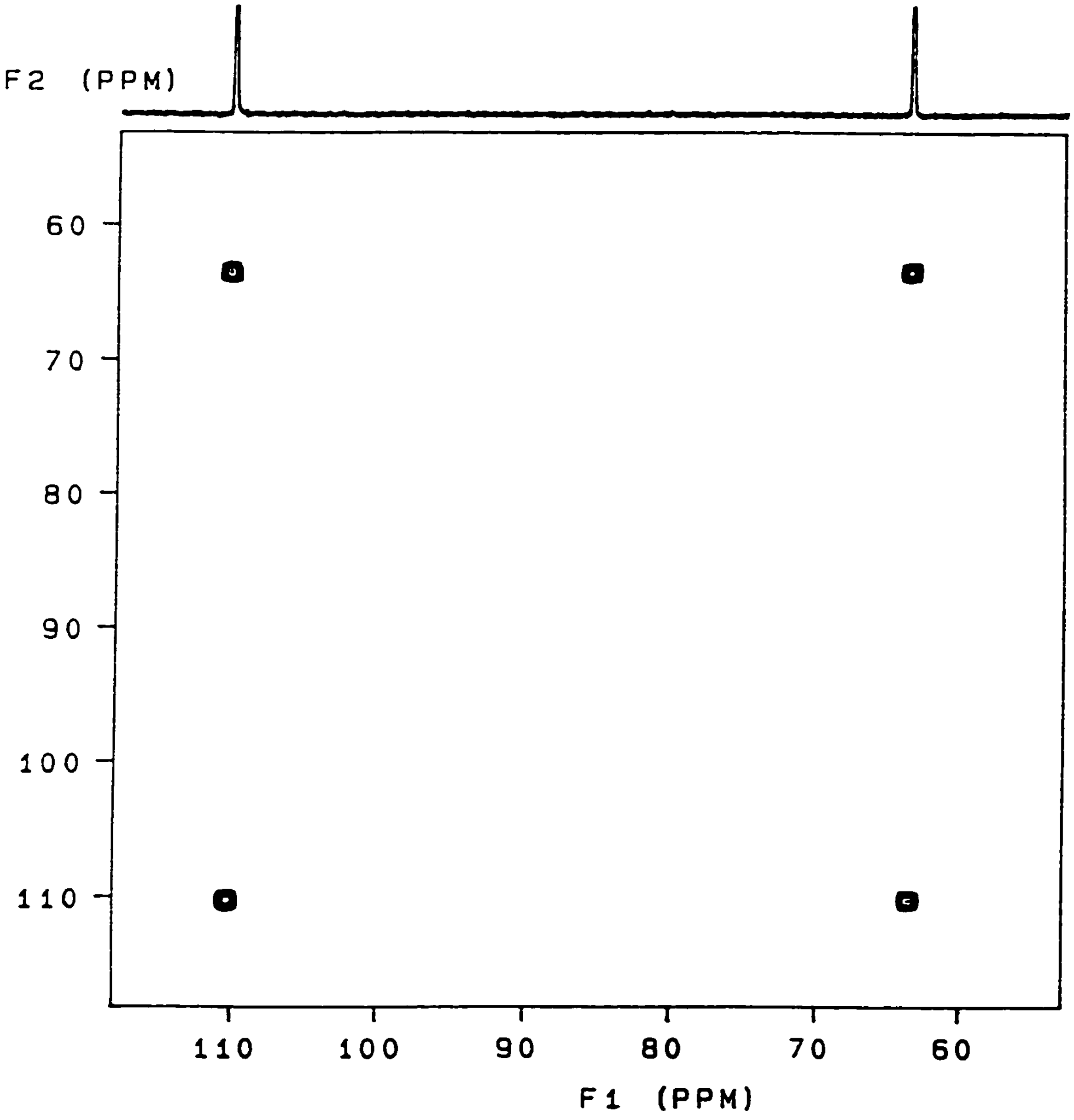


Fig. 8: A COSY-^{31}P spectrum of **2.18a** in the mother solution, showing the coupling between the two phosphorus atoms.

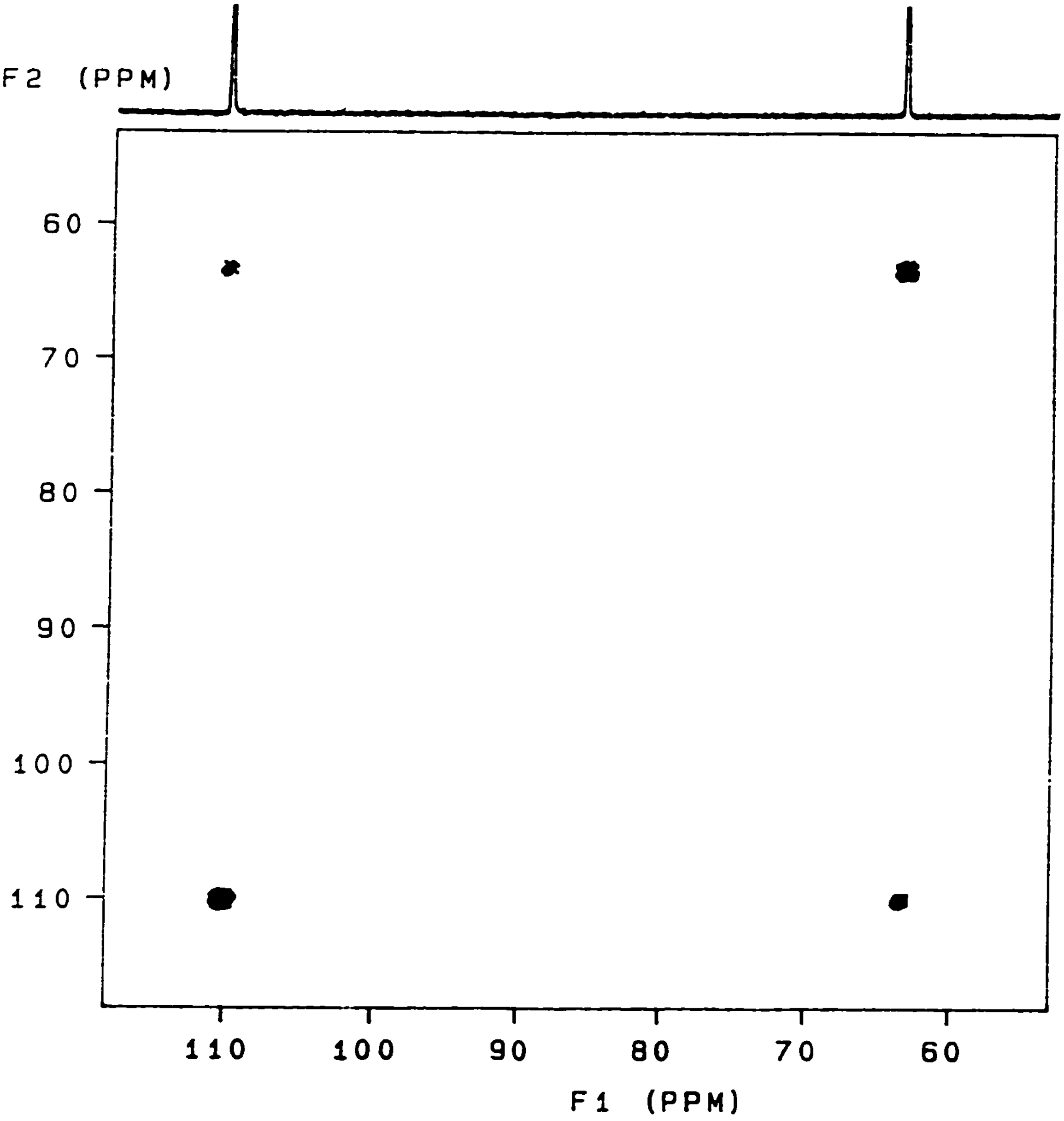


Fig. 9: A NOESY-^{31}P spectrum of **2.18a** in the mother solution, showing an exchange between the two phosphorus atoms.

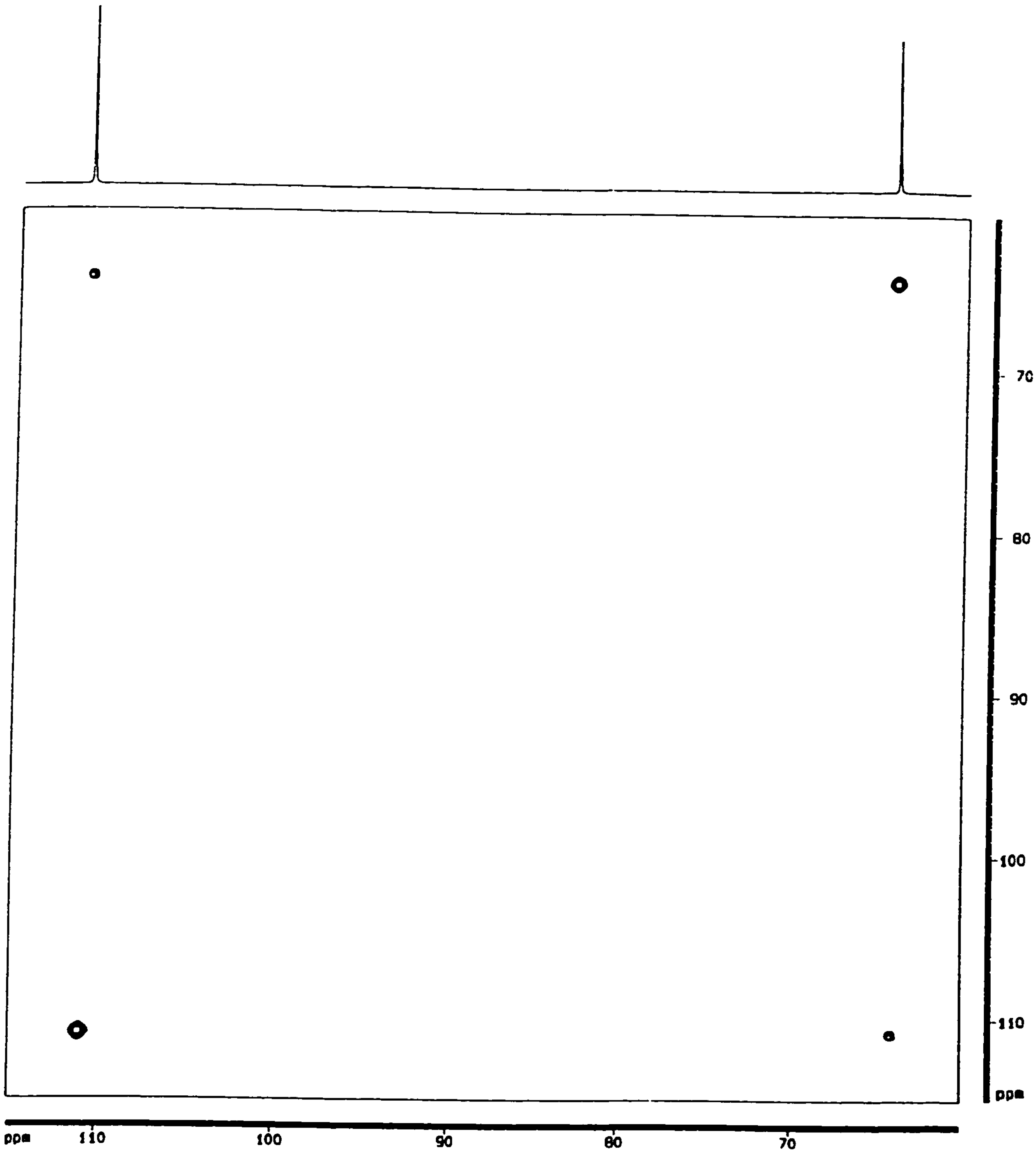


Fig. 10: A COSY-^{31}P spectrum of an isolated **2.18a**, showing the coupling between the two phosphorus atoms.

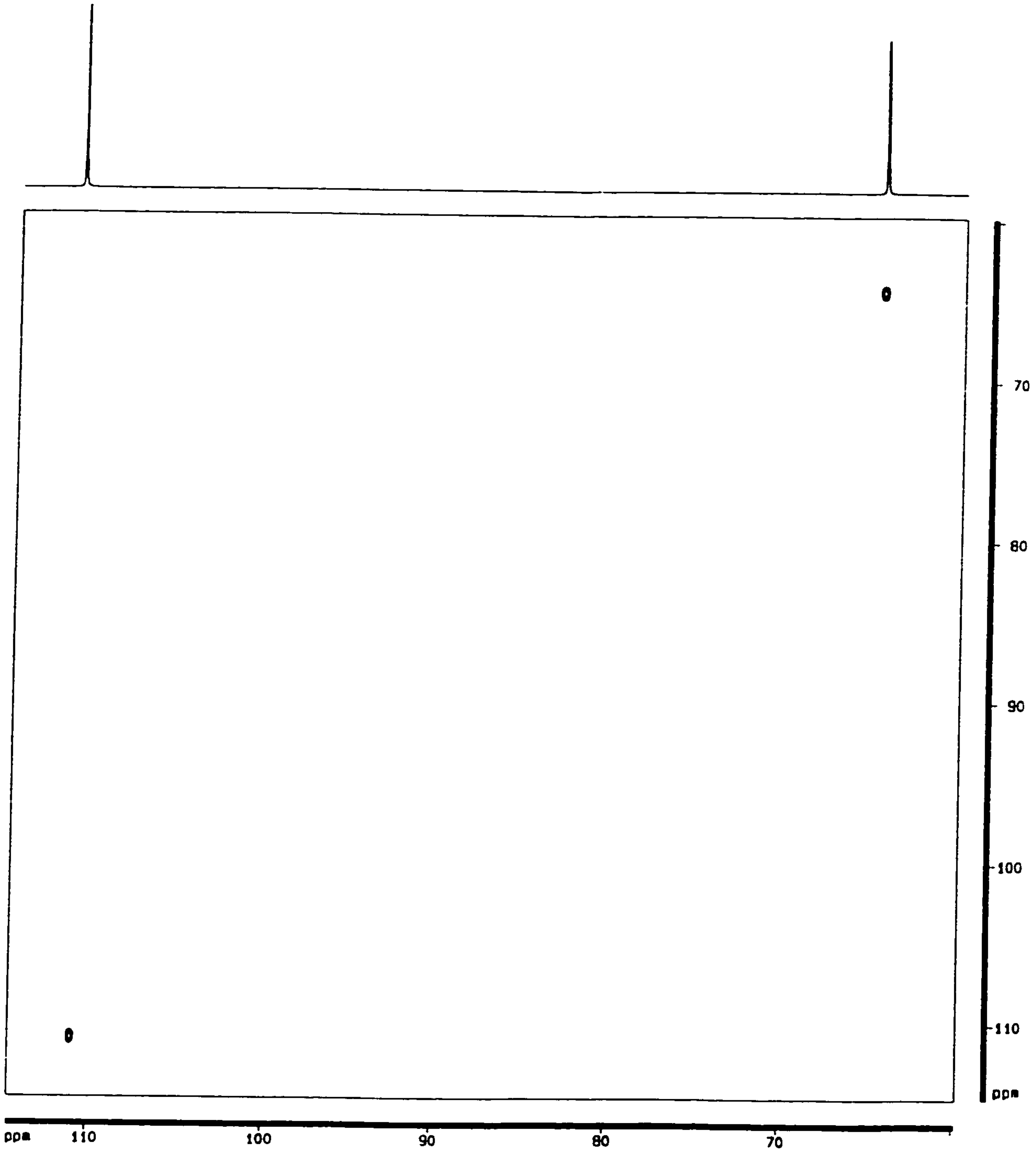
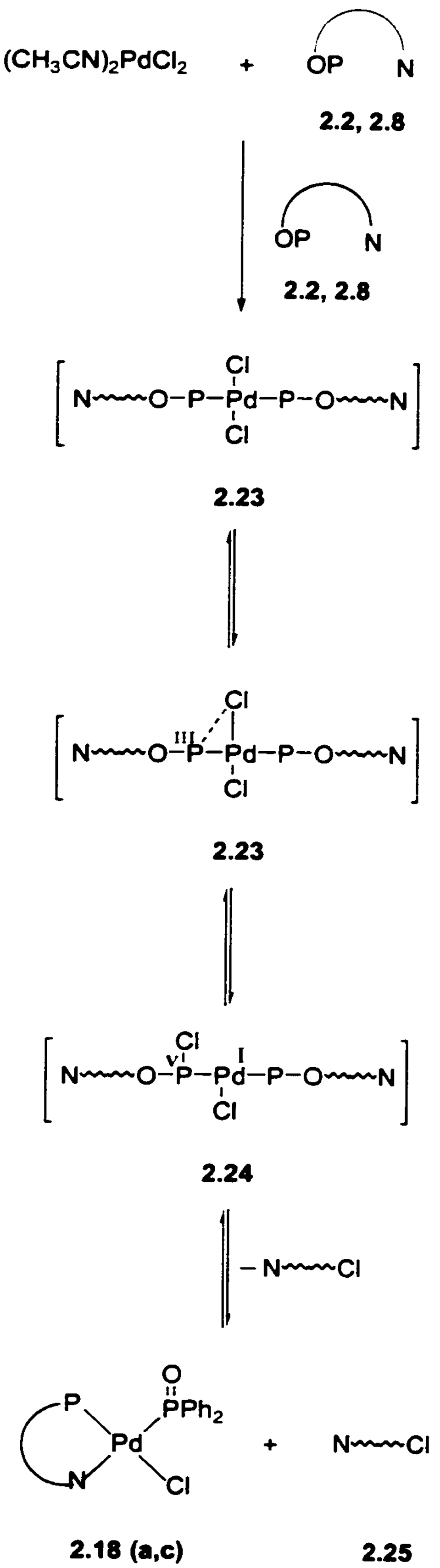


Fig. 11: A NOESY-^{31}P spectrum of an isolated **2.18a**, showing the two phosphorus atoms to no longer exchange with eachother.

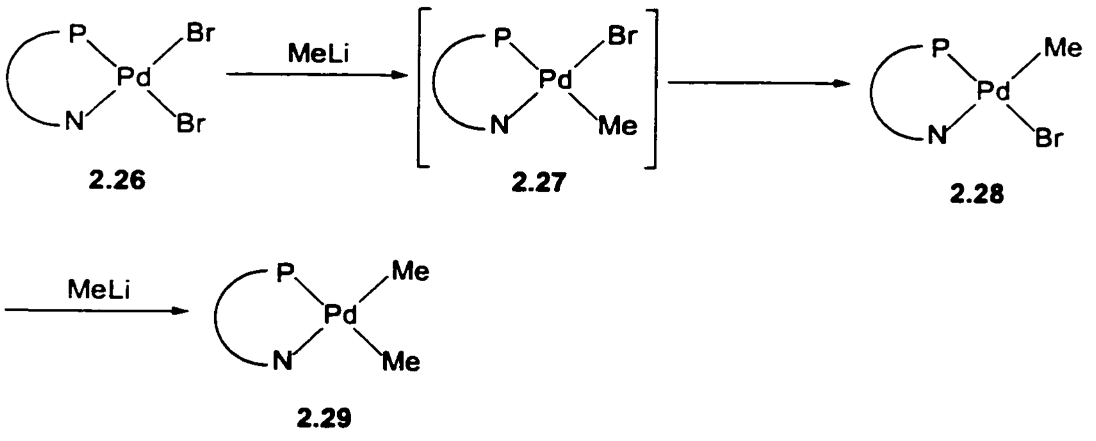


Scheme 5: A Possible Mechanism for the Formation of **2.18 (a,c)**

2.2.3 Attempted Modification of 2.15(a-c)

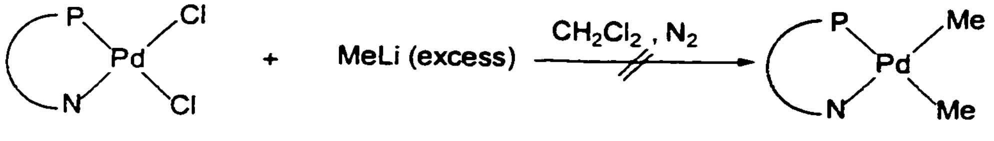
*2.2.3.1 Attempt to Methylate Complexes **2.15 (a-c)***

In 1988, a dimethylpalladium (II) complex containing the potentially (P,N)-chiral bidentate ligand (o-diphenylphosphino-α-methyl-N,N-dimethylbenzylamine) **2.2** was prepared by treating the dihalide complex **2.26** with an excess of MeLi, which was isolated as a cream-white air-stable solid (eq 27).[33g] Attempts to prepare **2.27**, the geometrical isomer of **2.28**, by treatment of (P,N)PdBr$_2$ with one equivalent of MeLi were unsuccessful. Substitution of the bromine trans to phosphorus was expected, as a consequence of the larger trans-influence of phosphines compared to amines,[55] but these reactions provided only a small amount of **2.28** (5%) together with **2.29** (45%) and starting material **2.26** (50%). The explanation of this result was that complex **2.27** was formed as an intermediate and rearranged to thermodynamically more stable **2.28**. The yields were dependent on the (P,N) ligands used: for example, a higher yield was obtained for the (P,N)-ligated dimethylpalladium (II) complex, [(P,N)= (Ph$_2$PCH$_2$CH$_2$NMe$_2$)] (82%), prepared in a similar fashion.[57]



(27)

An attempt to synthesize **2.29** from **2.15 (a-c)**, (eq 28), failed to give any results. Instead, decomposition into palladium-black occurred upon addition of MeLi. Various reaction conditions were explored to reduce this decomposition. However, the decomposition was still observed even though the reaction temperature was as low as -30°C. Changing the solvent from CH_2Cl_2 to methanol, THF and benzene did not reduce or slow down this decomposition.



2.15(a-c) **2.29** **(28)**

2.2.3.2 Attempt to Prepare Complexes 2.15 (a-c) With Other Chiral Ligands

(P,N)-bidentate chiral ligands **2.30** and **2.31**, analogous to ligand **2.2**, were prepared according to the same procedure (outlined in section 2.1.1). An attempt to synthesize the complexes **2.15** using these ligands was unsuccessful. Treatment of $(CH_3CN)_2PdCl_2$ with an equivalent amount of **2.30** in CH_2Cl_2 gave a homogeneous dark orange solution. A ^{31}P NMR spectrum of this solution was unclean and isolation of the desired product failed due to the high impurities present. The reaction with two equivalents of the ligand gave a similar result. The reactions were stirred for 3 days under a constant flow of N_2, and were monitored by ^{31}P NMR spectroscopy. Palladium black was observed after the reaction.

In contrast, the reaction of $(CH_3CN)_2PdCl_2$ with an equivalent amount of ligand **2.31** in methylene chloride gave a sharp signal at 108 ppm in the ^{31}P NMR spectrum, corresponding to the desired product. However, the reaction was unclean and the product was difficult to isolate in a pure form. When two equivalents of the ligand were used a similar ^{31}P NMR spectrum to that of **2.18a** was obtained. A set of doublets at (64.16 & 64.25 ppm) and (115.77 & 115.86 ppm) indicated the formation of the desired product. The reaction was also messy and the product couldn't be isolated in a pure form, and hence, was not fully characterized. Complexes **2.15** and **2.18** of this ligand were successfully prepared, however, since both were not pure, full characterization with ^1H & ^{13}C NMR spectroscopy and MS was not possible.

$Ph_2POCH(Ph)CH(CH_3)NCHPh(CH_3)$ $\quad\quad$ $Ph_2POCH(Ph)CH(CH_3)NH(CH_3)$

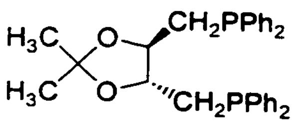
2.30 $\quad\quad$ **2.31**

2.2.3.3 Using Pd(0) instead of Pd(II)

In 1997 Amatore et al. reported the reaction of Pd(0) with chiral and achiral bidentate phosphine ligands.[58] The reaction of $Pd(dba)_2$ with two equivalents of DIOP generated a Pd(0) complex **2.32** in THF, (eq 29).

$$Pd(dba)_2 \quad + \quad 2\ DIOP \longrightarrow \underset{\textbf{2.32}}{Pd(DIOP)_2} \quad + \quad 2\ dba \qquad \textbf{(29)}$$

DIOP =



The attempt to synthesize $Pd(P,N)_2$ complexes by reacting $Pd(dba)_2$ with two equivalents of the ligand **2.2**, **2.7** or **2.8** failed, (eq 30). The ^{31}P NMR spectrum exhibited multiple signals. Identification, isolation and characterization of the major product were not possible.

$$Pd(dba)_2 \quad + \quad \underset{\textbf{2.2, 2.7, 2.8}}{2\ (P,N)} \quad \overset{\text{benzene}}{\not\longrightarrow} \quad Pd(P,N)_2 \qquad \textbf{(30)}$$

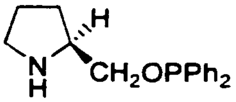
2.2.3.4 Using Ni(0)

In 1984, an aminophosphinite-Ni(0) complex was found to be the most active catalyst for the linear dimerization of butadienes.[49] The conversion was up to 100%, with high yields (98%) at low temperatures (40-60°C) in a 10 minutes duration time. Chiral bidentate aminophosphinite ligands such as **2.31** and **2.33** were used with $Ni(COD)_2$, however, the aminophosphinite-Ni(0) complexes were not isolated nor characterized. An attempt was made to isolate and fully characterize such complexes according to the following procedure:

The ligand **2.31** was added dropwise to a clear light yellow solution of $Ni(COD)_2$ in toluene under nitrogen atmosphere. The solution changed instantly to a darker yellow then into an orange color upon the complete addition of the ligand. A ^{31}P NMR spectrum was immediately obtained for this mixture which exhibited a single signal at $\delta=144.3$ppm, which was believed to be the characteristic peak of the aminophosphinite (P,N)-Ni(0) complex. The signal of the free ligand at $\delta=112.3$ppm was not detected. Unfortunately, the product started decomposing within minutes of the complete addition of the ligand. This decomposition was observed by ^{31}P NMR spectroscopy by the rapid disappearance of the complex peak and appearance of different signals at various chemical shifts, and by the black deposits that precipitated out of the reaction mixture.

$Ph_2POCH(Ph)CH(CH_3)NH(CH_3)$

2.31



2.33

2.3 CYCLOADDITION REACTION OF AZIRIDINES AND HETEROCUMULENES

In 1968 Bittler et al. reported the use of palladium (II) complexes possessing phosphorus and nitrogen ligands, such as $(PhCH_2NH_2)(PPh_3)PdCl_2$ and $(C_5H_{11}N)(PPh_3)PdCl_2$, for the carbonylation of olefins.[59] These catalysts exhibited a catalytic activity similar to that of diphosphine-palladium (II) complexes $(PPh_3)_2PdCl_2$ but higher than that of diamino-palladium (II) complexes $(C_5H_{11}N)_2PdCl_2$. The mechanism for this reaction was not proposed.

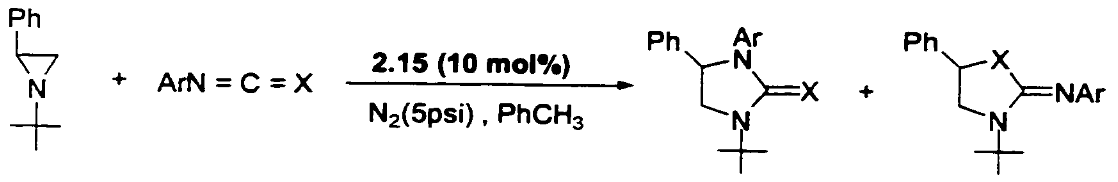
Cycloaddition reaction of aziridines with heterocumulenes was briefly discussed in section 1.2.2. Palladium (II) complexes were found to be the most suitable catalysts for such reactions.[26c,28n,o] Based on this fact, it was reasonable to assume that asymmetric cycloaddition reactions of aziridines with heterocumulenes could be achieved by using chiral palladium (II) complexes, such as complexes **2.15 (a-c)**. This asymmetry would be obtained by one of two possible routes:

1. Sequential dissociation of the two Pd-Cl bonds, leaving two vacant coordination sites for the aziridine and heterocumulene. The mechanism would then proceed according to Scheme 4. Crystal structures of several (P,N)-bidentate palladium (II) complexes showed the Pd-P and Pd-N bonds to be shorter than the two Pd-Cl bonds,[33f,h,k] which could support this hypothesis.

2. The Pd-Cl bond trans to the phosphorus atom would first dissociate, due to the trans-influence of the phosphorus, making it possible for the aziridine to coordinate to palladium. An insertion of the heterocumulene at the Pd-Cl bond trans to the nitrogen atom would then occur, similar to CO-insertion. This would generate a negative charge at one of the heterocumulene ends, which then would attack to the most substituted carbon of the aziridine.

2.3.1 Cycloaddition Reaction of Aziridines and Heterocumulenes Using Complexes 2.15 (a-c) as the Chiral Catalysts

In a glass autoclave, aziridine **2.11** was added dropwise to a suspension of the catalyst **2.15 (a-c)** (10 mol %) in toluene under a constant flow of nitrogen gas. The solution turned bright yellow upon stirring for 2 minutes. The heterocumulene (**2.12**, **2.14**) was added, the glass autoclave was purged and pressurized with 5psi of N_2, and then heated in an oil bath at the required temperature (70°C for carbodiimides **2.14** and 110°C for isocyanates **2.12**). The reaction was monitored by IR spectroscopy, showing the disappearance of the C=N and C=O signals of the carbodiimide and isocyanate respectively. The reaction times were varied from 24-48 hours, depending on the heterocumulene used. The resulting homogeneous red-brown solution was then filtered through Celite. The filtrate was concentrated by rotary evaporation and the crude product was purified by silica gel thin-layer chromatography. Spectroscopic analysis (^{1}H & ^{13}C NMR) indicated the formation of 3,4-disubstituted imidazolidine-2-imines (**2.34**, X=NAr) for the reaction of the aziridine with carbodiimides. The chemoselectivity of the reaction of aziridine with isocyanates was dependent on the type of catalyst. One product, 3,4-disubstituted imidazolidin-2-one (**2.34**, X=O), was formed when catalyst **2.15b** was used while two products, 3,4-disubstituted imidazolidin-2-one (**2.34**, X=O) and 3,5-disubstituted oxazolidin-2-imine (**2.35**, X=O), were obtained when complexes **2.15 (a,c)** were the catalysts, (eq 31). The results are summarized in Table I. It is worth noting that the activity of the three catalysts differs slightly from each other. Catalyst **2.15a** was the most active (affording up to 86% yield for carbodiimides and 82% yield for isocyanates), while **2.15b** exhibited the lowest activity (81% for carbodiimides and 79% for isocyanates).



(31)

2.11 X = O 2.12 2.34 2.35

X = NAr 2.14

Table 1:Cycloaddtion Reaction of Aziridine and Heterocumulenes Catalyzed by Complexes 2.15 (a-c) [a]

Ar	X	2.15	T (°C)	t (h)	yield %[b]	Proportion Of 2.34[c]	Proportion Of 2.35[c]
p-Cl-Ph-N	p-Cl-Ph-N	a	110	36	84	100	0
Ph-N	Ph-N	a	110	36	86	100	0
p-Cl-Ph-N	O	a	70	24	82	67	33
Ph-N	O	a	70	24	80	80	20
p-Cl-Ph-N	p-Cl-Ph-N	b	110	48	80	100	0
Ph-N	Ph-N	b	110	48	81	100	0
p-Cl-Ph-N	O	b	70	36	79	100	0
Ph-N	O	b	70	36	77	100	0
p-Cl-Ph-N	p-Cl-Ph-N	c	110	36	83	100	0
Ph-N	Ph-N	c	110	36	82	100	0
p-Cl-Ph-N	O	c	70	24	81	75	25
Ph-N	O	c	70	24	78	80	20

[a] Reaction conditions: **2.11** (1.0 mmol), **2.12** or **2.14** (1.0 mmol). **2.15** (0.1 mmol), $PhCH_3$ (7.0 mL), 5psi N_2. [b] Isolated yields of pure materials, combined yields of **2.34** & **2.35**. [c] Ratio obtained from an ^1H NMR spectrum.

2.3.2 The Palladium(II)-Catalyzed Cycloaddition Reaction of Aziridines with Carbodiimides

Treatment of aziridine **2.11** with carbodiimides **2.14** (Ar= Ph, *p*-Cl-C_6H_4) in the presence of the palladium catalysts **2.15 (a-c)** (10 mol %) in toluene (7.0 mL) at 110°C for 36-48 hours afforded only 3,4-disubstituted imidazolidine-2-imine (**2.34**, X = NAr) in 80-86% isolated yield. Unfortunately, the reaction did not show any stereoselectivity. A racemic mixture of the products was detected after the reaction. It is worth noting that the reaction was regioselective, since the cleavage of the more substituted ring carbon-nitrogen bond of the aziridine was favoured. In contrast, when bis(benzonitrile)palladium dichloride was the catalyst for this system, the yields were higher (86-95%), and the reaction conditions were slightly better (100°C, 24h).[28m,n] In addition, the economic benefits of using this catalyst, arising from the reduced cost of preparing it compared to the cost of making catalysts **2.15(a-c)**, makes it a better catalyst for this particular system.

2.3.3 The Palladium(II)-Catalyzed Cycloaddition Reaction of Aziridines with Isocyanates

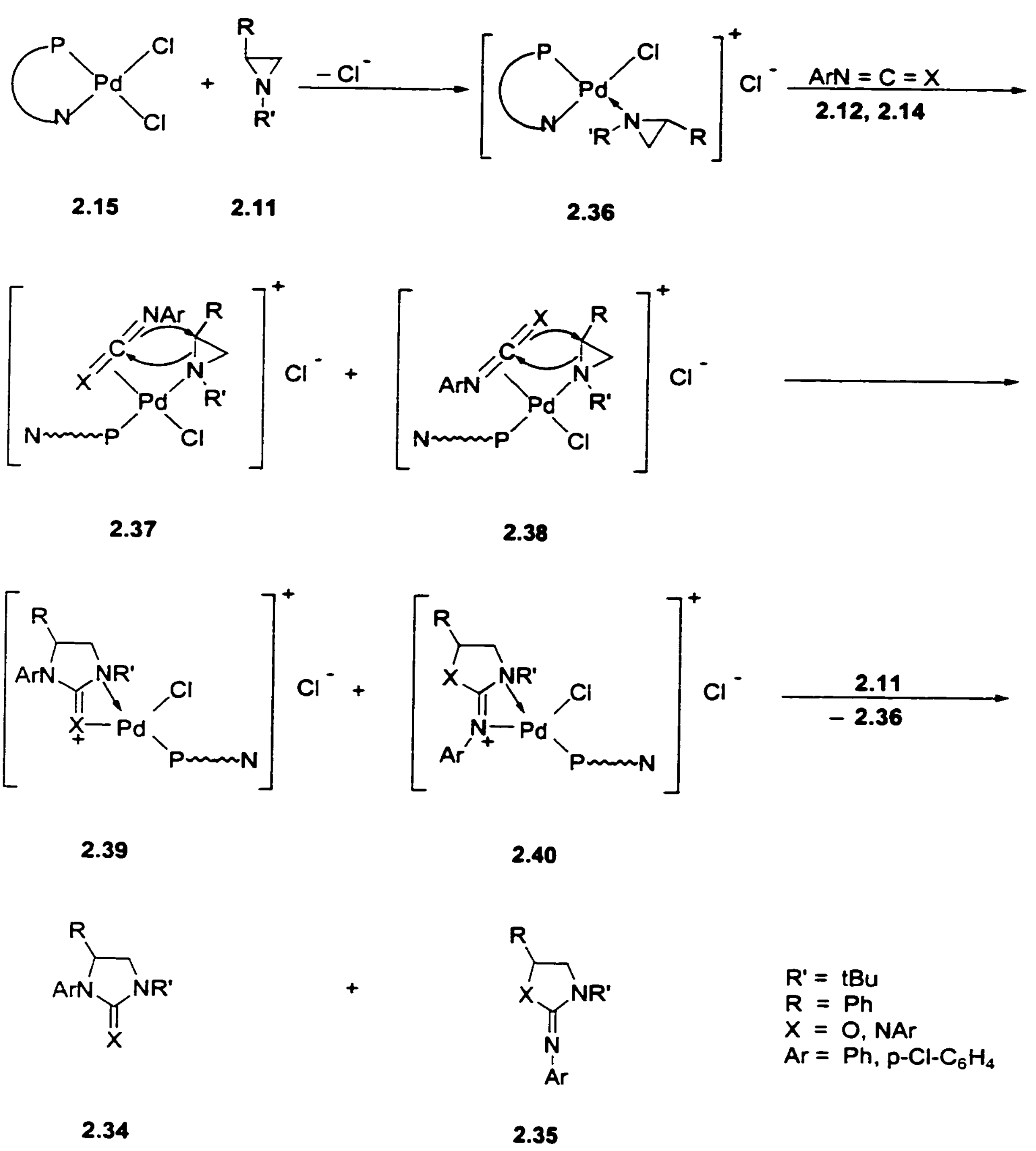
Treatment of aziridine **2.11** with carbodiimides **2.12** (Ar= Ph, *p*-Cl-C_6H_4) in the presence of palladium catalyst **2.15 (a,c)** (10 mol %) in toluene (7.0 mL) gave rise to two products. However, only one product was formed when palladium catalyst **2.15b** was used. Complete conversion occurred after 24-36 hours at 70°C in toluene as the solvent for all cases. The major product was identified as 3,4-disubstituted imidazolidin-2-one (**2.34**, X=O), by ^1H & ^{13}C NMR, IR and mass spectroscopy. The minor product was found to be the 3,5-disubstituted oxazolidin-2-imine (**2.35**, X=O). An NOE NMR experiment of the products confirmed that the major product contains an imidazolidine ring. This result eliminated the possibility of the minor product being the regio-isomer of **2.34**. This behaviour only occurred when the catalyst used was **2.15 (a,c)**. The product obtained was solely **2.34** (X=O) using **2.15b**. This implies that the phosphinite moiety of the ligand plays an important role in this reaction. It is still unclear of how and why the phosphinite moiety [-O-PPh_2] in catalysts **2.15 (a,c)** affects the chemoselectivity, as well as the yield, of this reaction compared to phosphine moiety [-PPh_2] in catalyst **2.15b**. The products in this case as well did not exhibit any stereoselectivity. It is worth noting that when the *t*-butyl group on aziridine **2.11** was replaced with an electron withdrawing group (EWG) such as BOC [-C(O)O-*t*Bu], the reaction was messy, and the ^{1}HNMR spectrum revealed the presence of numerous unidentified products and the desired product could not be isolated. This implies that the presence of an EWG at the nitrogen atom of the aziridine can significantly influence the mechanism of the reaction and, as a result, the outcome of the products. Bis(benzonitrile)palladium dichloride is a more suitable catalyst for this system since it affords **2.34** (X=O) in 81-87%yield,[28m] while **2.15(a-c)** results in two products (**2.34** and **2.35**, X=O) in combined yields of 77-82%. However, the reaction conditions for **2.15(a-c)** (70°C, 24-36h) are less harsh than those of $(PhCN)_2PdCl_2$ (120°C, 24h).

2.3.4 Possible Mechanism

The objective of the reaction of the aziridine with heterocumulenes using complexes **2.15(a-c)** as the chiral catalysts was to achieve significant asymmetric induction of the desired products. The failure to obtain products with enantiomeric excess, which is attributed to the catalysts used, implies that the mechanism does not proceed according to that predicted in section *2.3*. A possible mechanism explaining the results is outlined in Scheme 6. The palladium-catalyzed reaction of aziridine **2.11** with heterocumulene (**2.12**, **2.14**), a process which does not occur in the absence of a metal catalyst; results in the regiospecific formation of 3,4-imidazolidin-2-imines (**2.34**, X=NAr) and 3,4-imidazolidin-2-ones (**2.34**, X=O) in good yields, and in some cases 3,5-oxazolidin-2-imines (**2.35**, X=O) as the minor product. Ligand exchange of **2.15(a-c)** by the aziridine **2.11** may afford the N-coordinated complex **2.36**. This may be due to the trans-influence resulting in the loss of the chlorine atom trans to the phosphorus atom. Reaction of complex **2.36** with carbodiimide (**2.14**, X=NAr) forms complexes **2.37** and

2.38 in which there is a π-complexation of one of the cumulative double bonds to palladium. The need for a vacant coordination site for the heterocumulene is expected to result in Pd-N bond dissociation. The situation may explain the failure to obtain any degree of asymmetric induction. Then, cycloaddition of the aziridine to the uncomplexed double bond of the carbodiimide ligand occurs to give complexes **2.39** and **2.40**, respectively. The generation of the 3,4-imidazolidin-2-imine (**2.34**, X=NAr) may occur via ligand exchange with free aziridine in the reaction mixture, and regenerate **2.36**.

In the case of the reaction of an isocyanate with an aziridine in the presence of palladium catalyst **2.15**, the product formed is dependent on the catalyst used. When catalyst **2.15b** (which possesses a ligand with a phosphine moiety [-PPh_2]) is used, the mechanism of the reaction is similar to that of carbodiimide. The π-complexation to palladium in this case is specific to the carbon-oxygen double bond (C=X), resulting in the formation of intermediate **2.37**. Cycloaddition of the aziridine to the carbon-nitrogen double bond of the isocyanate afforded complex **2.39**. Note that 3,4-imidazolidin-2-one **2.34** (X=O) was the only product formed from this reaction. However, when catalysts **2.15 (a,c)** (which contain ligands with a phosphinite moiety [-O-PPh_2]) are used, two compounds were obtained in the ratio of 2-4:1. There are two possible intermediates formed for the latter case. Intermediate **2.37** consists of π-coordination of palladium to the carbon-oxygen double bond can then afford the 3,4-imidazolidin-2-imine **2.34**. Electron delocalization in palladium-ligated isocyanate may also form intermediate **2.38**, followed by nucleophillic ring opening of the aziridine giving the 3,5-oxazolidin-2-imine **2.35**. The reason for **2.34** being the major product maybe due to the preferential formation of intermediate **2.37** over **2.38** during the catalytic cycle. The regioselective ring opening of the aziridine is observed for this reaction since the reaction involves the cleavage of the most substituted carbon of the aziridine.



R' = tBu
R = Ph
X = O, NAr
Ar = Ph, p-Cl-C_6H_4

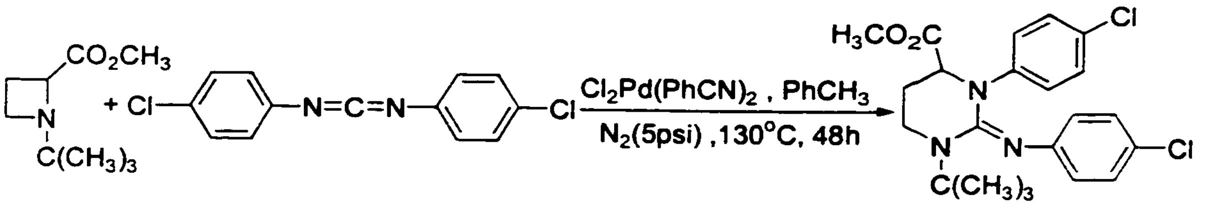
Scheme 6: A possible mechanism for the cycloaddition reaction of aziridine and heterocumulenes using the chiral catalysts **2.15(a-c)**

The mechanistic concept of how the phosphine moiety in catalyst **2.15b** leads to the formation of one product while two products were obtained when the catalyst containing the phosphinite moiety was used is not known. A possible explanation may involve the steric bulkiness of the phosphine moiety compared to that of the phosphinite. It is worth noting that the NAr group is also sterically larger than the oxygen atom at X. The bulkiness of the NAr group and the phosphine moiety of the ligand in catalyst **2.15b** discourage the formation of intermediate **2.38**. In this intermediate, the NAr group is closer to the phosphorus atom of the ligand than that of **2.37**. The formation of this intermediate takes place for catalysts **2.15 (a,c)** with the less bulky aminophosphinite moiety being close to the bulky NAr, but is discouraged for catalyst **2.15b** which has a bulky aminophosphine moiety.

2.3.5 *Attempts to Use Complexes **2.15(a-c)** in Asymmetric Catalysis*

2.3.5.1 *Regioselective Palladium (II)-Catalyzed Cycloaddition of Azetidine and Carbodiimide*

In principle, six-membered ring heterocycles can be synthesized by the cycloaddition of four-membered ring heterocycles and heterocumulenes. The procedure was similar to that of the aziridines, (eq 16, section 1.2.2). When 1-*tert*-butyl-2-carbomethoxyazetidine **2.41** was reacted with an equivalent amount of di-*p*-chlorophenylcarbodiimide **2.42** in toluene at 130°C, using bis(benzonitrile)palladium dichloride as the catalyst, tetrahydropyrimidin-2-imine **2.43** was formed in 95% yield, (eq 33).[28p] Replacing bis(benzonitrile)palladium (II) dichloride with **2.15 (a-c)** gave the six-membered ring heterocycle **2.43** in a 40% yield, but with no enantiomeric excess.



2.41 **2.42** **2.43**

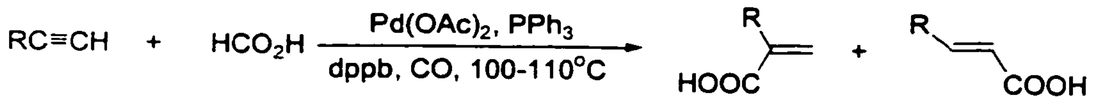
(32)

2.3.5.2 Palladium-Catalyzed Cycloaddition of Vinyl Oxiranes with Heterocumulenes

In section 1.2.1, the cycloaddition reaction of vinyloxiranes with heterocumulenes using Pd(0) catalyst and a ligand was briefly discussed. It was also mentioned that by using chiral ligands, such as TolBINAP, high asymmetric induction could be obtained, eq 7.[26g] An attempt to replace the Pd(0)-TolBINAP catalyst with **2.15 (a-c)** resulted in the recovery of the vinyloxirane and dimerization of the carbodiimide, which precipitated out as a white solid.

2.3.5.3 Palladium-Catalyzed Hydrocarboxylation of Alkynes with Formic Acid

Alkynes **2.44** were hydrocarboxylated with formic acid **2.45** in the presence of catalytic amounts of Pd(0) and suitable phosphine ligands (120psi of CO gas pressure, 100-110°C) to produce the corresponding unsaturated carboxylic acids in 60-90% yields, (eq 33). The products of terminal alkyne reactions were **2.46** and **2.47**. The regioselectivity was approximately 90:10 in favor of **2.46** when R was a phenyl or a straight chain alkyl group; **2.47** was the favored product when R was *t*-Bu and the exclusive one when R was $SiMe_3$.[60]



2.44 **2.45** **2.46** **2.47**

(33)

The activity observed with Pd(II) catalysts was much less than that of Pd(0), (15% yield), with a ratio of 96:4 of **2.46**:**2.47**. Many reports[61] have indicated that chloride ions can strongly influence the catalytic activity of Pd catalysts, which was responsible for the low reactivity of $PdCl_2$ in this system. It was reasoned that adding some NaOAc to the reaction mixture would bring about a ligand-exchange equilibrium, trapping the chloride ions as insoluble NaCl and removing them from the catalytic cycle. The presence of NaOAc dramatically improved the activity of Pd(II), 77%yield.

The hydrocarboxylation reaction of alkynes with formic acid using catalyst **2.15 (a-c)** was expected to give a low yield as described above for Pd(II) catalysts. The reaction of phenylacetylene with formic acid, in the presence of a catalytic amount of catalyst **2.15 (a-c)** under 120 psi of CO gas pressure and 100°C in DME for 18 hours, gave a brown solution with palladium black precipitated from solution. The catalyst was inactive in this system and phenylacetylene was completely recovered. The presence of the two chloride ligands strongly bound to the palladium inhibits the activity of the catalyst and prevents the formation of the active species of the form PdL_4. The purpose was to examine the behaviour of catalysts **2.15 (a-c)** in this particular system without the presence of NaOAc and compare it to the catalyst used previously, (dppb)$PdCl_2$, dppb = [1,4-bis(diphenylphosphino)butane]. The activity of the (P,N)-bidentate palladium (II) catalyst seems to be much lower than that of a (P,P)-bidentate palladium (II) complexes. This may be due to the two strong Pd-P bonds in (dppb)$PdCl_2$ complex compared to the strong Pd-P and weaker Pd-N bonds in **2.15 (a-c)**.

3. CONCLUSION

Chiral bis-chelated palladium (II) dichloride complexes, **2.15(a-c)**, were successfully synthesized from the one pot reaction of bis(acetonitrile)palladium (II) dichloride with an equivalent amount of the ligand (**2.2**, **2.7**, **2.8**). Toluene was the most suitable solvent for this system since the products were insoluble in toluene and precipitated out upon formation. ^{31}P-NMR spectroscopy was used to monitor the formation of these complexes and the end of the reaction was observed by the disappearance of the ligand signal. These complexes were air stable and were found to survive heating up to 120°C. Several attempts to modify catalysts **2.15(a-c)** resulted in their decomposition into palladium black. One of the attempts was to methylate these complexes using excess MeLi at low temperatures. Surprisingly, decomposition into palladium black was observed instead. Other attempts such as reduction with $LiAlH_4$, replacing one of the chlorine atoms with a CO group, using two linear chiral ligands analogous to **2.2**, and replacing Pd(II) with Pd(0) and Ni(0), all failed.

Complexes **2.15(a-c)** were found to be catalytically active but failed to produce an optical bias in any of the systems investigated. They exhibited a slightly different activity, **2.15a** being the most active and **2.15b** being the least active. The cycloaddition reaction of aziridines to carbodiimides, using **2.15(a-c)** as the chiral catalysts, afforded 3,4-disubstituted imidazolidine-2-imine (**2.34**, X=NAr) in good yields. Unfortunately, the reaction did not show any stereoselectivity. The scope of this investigation was extended to include isocyanates. The cycloaddition reaction of aziridines to isocyanates afforded 3,4-disubstituted imidazolidin-2-ones (**2.34**, X=O) as the main product, and, in some cases, 3,5-disubstituted oxazolidin-2-imine (**2.35**, X=O) as the minor product. Oxazolidinimine, being the intermediate for the cycloaddition reaction of oxiranes to carbodiimides, was isolated when **2.15(a,c)** were the catalysts. However, **2.34** (X=O) was the only product formed when **2.15b** was used. The products in this system did not exhibit any stereoselectivity. This may be attributed to the steric bulkiness of the phosphine moiety in **2.15b**, compared to the phosphinite in **2.15(a,c)**, which may prevent the intermediate leading to the formation of **2.35** (X=O) from forming. The dissociation of the Pd-N bond, of the bidentate ligand was a possible explanation for the failure to obtain any degree of asymmetric induction.

In addition to the cycloaddition reaction of an aziridine to heterocumulenes, an attempt to use these catalysts in the same system but using azetidines (4-membered ring heterocycle) instead of the aziridines, afforded the product (tetrahydropyrimidinimine **2.43**) in 40% yield but with no enantiomeric excess. The yield obtained was much lower than that obtained with bis(benzonitrile)palladium dichloride (95%). In other attempted reactions such as cycloaddition of vinyl oxiranes with heterocumulenes and hydrocarboxylation of alkynes with formic acid, **2.15(a-c)** were not active.

An interesting result was obtained when bis(acetonitrile)palladium dichloride was reacted with two equivalents of ligand **2.2** or **2.8**. Complex **2.17** of the form $(P,N)_2PdCl_2$ was the predicted product for this reaction. However, complex **2.18** $Ph_2P(O)Pd(P,N)Cl$ was obtained instead. An X-Ray crystal structure was obtained showing the phosphorus atoms being cis to each other as required by the trans-influence. The structure was square-planar with a slight distortion in the geometry. Complexes **2.18(a,c)** could also be obtained by the reaction of **2.15(a,c)** with an equivalent amount of the corresponding ligand. This reaction could be reversed to produce **2.15(a,c)** by simply reacting **2.18(a,c)** with $(CH_3CN)_2PdCl_2$. This reaction was slow and the conversion was incomplete. The lack of phosphinite moiety from ligand **2.7** prevented the formation of **2.18**, when $(CH_3CN)_2PdCl_2$ reacted with two equivalents of the ligand, and the formation of complex **2.17** was expected. However, because of the high degree of impurity of the solid obtained from this reaction, identification of the product was not possible.

The behaviour of **2.18(a,c)** in solution was investigated. It was observed, based on a series of COSY-^{31}P and NOESY-^{31}P experiments, that the phosphorus atoms not only couple, but also exchange with each other while in solution. This exchange was attributed to the presence of an organic halide (**2.25**) in the mother solution. A NOESY-^{31}P experiment performed on **2.18**, which was isolated an crystallized, showed the two phosphorus atoms to no longer exchange with each other.

4. EXPERIMENTAL

4.1 General Comments

Bruker AMX 500, Varian XL 300 and Gemini 200 NMR spectrometers were used for recording ^{1}H, ^{13}C and ^{31}P spectra. ^{1}H and ^{13}C chemical shifts are reported in ppm and referenced to residual protons in the deuterated solvents (7.24 ppm for $CDCl_3$). ^{31}P NMR chemical shifts are reported in ppm relative to the external standard (85% H_3PO_4). Chemical shifts reported upfield of zero are defined as negative.

A Bomem MB100 FT-IR spectrometer was used with Bomem version 1.45 Michelson series software for all infrared analyses. The samples were run in solution or as KBr pellets.

A VG7070E spectrometer was used for mass spectral determinations. The energy of ionization was 70 eV. For complex mixtures, the mass spectrometer was coupled to a gas chromatograph for GC-MS analysis.

Varian 3300 and Hewlett Packard chromatographs were used for GC analyses. Both instruments were equipped with flame ionization detectors and packed columns containing OV-101 and 1.5% OV-17 + 1.95% OV-210 on Chromosorb W-HP (100-200 mesh), respectively. A Perkin-Elmer 241 polarimeter was used for measuring optical rotations. A standard vacuum line equipped with a two stage Edwards pump was used for handling air and moisture sensitive materials.

A Perkin-Elmer PE CHN 4000 spectrometer was used for elemental analysis. Fischer and Porter glass autoclaves were used for all reactions of aziridine with heterocumulene. For experiments at elevated temperatures, a silicone oil bath was used.

The palladium catalyst, $[(CH_3CN)_2PdCl_2]$, was prepared according to the literature procedure.[62] Organic solvents were dried, purified and distilled as described in the literature.[63] Reagents and palladium acetate were purchased from Aldrich Chemical Company, Inc., Strem Chemicals Co., and Lancaster Co. Carbon monoxide, hydrogen and nitrogen were obtained from Air products Co. Preparative thin layer chromatography was run on silica gel and neutral alumina plates, which were purchased from E.M. Science Co.

4.2 Synthesis of the Chiral Ligands

4.2.1 Synthesis of (+)O-diphenylphosphino-N-methylephedrine 2.2

The procedure reported by Kagan[14] for preparing ligand **2.2** was modified by Alper et al.[37] as follows:

A solution of Ph_2PCl (2.0mL, 11.14.mmol) and an excess of Et_3N (4.0mL) in 30mL of benzene was added to a solution of N-methylephedrine (2.0g, 11.16mmol) in 30mL of benzene. The resulting suspension was refluxed for 1 hour, allowed to cool to room temperature and then filtered. The white solid was washed with benzene (3×10mL), and the combined filtrates were evaporated and dried under vacuum at 100°C. The resulting oil was stirred with hexane:ether (4:1, 15mL), then passed through a short alumina column (50×25mm) using hexane:ether (2:1, 30mL) as the eluant. The solvent was then removed under vacuum affording (+)O-diphenylphosphino-N-methylephedrine **2.2** as a colorless oil. Some characteristic data of the ligand are presented below.

81% yield; ^1H NMR ($CDCl_3$) δ 1.2 (d, J=6.6 Hz, 3H, CH_3), 2.3 (s, 6H, CH_3), 3.0 (m, 1H, CH-N), 5.1 (dd, J=5.5, 8.9 Hz, 1H, CH-O), 7.3-7.8 (m, 15H, aromatic ring protons); ^{13}C NMR ($CDCl_3$) δ 9.8 (s, CH_3), 41.7 (s, CH_3), 65.3 (d, J=6.2 Hz, CH-N), 85.1 (d, J=18.5 Hz, CH-O), 126.52-141.65 (aromatic carbons), 142.2 (d, J=27 Hz, quaternary aromatic carbon), 142.4 (d, J=2.4 Hz, quaternary aromatic carbon); ^{31}P NMR ($CDCl_3$) δ 111.9.

4.2.2 Synthesis of (S)-Prophos 2.7

According to Bowman's procedure,[42] the (S)-proline **2.3** was methylated by reductive condensation with formaldehyde and hydrogen in the presence of Pd/C in water. The N-methylproline **2.4**, obtained by removing the catalyst, excess formaldehyde and the solvent, was subjected to the subsequent reduction without further purification by recrystallization. (S)-1-methyl-2-(hydroxymethyl)pyrrolidine **2.5** was prepared, according to Hayashi's method[16a] by reducing N-methylproline **2.4** with lithium aluminum hydride in THF which was then treated with hydrochloric acid and thionyl chloride in chloroform to give (S)-1-methyl-2-(chloromethyl)pyrrolidine hydrochloride **2.6**. Conversion of **2.6** into (S)-Prophos **2.7** according to Whitesides' method,[44] which was later modified by Hayashi,[16a] was achieved by the addition of tert-butoxide followed by diphenylphosphine in dry THF under a constant flow of nitrogen. Some characteristic data of the ligand are presented below.

78% yield; ^{1}H NMR (C_6D_6) δ 1.27-2.22, 2.50-2.61, 2.89-3.00 (m, 9H, CH_2's & CH), 2.18 (s, 3H, CH_3), 7.1-7.6 (m, 10H, aromatic ring protons); ^{13}C NMR (C_6D_6) δ 22.9 (s, CH_2-ring), 32.6 (d, J=8.5 Hz, CH_2-ring), 34.2 (d, J=14.1 Hz, CH_2-PPh_2), 40.03 (s, CH_3), 57.2 (s, CH_2-N), 63.9 (d, J=17.9 Hz, CH), 128.4-133.6 (aromatic carbons), 139.7 (d, J=14.8 Hz, quaternary aromatic carbon), 140.6 (d, J=14.4 Hz, quaternary aromatic carbon); ^{31}P NMR (C_6D_6) δ -20.6.

4.2.3 Synthesis of (S)-1-methyl-2-(diphenylphosphinomethyl)pyrrolidine 2.8

The (S)-1-methyl-2-(diphenylphosphinomethyl)pyrrolidine **2.8** was prepared according to the procedure described in 3.1.1 used to prepare (+)O-diphenylphosphino-N-methylephedrine **2.2** by treating (S)-1-methyl-2-(hydroxymethyl)pyrrolidine **2.5** with Ph_2PCl in the presence of excess Et_3N. The ligand was isolated as a colorless oil. Some characteristic data of the ligand are presented below.

83% yield; ^{1}H NMR ($CDCl_3$) δ 1.61-2.59 (m, 6H, CH_2's ring), 2.42 (s, 3H, CH_3), 3.01 (t, J=7.1 Hz, 2H, CH_2-O), 3.75 (m, 1H, CH), 7.29-7.62 (m, 10H, aromatic ring protons); ^{13}C NMR ($CDCl_3$) δ 22.4 (s, CH_2-ring), 28.8 (s, CH_2-ring), 41.07 (s, CH_3), 57.5 (s, CH_2-N), 65.8 (d, J=7.7 Hz, CH_2-$OPPh_2$), 72.5 (d, J=17 Hz, CH), 127.8-130.2 (aromatic carbons), 141.7 (d, J=17.6 Hz, quaternary aromatic carbon), 141.9 (d, J=17.8 Hz, quaternary aromatic carbon); ^{31}P NMR ($CDCl_3$) δ 115.2.

4.3 Synthesis of cis-Dichloro[(+)*O*-diphenylphosphino-N-methylephedrine] Palladium (II), cis-Dichloro[(*S*)-Prophos] Palladium (II), and cis-Dichloro[(*S*)-1-methyl-2-(diphenylphosphinomethyl)pyrrolidine] Palladium (II) complexes ([Cl_2PdL^*])

General Procedure

In a Schlenk flask, (N_2 atmosphere), a solution of the ligand (0.193mmol, 0.325M in C_6H_6) was added to a suspension of bis(acetonitrile)palladium dichloride (50mg, 0.193mmol) in toluene (3.0mL). The mixture was stirred for five minutes at room temperature. The resulting light yellow solid was separated by decantation, washed with toluene several times (3×5mL) and dried under vacuum. The product was crystallized from CH_2Cl_2 (5mL)/ Et_2O (15mL) for elemental analyses. Some characteristic data of the ligand are presented below.

Synthesis of Cl_2PdL^* (2.15a), L*= (2.2)

81% yield; ^{1}H NMR ($CDCl_3$) δ 1.33 (d, J=6.2 Hz, 3H, CH_3), 2.23 (m, 1H, CH-N), 3.07 (s, 3H, N-CH_3), 5.13 (d, J=7.3Hz, 1H, CHPh), 7.21-8.20 (m, 15H, aromatic ring protons); ^{13}C NMR ($CDCl_3$) δ 12.13 (CH_3), 52.04 (NCH_3), 52.11 (NCH_3), 70.06 (CH-N), 77.34 (CHPh), 125.56-134.21 (aromatic carbons); ^{31}P NMR ($CDCl_3$) δ 102.79 (s). Anal. Calcd. for $C_{23}H_{26}Cl_2NOPPd$: C, 51.09; H, 4.85; N, 2.59. Found: C, 50.77; H, 4.80; N, 2.54.

Synthesis of Cl_2PdL^* (2.15b), L*= (2.7)

87% yield; ^1H NMR ($CDCl_3$) δ 1.51-2.98 (m, 8H, CH_2's), 3.11 (s, 3H, CH_3), 4.59 (m, 1H, CH), 7.32-8.17 (m, 10H, aromatic ring protons); ^{13}C NMR ($CDCl_3$) δ 21.57 (s, CH_2 ring), 28.45 (d, J= 6.0 Hz, CH_2 ring), 34.53 (d, J= 26.0 Hz, CH_2-PPh_2), 49.20 (s, CH_3), 62.99 (s, N-CH_2 ring), 73.60 (d, J= 5.0 Hz, CH), 127.52-134.05 (aromatic carbons); ^{31}P NMR ($CDCl_3$) δ 47.31 (s). Anal. Calcd. for $C_{18}H_{22}Cl_2NPPd$: C, 46.93; H, 4.81; N, 3.04. Found: C, 47.12; H, 4.81; N, 3.10.

Synthesis of Cl_2PdL^* (2.15c), L*= (2.8)

91% yield; ^1H NMR ($CDCl_3$) δ 1.76-2.89 (m, 6H, CH_2's-ring), 3.10 (s, 3H, CH_3), 3.88 (m, 2H, CH_2-O), 4.64 (m, 1H, CH), 7.34-8.22 (m, 10H, aromatic ring protons); ^{13}C NMR ($CDCl_3$) δ 21.42 (s, CH_2 ring), 24.01 (s, CH_2 ring), 49.56 (s, CH_3), 64.28 (s, N-CH_2 ring), 64.96 (s, CH_2-O), 67.98 (d, J= 5.1 Hz, CH), 128.24-134.32 (aromatic carbons); ^{31}P NMR ($CDCl_3$) δ 102.85 (s). Anal. Calcd. for $C_{18}H_{22}Cl_2NOPPd$: C, 45.36; H, 4.65; N, 2.94. Found: C, 45.25; H, 4.55; N, 2.84.

4.4 Synthesis of [Diphenylphosphine oxide][(+)O-diphenylphosphino-N-methylephedrine] and [Diphenylphosphine oxide][(*S*)-1-methyl-2-(diphenylphosphinomethyl)pyrrolidine] Palladium Chloride Complexes [Cl(POPh$_2$)PdL*]

General Procedure

In a Schlenk flask, (N_2 atmosphere), a solution of the ligand (0.386mmol, 0.325M in C_6H_6) was added to a suspension of bis(acetonitrile)palladium dichloride (50mg, 0.193mmol) in methylene chloride (3.0mL) at room temperature. The resulting yellow homogeneous solution was then taken to dryness. The light yellow solid was dissolved in methylene chloride (5mL) followed by dilution with ether (15mL), then left standing overnight. The precipitated colorless crystals were separated, rinsed with ether (3×5mL) and dried under vacuum.

Synthesis of ClPd(POPh$_2$)L* (2.18a), L*= 2.2

85% yield; IR ν (P=O) 1106 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (d, J=6.3 Hz, 3H, CH_3), 2.18 (m, 1H, CH-N), 2.72 (s, 3H, CH_3N), 2.85 (s, 3H, CH_3N), 4.96 (d, J=8.6Hz, 1H, CHPh,), 7.04-8.24 (m, 25H, aromatic ring protons); ^{13}C NMR ($CDCl_3$) δ 12.11 (CH_3), 48.46.04 (NCH_3), 49.32 (NCH_3), 70.01 (CH-N), 75.62 (CHPh), 125.46-136.19 (aromatic carbons); ^{31}P NMR ($CDCl_3$) δ 63.88 (d, J=15.2 Hz), 110.51 (d, J=15.2Hz); ^{15}N NMR ($CDCl_3$: $CHCl_3$ = 1 : 5) δ -388.9 (d, J= 5.6 Hz), -389.6 (d, J= 5.6 Hz). Anal. Calcd. for $C_{35}H_{36}ClNO_2P_2Pd$: C, 59.50; H, 5.14; N, 1.98. Found: C, 59.20; H, 5.14; N, 2.00.

Synthesis of ClPd(POPh$_2$)L* (2.18c), L*= 2.8

90% yield; IR ν (P=O) 1109 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51-2.59 (m, 6H, CH_2's ring), 2.68 (s, 3H, CH_3), 3.92 (m, 2H, CH_2-O), 4.62 (m, 1H, CH), 7.05-8.29 (m, 20H, aromatic ring protons); ^{13}C NMR ($CDCl_3$) δ 21.89 (CH_2 ring), 24.33 (CH_2 ring), 45.28 (CH_3), 60.13 (N-CH_2 ring), 62.78 (CH_2-O), 67.52 (CH), 126.91-135.14 (aromatic carbons); ^{31}P NMR ($CDCl_3$) δ 62.40

(d, J=15.0 Hz), 112.26 (d, J=15.0Hz) Anal. Calcd. for $C_{30}H_{32}ClNO_2P_2Pd$: C, 56.16; H, 5.03; N, 2.18. Found: C, 55.94; H, 5.01; N, 2.17.

4.5 Cycloaddition Reactions of An Aziridine and Heterocumulenes

4.5.1 General Procedure for the Palladium-Catalyzed Cycloaddition Reaction of 1,2-Disubstituted Aziridines and Carbodiimides

A mixture of aziridine (1.0mmol), carbodiimide (1.0mmol), and palladium catalyst **2.15(a-c)** (0.10mmol) in toluene (7.0mL) was heated with stirring in a glass autoclave for 36h, at 110°C (oil bath temperature) under a slight pressure of nitrogen (5psi). After being cooled to room temperature, the autoclave was opened and the red-brown homogeneous solution was filtered through Celite. The filtrate was concentrated by rotary evaporation, and the crude product was purified by silica gel thin-layer chromatography using 1:1 heptane/ether as the developer. IR, NMR and MS data for the products are as follows:

Synthesis of 1-tert-Butyl-3,4-diphenylimidazolidine-2-phenylimine (2.34). (X=Ar=Ph)

86%**a**, 82%**b**, 81%**c**; IR ν (C=N) 1641 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.56 (s, 9H, CH_3), 3.30 (dd, J= 7.8, 8.8 Hz, 1H, CH_2), 3.88 (t, J= 8.6 Hz, 1H, CH_2), 4.52 (t, J= 8.0 Hz, 1H, CHPh), 6.49-7.45 (m, 15H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 27.24 (CH_3), 51.84 (CH_2), 54.40 ($C(CH_3)_3$), 65.61 (CHPh), 119.35, 122.20, 125.40, 126.76, 127.86, 128.07, 128.77, 128.86 (aromatic carbons), 142.24, 143.61, 149.73 (quaternary aromatic carbons), 151.82 (C=N); MS (m/e) 369 $[M]^+$.

Synthesis of 1-tert-Butyl-4-phenyl-3-p-chlorophenylimidazolidine-2-p-chlorophenylimine (2.34). (X=Ar=p-Cl-C_6H_5N)

84%**a**, 83%**b**, 80%**c** yield; IR ν (C=N) 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$) of δ 1.54 (s, 9H, CH_3), 3.32 (dd, J= 7.9, 8.9 Hz, 1H, CH_2), 3.88 (t, J= 8.6 Hz, 1H, CH_2), 4.46 (t, J= 8.2 Hz, 1H, CHPh), 6.52-7.40 (m, 13H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 27.30 (CH_3), 51.85 (CH_2), 54.63 ($C(CH_3)_3$), 65.86 (CHPh), 123.27, 125.71, 127.14, 127.77, 128.29, 128.65, 128.78, 130.41, 141.21, 141.86, 148.01 (aromatic carbons), 152.14 (C=N); MS (m/e) 438 $[M]^+$.

4.5.2 General Procedure for the Palladium-Catalyzed Cycloaddition Reaction of Aziridines and Isocyanates

A mixture of aziridine (1.0mmol), heterocumulene (1.0mmol), and palladium catalyst **2.15(a-c)** (0.10mmol) in toluene (7.0mL) was heated with stirring in a glass autoclave for 24h, at 70°C (oil bath temperature) under a slight pressure of nitrogen (5psi). After being cooled to room temperature, the autoclave was opened and the red-brown homogeneous solution was filtered through Celite. The filtrate was concentrated by rotary evaporation, and the crude product was purified by silica gel thin-layer chromatography using 9:1 hexane/ether as the developer. IR, NMR and MS data for the products are as follows:

Synthesis of 1-tert-Butyl-3,4- diphenylimidazolidin-2-one (2.34) and 1-tert-Butyl-3,5- diphenyloxazolidin-2-imine (2.35). (X=O, Ar=PhN)

78%**a**, 77%**b**, 80%**c** yield; **2.34**: IR ν (C=O) 1699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 9H, CH_3), 3.38 (dd, J= 6.5, 8.7 Hz,1H, CH_2 ring), 3.86 (dd, J= 6.8, 8.5 Hz,1H, CH_2 ring), 5.34 (t, J= 7.8Hz,1H, CHPh), 6.97-7.41 (m, 10H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 27.06 (CH_3), 51.80 (CH_2 ring), 53.72 ($C(CH_3)_3$), 56.79 (CHPh), 120.07, 123.41, 126.09, 128.29, 128.59, 128.72 (aromatic carbons), 139.15, 140.06 (quaternary aromatic carbons), 158.89 (C=O);
2.35: IR ν (C=N) 1675 cm^{-1}; ^{1}H NMR ($CDCl_3$) of δ 1.47 (s, 9H, CH_3), 3.21 (dd, J= 6.5, 8.6 Hz,1H, CH_2 ring), 3.83 (t, J= 7.8 Hz,1H, CH_2 ring), 5.06 (dd, J= 6.6, 8.9 Hz, 1H, CHPh), 6.97-

7.41 (m, 10H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 27.40 (CH_3), 49.73 (CH_2 ring) 53.45 ($C(CH_3)_3$), 57.12 (CHPh), 75.68 (C-O), 121.42, 125.63, 127.86, 128.39, 128.68, 128.86 (aromatic carbons), 139.31, 140.10 (quaternary aromatic carbons), 150.57 (C=N); MS (m/e) 294 $[M]^+$.

Synthesis of 1-tert-Butyl-3-p-chlorophenyl-4-phenylimidazolidin-2-one (2.34) and 1-terty-Butyl-3-p-chlorophenyl-5-phenyloxazolidin-2-imine (2.35). (X=O, Ar=p-Cl-C_6H_4N)

82%**a**,81%**b**, 79%**c**; **2.34**: IR ν 1681 cm^{-1}; ^{1}H NMR ($CDCl_3$) of δ 1.51 (s, 9H, CH_3), 3.38 (dd, J= 6.3, 8.3 Hz, 1H, CH_2 ring), 3.87 (dd, J= 6.5, 8.9 Hz, 1H, CH_2 ring), 5.30 (t, J= 7.8Hz, 1H, CHPh), 7.03-7.50 (m, 9H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 27.07 (CH_3), 51.79 (CH_2 ring), 53.90 ($C(CH_3)_3$), 56.96 (CHPh), 121.14, 126.35, 128.68, 128.97, 129.49 (aromatic carbons), 128.18, 138.61, 140.73 (quaternary aromatic carbons), 158.49 (C=O);

2.35: IR ν (C=N) 1691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 9H, CH_3), 3.18 (dd,J= 6.9, 9.2 Hz, 1H, CH_2 ring), 3.82 (t, J= 7.9 Hz, 1H, CH_2 ring), 5.02 (dd, J= 6.9, 9.0 Hz, 1H, CHPh), 7.03-7.50 (m, 9H, aromatic protons); ^{13}C NMR ($CDCl_3$) δ 27.37 (CH_3), 49.45 (CH_2 ring), 53.55 ($C(CH_3)_3$), 57.03 (CHPh), 75.73 (C-O), 124.82, 125.61, 126.00, 128.07, 128.27 (aromatic carbons), 128.56, 139.28, 140.16 (quaternary aromatic carbons), 152.53 (C=N); MS (m/e) 328 $[M]^+$.

4.6 Single Crystal Diffraction Study of 2.18a

Crystals of **2.18a** were obtained by layering a concentrated solution of methylene chloride with ether. One of the crystals, having approximate dimensions of 0.3 × 0.1 × 0.06 mm, was mounted on a thin glass fibre using paraffin oil, and cooled to the data collection temperature of -70°C. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. The monoclinic cell had dimensions of a = 10.182(3) A, b = 24.630(7) A, c = 13.654(4) A, β = 101.530(3). For Z = 4 and FW = 706.44, the calculated density was 1.399 g/cm^3. Semi-empirical absorption corrections based on equivalent reflections were applied.[64] All the measurements were made on a Rigaku diffractometer with Mo Kα radiation. A total of 21166 reflections were collected. The unique set contains only 13913 reflections.

Systematic absences in the diffraction data and unit-cell parameters were consistent with $P2_1$ and $P2_1/m$. Although the centric space group was thoroughly investigated, only the solution in $P2_1$ was computationally stable and chemically reasonable. The structure was solved by direct methods, completed with difference Fourier syntheses and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Refinement of the Flack parameter yielded nil indicating the true hand of the data was determined. Weights based on counting statistics were used, and the maximum and minimum peaks on the final difference Fourier map corresponded to 0.975 and -1.315 e/a^3, respectively. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library.[65]

Table 2: Crystal Data Collection and Refinement Information for Compound 2.18a.

Empirical formula	C35 H36 Cl N O2 P2 Pd
Formula weight	706.44
Temperature	203(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 10.182(3) A alpha = 90 deg. b = 24.630(7) A beta = 101.530(3) deg c = 13.654(4) A gamma = 90 deg.
Volume	3355(2) A^3
Z, Calculated density	4, 1.399 Mg/m^3
Absorption coefficient	0.759 mm^-1
F(000)	1448
Crystal size	0.3 x 0.1 x 0.06 mm
Theta range for data collection	1.52 to 28.59 deg.
Limiting indices	-13<=h<=13, -29<=k<=33, 0<=l<=18
Reflections collected / unique	21166 / 13913 [R(int) = 0.0609]
Completeness to theta = 28.59	90.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.801508 and 0.585780
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13913 / 1 / 757
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I)]	R1 = 0.0547, wR2 = 0.1000
R indices (all data)	R1 = 0.1039, wR2 = 0.1083
Absolute structure parameter	-0.01(3)
Largest diff. peak and hole	0.975 and -1.315 e.A^-3

Table 3: Atomic Parameters X, Y, Z and U(eq) for 2.18a.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Pd(1)	9149(1)	6717(1)	1523(1)	25(1)
Pd(2)	4365(1)	8244(1)	6551(1)	23(1)
P(1)	11416(2)	6806(1)	1953(2)	25(1)
P(2)	9538(2)	6027(1)	569(2)	28(1)
P(3)	6622(2)	8169(1)	6837(2)	26(1)
P(4)	4594(2)	8889(1)	5438(2)	22(1)
Cl(1)	8912(2)	7468(1)	2542(2)	36(1)
Cl(2)	4290(2)	7546(1)	7736(2)	33(1)
N(1)	6856(7)	6639(4)	1078(6)	35(2)
N(2)	2108(7)	8430(3)	6459(6)	27(2)
O(1)	12204(6)	6356(3)	1615(5)	30(2)
O(2)	8214(6)	5782(2)	-129(5)	32(2)
O(3)	7317(6)	8623(3)	6409(5)	29(2)
O(4)	3133(5)	9019(2)	4735(5)	26(2)
C(1)	11709(9)	7959(4)	1807(8)	26(2)
C(2)	12110(10)	8407(5)	1365(9)	46(3)
C(3)	12701(9)	8365(5)	519(9)	48(4)
C(4)	12912(10)	7855(5)	157(10)	45(3)
C(5)	12508(8)	7407(4)	620(8)	32(3)
C(6)	11882(8)	7441(4)	1424(8)	24(2)
C(7)	11240(9)	6688(4)	4002(8)	37(2)
C(8)	11796(11)	6685(5)	5002(7)	50(3)
C(9)	13106(11)	6877(4)	5334(8)	48(3)
C(10)	13833(10)	7049(4)	4669(9)	38(3)
C(11)	13264(9)	7062(4)	3681(8)	30(2)
C(12)	11966(8)	6871(4)	3310(7)	24(2)
C(13)	10050(11)	6555(5)	-1100(9)	47(3)
C(14)	10765(10)	6715(5)	-1811(7)	45(3)
C(15)	12000(12)	6435(5)	-1794(9)	48(4)
C(16)	12435(10)	6051(5)	-1106(9)	48(3)
C(17)	11731(9)	5916(4)	-394(8)	37(3)
C(18)	10546(9)	6182(4)	-352(7)	25(2)
C(19)	10572(10)	5360(5)	2188(9)	47(3)
C(20)	10939(10)	4869(6)	2631(11)	65(4)
C(21)	10851(11)	4398(6)	2060(12)	70(5)
C(22)	10431(12)	4438(6)	1045(12)	69(4)
C(23)	10043(11)	4935(6)	607(9)	58(4)
C(24)	10140(9)	5403(4)	1173(9)	31(3)
C(25)	6992(8)	6061(3)	-415(7)	33(2)
C(26)	6194(11)	5193(5)	-1309(10)	55(4)
C(27)	5416(13)	4881(5)	-2055(12)	79(5)
C(28)	4538(10)	5164(4)	-2798(8)	56(3)
C(29)	4483(9)	5721(4)	-2830(7)	41(2)
C(30)	5256(8)	6010(4)	-2033(6)	39(2)
C(31)	6160(8)	5741(3)	-1273(8)	35(2)
C(32)	6285(10)	6152(4)	468(8)	35(3)
C(33)	6392(10)	5635(4)	1114(7)	69(3)
C(34)	6299(9)	6655(4)	2003(7)	54(3)
C(35)	6390(8)	7135(3)	511(8)	51(3)

C(36)	7583(9)	7551(5)	5490(8)	38(3)
C(37)	7938(11)	7062(5)	5065(10)	49(4)
C(38)	7895(11)	6575(5)	5547(11)	53(4)
C(39)	7390(10)	6549(4)	6390(10)	46(3)
C(40)	7022(9)	7039(4)	6810(8)	35(3)
C(41)	7109(8)	7521(4)	6369(8)	28(3)
C(42)	8491(9)	7934(4)	8564(8)	29(2)
C(43)	9066(11)	7964(5)	9586(9)	56(4)
C(44)	8387(10)	8259(5)	10223(7)	45(3)
C(45)	7166(10)	8484(4)	9848(8)	44(3)
C(46)	6531(9)	8435(4)	8847(7)	35(3)
C(47)	7245(8)	8147(4)	8188(7)	26(2)
C(48)	6704(9)	8981(4)	4402(8)	29(2)
C(49)	7277(10)	8857(5)	3581(8)	42(3)
C(50)	6676(12)	8493(4)	2835(8)	41(3)
C(51)	5466(11)	8279(5)	2865(8)	48(3)
C(52)	4844(9)	8395(4)	3692(8)	33(3)
C(53)	5453(9)	8757(4)	4426(7)	19(2)
C(54)	4927(11)	10009(4)	5304(8)	40(3)
C(55)	5222(11)	10524(5)	5669(10)	54(3)
C(56)	5775(10)	10595(5)	6661(9)	41(3)
C(57)	5982(9)	10162(4)	7313(9)	42(3)
C(58)	5645(9)	9624(4)	6947(8)	33(3)
C(59)	5117(9)	9546(4)	5941(8)	27(2)
C(60)	2070(8)	9184(3)	5208(6)	24(2)
C(61)	1251(13)	9623(6)	3540(10)	86(5)
C(62)	314(16)	9970(8)	2921(13)	125(8)
C(63)	-571(13)	10253(7)	3330(14)	126(7)
C(64)	-674(12)	10209(5)	4329(13)	98(5)
C(65)	231(9)	9863(3)	4871(9)	56(3)
C(66)	1142(8)	9564(3)	4515(7)	36(2)
C(67)	1359(8)	8694(4)	5528(8)	28(3)
C(68)	1061(8)	8286(3)	4656(6)	42(2)
C(69)	2167(9)	8781(4)	7324(7)	54(3)
C(70)	1336(9)	7934(4)	6684(8)	54(3)

Table 4: Table of U(i,j) or U values *100.

	U11	U22	U33	U23	U13	U12
Pd(1)	23(1)	29(1)	25(1)	-1(1)	5(1)	2(1)
Pd(2)	23(1)	26(1)	20(1)	3(1)	6(1)	2(1)
P(1)	25(1)	27(2)	21(1)	0(1)	4(1)	0(1)
P(2)	25(1)	31(2)	29(2)	0(1)	6(1)	0(1)
P(3)	25(1)	30(2)	22(1)	2(1)	3(1)	2(1)
P(4)	22(1)	22(2)	21(2)	2(1)	5(1)	2(1)
Cl(1)	34(1)	42(2)	31(2)	-11(1)	6(1)	7(1)
Cl(2)	32(1)	37(1)	29(1)	7(1)	8(1)	1(1)
N(1)	18(4)	50(6)	38(5)	5(5)	9(4)	3(4)
N(2)	26(4)	30(5)	26(5)	20(4)	12(4)	7(3)
O(1)	32(4)	35(4)	23(4)	-2(3)	5(3)	3(3)
O(2)	21(3)	26(4)	48(5)	-5(3)	4(3)	-1(3)
O(3)	30(4)	31(4)	27(4)	-2(3)	8(3)	-8(3)
O(4)	22(3)	40(4)	15(3)	5(3)	1(3)	7(3)
C(1)	27(5)	26(6)	25(6)	-2(5)	2(4)	-1(4)
C(2)	56(7)	50(9)	31(7)	2(6)	4(6)	-3(5)
C(3)	29(6)	65(10)	47(8)	29(7)	1(5)	-10(6)
C(4)	39(7)	53(9)	45(8)	-1(7)	12(6)	-13(6)
C(5)	23(5)	30(7)	39(7)	-8(6)	-2(5)	-4(4)
C(6)	16(5)	33(6)	22(6)	6(5)	2(4)	3(4)
C(7)	41(5)	26(5)	44(6)	-8(5)	8(5)	-2(5)
C(8)	72(8)	67(7)	10(5)	8(6)	5(5)	15(7)
C(9)	71(8)	43(7)	22(6)	-9(5)	-8(6)	1(5)
C(10)	44(6)	40(7)	27(7)	-8(5)	0(5)	-1(5)
C(11)	36(6)	35(6)	19(6)	-1(5)	6(5)	0(4)
C(12)	24(5)	25(6)	23(5)	6(4)	5(4)	3(4)
C(13)	37(6)	49(9)	56(8)	-1(6)	9(6)	-5(5)
C(14)	67(7)	30(6)	42(7)	9(6)	21(6)	-16(6)
C(15)	60(8)	55(8)	39(8)	-23(6)	34(6)	-25(6)
C(16)	31(6)	75(9)	39(7)	-1(6)	5(5)	3(6)
C(17)	24(5)	50(7)	33(7)	-7(5)	-1(5)	-1(5)
C(18)	19(5)	32(6)	22(6)	-7(4)	1(4)	-3(4)
C(19)	50(7)	49(8)	46(8)	22(6)	21(6)	5(6)
C(20)	25(6)	85(10)	90(11)	34(9)	21(6)	-2(6)
C(21)	28(7)	75(10)	108(14)	36(10)	18(7)	12(7)
C(22)	73(9)	39(8)	91(12)	-3(9)	7(9)	13(6)
C(23)	55(8)	83(10)	40(8)	-11(7)	16(6)	12(7)
C(24)	23(5)	29(6)	41(7)	3(5)	6(5)	-5(4)
C(25)	30(5)	19(5)	50(6)	-12(4)	8(5)	-6(4)
C(26)	52(7)	46(7)	59(9)	15(6)	-5(6)	-17(6)
C(27)	83(10)	38(7)	105(14)	-19(8)	-5(9)	-10(7)
C(28)	57(8)	53(7)	59(8)	-34(6)	17(6)	-15(6)
C(29)	44(6)	49(6)	30(6)	-10(5)	10(5)	-2(5)
C(30)	39(6)	40(5)	39(6)	-7(5)	12(5)	-17(5)
C(31)	30(5)	24(5)	56(7)	-11(5)	20(5)	-4(4)
C(32)	26(5)	44(7)	35(7)	-12(5)	6(5)	-16(5)
C(33)	95(9)	71(7)	53(8)	4(6)	39(7)	-36(7)
C(34)	50(6)	68(7)	49(7)	-20(7)	21(5)	-14(6)
C(35)	23(5)	32(5)	87(9)	-21(5)	-18(5)	18(4)
C(36)	31(6)	55(8)	32(7)	-1(6)	15(5)	2(5)

C(37)	47(7)	58(9)	46(8)	-21(7)	21(6)	12(6)
C(38)	63(8)	29(8)	67(10)	-1(7)	14(7)	6(6)
C(39)	55(7)	23(7)	65(10)	8(6)	29(6)	19(5)
C(40)	48(7)	34(7)	24(6)	-2(5)	9(5)	1(5)
C(41)	15(5)	32(6)	36(7)	-8(6)	0(4)	-3(4)
C(42)	30(5)	29(6)	29(6)	5(5)	6(5)	8(4)
C(43)	50(7)	67(9)	38(8)	6(7)	-19(6)	0(6)
C(44)	54(6)	52(7)	22(6)	5(6)	-10(5)	-10(6)
C(45)	51(7)	57(7)	29(6)	-19(5)	18(5)	-9(5)
C(46)	34(5)	43(7)	24(6)	3(5)	0(5)	0(4)
C(47)	29(5)	23(6)	26(5)	7(4)	1(4)	-4(4)
C(48)	30(6)	37(6)	22(6)	2(5)	9(4)	3(4)
C(49)	28(6)	56(8)	44(8)	15(6)	16(5)	8(5)
C(50)	54(7)	41(6)	34(7)	14(5)	22(6)	30(5)
C(51)	71(7)	44(7)	29(6)	6(6)	11(5)	22(7)
C(52)	30(5)	32(7)	36(6)	-2(5)	8(5)	0(4)
C(53)	27(5)	20(5)	13(5)	8(4)	6(4)	2(4)
C(54)	66(7)	26(6)	27(6)	4(5)	8(5)	-6(5)
C(55)	71(8)	25(6)	72(9)	7(6)	31(7)	-7(6)
C(56)	34(6)	34(6)	57(8)	-19(6)	16(6)	-5(5)
C(57)	32(6)	44(7)	50(8)	-25(6)	8(5)	-2(5)
C(58)	30(6)	30(6)	37(7)	4(5)	-2(5)	6(4)
C(59)	26(5)	36(6)	20(5)	-4(5)	8(4)	-11(4)
C(60)	26(5)	27(5)	19(5)	-2(4)	2(4)	10(4)
C(61)	65(9)	140(15)	52(9)	55(10)	12(7)	45(9)
C(62)	116(14)	186(19)	75(13)	88(13)	24(11)	85(13)
C(63)	62(10)	133(14)	167(18)	80(14)	-15(11)	36(9)
C(64)	74(10)	49(8)	158(15)	9(9)	-13(10)	23(7)
C(65)	46(7)	32(5)	92(9)	10(6)	17(6)	13(5)
C(66)	16(5)	31(5)	57(7)	13(5)	-3(5)	1(4)
C(67)	14(5)	35(6)	34(7)	1(5)	1(4)	1(4)
C(68)	36(5)	37(5)	50(6)	3(5)	-1(4)	7(5)
C(69)	51(7)	79(8)	34(6)	-5(6)	15(5)	30(6)
C(70)	33(6)	64(7)	66(8)	33(6)	8(6)	4(5)

Table 5: Atomic Bond Distances in Angstroms and Bond Angles in Degrees for 2.18a.

Pd(1)-P(2)	2.225(3)
Pd(1)-P(1)	2.276(3)
Pd(1)-N(1)	2.300(7)
Pd(1)-Cl(1)	2.356(3)
Pd(2)-P(4)	2.243(3)
Pd(2)-P(3)	2.260(3)
Pd(2)-N(2)	2.322(7)
Pd(2)-Cl(2)	2.371(3)
P(1)-O(1)	1.495(7)
P(1)-C(6)	1.825(10)
P(1)-C(12)	1.832(10)
P(2)-O(2)	1.606(7)
P(2)-C(24)	1.791(11)
P(2)-C(18)	1.816(10)
P(3)-O(3)	1.504(6)
P(3)-C(41)	1.824(11)
P(3)-C(47)	1.827(10)
P(4)-O(4)	1.632(6)
P(4)-C(59)	1.796(11)
P(4)-C(53)	1.806(9)
N(1)-C(35)	1.474(11)
N(1)-C(34)	1.485(10)
N(1)-C(32)	1.508(12)
N(2)-C(69)	1.454(10)
N(2)-C(67)	1.495(12)
N(2)-C(70)	1.517(10)
O(2)-C(25)	1.406(9)
O(4)-C(60)	1.426(9)
C(1)-C(2)	1.359(13)
C(1)-C(6)	1.404(13)
C(2)-C(3)	1.409(15)
C(3)-C(4)	1.383(15)
C(4)-C(5)	1.376(14)
C(5)-C(6)	1.378(13)
C(7)-C(8)	1.369(13)
C(7)-C(12)	1.387(12)
C(8)-C(9)	1.403(13)
C(9)-C(10)	1.349(13)
C(10)-C(11)	1.358(14)
C(11)-C(12)	1.399(12)
C(13)-C(14)	1.383(13)
C(13)-C(18)	1.390(15)
C(14)-C(15)	1.431(14)
C(15)-C(16)	1.344(15)
C(16)-C(17)	1.359(14)
C(17)-C(18)	1.385(12)
C(19)-C(20)	1.370(16)
C(19)-C(24)	1.372(15)

C(20)-C(21)	1.390(18)
C(21)-C(22)	1.369(18)
C(22)-C(23)	1.385(16)
C(23)-C(24)	1.382(15)
C(25)-C(31)	1.521(12)
C(25)-C(32)	1.540(13)
C(26)-C(31)	1.350(13)
C(26)-C(27)	1.390(18)
C(27)-C(28)	1.397(17)
C(28)-C(29)	1.373(12)
C(29)-C(30)	1.403(11)
C(30)-C(31)	1.408(12)
C(32)-C(33)	1.539(14)
C(36)-C(41)	1.383(13)
C(36)-C(37)	1.416(15)
C(37)-C(38)	1.372(16)
C(38)-C(39)	1.352(15)
C(39)-C(40)	1.418(13)
C(40)-C(41)	1.342(14)
C(42)-C(47)	1.375(12)
C(42)-C(43)	1.403(15)
C(43)-C(44)	1.415(15)
C(44)-C(45)	1.364(13)
C(45)-C(46)	1.396(13)
C(46)-C(47)	1.449(12)
C(48)-C(53)	1.395(12)
C(48)-C(49)	1.398(13)
C(49)-C(50)	1.401(15)
C(50)-C(51)	1.349(14)
C(51)-C(52)	1.429(12)
C(52)-C(53)	1.392(13)
C(54)-C(55)	1.375(14)
C(54)-C(59)	1.423(14)
C(55)-C(56)	1.371(15)
C(56)-C(57)	1.379(15)
C(57)-C(58)	1.433(13)
C(58)-C(59)	1.384(14)
C(60)-C(66)	1.518(10)
C(60)-C(67)	1.516(12)
C(61)-C(66)	1.365(14)
C(61)-C(62)	1.426(17)
C(62)-C(63)	1.346(19)
C(63)-C(64)	1.394(19)
C(64)-C(65)	1.360(14)
C(65)-C(66)	1.349(11)
C(67)-C(68)	1.542(12)

P(2)-Pd(1)-P(1)	86.23(10)
P(2)-Pd(1)-N(1)	94.1(2)
P(1)-Pd(1)-N(1)	179.2(2)
P(2)-Pd(1)-Cl(1)	175.53(9)
P(1)-Pd(1)-Cl(1)	89.43(10)
N(1)-Pd(1)-Cl(1)	90.2(2)
P(4)-Pd(2)-P(3)	86.30(10)
P(4)-Pd(2)-N(2)	93.38(18)
P(3)-Pd(2)-N(2)	170.6(2)
P(4)-Pd(2)-Cl(2)	175.83(9)
P(3)-Pd(2)-Cl(2)	89.59(9)
N(2)-Pd(2)-Cl(2)	90.79(18)
O(1)-P(1)-C(6)	108.4(4)
O(1)-P(1)-C(12)	107.6(4)
C(6)-P(1)-C(12)	105.9(5)
O(1)-P(1)-Pd(1)	115.4(3)
C(6)-P(1)-Pd(1)	108.1(3)
C(12)-P(1)-Pd(1)	111.0(3)
O(2)-P(2)-C(24)	97.0(4)
O(2)-P(2)-C(18)	101.0(4)
C(24)-P(2)-C(18)	108.1(5)
O(2)-P(2)-Pd(1)	114.1(3)
C(24)-P(2)-Pd(1)	118.1(4)
C(18)-P(2)-Pd(1)	115.8(4)
O(3)-P(3)-C(41)	109.4(4)
O(3)-P(3)-C(47)	108.6(4)
C(41)-P(3)-C(47)	105.3(5)
O(3)-P(3)-Pd(2)	114.4(3)
C(41)-P(3)-Pd(2)	110.5(3)
C(47)-P(3)-Pd(2)	108.2(3)
O(4)-P(4)-C(59)	102.4(4)
O(4)-P(4)-C(53)	96.3(4)
C(59)-P(4)-C(53)	107.6(5)
O(4)-P(4)-Pd(2)	109.3(3)
C(59)-P(4)-Pd(2)	116.2(4)
C(53)-P(4)-Pd(2)	121.5(3)
C(35)-N(1)-C(34)	106.7(8)
C(35)-N(1)-C(32)	108.7(7)
C(34)-N(1)-C(32)	108.6(7)
C(35)-N(1)-Pd(1)	105.8(5)
C(34)-N(1)-Pd(1)	108.3(6)
C(32)-N(1)-Pd(1)	118.2(6)
C(69)-N(2)-C(67)	111.3(7)
C(69)-N(2)-C(70)	104.6(7)
C(67)-N(2)-C(70)	109.0(7)
C(69)-N(2)-Pd(2)	101.2(5)
C(67)-N(2)-Pd(2)	117.6(5)
C(70)-N(2)-Pd(2)	112.2(5)
C(25)-O(2)-P(2)	124.9(5)
C(60)-O(4)-P(4)	118.4(5)
C(2)-C(1)-C(6)	120.0(10)

C(1)-C(2)-C(3)	121.4(11)
C(4)-C(3)-C(2)	118.8(11)
C(3)-C(4)-C(5)	118.9(11)
C(6)-C(5)-C(4)	123.0(11)
C(5)-C(6)-C(1)	117.8(10)
C(5)-C(6)-P(1)	117.5(8)
C(1)-C(6)-P(1)	124.7(8)
C(8)-C(7)-C(12)	120.7(9)
C(9)-C(8)-C(7)	119.9(10)
C(10)-C(9)-C(8)	120.1(10)
C(9)-C(10)-C(11)	119.6(10)
C(10)-C(11)-C(12)	122.5(10)
C(7)-C(12)-C(11)	117.1(9)
C(7)-C(12)-P(1)	124.4(7)
C(11)-C(12)-P(1)	118.1(7)
C(14)-C(13)-C(18)	122.6(10)
C(13)-C(14)-C(15)	115.8(11)
C(16)-C(15)-C(14)	121.1(10)
C(17)-C(16)-C(15)	121.6(11)
C(16)-C(17)-C(18)	120.2(11)
C(13)-C(18)-C(17)	118.3(10)
C(13)-C(18)-P(2)	118.4(8)
C(17)-C(18)-P(2)	123.1(8)
C(20)-C(19)-C(24)	121.2(13)
C(19)-C(20)-C(21)	120.5(15)
C(20)-C(21)-C(22)	118.7(14)
C(23)-C(22)-C(21)	120.3(14)
C(22)-C(23)-C(24)	121.0(12)
C(23)-C(24)-C(19)	118.2(11)
C(23)-C(24)-P(2)	118.6(9)
C(19)-C(24)-P(2)	122.9(9)
O(2)-C(25)-C(31)	106.6(6)
O(2)-C(25)-C(32)	112.4(8)
C(31)-C(25)-C(32)	113.7(7)
C(31)-C(26)-C(27)	124.4(13)
C(28)-C(27)-C(26)	116.4(12)
C(29)-C(28)-C(27)	122.5(11)
C(28)-C(29)-C(30)	118.0(9)
C(29)-C(30)-C(31)	121.0(8)
C(26)-C(31)-C(30)	117.4(10)
C(26)-C(31)-C(25)	122.1(10)
C(30)-C(31)-C(25)	120.3(7)
N(1)-C(32)-C(33)	111.5(9)
N(1)-C(32)-C(25)	111.0(7)
C(33)-C(32)-C(25)	109.7(8)
C(41)-C(36)-C(37)	118.2(12)
C(38)-C(37)-C(36)	120.8(12)
C(39)-C(38)-C(37)	120.3(12)
C(38)-C(39)-C(40)	118.7(11)
C(41)-C(40)-C(39)	121.7(10)
C(40)-C(41)-C(36)	120.2(11)
C(40)-C(41)-P(3)	124.7(9)
C(36)-C(41)-P(3)	115.1(9)

C(47)-C(42)-C(43)	121.5(10)
C(44)-C(43)-C(42)	118.7(10)
C(45)-C(44)-C(43)	119.9(10)
C(44)-C(45)-C(46)	122.8(10)
C(45)-C(46)-C(47)	117.3(9)
C(42)-C(47)-C(46)	119.7(9)
C(42)-C(47)-P(3)	119.8(7)
C(46)-C(47)-P(3)	119.8(7)
C(53)-C(48)-C(49)	117.5(10)
C(50)-C(49)-C(48)	122.1(10)
C(51)-C(50)-C(49)	119.8(10)
C(50)-C(51)-C(52)	119.9(11)
C(53)-C(52)-C(51)	119.6(10)
C(48)-C(53)-C(52)	120.9(9)
C(48)-C(53)-P(4)	122.1(7)
C(52)-C(53)-P(4)	116.9(7)
C(55)-C(54)-C(59)	121.7(11)
C(56)-C(55)-C(54)	119.5(12)
C(55)-C(56)-C(57)	121.3(11)
C(56)-C(57)-C(58)	119.7(10)
C(59)-C(58)-C(57)	119.5(10)
C(58)-C(59)-C(54)	118.3(10)
C(58)-C(59)-P(4)	122.1(9)
C(54)-C(59)-P(4)	119.6(8)
O(4)-C(60)-C(66)	109.2(7)
O(4)-C(60)-C(67)	110.7(7)
C(66)-C(60)-C(67)	113.4(7)
C(66)-C(61)-C(62)	117.8(13)
C(63)-C(62)-C(61)	119.4(15)
C(62)-C(63)-C(64)	123.5(13)
C(65)-C(64)-C(63)	114.0(13)
C(64)-C(65)-C(66)	125.8(12)
C(61)-C(66)-C(65)	119.3(10)
C(61)-C(66)-C(60)	120.7(9)
C(65)-C(66)-C(60)	119.9(9)
N(2)-C(67)-C(60)	113.6(7)
N(2)-C(67)-C(68)	111.2(8)
C(60)-C(67)-C(68)	109.1(8)

5. CLAMIS TO ORIGINAL RESEARCH

1. The synthesis of the cis-dichloro[(+)*O*-diphenylphosphino-N-methylephedrine] palladium dichloride (**2.15a**), cis-dichloro[(*S*)-Prophos] palladium dichloride (**2.15b**), and cis-dichloro[(*S*)-1-methyl-2-(diphenylphosphinomethyl)pyrrolidine] palladium dichloride (**2.15c**) complexes from the one pot reaction of bis(acetonitrile)palladium dichloride with an equivalent amount of ligands **2.2**, **2.7** and **2.8**, respectively.

2. The novel synthesis of [diphenylphosphine oxide][(+)*O*-diphenylphosphino-N-methylephedrine] palladium chloride (**2.18a**) and [diphenylphosphine oxide][(*S*)-1-methyl-2-(diphenylphosphinomethyl)pyrrolidine] palladium chloride (**2.18c**) from the one pot reaction of bis(acetonitrile)palladium dichloride with two equivalent amounts of ligands **2.2** and **2.8**, respectively, or from the reaction of complexes **2.15(a,c)** with an equivalent amount of the corresponding ligand. An X-Ray crystal structure of **2.18a** was obtained.

3. The mechanistic aspect of the formation of **2.18(a,c)**, supported by COSY-^{31}P and NOSEY-^{31}P spectra. As well as the reversibility behaviour of **2.18(a,c)** to **2.15(a,c)** and vice-versa.

6. REFERENCES

1. a) Morrison, J.D.; Mosher, H.S. in *Asymmetric Organic Reactions*, Prentice-Hall, Englewood Cliffs, New Jersey, 1971. b) Scott, J.W.; Valentine, D. *Science* **1974**, *184*, 943. c) Valentine, D.; Scott, J.W. *Synthesis* **1978**, 329.
2. a) James, B. R. *Homogeneous Hydrogenation*, John Wiley & Sons, New York, 1973, p. 83, 204-208. b) Horner, L.; *Kontakte (Merck)* **1979** (3), 3; **1980** (1), 37. c) Morrison, J.D.; Masler, W.F.; Neuberg, M.K. *Advances in Catalysis*, Vol. 25, Academic Press, New York, San Francisco, London, 1976, p.81-124, 98, 112.
3. a) Osborn, J. A.; Jardine, F.J.; Young, J.F.; Wilkinson, G. *J. Chem. Soc. [A]* **1966**, 1711. b) Montelatici, S.; van der Ent, A.; Osborn, J. A.; Wlkinson, G. *J. Chem. Soc. [A]* **1968**, 1954.
4. a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, 1994, ch. 2. b) Hiroi, K.; Abe, J. *Chem. Pharm. Bull.* **1991**, *39*, 616. c) Brunner, H. *Synthesis* **1988**, 645; Blystone, S.L. *Chem. Rev.* **1989**, *89*, 1663. d) Kagan, H.B.; Frian, J.C. *Top. Stereochem.* **1977**, 10.
5. Ojima, I.; Hirai, K. *Asymmetric Synth.* **1985**, *3*, 103.
6. Hayashi, T. *Catalytic Asymmetric Synthesis*, ed. I. Ojima (VCH, New York, 1993) ch. 7.
7. a) Trost, B.M.; Dietsche, T.S. *J. Am. Chem. Soc.* **1973**, *95*, 8200. b) Trost, B.M.; Strege, P.E. *J. Am. Chem. Soc.* **1977**, *99*, 1649. c) Frost, C.G.; Howarth, J.; Williams, J.M.J. *Tetrahedron Asymmetry* **1992**, *3*, 1089. d) Togni, A.; Venanzi, L.M. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497-526.
8. yamamoto, K. *J. Tetrahedron Lett.*, **1982**, *23*, 3089.
9. a) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 669. b) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 99.
10. a) Kosolapoff, G.M.; Maier, L. *Organic Phosphorus Compounds*, 1973, vol. 4, p. 504. b) Caplar, V.; Comisso, G.; Sunjic, V. *Synthesis* **1981**, 85. c) Mortreux, A.; Petit, F.; Buono, G.; Peiffer, G. *Bull. Soc. Chim.. France* **1987**, *4*, 631.

11. a) Cesarotti, E.; Chiesa, A.; D'Alfonso, G. *Tetrahedron Lett.* **1982**, *23*, 2995. b) Petit, M.; Mortreux, A.; Petit, F.; Buono, G.; Peiffer, G. *Nouv. J. Chim.*, **1983**, *7*, 593. c) Pracejus, G.; Pracejus, H. *J. Mol. Catal.* **1984**, *24*, 227.
12. a) Knowles, W.S.; Sabacky, M.J.; Vineyard, B.D.; Weinkauff, D.J.J. *Am. Chem. Soc.*, **1975**, *97*, 2567. b) Brunner, H. *J. Organomet. Chem.* **1986**, *300*, 39. c) Bosnich, B.; Fyzuk, M.D. *Top. Stereochem.* **1981**, *12*, 119. d) Halpern, J. *Asymmetric Synth.* **1985**, *5*, 41. e) Koenig, K. E. *Asymmetric Synth.* **1985**, *5*, 71. f) Kagan, H.B.; Frian, J.C. *Top. Stereochem.* **1977**, 10. g) Morrison, J.D.; Masler, W.F.; Neuberg, M.K. *Adv. Catal.* **1976**, *25*, 81. h) Achiwa, K. *J. Am. Chem. Soc.*, **1976**, *98*, 8265.
13. a) Ojima, I.; Kogure, T.; Nakai, Y. *Chem. Lett.* **1973**, 541. b) Johnson, T.H.; Klein, K.C.; Thomen, S. *J. Mol. Catal.* **1981**, *12*, 37. c) Brunner, H.; Riepl, G.; Weitzer, H. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 331. d) Karim, A.; Mortreux, A.; Petit, F. *Tetrahedron Lett.* **1986**, *27*, 345.
14. Peyronel, J. F.; Fiaud, J.C.; Kagan, H. B. *Bull. Soc. Chim. France* **1980**,4057.
15. Hayashi, T.; Konishi, M.; Fukushima, M.; Kanehira, K.; Kioki, T.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2195.
16. a) Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.; Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180; Brunner, H.; Probseter, M. *J. Organomet. Chem.* **1981**, *209*, C1. b) Hayashi, T.; Kumada, M. *Asymmetric Synth.* **1985**, *5*, 147.
17. a) Brown, J. M.; Hulmes, D.I.; Guiry, P.J. *Tetrahedron* **1994**, *50*, 4493. b) ahn, K.H.; Cho, C.; Park, J.; Lee, S. *Tetrahedron: Asymmetry* **1997**, *8*, 1179. c) Langer, T.; Jassen, J.; Helmchen, G. *Tetrahedron: Asymmetry* **1996**, *7*, 1599. d) von Matt, P.J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769; Allen, J.V.; Coote, S.J.; Dawson, G.J.; Frost, C.G.; Martin, C.J.; Williams, J.M.J. *J. Chem. Soc., Perkin Trans. 1* **1994**, *15*, 2065.
18. a) Fiorini, M.; Giongo, G.M.; Marcati F.; Marconi, W. *J. Mol. Catal.* **1978**, 143. b) Pracejus G.; Pracejus, H. *Tetrahedron Lett.* **1977**, 3497. c) Omuma, K.; Ito, T.; Nakamura, A. *Tetrahedron Lett.* **1979**, 3163.
19. Marko L.; Bakos, J. *Aspects Homog. Catal.* **1980**, *4*, 145.

20. Kagan, H.B. *Asymmetric Synthesis*, J.D. Morrison Ed., Academic Press, Orlando, 1985, vol. 5, p. 1.

21. Achiwa, K. *Fundamental Research in Homogeneous Catalysis*, M. Tsutsui Ed., Plenum, New York, 1979, Vol. 3, p. 549.

22. Ojima, I.; Yodo, M. *Tetrahedron Lett.* **1980**, 1951.

23. Kinoshita, I.; Kashiwabara, K.; Fujita, J.; Yamane, T.; Ukai, H.; Ashida, T. *Bull. Chem. Soc. Japan.* **1979**, *52*, 1413.

24. V. Kuznetsov, H. Alper, Unpublished Results.

25. Buono, G.; Siv, C.; Peiffer, G.; Triantaphylides, C.; Denis, P.; Mortreux, A.; Petit, F. *J. Org. Chem.* **1985**, *50*, 1782.

26. a) Corey, E.J.; Cheng, X. *The Logic of Chemcial Synthesis*; Wiley-Interscience: New York, 1989; Fleming, I. *Selected Organic Sythesis*; Wiley: London, 1973; Anand, J.; Bindra, J.S.; Ranganathan, S. *Art in Organic Synthesis*, 2nd ed.; Wiley-Interscience: New York, 1988. b) Trost, B.M. *Angew. Chem., Int. ed. Engl.* **1995**, *34*, 259. c) Ojima, I. *Catalytic Asymmetric Synthesis*; VCH Publishers: New York, 1993; Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; John Wiley & Sons: New York, 1993; Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. d) Kagan, H.B.; Girard, C.; Giullaneux, D.; Rainford, D.; Samuel, O.; Zhang, S.; Zhao, S. *Acta Chem. Scand.* **1996**, *50*, 345; Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49; Berrisford, D.J.; Bolm, C.; Sharpless, K.B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1059. e) Larksarp, C.; Alper, H. *J. Org. Chem.*, **1998**, *63*, 6229. f) Nadri, U.K.; Basu, N.J. *J. Org. Chem.* **1995**, *60*, 1458; SepUlveda-Arques, T. Armero_Alarte, A. Acero-AlarcOn, E. Zaballos-Garcia, B. Yruretagoy-ena, J.; Carrera, J.E. *Tetrahedron* **1996**, *52*, 2097. g) Larksarp, C.; Alper, H. *J. Am. Chem. Soc.* **1997**, *119*, 3709. h) Baba, A.; Seki, K.; Matsuda, H. *J. heterocycl. Chem.* **1990**, *27*, 1925; Qian, C.; Zhu, D. *Syn Lett.* **1994**, 129; Brunner, M.; Mussmann, D.V. *Syn Lett.* **1994**, 69. i) Tsuji, J. *Palladium Reagents and Catalysts. Innovations in Organic Synthesis*; John Wiley & Sons: U.K., 1995. j) Hayashi, T.; Yamamoto, A.; Ito, Y. *Chem. Lett.* **1987**, 177; Fiaud, J-C.; Legros, J. Y. *J. Org. Chem.* **1990**, *55*, 4840. k) Trost, B.M.; Van Vrenken, D.L. *Chem. Rev.* **1996**, *96*, 395; Trost, B. M.; Bunt, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*,

99. l) (–)DIOP = (R,R)-2, 3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis-(diphenylphosphino)butane. See: Kagan, H.B.; Dang, T.P. *J. Am. Chem. Soc.* **1972**, *94*, 6429. m) (–)MeDUPHOS = (–)-1,2-bis(2R,5R)-2,5-dimethylphospholano)-benzene. See: Burk, M.J. *J. Am. Chem. Soc.* **1991**, *113*, 8518. n) (R,R)-NORPHOS = (R,R)-5,6-bis(diphenylphosphino)-2-norbornene. See: Brunner, H.; Pieronczyk, W.; Schinhammer, B.; Streng, K.; Bernal, I.; Korp, J. *Chem. Ber.* **1981**, *114*, 1137. o) (R)- PROPHOS = (R)-1,2-bis(diphenylphosphino)propane. See: Fyzuk, M.D.; Bosnich, B. *J. Am. Chem. Soc.* **1978**, *100*, 5491. p) (R)-BINAP = (R)-2,2'-bis(diphenylphosphino)1,1'-binaphthyl. See: Miyashita, A.; Yasuda, A.; Takay, H.; Toriumi, K.; Ito, T.; Souchi, Y.; Noyori, R. *J. Am Chem. Soc.* **1980**, *102*, 7932. q) (S)-TolBINAP = (S)-2,2'-bis(di-*p*-tolylphosphino)-1,1'-binaphthyl. See: Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* **1986**, *51*, 629. r) Fujiwara, M.; Baba, A.; Matsuda, H. *J. Heterocyclic Chem.* **1988**, *25*, 1351.

27. a) Negishi, E. in *Organometallics in Organic Synthesis*; Wiley: New York, 1980; Vol. 1, p 394; Davies, A.G.; Smith, P.J. *Comprehensive Organometallic Chemistry*; Pregamon: Oxford, 1982; Vol. 2, p 519. b) Baba, A.; Shibata, I.; Masuda, K.; Matsuda, H. *Synthesis* **1985**, 1144. c) Gulbins, K.; Benzing, G.; Maysenholder, R.; Hamann, K. *Chem. Ber.* **1960**, *93*, 1975. d) Gulbins, K.; Hamann, K. *Angew. Chem.* **1961**, *73*, 434; Mukaiyama, T.; Fujisawa, T.; Nohira, H.; Hyugaji, T. *J. Org. Chem.* **1962**, *27*, 3337. e) Gulbins, K.; Hamann, K. *Chem. Ber.* **1961**, *94*, 3287. f) Vowinkel, E.; Gleichenhagen, P. *Tetrahedron Lett.* **1974**, 143; Beachell, H.C.; Ngoc Son, C.P.; Tinh, N.H. *J. Org. Chem.* **1972**, *37*, 422. g) Shibata, I.; Baba, A.; Iwasaki, H.; Matusda, H. *J. Org. Chem.* **1986**, *51*, 2177. h) Evans, D.A.; Ennis, M.D.; Lee, T. *J. Am. Chem. Soc.* **1984**, *106*, 1154. i) Umezawa, S. *Pure Appl. Chem.* **1978**, *50*, 1453. j) Dyen, M.E.; Swern, D. *Chem. Rev.* **1967**, *67*, 197.

28. a) Dyer, M.E.; Swern, D. *Chem. Rev.* **1967**, *67*, 197. b) Matsuda, H.; Ninagawa, A.; Normura, R. *Chem. Lett.* **1979**, 1261. c) Nomura, R.; Ninagawa, A.; Matsuda, H. *J. Org. Chem.* **1980**, *45*, 3735. d) Matsuda, H.; Ninagawa, A.; Hasegawa, H.

Bull. Chem. Soc. Jpn. **1985**, *58*, 2717. e) Fujinami, T.; Suziki, T.; Kamiya, M. *Chem. Lett.* **1985**, 199. f) Kisch, H.; Millini, R.; Wang, I. *J. Chem. Ber.* **1986**, *119*, 1090. g) Shibaa, I.; Baba, A.; Iwasaki, H.; Matsuda, H. *J. Org. Chem.* **1988**, *25*, 1351. h) Trost, B. M.; Sudhakar, A.R. *J. Am. Chem. Soc.* **1987**, *109*, 3792. i) Nomura, R.; Nakano, T.; Nishio, Y.; Ogawa, S.; Ninagawa, A.; Matsuda, H. *Chem. Ber.* **1989**, *122*, 2409. j) Haddadin, M.J.; Hassner, A.J. *J. Org. Chem.* **1973**, *38*, 3466. k) Baba, A.; Shibata, I.; Fujiwara, M.; Matsuda, H. *Tetrahedron Lett.* **1985**, *26*, 5167. l) Fujiwara, M.; Imada, M.; Baba, A.; Matsuda, H. *J. Org. Chem.* **1988**, *53*, 5974. m) Baeg, J.O.; Bensimon, C.; Alper, H. *J. Am. Chem. Soc.* **1995**, *117*, 4700. n) Baeg, J.O.; Alper, H. *J. Org. Chem.* **1992**, *57*, 157. o) Baeg, J.O.; Bensimon, C.; Alper, H. *J. Org. Chem.* **1995**, *60*, 253. p) Baeg, J.O.; Alper, H *J. Am. Chem. Soc.* **1994**, *116*, 1220.

29. Stamm, H.; Onistaschenko, A.; Buchholz, B.; Mall, T. *J. Org. Chem.* **1989**, *54*, 193.

30. Stamm, H.; Mall, T.; Folkenstein, R.; Werry, J.; Speth, D. *J. Org. Chem.* **1989**, *54*, 1603.

31. a) Dureault, A.; Greck, C.; Depezay, J.G. *Tetrahedron Lett.* **1986**, *27*, 4157. b) Takeuchi, H.; Shiobara, Y.; Mitani, M.; Koyama, K. *J.Chem. Soc.Chem. Commun.* **1985**, 1251. c) Eis, M.J.; Ganem, B. *Tetrahedron Lett.* **1985**, *26*, 1153. d) Hatta, Y.; Watanabe, M. *Tetrahedron* **1974**, *30*, 3572. e) Stamm, H. *Pharm.Aentralbl.* **1968**, 440. f) Barby, D.; Couturier, D. *Chem. Ber.* **1987**, *120*, 1073.

32. Gulbins, E.; Morlock, R.; Hamann, K. *Justus Liebigs Ann. Chem.* **1966**, *698*, 180.

33. a) Smith, D.J. *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon: Oxford, England, 1979; Vol. 2, Chapter 10, p 1121. b) Kumada, M. *Pure & Appl. Chem.* **1980**, *52*, 669. c) de Graaf, W.; Boersma, J.; Smeets, W.J.J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907. d) Steffen, W.L.; Palenik, G.J *Inorganic Chemistry* **1976**, *15*, 2432. e) Rauchfuss, T.B.; Patino, F.T.; Roundhill, D.M. *Inorg. Chem.* **1975**, *14*, 652. f) van der Steen, F.H.; Kanters, J. A. *Acta Cryst.C* **1986**, *42*, 547. g) de Graaf, W.; Harder, S.; Boersma, J.; van Koten, G.; Kanters, J. *J. Organomet. Chem.* **1988**, *358*, 545. h) Tanaka, A.;

Sasada, Y.; Yamamoto, K.; Tsuji, J. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3177. i) Rauchfuss, T.B.; Patino, F.T.; Roundhill, D.M. *Inorganic chemistry* **1975**, *14*, 652. j) Appleton, T.G.; Clark, H.C.; Manzer, L.E. *Coord. Chem. Rev.* **1973**, *10*, 335. k) Hynes, R.C., Willis, C.J.; Payne, N.C. *Acta Cryst.* **1992**, *C48*, 45. l) Ghilardi, C.A.; Midollini, S.; Monetti, S.; Orlandini, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1771. m) Livingstone, S.E. in Vol. 4, A.F. Trotman-Dickenson (Ed.) *Comprehensive Inorganic Chemistry*, Pergamon Press, 1973, p. 1304.

34. a) Airey, A.L.; Swiegers, G.F; Willis, A.C.; Wild, S.B. *Inorg. Chem.* **1997**, *36*, 1588. b) Molani, B.; Vicentini, L.; Sommazzi, A.; Barbassi, F.; Chiarparin, E.; Zangrando, E.; Mestroni, G. *J. Chem. Soc., Dalton Trans.* **1996**, 3139.
35. Bray, K. L.; Butts, C.P.; Lloyd-Jones, G.C.; Murray, M. *J. Chem. Soc., Dalton Trans.* **1998**, 1421.
36. Helmchen, G.; Kudis, S.; Sennhenn, P.; Steinhagen, H. *Pure Appl. Chem.* **1997**, *69*, 513; Sprinz, J.; Kiefer, M.; Helmchen, G.; reggelin, M.; Huttner, G.; Walter, O.; Zsolnai, L. *Tetrahedron Lett.* **1994**, *35*, 1523.
37. Kuznetsov, V.; Alper, H. *Organometallics*, In Press.
38. Milani, B.; Anzilutti, A.; Vicentini, L.; Sessanta A.; Santi, O.; Zangrando, E.; Germia, S.; Mestroni, G. *Organometallics* **1997**, *16*, 5064.
39. Milani, B.; Alessio, E.; Mestroni, G.; Zangrando, E.; Randaccio, L.; Consiglio, G. *J. Chem. Soc., Dalton Trans.* **1996**, 1021.
40. Sommazzi, A.; Grabassi, F.; Milani, B. *8th International Symposium on Homogenous Catalysis*, Amsterdam, 1992; Milani, B.; Mestroni, G. Unpublished results
41. Togni, A.; Venanzi, L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497.
42. Bowman, R. E ; Stroud, H.H. *J. Chem. Soc.* **1950**, 1342.
43. Vogl, O.; Pohm, M. ; *Monatsh. Chem.* **1952**, *83*, 541.
44. Nuzzo, R.G.; Haynie, S.L.; Wilson, M.E.; Whitesides, G.M. *J. Org. Chem.* **1981**, *46*, 2861.
45. Okada, I.; Ichimura, K.; Sudo, R. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1185.
46. Campbell, T.W.; Monagle, J.J.; Foldi, V.S. *J. Am. Chem. Soc.* **1962**, *84*, 3673.

47. Cullen, W.R.; Einstein, F.B.W.; Huang, C. H.; Willis, A.C.; Yeh, E. S. *J. Am. Chem. Soc.* **1980**, *102*, 988.

48. Pidcock, A.; Richards, R.E.; Venanzi, L.M. *J. Chem. Soc. A.* **1966**, 1707.

49. Denis, P.; Mortreux, A.; Petit, F.; Buono, G.; Peiffer, G. *J. Org. Chem.* **1984**, *49*, 5275.

50. Alcock, N.W.; Bergamini, P.; Kemp, T.J.; Pringle, P.G.; Sostero, S. *Inorg. Chem.* **1991**, *30*, 1594.

51. Barrow, M.J., Sim, G.A *J. Chem. Soc., Dalton Trans.* **1975**, 291.

52. Beck, W., Keubler, M.; Leidl, E.; Nagel, U.; Schall, M. *J. Chem. Soc., Dalton Trans.* **1981**, 446.

53. Balegroune, F.; Braunstein, P.; Grandjean, D.; Matt, D.; Nobel, D. *Inorg. Chem.* **1988**, *27*, 3320.

54. Walther, B. *Coord. Chem. Rev.* **1984**, *60*, 67.

55. Basolo, F. *Mechanisms of Inorganic Reactions, in Adv. In Chem. Series* **1965**, *49*, 90.

56. Kapteijn, G. M.; Spee, M. P.; Grove, D.M.; Kooijman, H.; Spek, A.L.; van Koten, G. *Organometallics* **1996**, *15*, 1405.

57. de Graaf, W.; Boersma, J.; Smeets, W.J.; Spek, A.L.; van Koten, G. *Organometallics* **1989**, *8*, 2907.

58. Amatore, C.; Broeker, G.; Jutand, A.; Khalil, F. *J. Am. Chem. Soc.* **1997**, *119*, 5176.

59. Bittler, K.; Kutepov, N.V.; Neubauer, D.; Reis, H. *Angew. Chem.* **1968**, *80*, 352.

60. Zargarian, D.; Alper, H. *Organometallics* **1993**, *12*, 712.

61. Scott, W.J.; Stille, J.K. *J. Am. Chem. Soc.* **1986**, *108*, 3033; Scott, W.J.; Crisp, G.T.; Stille, J.K. *J. Am. Chem. Soc.* **1984**, *106*, 4630; Backvall, J.E.; Bystrom, S.E.; Nordberg, R.E. *J. Org. Chem.* **1984**, *49*, 4619.

62. Doyle, J.R.; Slade, P.E.; Johassen, H.B. *Inorg. Synth.* **1960**, *6*, 218.

63. Perrin, D.D.; Armarego, W.L.F. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1988.

64. Blessing, R. *Acta Cryst.* **1995**, *A51*, 33-38.

65. Sheldrick, G. M., Bruker AXS, Madison, WI, 1997.