SYNTHESIS AND REACTIVITY OF LATE METAL COMPLEXES FEATURING NEW HETEROBIDENTATE ANCILLARY LIGANDS

by

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Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

at

Dalhousie University
Halifax, Nova Scotia
August 2007

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ISBN: 978-0-494-31506-4
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ISBN: 978-0-494-31506-4

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Abstract

Homogeneous transition metal catalysts are commonly made up of transition metals bound to one or more ligands, where the electronic and steric contributions of the ligands can have a significant impact upon the reactivity and selectivity of the catalyst in mediating various substrate transformations, such as the activation of E-H bonds (E = main group element) in small molecule substrates. The development of new catalyst structural motifs through the design of new ancillary ligands is a persistent challenge in organometallic chemistry.

In this thesis, the development of new ancillary ligands derived from a P,N substituted indene backbone (**1-3a**) has been discussed. 1-P(S)^{i}Pr$_2$-2-NMe$_2$-indene **2-3a** was prepared *via* a one-step synthetic pathway from **1-3a** and has been shown to support neutral and cationic Rh(I) and Ir(I) fragments, in a κ^2-*C,S* and κ^2-*N,S* fashion (respectively). The neutral κ^2-*C,S* Rh complex **2-7a** (the first complex featuring a Rh-C-P-S ring system, as well as the first η^1-indenylrhodium species to be crystallographically characterized) has shown similar catalytic activity and regioselectivity to that of Wilkinson's catalyst **1-1** under some conditions. In the presence of water, clean conversion of complexes **2-6a,b** to the (COD)M(κ^2-P(*S*),*O*) complexes **2-10a,b** has been demonstrated; **2-10a,b** have shown similar catalytic activity and regioselectivity to those observed with **2-7a** for the addition of triethylsilane to styrene. The incorporation of chirality into the P,N binding site of ligand **1-3a** afforded ligand **2-11b** and the metal coordination chemistry and catalytic activity of **2-11b** is unlike that observed with **1-3a**.

The ability of the P,N ligand (**1-3a**) to support two metal fragments (η^5-MLn and κ^2-*P,N*) has been demonstrated confirming its ambidentate function. The catalytic ability of these racemic bimetallic complexes **3-3a-c** has also been explored in the hydroboration of styrene with pinacolborane. The results of this preliminary catalytic survey revealed that structural changes to the η^5-coordinated metal fragment (MLn = Mn(CO)$_3$ **3-3a**, RuCp* **3-3b** or FeCp* **3-3c**) may provide a systematic way to modify and influence the steric and electronic properties of the κ^2-*P,N*-ligated metal fragment in these complexes.

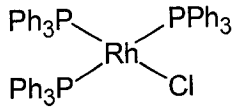
The development of a new chiral P,N ligand **4-1** derived from 7-azaindole was also discussed. Ligand **4-1** was prepared in an easy and modular manner and showed divergent metal coordination chemistry with transition metals such as Rh, Ir and Pd. In certain catalytic asymmetric transformations (hydrogenation and allylic alkylation reactions) some of these metal complexes have demonstrated good catalytic activity and enantioselectivity.

List of Abbreviations and Symbols Used

Å	angstrom(s)
atm	atmosphere(s)
Aza.	7-azaindole
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINOL	1,1'-bi-2-naphthol
br	broad
n-BuLi	normal-butyllithium
COD	η^4-1,5-cyclooctadiene
COE	η^2-cyclooctene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
d	day(s) or doublet
DCE	1,2-dichloroethane
DiPAMP	[(*R*,*R*)-1,2-Bis(o-methoxyphenyl)(phenyl)phosphino)ethane]
E	main group element
ee	enantiomeric excess
eq	equation
equiv	equivalent(s)
FID	Flame Ionization Detection
GC	gas chromatography
HBcat	catecholborane

HBpin	pinacolborane
hfc	3-(heptafluoropropylhydroxymethylene)-(+)-camphorate
HPLC	high pressure liquid chromatography
Hz	hertz
IR	infrared
$^{n}J_{xy}$	n bond coupling constant between atoms x and y
κ	kappa
L	ligand
L-DOPA	3,4-dihydroxy-L-phenylalanine
m	multiplet
M	transition metal or concentration in mol/L
min	minute(s)
mmol	millimole(s)
mol	mole(s)
MS	mass spectrometry
η	eta
Naph.	naphthyl
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermo Ellipsoid Plot
PCM	planar chiral metalloligand
PHOX	phosphinooxazolines
ppm	parts per million
psi	pounds per square inch

PTFE	poly(tetrafluoroethene)
Py	pyridine
PyrPHOX	phosphinopyrrolyl-oxazolines
q	quartet
s	singlet
(*S*)-(*R*)-Xyliphos	(*S*)-1-[(*R*)-2-(diphenylphosphanyl)ferrocenyl]ethyldi(3,5-xylyl)phosphine
t	triplet
RT	room temperature
THF	tetrahydrofuran
TOF	turn over frequency
TON	turn over number
X	non-coordinating counteranion



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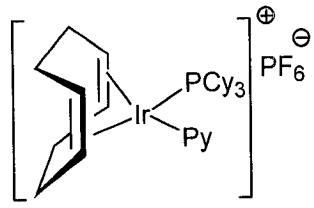

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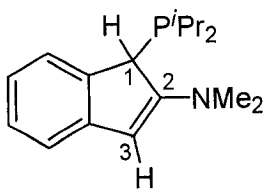

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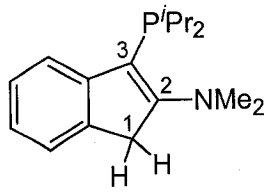

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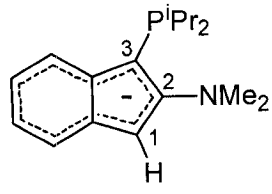
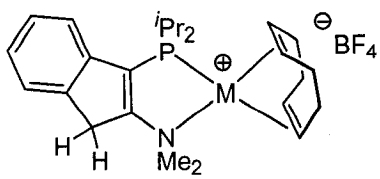


1-3c



cationic

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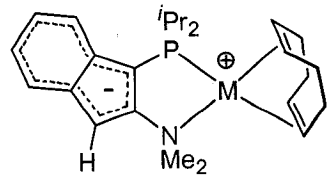
2-1b, M = Ir



zwitterionic

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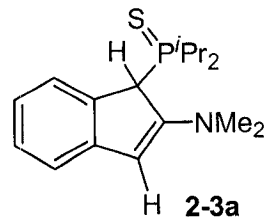

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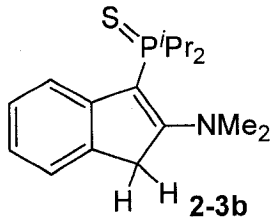

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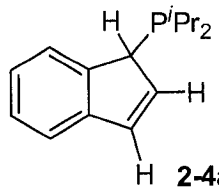

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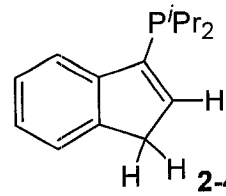

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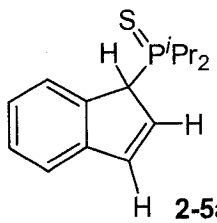

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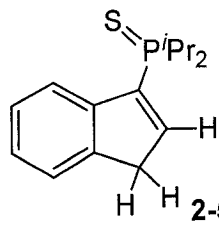

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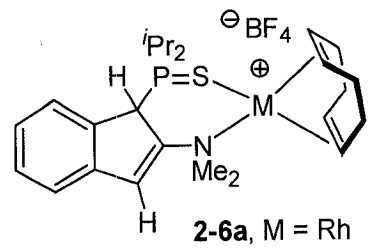

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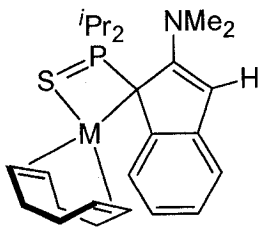

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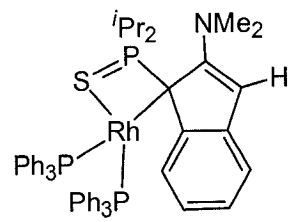
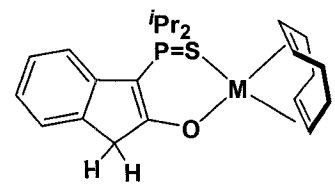


2-8a



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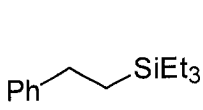

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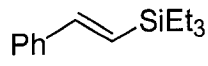

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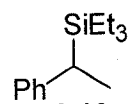

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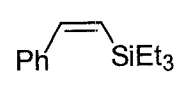

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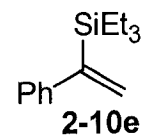

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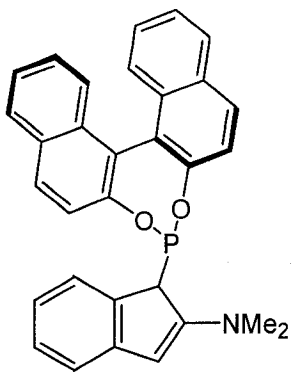

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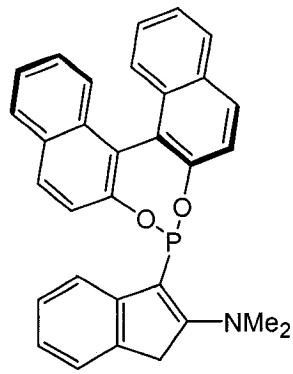

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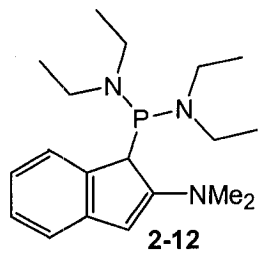

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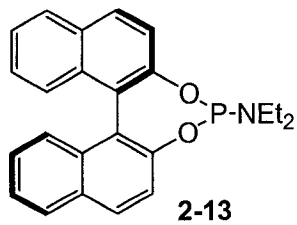

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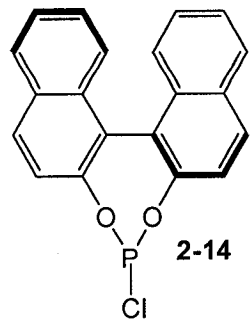

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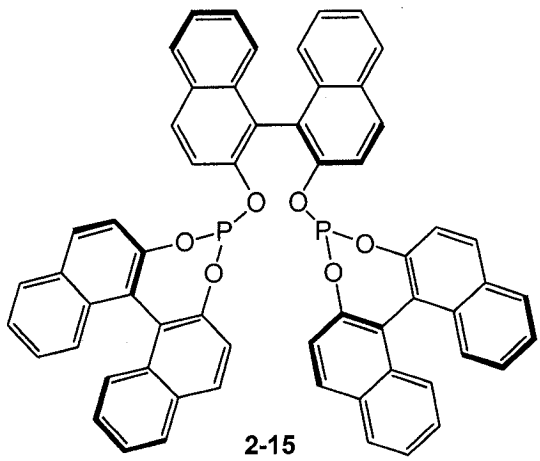

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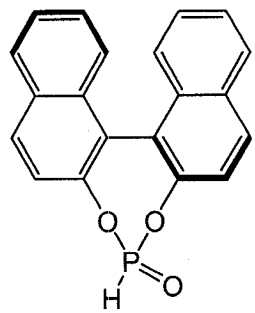

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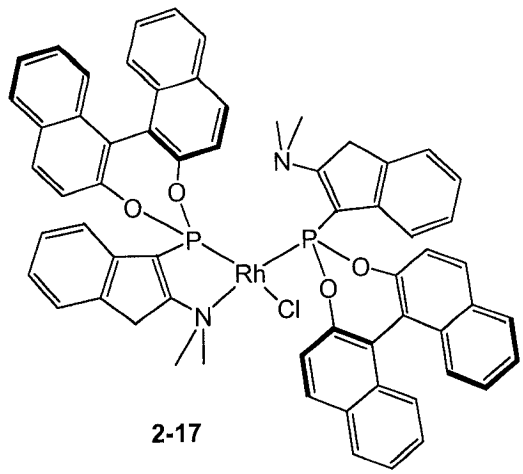

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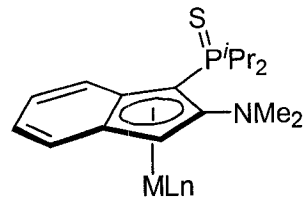

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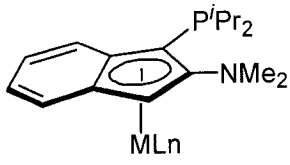
3-1b, MLn = Cp*Ru
3-1c, MLn = Cp*Fe



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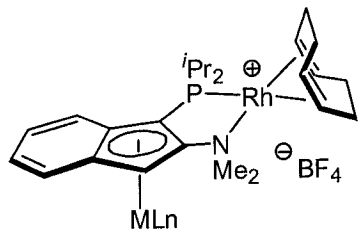

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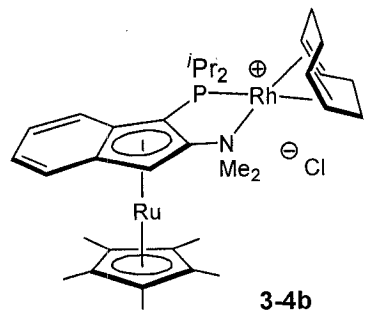
3-3b, MLn = Cp*Ru
3-3c, MLn = Cp*Fe



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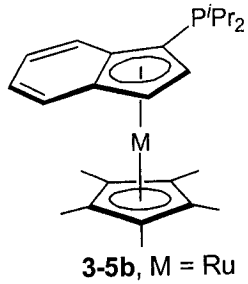

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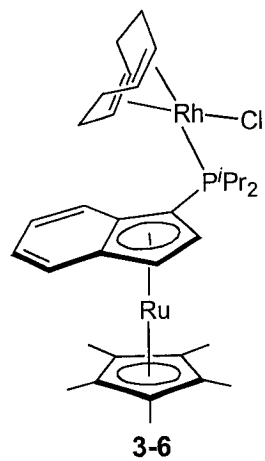

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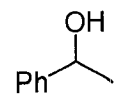

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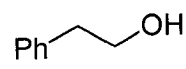

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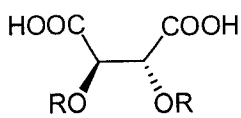

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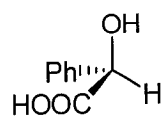
3-8b, R = CONHPh



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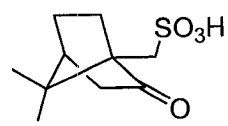

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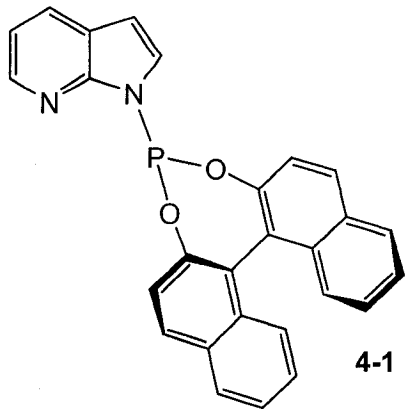

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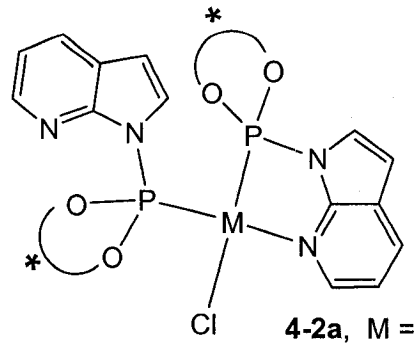

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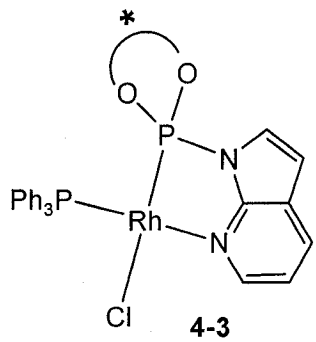

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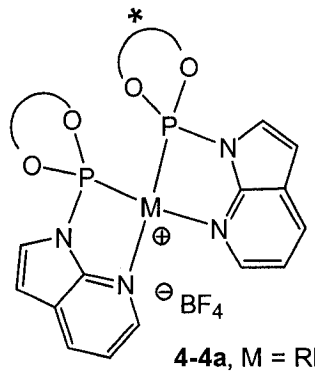
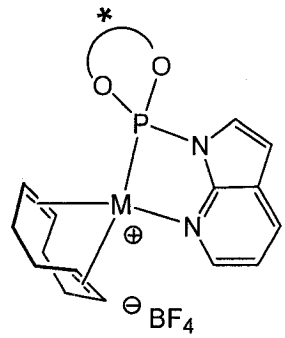


4-4a, M = Rh
4-4b, M = Ir



4-5a, M = Rh
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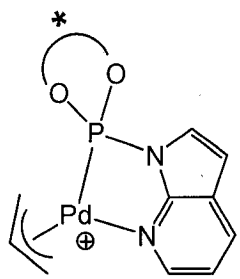

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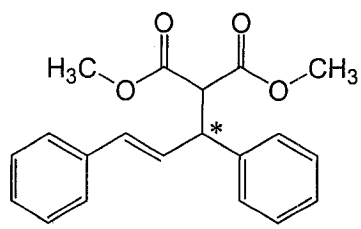

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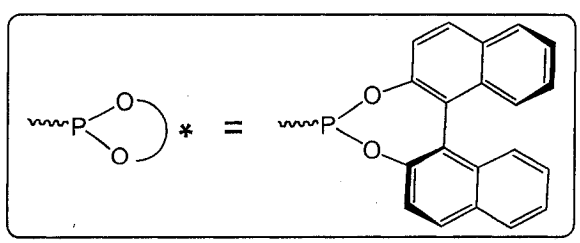


Acknowledgements

Over the course of the last four years, I have had the opportunity to work with an outstanding group of individuals who have enriched my time at Dalhousie in immeasurable ways. First of all, I would like to thank my supervisor, Dr. Mark Stradiotto, for his guidance, encouragement, enthusiasm and patience as I have moved forward in the pursuit of this degree. I appreciate the challenges and opportunities that being a member of his research group have provided to me, and the ability to undertake my research in a state-of-the-art laboratory.

The people I have worked with in the Stradiotto group deserve special recognition as sources of invaluable discussion, information, and support: thanks to Judy Cipot, Brad Wile, Matthew Rankin, Rylan Lundgren, Kevin Hesp and Stephen Scully. I also need to thank the members of the Burford group, especially Heather Phillips, Cheryl Saunders, Robyn Ovans and Katie Groom for their friendship and support. The Turculet, Pincock and Thompson groups have also been extremely helpful when it came to borrowing equipment and for offering useful discussions. Special thanks go to Dr. James Pincock for allowing me to use his GC instruments and Dr. Alison Thompson for allowing me to use her chiral HPLC.

Of all the people that I have worked with, I extend special thanks to Anne Myers, the undergraduate honors project student that I had the opportunity to supervise and mentor over the course of my time here. Anne Myers enriched my program in countless ways, she made significant contributions to the work on the synthesis, stability and catalytic studies of the metal complexes of the P(S),N ligand. Anne was also part of the

initial discovery of the formation of the κ^2-*S,O* complexes from the κ^2-*N,S* complexes in the presence of water.

The members of my supervisory committee, Dr. Neil Burford, Dr. Jean Burnell, and Dr. Norman Schepp need to be acknowledged for their continued support over the course of my time here. They have provided useful input and discussions, and have always made themselves available to me when I needed them.

I must give credit to Drs. Robert McDonald and Mike Ferguson at the University of Alberta and Dr. Gabriele Schatte at the Saskatchewan Structural Science Centre, University of Saskatchewan, for their excellent X-ray crystallography work. I need to thank the ARMRC, especially Drs. Mike Lumsden, Bob Berno, and Kathy Robertson for access to, and support of, the NMR instrumentation, and for helpful suggestions on solving chemistry problems with NMR experiments.

At Dalhousie, there are many people in the department of chemistry who I would like to acknowledge. The main office staff (Giselle Andrews, Deanna Wentzell, Cheryl Stanton, and Shelley Dorey) has been extremely helpful with all manners of things; Mr. Jürgen Müller has prepared all of the custom Schlenk and other glassware used in the lab, without which this research would not have been possible. The machine shop staff, Rick Conrad and Mike Boutilier, has helped tremendously to keep the lab equipment running smoothly, and Brian Millier has been irreplaceable for his skills in keeping the electronic equipment working. The chemical stores staff, John Sutton and Barry Moore, has been very helpful in ordering chemicals and supplies.

My family has been by my side each step of the way and I cannot thank them enough for their constant love and support. I would also like to thank my friends Mark Hodder, Amanda Hodder and Chris Andrews for helping to keep me sane.

Finally, I must thank my best friend and wife, Judy Cipot-Wechsler, who I met during my honors project, and who continues to stand by me and offer endless advice, support, strength and guidance.

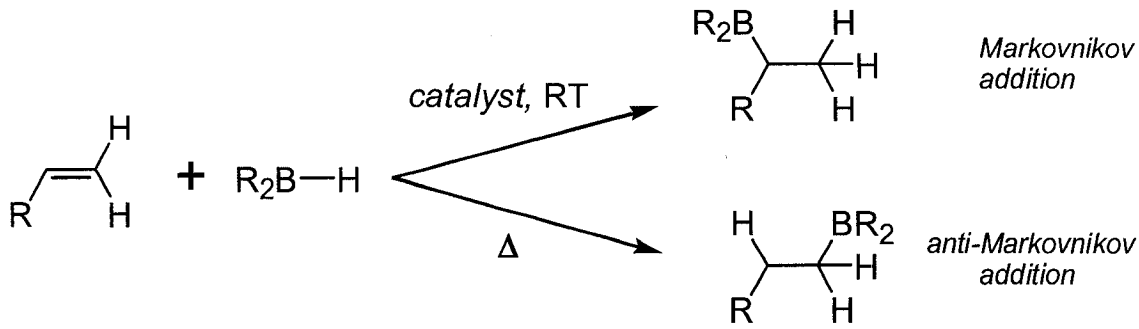
My graduate program was funded by the National Science and Engineering Research Council of Canada and Dalhousie University.

Chapter One: Introduction

1.1 Goals in Modern Synthetic Chemistry

The need to establish new and efficient routes to value-added products is becoming increasingly more important in modern society.[1] To meet this need, the discovery of new chemical transformations, or the development of improved methodologies for currently used transformations, will figure prominently. Because we live in an economically based world, it is advantageous to exploit cheap and abundant resources including hydrocarbons.[2, 3] One difficulty associated with the functionalization of these species is the strength of the carbon-hydrogen bond, which diminishes their utility as reagents in synthesis. Indeed, carbon-hydrogen bond cleavage in hydrocarbons represents a significant challenge in modern synthetic chemistry, and as such, the development of metal complexes that mediate E-H bond (E = main group elements such as H, B, C, N, Si, etc.) cleavage reactions can provide important contributions to the understanding of hydrocarbon functionalization.[4-13] Furthermore, in order to reduce the environmental impact, minimizing the number of side-products formed during a chemical transformation is advantageous. In general, addition reactions are more environmentally friendly and more atom economical than substitution reactions.[2] In this regard, the development of synthetic methods based on E-H additions to unsaturated substrates is particularly appealing. The use of a catalyst is often required in order to enhance the rate of reaction to make these transformations possible and can direct reactants to specific products leading to highly selective processes.[14] A prototypical example of such selectivity in E-H addition reactions is provided in Scheme 1-1, whereby the regioselectivity observed in the hydroboration of alkenes can be altered

relative to the thermal (non-catalyzed) reaction by use of an appropriately designed metal catalyst.



Scheme 1-1. A generic representation of selectivity in alkene hydroboration.

1.2 Classes of Catalysts Used in Synthetic Chemistry

There are two main types of catalysts, heterogeneous and homogeneous catalysts. Heterogeneous catalysis is implemented for many different aspects of chemical transformations such as carbon-carbon coupling reactions[15, 16] and hydrogenations,[17] among other applications.[18, 19] The catalyst exists in one phase, normally solid, while the reactants and products are in another phase. Separation of catalyst and products is easy, but the reaction is often less selective, and usually higher reaction temperatures and pressures are required.[20] In homogeneous catalysis the catalyst, reactants and products are all in one phase, normally the liquid phase. These reactions usually proceed at more reasonable temperatures and pressures than their heterogeneous counterparts. Homogeneously catalyzed reactions are often highly selective, but separation of the products and the catalyst is more difficult than in heterogeneous systems.[20] This shows that each catalyst system has its advantages and the choice of catalyst depends on the desired application.

A homogeneous catalyst commonly consists of a transition metal (or other metal) supported by one or more coordinated ligands. The electronic and steric contributions of the ligands can have a significant impact upon the reactivity and selectivity of the catalyst in mediating various substrate transformations. As such, the development and incorporation of carefully chosen ligand components in the design of new homogeneous metal catalysts continues to be an active area of research. This thesis will focus exclusively on homogeneous catalysts development, and primarily on the chemistry of the Group 9 elements rhodium and iridium.

The word "ligand" was first coined by Alfred Stock in 1917, but it had not been used by the English-speaking chemical community until the 1940's.[21] Ligands can be classified into two main groups: reactive and ancillary. Reactive ligands are those that may be consumed or ultimately utilized in a reaction facilitated by the catalyst and are thought not to offer any real influence on the reactivity of the metal center during catalysis. Ancillary is the term used to classify a second group of ligands whose electronic and/or steric components are rationally chosen so as to tune the selectivity or reactivity of a metal complex during the course of a given metal-catalyzed reaction. Although ancillary ligands are selected such that they remain coordinated to the metal and are not degraded during substrate transformations, the line between reactive and ancillary ligands is not always clear. In some cases, new or unprecedented reactions can be uncovered simply by altering the ancillary ligand characteristics, which makes these transition metal complexes attractive targets for mediating homogeneous catalysis, as is demonstrated by their synthetic utility, including on industrial scales.[20, 22-24]

One of the first examples of a homogeneous transition-metal catalyst used to facilitate E-H bond activation, chlorotris(triphenylphosphine)rhodium(I) (**1-1**), was introduced by Wilkinson in the 1960s,[25] which proved to be the most effective hydrogenation and hydroformylation catalyst at the time (Figure 1-1).[26, 27] Wilkinson's catalyst **1-1** has also been shown to facilitate the hydrosilylation[28] and hydroboration[29] of alkenes.[2] Furthermore, in the 1970's, Crabtree developed a new cationic mixed donor Group 9 metal complex, $[Ir(COD)(PCy_3)(Py)]^+ PF_6^-$, (**1-2**, Cy = cyclohexyl, Py = pyridine, COD = η^4-1,5-cyclooctadiene), which turned out to be a substantially more active hydrogenation catalyst than **1-1**.[30-32] More recently, Peters and co-workers have advanced further such ligand design concepts in the development of cationic and zwitterionic Group 9 metal complexes supported by bidentate ligands for the activation of E-H bonds in hydroboration, hydrogenation, hydrosilylation and hydroacylation reactions.[33, 34] Notably, the overall neutral character of such zwitterionic catalysts provided significant selectivity and reactivity advantages over more traditional cationic complexes. These examples illustrate that ligand design has an immense influence on the reactivity and selectivity of the metal center during catalysis.

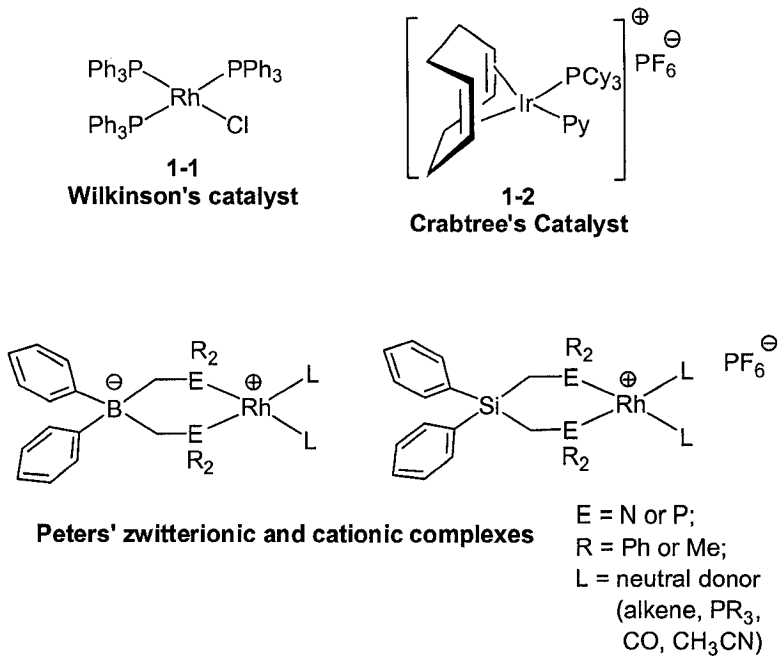


Figure 1-1. Examples of homogeneous Group 9 transition metal catalysts for the addition of E-H bonds to unsaturated substrates.

A wide variety of transition metals and ancillary ligands, both chiral and achiral, are currently in use for many different types of chemical transformations. At first it was thought that for each catalytic reaction, a new catalyst structure would have to be developed, but it turns out that certain catalyst structures have the ability to promote a wide range of different reactions; these have been termed "privileged structures" (Figure 1-2).[35] Despite the emergence of such privileged ligand/catalyst structures, our understanding of how ancillary ligands influence the reactivity properties of the associated metals is still underdeveloped. In this context, the study of complexes featuring new ancillary ligands continues to provide important breakthroughs in metal-mediated reaction chemistry.

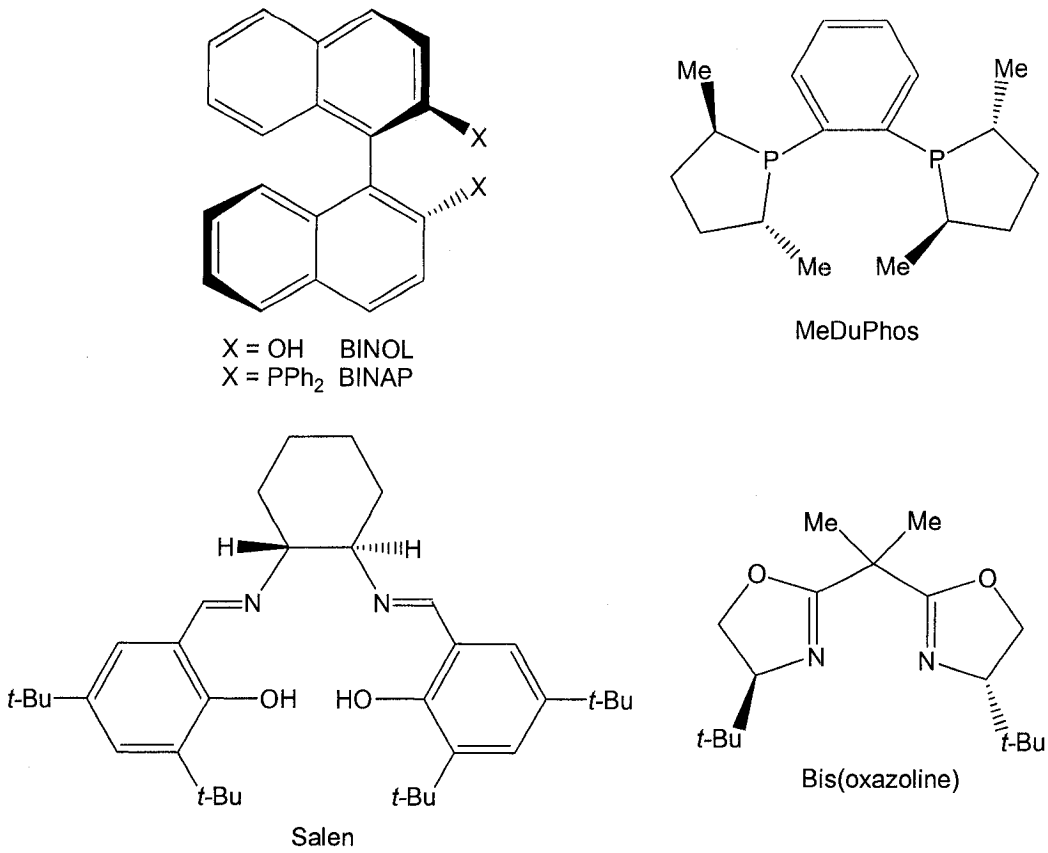


Figure 1-2. Examples of some chiral ligands that fall into the privileged structures category.

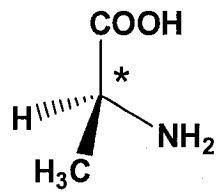
1.3 Chirality and Homogeneous Catalyst Systems

The concept of chirality was first introduced in the late 1800's,[36] but concrete rules to describe chirality were not established until later in the 1900's. In 1966, the first version of the Cahn, Ingold and Prelog classification[37] was published, where the three general types of chirality were initially discussed: central, axial and planar. The incorporation of chirality into the design of ancillary ligand architectures (including those in Figure 1-2) has enabled the preparation of catalysts that can offer remarkably high levels of both activity and enantioselectivity in a diversity of metal-mediated transformations. In the following sections, representative examples of industrially

relevant Group 9 catalysts for E-H bond activation that feature central, axial, and planar chirality are presented.

1.3.1 Chiral Catalyst Systems Based on Central Chirality

All chiral molecules lack a plane of symmetry and can exist as two mirror-image forms (enantiomers) that are non-superimposable. In order for a molecule to possess central chirality, there typically needs to be one atom (carbon, phosphorus, etc.) present that carries four different groups. In the case of phosphorus, one of the groups usually consists of a stereochemically active lone pair of electrons; this atom is considered the chiral center or a stereogenic atom.[38-40] This type of chirality is most commonly found in both naturally occurring and synthetically made chiral molecules. Figure 1-3 features (*S*)-alanine, a naturally occurring example of a molecule that possesses central chirality.



(*S*)-alanine

Figure 1-3. The structure of (*S*)-alanine a naturally occurring amino acid possessing central chirality.

The DiPAMP [(*R*,*R*)-1,2-bis(o-methoxyphenyl)(phenyl)phosphino)ethane] ligand developed by Knowles and co-workers serves as a prototypical example of an effective chiral ancillary ligand featuring central chirality.[42] Once it was discovered that a fairly massive dose of 3,4-dihydroxy-L-phenylalanine (L-DOPA) (an amino acid derivative) is useful in treating Parkinson's disease, the demand for this rare amino acid jumped

dramatically, making the process used at the time (the Hoffman-LaRoche L-DOPA process) too inefficient to keep up with new demands:[41] the hydrogenation step of the prochiral enamide intermediate was achieved by use of palladium on carbon with low enantiomeric excess (*ee*), requiring resolution of stereoisomers and in turn making isolation of pure material in high yields difficult. Improvements to the enantioselectivity of the rhodium-catalyzed hydrogenation step were sought by Knowles and co-workers,[42] by developing a new chiral bis-phosphine ligand. After exploring different side groups on the phosphorus atom and determining the structure-activity relationship of these changes, the Knowles group identified (*R*,*R*)-DiPAMP, where the phosphorus atom has central chirality, as the most effective ligand (Figure 1-4). The resulting catalyst $[(COD)Rh(DiPAMP)]^{+}BF_4^{-}$ has since been used by Monsanto for the key step of the commercial synthesis of L-DOPA (Scheme 1-2).[24, 42]

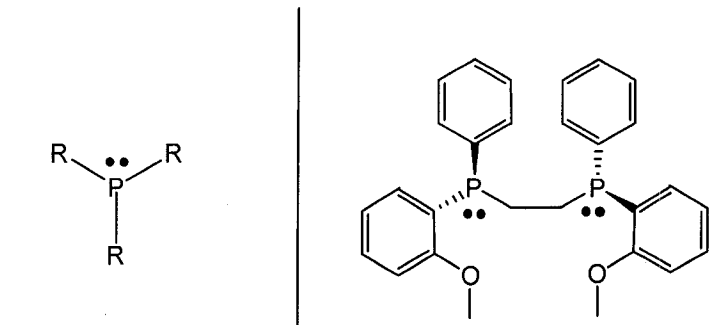
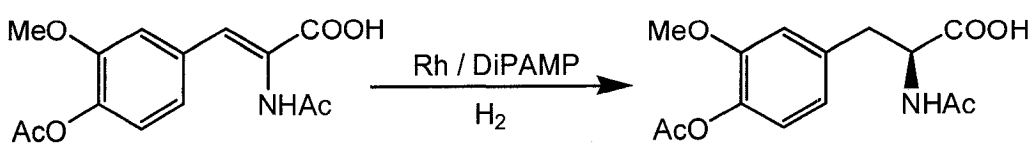


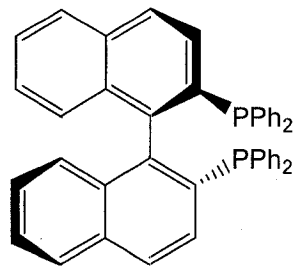
Figure 1-4. The DiPAMP ligand used in the L-DOPA process.



Scheme 1-2. The enantioselective step in the L-DOPA process.

1.3.2 Chiral Catalyst Systems Based on Axial Chirality

Axial chirality results from hindered rotation about a single bond (substituents are held in a spatial arrangement which is not superimposable on its mirror image) where the steric strain barrier to rotation is high enough to allow the isolation of conformers,[43] and to avoid the possible planar arrangement and subsequent racemization.[37, 40] The BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) ligand (Figure 1-5), first synthesized by Noyori and co-workers in 1986,[44-46] is a good example of an axially chiral bis(triaryl)phosphine.



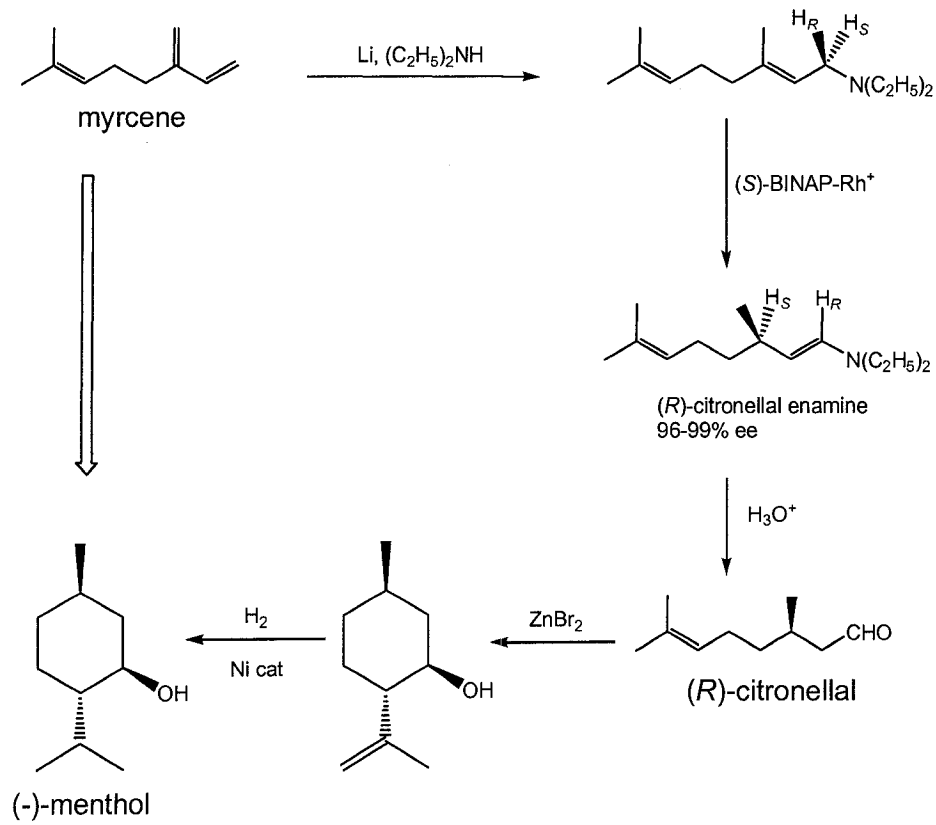
(*R*)-BINAP
(2,2'-bis(diphenylphosphino)-1,1'-binaphthyl)

Figure 1-5. The structure of (*R*)-BINAP, a chiral molecule possessing axial chirality.

The BINAP ligand design is modular so the properties of the ligand can easily be fine-tuned by substitutions on the aromatic ring. As well, the flexible chelating angle between the two phosphines allows this ligand to bind a variety of transition metals. The initial synthesis was more difficult than expected due the issue of resolving the conformers, but eventually a reliable method was discovered by using an optically active dimethyl(1-phenylethyl)aminopalladium(II) chloride complex. More convenient methods, not requiring an expensive metal such as palladium, were later developed to

resolve the BINAP dioxide analogue, using camphorsulfonic acid or 2,3-O-dibenzoyltartaric acid.[47]

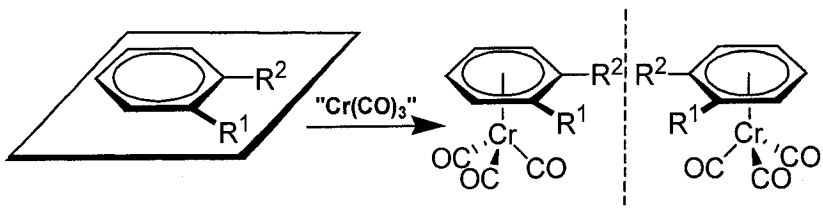
Cationic BINAP-Rh complexes exhibit useful reactivity in the asymmetric isomerization of allylic amines, making it possible for the synthesis of (-)-menthol from myrcene on an industrial scale (Scheme 1-3). The key step in the menthol synthesis is the asymmetric isomerization of geranyldiethylamine, catalyzed by a (*S*)-BINAP-Rh complex forming (*R*)-citronellal enamine, that upon hydrolysis gives (*R*)-citronellal in 96 – 99 % *ee* (Scheme 1-3). Although (*R*)-citronellal is a naturally occurring compound available from rose oil, it can only be obtained in 80 % *ee* from natural sources, making the catalyzed process much more appealing.[47]



Scheme 1-3. The industrial process for the synthesis of (-)-menthol using cationic (*S*)-BINAP-Rh as the catalyst in the key enantioselective step.

1.3.3 Chiral Catalyst Systems Based on Planar Chirality

Planar chirality represents the third type of chirality; as the name suggests this type results from the arrangement of out-of-plane groups with respect to a plane (chirality plane).[40] This concept can be used to transform traditionally achiral aromatic ligands into chiral ligands by introducing planar chirality through simple chemical transformations. For example, while unsymmetrical 1,2- or 1,3-disubstituted arenes possess mirror-plane symmetry, the top and bottom faces of this plane can be differentiated by the complexation of a metal fragment, as shown in Scheme 1-4.[48] The metal fragments used to label a face of these substituted achiral arene ligands are usually catalytically inactive or spectator π-bound metal fragments, and the resulting planar chiral ligands have been termed 'metalloligands' that can be resolved into enantiopure form. If a second metal (catalytically active) is coordinated into the primary metal chelation site defined by the donor arms (e.g. R^1 and R^2), a chiral bimetallic complex is formed from an initially achiral arene (or related) ligand. Collectively, these examples demonstrate that the design and synthesis of chiral metal complexes do not have to rely on traditional chiral organic ligands derived from the 'chiral pool'.[49] Planar-chiral ferrocene chelating ligands are perhaps the most widely used class of planar-chiral metalloligands. The following section provides an account of the use of such ligands in a large-scale industrial system.



Scheme 1-4. Conversion of an achiral arene to a planar chiral complex through the facial complexation of a metal fragment, resulting in the formation of enantiomers.

In 1976 the industrial production of racemic Metolachlor (a herbicide, consisting of four stereoisomers, Figure 1-6), was introduced.[50] Shortly after, in 1982, it was discovered that 95 % of the herbicide activity is actually attributed to only two stereoisomers (*S*-configuration at stereocenter). Many possibilities exist to prepare the (*S*)-Metolachlor isomers in enantiomerically pure form, but due to the relative low cost and large volume of the racemic Metolachlor synthesis, a highly efficient chiral variation of this transformation was pursued. This discovery initiated intensive research to find new ways of producing only the active stereoisomers,[50] a strategy that is of widespread relevance to modern pharmaceutical syntheses.

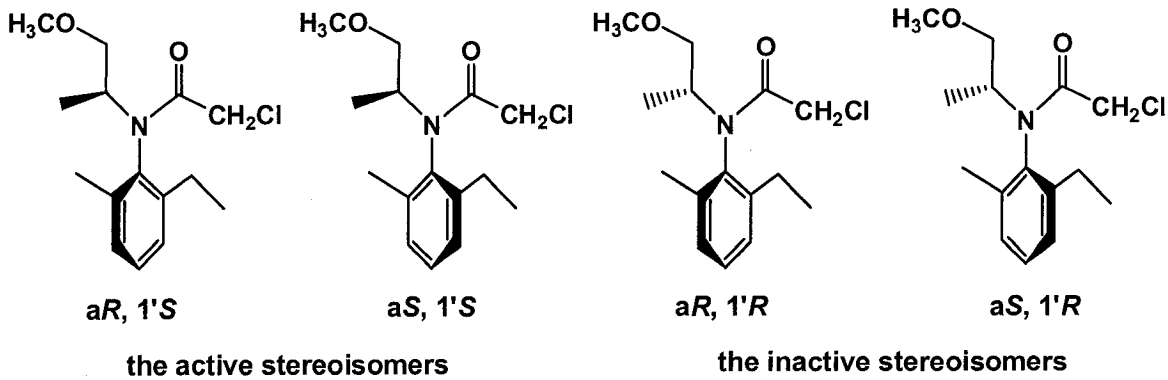
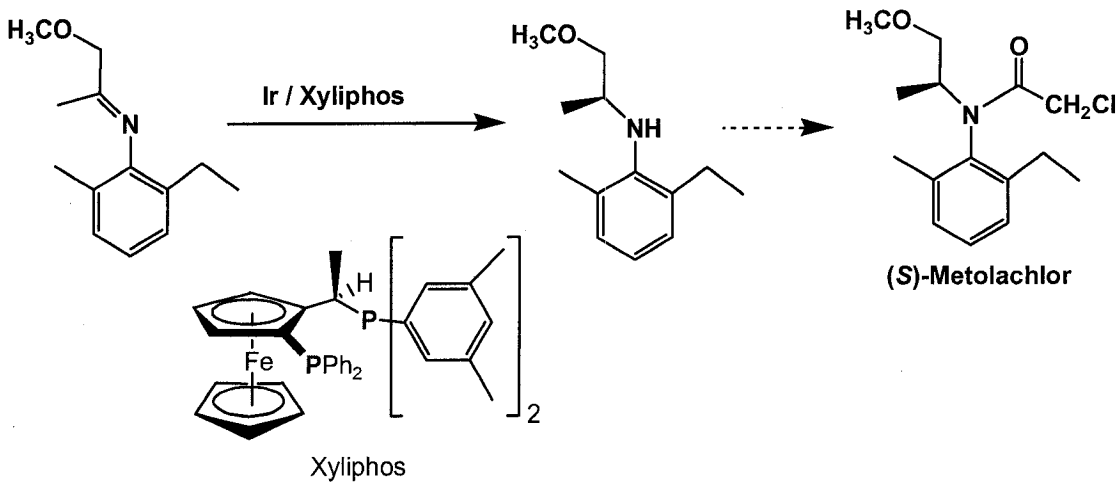


Figure 1-6. The four possible stereoisomers of Metolachlor (active and inactive).

The commercial synthesis of racemic Metolachlor is achieved through an imine intermediate, and as such chiral catalysts that could effect the enantioselective hydrogenation of this imine intermediate were targeted. However, only one single imine hydrogenation had been reported previously in the literature, and only very low enantioselectivity was achieved. Therefore, a more efficient imine hydrogenation catalyst was required. After screening a variety of Rh-diphosphine catalysts, higher levels of *ee* (69 %) were achieved, but the turnover frequencies (TOF's) were still too low for these

catalysts to be used in an industrial application. When rhodium was replaced by iridium, inspired by the ability of Crabtree's catalyst **1-2** to hydrogenate even tetra-substituted olefins, the levels of *ee* surpassed 80 %, but the activity levels were still unsatisfactory. At the same time, Togni and Spindler[51] had developed a series of planar chiral ferrocenyl-diphosphine ligands, and iridium complexes of these ligands were explored and found to be highly efficient catalysts. The (*S*)-1-[(*R*)-2-(diphenylphosphanyl)ferrocenyl]ethyldi(3,5-xylyl)phosphine [(*S*)-(*R*)-Xyliphos] ligand (Scheme 1-5) provided the most active catalyst that did not deactivate during the catalytic cycle and is currently used in the industrial synthesis of (*S*)-Metolachlor. This catalyst is able to hydrogenate the imine intermediate with an *ee* of 79 %, turnover number (TON) of 1,000,000 and a TOF of >200,000 h^{-1}.[24, 50, 52]



Scheme 1-5. The key enantioselective step in the synthesis of (*S*)-Metolachlor promoted by a planar chiral iridium catalyst.

1.4 The Development of New Ancillary Ligands and Their Corresponding Metal Complexes

As mentioned earlier, the pursuit of new and synthetically useful transition metal-mediated reaction chemistry represents a persistent challenge in organometallic research.[53] New catalyst structural motifs are being developed through the design of new ancillary ligands, or by the modification of known complexes that in turn may lead to new reactivity and better understanding of the influence of the ancillary ligand on the metal center. Serendipity can be a viable method for identifying new ancillary ligand systems, but more reliable and systematic techniques for the design and synthesis of new ligand sets include: i) experience and insight – ligand design can be based on a known mechanism of a specific reaction for which a new catalyst is being developed; ii) molecular modeling; iii) and fast screening methods, such as high throughput screening techniques.[1]

An attractive strategy for the design and synthesis of new classes of reactive metal complexes that will be implemented in this thesis is to have a systematic approach which starts from a basic ligand framework that can be built upon in a rational and modular manner. Ideally, the design concept of new multidentate ligand frameworks that are able to support a wide variety of metal fragments, should: i) be accessible from high-yielding, modular and inexpensive synthetic steps; ii) have the ability to incorporate different combinations of donor fragments; iii) be able to bind one or more metal fragments of different electronic configurations; iv) and have the possibility of incorporating stereogenic centers within the framework. Although not all of these elements might be represented in a single, effective ligand design, the combination of two or more of these characteristics can potentially enhance the performance of the resulting metal complex in

catalytic reactions. The choice of design elements that should be incorporated into the ancillary ligand are dictated by the desired properties of the resulting metal complex in its given target application.

Two specific key ligand design features that are commonly sought after in the development of new homogeneous catalysts include hemilability and chirality. Hemilabile ligands are widely used in catalysis and usually, although not necessarily, contain two different donor atoms. The term hemilabile was first coined by Jeffrey and Rauchfuss[53] in 1979 and is now widely used to describe ligands that have one weakly coordinating donor atom that is capable of temporarily occupying a coordination site at the reactive transition metal center in the absence of small molecule substrates.[54] The hemilabile donor atom also helps to stabilize the otherwise electronically and coordinatively unsaturated metal center in the absence of substrates. Chiral ligands can play an important role by influencing the active metal center during the course of a metal-mediated asymmetric transformation. The types of chiral ligands available can range greatly in size, structure and chirality, as outlined in Section 1.3.

Once an ancillary ligand design has been identified, there are different techniques that can be used to evaluate the influence of the ancillary ligands on the metal center in new potential catalyst systems. Rapid evaluation methods such as high throughput screening are used to synthesize a large number of metal complexes in a very short time period, and to explore their efficiency in mediating a specific catalytic reaction. This approach enables the researchers to identify quickly new effective catalysts, but very large volumes of information need to be analyzed and the understanding of how the structure and properties of the catalyst influence reactivity is minimal. Another approach

to catalyst development is to start with a systematic ligand design and generate a small number of metal complexes. From this small group of complexes, the binding patterns, stability, and reactivity of the catalysts can be related back to the ancillary ligand design, expanding the understanding of the ancillary ligand influence on the metal center. Although this process requires more time, the metal complex properties are better understood and structure-activity relationships can be developed, even though the most efficient catalyst (in a global sense) may not have been identified. Unlike in high throughput screening methods, only minor modifications are made within the metal complex and the structure-activity relationship is assessed with each change, ultimately helping in the catalyst development process and understanding of ancillary ligand influence. The latter screening method is applied for the work discussed in this thesis.

1.5 Goals and Outline of This Thesis

The goals of this thesis involve the synthesis of new bidentate ancillary ligands and their coordination to transition metals, in particularly the Group 9 metals rhodium and iridium. The major part of this thesis discusses the development of new ancillary ligands derived from a P,N substituted indene backbone (**1-3**, Figure 1-7), that was recently developed in the Stradiotto research group.[55] This general ligand class has the possibility of being systematically modified in a variety of ways; the types of modifications that will be explored are outlined in Figure 1-7.

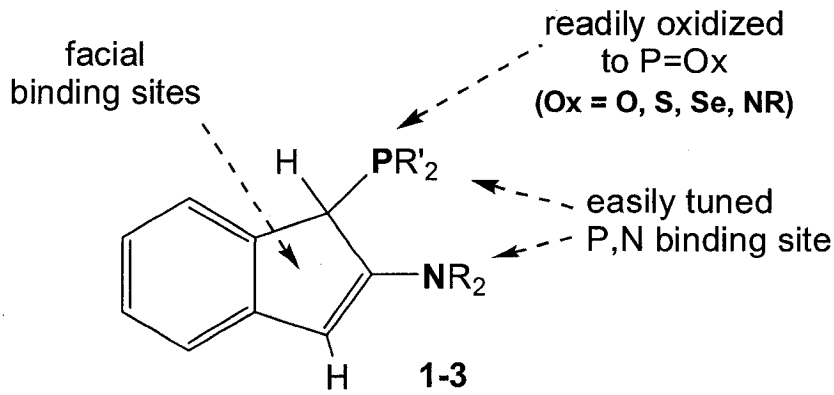


Figure 1-7. The modifications and structural motifs of the P,N functionalized indene ligand that will be explored in this thesis.

Chapter Two describes a one step synthetic route to an oxidized version of the P,N ligand **1-3** using elemental sulfur, in addition to evaluation of the binding properties and preparative methods for the formation of the corresponding neutral and cationic Group 9 N,S complexes. Reactivity studies described in this thesis also show that in the presence of water, the cationic N,S Group 9 complexes can be converted to neutral S,O metal complexes. In addition to the exploration of the oxidized P,N ligand, Chapter Two also examines the effects of tuning the P,N binding site by incorporating chirality into the phosphine donor fragment and the ability of such a chiral P,N ligand to form Group 9 metal complexes. Some preliminary reactivity studies were undertaken to explore the catalytic ability of the prepared metal complexes in E-H bond activation reactions. After establishing the efficacy of the modified P,N ligand sets to support single transition metal fragments, a synthetic survey was undertaken to explore the facial binding sites of the indenyl backbone in such ligands. Chapter Three explores the ability of the P,N and N,S ligands to support two metal fragments. Finally, while the bidentate ligands discussed in Chapters Two and Three were based on an indenyl backbone, the development of a new chiral P,N ligand, based on 7-azaindole, and its metal complexes, is discussed in Chapter

Four. The overall conclusions and a summary of key results of the work presented in this thesis, along with suggestions for future work, are the subject of Chapter Five.

1.6 References

1. Elsevier, C. J.; Reedijk, J.; Walton, P. H.; Ward, M. D. *Dalton Trans.* **2003**, 1869.
2. Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals*. 3rd ed. 2001, New York: John Wiley & Sons.
3. Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.
4. Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079.
5. Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3.
6. Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731.
7. Jia, C. G.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633.
8. Harrod, J. F. *Coord. Chem. Rev.* **2000**, *206*, 493.
9. Dyker, G. *Angew. Chem. Int. Ed.* **1999**, *38*, 1699.
10. Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1999**, *43*, 197.
11. Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363.
12. Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.
13. Schneider, J. J. *Angew. Chem. Int. Ed.* **1996**, *35*, 1069.
14. Vecchio, B. M.; de Maria, G. *Chim. Oggi-Chem. Today* **2006**, *24*, 3.
15. Tungler, A.; Sipos, E.; Hada, V. *Curr. Org. Chem.* **2006**, *10*, 1569.
16. Yin, L. X.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133.
17. Bartok, M. *Curr. Org. Chem.* **2006**, *10*, 1533.
18. Hutchings, G. J. *Ann. Rev. Mater. Res.* **2005**, *35*, 143.
19. Tundo, P.; Perosa, A. *Chem. Soc. Rev.* **2007**, *36*, 532.

20. Spessard, G. O.; Miessler, G. L., *Organometallic Chemistry*. 1996, Upper Saddle River, New Jersey: Prentice-Hall Inc.

21. Brock, W. H.; Jensen, K. A.; Jorgensen, C. K.; Kauffman, G. B. *Polyhedron* **1983**, *2*, 1.

22. Blaser, H. U.; Schmidt, E. eds., *Asymmetric Catalysis on Industrial Scale: Challenges, Approaches and Solutions*. 1st ed. 2004, Weinheim: Wiley-VCH Verlag GmbH & Co.

23. Blaser, H. U.; Pugin, B.; Spindler, F. *J. Mol. Catal. A-Chem.* **2005**, *231*, 1.

24. Blaser, H. U.; Spindler, F.; Studer, A. *Appl. Catal. A-Gen.* **2001**, *221*, 119.

25. Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1965**, 131.

26. Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. (A)* **1966**, 1711.

27. Jardine, F. H.; Osborn, J. A.; Wilkinson, G.; Young, J. F. *Chem. Ind. (London)* **1965**, 560.

28. Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748.

29. Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671.

30. Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395.

31. Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205.

32. Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331.

33. Betley, T. A.; Peters, J. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 2385.

34. Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2002**, *41*, 6541.

35. Yoon, T. P.; Jacobsen, E. N. *Science* **2003**, *299*, 1691.

36. Kalsi, P. S., *Stereochemistry - Conformation and Mechanism*. 1990, New Delhi: Wiley Eastern Ltd.

37. Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem. Int. Ed.* **1966**, *5*, 385.

38. Clayden, J.; Greeves, N.; Warren, S.; Wothers, P., *Organic Chemistry*. 2001, New York: Oxford University Press.

39. Munowitz, M., *Principles of Chemistry*. 2000, New York: W. W. Norton & Company, Inc.

40. Moss, G. P. *Pure App. Chem.* **1996**, *68*, 2193.

41. Knowles, W. S., *Asymmetric Hydrogenations - Monsanto L-Dopa Process*, in *Asymmetric Catalysis on Industrial Scale: Challenges, Approaches and Solutions*., Blaser, H. U. and Schmidt, E., Editors. 2004, Wiley-VCH Verlag GmbH & Co.: Weinheim. p. 23.

42. Knowles, W. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 1999.

43. Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem. Int. Ed.* **1990**, *29*, 977.

44. Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* **1986**, *51*, 629.

45. Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932.

46. Cai, D. W.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *Org. Syn.* **1999**, *76*, 6.

47. Noyori, R. *Angew. Chem. Int. Ed.* **2002**, *41*, 2008.

48. Gibson, S. E.; Ibrahim, H. *Chem. Commun.* **2002**, 2465.

49. Delacroix, O.; Gladysz, J. A. *Chem. Commun.* **2003**, 665.

50. Blaser, H. U.; Buser, H. P.; Coers, K.; Hanreich, R.; Jalett, H. P.; Jelsch, E.; Pugin, B.; Schneider, H. D.; Spindler, F.; Wegmann, A. *Chimia* **1999**, *53*, 275.

51. Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.

52. Spindler, F.; Blaser, H. U. *Enantiomer* **1999**, *4*, 557.

53. Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658.

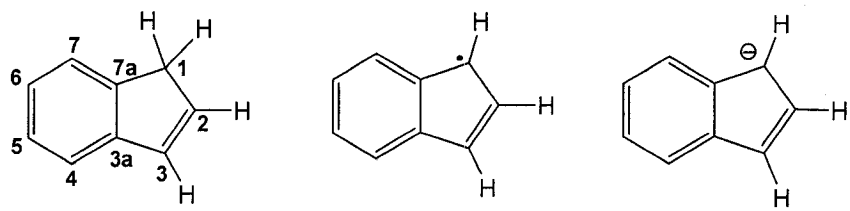
54. Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.

55. Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618.

Chapter Two: κ^2-*S,N*, κ^2-*S,O* and Chiral κ^2-*P,N* Complexes of Donor-Substituted Indene Ligands: Synthetic, Structural, and Catalytic Studies

2.1 Preamble: Indene Nomenclature

Indene (C_9H_8) is a bicyclic organic molecule featuring a benzo unit fused to a cyclopentadiene ring (Figure 2-1). Substitution of indene with various groups leads to functionalized indenes. Whenever there is at least one M-C linkage between a metal fragment and a C_9H_7 unit or functionalized derivative, the bound ligand is termed "indenyl". The uncoordinated C_9H_7 ligand yields an anionic version that is called "indenide". The numbering convention used in indene chemistry is shown in Figure 2-1, whereby the C1 position is assigned to the sp^3 hybridized carbon.



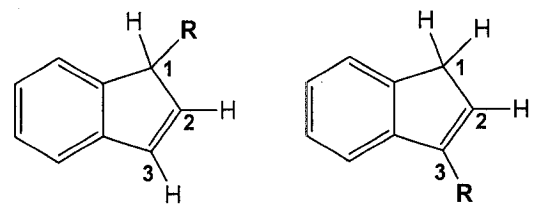


Figure 2-1. Nomenclature of indene and its derivatives.

2.2 Introduction

Innovations in multidentate ancillary ligand design continue to enable significant breakthroughs in the field of metal-mediated reaction chemistry.[1-4] It has been demonstrated in a variety of coordination complexes that even subtle modifications to the ancillary ligand topology can alter the coordination behavior of the ligand, as well as influence the stability and reactivity properties of the associated metal fragment.[5, 6] With the aim of identifying new ligand classes and subsequent metal complexes that display interesting and synthetically useful patterns of reactivity with substrate E-H bonds (E = main group element), one research focus in the Stradiotto group is the study of complexes supported by donor-functionalized indene and indenide ancillary ligands. Previous work done in the group was aimed at evaluating how the geometric differences between isomeric neutral ligands such as 1-diisopropylphosphino-2-dimethylaminoindene (κ^2-1-*P*^{i}Pr$_2$-2-*N*Me$_2$-indene, κ^2-**1-3a**) and 2-dimethylamino-3-diisopropylphosphinoindene (κ^2-2-*N*Me$_2$-3-*P*^{i}Pr$_2$-indene, κ^2-**1-3b**) impact the reactivity behavior of coordinated metal fragments. Ligand **1-3b** and related neutral bidentate ligands were also compared with those of analogous complexes featuring isosteric anionic ligands including 2-dimethylamino-3-diisopropylphospinoindenide (κ^2-2-*N*Me$_2$-3-*P*^{i}Pr$_2$-indenide, κ^2-**1-3c**) (Figure 2-2) in terms of their structural and reactivity properties.[7-11]

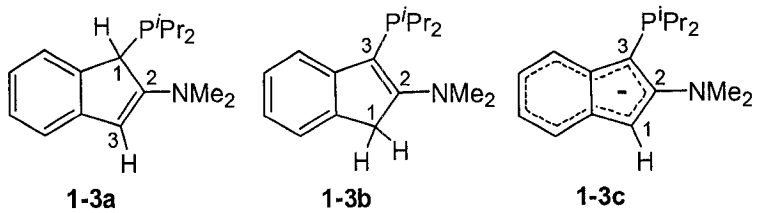
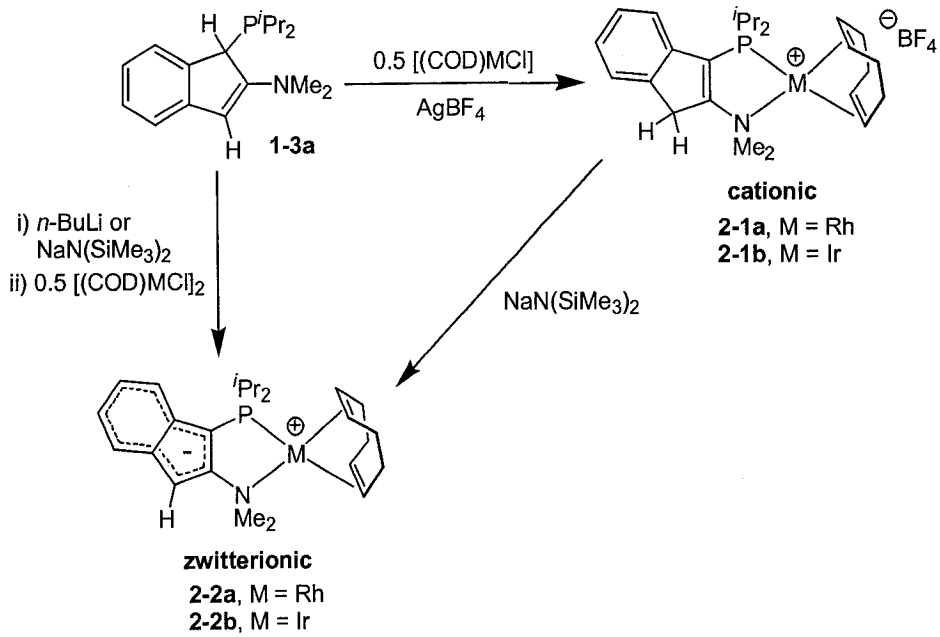


Figure 2-2. C1 and C3 indene and indenide versions of P,N ligand **1-3**.

The synthesis and characterization of Rh and Ir cations of the type [(COD)M(κ^2-**1-3b**)]$^+$X$^-$ (M = Rh, **2-1a**; M = Ir, **2-1b**; COD = η^4-1,5-cyclooctadiene) as well as the structurally related and formally zwitterionic species, (COD)M(κ^2-**1-3c**) (M = Rh, **2-2a**; M = Ir, **2-2b**; Scheme 2-1) were described previously.[9-11] Such zwitterions represent an unusual class of substituted indenyl-metal complexes that can be viewed as being comprised of a formally cationic [(COD)M]$^+$ fragment counterbalanced by an uncoordinated 10π-electron indenide unit that is built into the backbone of the κ^2-*P,N* ligand, **1-3c**, and which functions as a sequestered anionic charge reservoir for non-facial binding[12-14] rather than as a locale for facial metal binding.[15-23] Preliminary reactivity investigations have revealed that **2-1a** and **2-2a** are active catalysts for the dehydrogenative silylation of styrene,[10] while **2-1b** and **2-2b** have proven capable of mediating the hydrogenation of substituted alkenes under mild experimental conditions.[9]



Scheme 2-1. Synthesis of cationic (**2-1a,b**) and zwitterionic (**2-2a,b**) κ^2-*P,N* Rh(I) and Ir(I) complexes derived from **1-3a**.

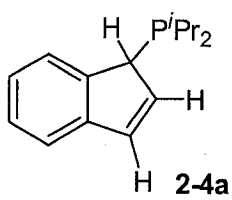
Intrigued by the tendency of **1-3c** for κ^2-*P,N* binding, rather than the usual η^5-coordination as is traditionally observed in indenyl-rhodium and -iridium complexes,[15-23] and motivated by the catalytic abilities exhibited by **2-1a,b** and **2-2a,b**, the development of chiral variants of these complexes as well as new bidentate Rh and Ir coordination complexes derived from alternative donor-substituted indenes was sought after, including those featuring oxidized phosphine donors. Phosphine sulfide type ligands represented appealing targets from a practical perspective since phosphine sulfides typically exhibit increased oxygen stability relative to the parent phosphines, while at the same time providing a relatively soft sulfur donor atom for binding to the heavier Group 9 metals.[24, 25] In particular, it was of interest to determine if the phosphine sulfide derivative of **1-3c** would support κ^2-P(*S*),*N* binding to $[(COD)M]^+$ fragments, reminiscent of the κ^2-*P,N* coordination of **1-3c** found in **2-2a,b**.

Within this chapter the synthesis of the phosphine sulfide derivative of **1-3a** (i.e. **2-3a**) as well as the use of this new ligand in the preparation of cationic (κ^2-*N,S*) and neutral (κ^2-*C,S*) Rh and Ir coordination complexes, and the application of these complexes as catalysts for the addition of triethylsilane to styrene are discussed. These catalytic results are also placed in the context of the same reaction catalyzed by Wilkinson's catalyst **1-1** and Crabtree's catalyst $[(COD)Ir(PCy_3)(Py)]^+PF_6^-$; **1-2**). Discussions also include the preparation and characterization of related (κ^2-P(*S*),*O*) Rh and Ir phosphinosulfide-enolate complexes in addition to the examination of their catalytic abilities in hydrosilylation of styrene. Following the exploration of the phosphine sulfide complexes, the synthesis of a chiral version of **1-3**, its coordination chemistry, and some preliminary catalytic studies are discussed.

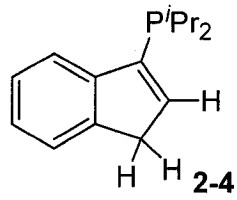
2.3 Results and Discussion

2.3.1 Synthesis and Characterization of 2-3a

Treatment of **1-3a** with elemental sulfur resulted in the clean conversion to **2-3a** (^{31}P NMR), which was isolated as an analytically pure yellow solid in 85 % yield and spectroscopically characterized (Scheme 2-2). The previously reported monosubstituted indene complexes 1-diisopropylphosphinoindene (**2-4a**) rearranges over the course of several hours to 3-diisopropylphosphinoindene (**2-4b**) in solution, and this transformation is accelerated upon treatment with alumina.[26]

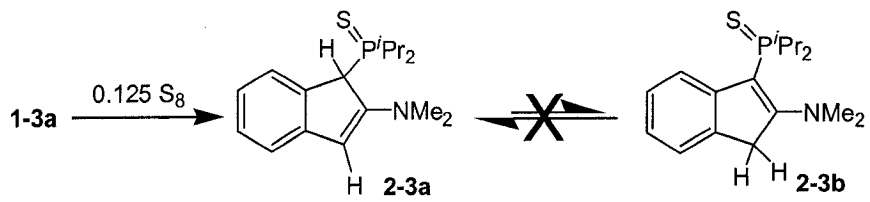


2-4a



2-4b

Employing **1-3a** and alumina under analogous conditions, an equilibrium mixture of **1-3a** and **1-3b** (~3:1; ^{1}H and ^{31}P NMR) is obtained.[26] In contrast, the vinylic isomer **2-3b** was not detected by use of NMR spectroscopic methods upon extended exposure of solutions of **2-3a** to alumina or triethylamine, or with prolonged heating (80 °C). It is unclear whether steric or electronic factors predominate in altering the equilibrium distribution of isomers in the **1-3a,b** versus **2-3a,b** systems.



Scheme 2-2. Synthesis of **2-3a**.

The possible electronic involvement of the phosphine sulfide unit in preventing the rearrangement of **2-3a** to **2-3b** was ruled out through the oxidation of **2-4a** with elemental sulfur. This reaction yielded directly a mixture of 1- and 3-diisopropylphosphinosulfide indene (**2-5a,b**, ~5:95; ^{1}H and ^{31}P NMR) after only one hour, an observation which is inconsistent with the formation of **2-5b** via sulfur oxidation of **2-4b** formed *in situ* from **2-4a**. Pure **2-5b** was isolated as a light yellow analytically pure solid in 81 % yield.

In an effort to complement the solution characterization of **2-3a**, the structure of this compound was confirmed by use of X-ray diffraction techniques. Moreover, in the course of recrystallizing **2-3a**, a crystal whose morphology was different from that of **2-3a** was isolated and subsequently identified as **2-3b** following single-crystal X-ray diffraction analysis. The crystal structures of **2-3a** and **2-3b** are provided in Figure 2-3, and can be compared with other crystallographically characterized 1- and 3-indenylphosphine sulfides.[27-30] The metrical parameters and X-ray experimental data for the crystallographically characterized complexes **2-3a** and **2-3b** are collected in Tables 2-1 and 2-2, respectively. While the P-S distances in **2-3a** and **2-3b** are equivalent, the P-C_{ind} distance in **2-3a** (1.873(2) Å) is longer than the related distance in **2-3b** (1.803(1) Å), in keeping with the P-$C_{ind}(sp^3)$ > P-$C_{ind}(sp^2)$ trend in bond lengths found in 1,3-($^{i}Pr_2P(S))_2$-indene,[27] and related compounds. As well, the contracted N-C2 distance in **2-3b** (1.351(2) Å) in comparison to that found in **2-3a** (1.392(2) Å), and the diminished pyramidalization at nitrogen in **2-3b** ($\Sigma_{angles\ at\ N}$ ~ 357°) versus **2-3a** ($\Sigma_{angles\ at\ N}$ ~ 342°) are both indicative of more extensive conjugation of the nitrogen lone pair with the adjacent indene framework in **2-3b**, relative to **2-3a**.

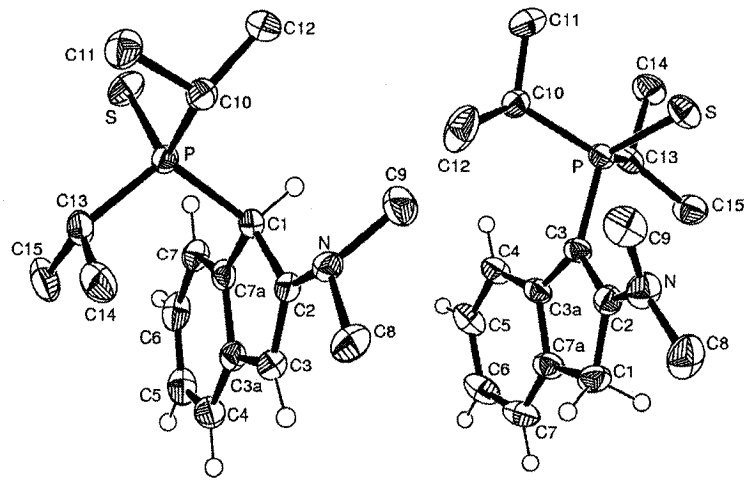


Figure 2-3. ORTEP diagrams for **2-3a** (left) and **2-3b** (right), shown with 50 % displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity.

Table 2-1. Selected Interatomic Distances (Å) and Angles (°) for **2-3a**, **2-3b**, **2-7a**, and **2-7b**.

	2-3a	**2-3b**	**2-7a**	**2-7b**
P-S	1.9665(6)	1.9657(5)	2.0127(8)	2.019(1)
P-C_{ind}	1.873(2)	1.803(1)	1.783(2)	1.799(3)
N-C2	1.392(2)	1.351(2)	1.407(3)	1.406(4)
C1-C2	1.533(2)	1.519(2)	1.504(3)	1.507(4)
C2-C3	1.351(2)	1.388(2)	1.364(4)	1.362(5)
M-S	---	---	2.3811(7)	2.3653(8)
M-C1	---	---	2.233(2)	2.214(3)
M-C11	---	---	2.116(2)	2.108(3)
M-C12	---	---	2.137(3)	2.122(3)
M-C15	---	---	2.135(2)	2.112(3)
M-C16	---	---	2.153(3)	2.137(3)
C2-N-Me^a	114.9(1)	120.3(2)	119.2(2)	119.7(3)
C2-N-Me^b	116.3(1)	123.7(1)	115.5(2)	115.6(3)
Me^a-N-Me^b	110.9(1)	113.0(1)	110.7(2)	110.6(3)
M-C1-P	---	---	90.9(1)	92.2(1)
C1-P-S	---	---	104.30(8)	102.1(1)
P-S-M	---	---	81.41(3)	82.63(4)
S-M-C1	---	---	81.07(6)	80.88(8)

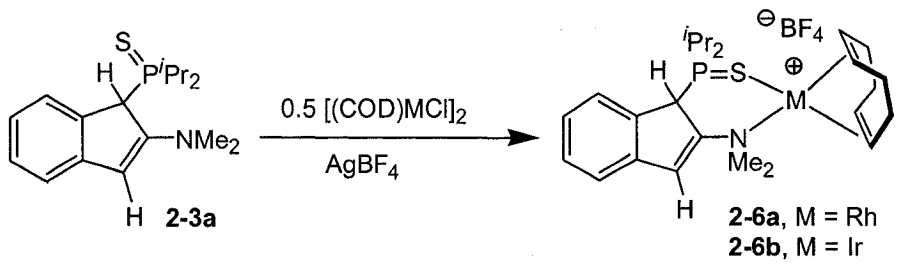
Table 2-2. Crystallographic Data for **2-3a**, **2-3b**, **2-7a**, **2-7b**, **2-9a**, **2-9b**, and **2-11b**.

	2-3a	**2-3b**	**2-7a**	**2-7b**
Empirical formula	$C_{17}H_{26}NPS$	$C_{17}H_{26}NPS$	$C_{25}H_{37}NPSRh$	$C_{25}H_{37}NPSIr$
Formula weight	307.42	307.42	517.50	606.79
Crystal dimensions	0.51 × 0.14 × 0.12	0.70 × 0.52 × 0.41	0.64 × 0.20 × 0.08	0.42 × 0.18 × 0.15
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	17.316(2)	10.5482(4)	10.1379(7)	10.1288(5)
b (Å)	10.834(1)	11.2705(5)	12.4282(8)	12.3895(7)
c (Å)	17.787(2)	14.3990(6)	18.848(1)	18.927(1)
β (deg)	90	98.752(1)	93.763(1)	93.2465(8)
V (Å^3)	3337.0(6)	1691.9(1)	2369.6(3)	2371.4(2)
Z	8	4	4	4
ρcalcd (g cm^{-3})	1.224	1.207	1.451	1.700
μ (mm^{-1})	0.281	0.277	0.888	5.798
2θ limit (deg)	52.84	52.74	52.74	52.78
	$-21 \le h \le 21$	$-13 \le h \le 13$	$-12 \le h \le 11$	$-12 \le h \le 12$
	$-13 \le k \le 13$	$-14 \le k \le 14$	$-15 \le k \le 15$	$-15 \le k \le 14$
	$-21 \le l \le 22$	$-18 \le l \le 17$	$-23 \le l \le 23$	$-23 \le l \le 23$
Total data collected	22338	10798	15830	13444
Independent reflections	3424	3442	4830	4856
R_{int}	0.0440	0.0162	0.0314	0.0248
Observed reflections	2883	3227	4087	3914
Absorption correction	multi-scan (SADABS)	multi-scan (SADABS)	multi-scan (SADABS)	multi-scan (SADABS)
Range of transmission	0.9670–0.8698	0.8948–0.8295	0.9323–0.6002	0.4767–0.1945
Data/restraints/parameters	3424 / 0 / 187	3442 / 0 / 183	4830 / 0 / 262	4856 / 0 / 262
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0338	0.0350	0.0281	0.0217
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0887	0.0978	0.0770	0.0544
Goodness-of-fit	1.064	1.057	1.020	1.029
Largest peak, hole (eÅ^{-3})	0.433, -0.178	0.721, -0.190	0.734, -0.274	1.040, -0.415

	2-9a	**2-9b**	**2-11b**
Empirical formula	$C_{23}H_{32}OPSRh$	$C_{23}H_{32}OPSIr$	$C_{31}H_{24}N_1O_2P_1$
Formula weight	490.43	579.72	473.82
Crystal dimensions	0.31 × 0.08 × 0.04	0.56 × 0.08 × 0.03	0.20 × 0.20 × 0.10
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	P21 [No. 4]
a (Å)	11.5449(8)	11.238(1)	9.4950(6)
b (Å)	16.358(1)	16.826(2)	7.2100(4)
c (Å)	12.4929(9)	12.621(1)	17.9760(8)
β (deg)	111.797(1)	112.260(1)	103.444(3)
V (Å^3)	2190.6(3)	2208.7(3)	1196.90(11)
Z	4	4	2
ρ_{calcd} (g cm^{-3})	1.487	1.743	1.314
μ (mm^{-1})	0.958	6.222	0.145
2θ limit (deg)	52.80	52.78	52.74
	$-14 \le h \le 14$	$-14 \le h \le 14$	$-11 \le h \le 11$
	$-20 \le k \le 20$	$-20 \le k \le 21$	$-8 \le k \le 9$
	$-15 \le l \le 15$	$-15 \le l \le 15$	$-22 \le l \le 22$
Total data collected	16430	17208	4656
Independent reflections	4490	4512	4656
Rint	0.0759	0.0406	0.0000
Observed reflections	3296	3840	3840
Absorption correction	multi-scan (SADABS)	multi-scan (SADABS)	multi-scan (SCALEPACK)
Range of transmission	0.9627–0.7554	0.8353–0.1283	0.9857–0.9716
Data/restraints/parameters	4490 / 0 / 244	4512 / 0 / 244	4656/ 1 / 319
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0375	0.0243	0.0561
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0796	0.0564	0.1331
Goodness-of-fit	0.992	1.038	1.057
Largest peak, hole (eÅ-3)	0.572, –0.408	0.789, –0.580	0.257, –0.270

2.3.2 Cationic κ^2-*N,S* Complexes of 2-3a

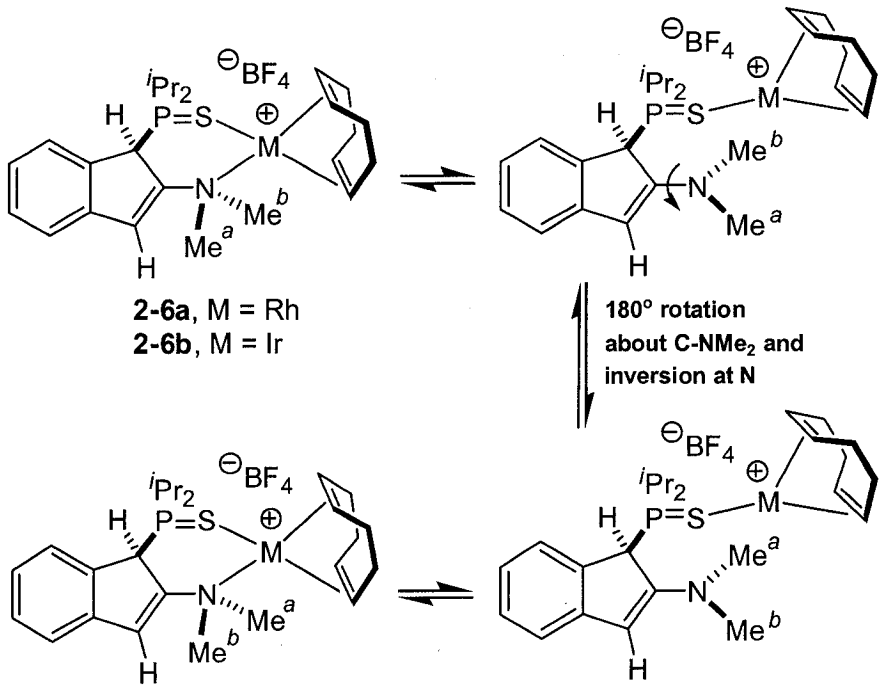
Treatment of **2-3a** with $[(COD)M(THF)_2]^+BF_4^-$ (M = Rh or Ir, prepared *in situ*) afforded **2-6a** and **2-6b** as analytically pure orange-red solids in 76 % and 59 % yield, respectively (Scheme 2-3). In contrast to the facile isomerization of **1-3a** to **1-3b** that occurs upon coordination to $[(COD)M]^+$ fragments,[9-11] both ^1H and ^{13}C NMR data confirm that the allylic structure of **2-3a** is retained when coordinated in **2-6a** and **2-6b**, in keeping with the observed stability of **2-3a** over **2-3b** in solution (Section 2.3.1).



Scheme 2-3. Synthesis of cationic κ^2-*N,S* (**2-6a,b**) Rh(I) and Ir(I) derivatives of **2-3a**.

Whereas the C_1 symmetry of **2-6a** and **2-6b** should result in the observation of two NMe ^1H NMR resonances for each complex, at 298 K only a single broad NMe_2 signal is detected in $CDCl_3$; however, in both cases two distinct NMe resonances are observed at 223 K. These temperature-dependent spectroscopic data are consistent with a dynamic process involving M-N dissociation, rotation about the C2-NMe_2 bond, inversion at N, and re-coordination to M, as depicted in Scheme 2-4. Analysis of variable-temperature ^1H NMR data for both **2-6a** and **2-6b** yielded a value for $\Delta G^{\ddagger}_{Tc}$ of ca. 14 kcal/mol for these processes (*Tc* = 279 K for **2-6a**; 284 K for **2-6b**).[31] The $^{31}P\{^1H\}$ NMR spectra of **2-6a** are also temperature-dependent; at 298 K, the spectrum in $CDCl_3$ is comprised of a broad resonance centered at 103 ppm, while at 223 K a sharp

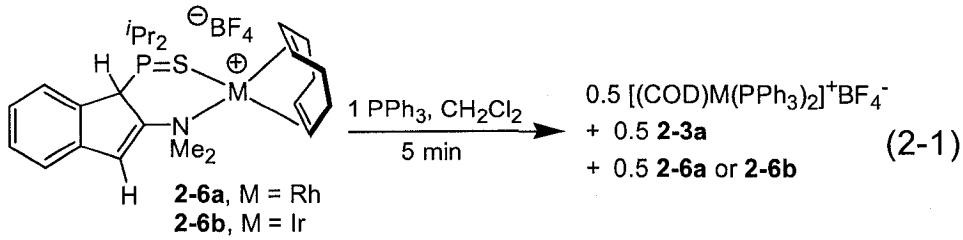
doublet ($^2J_{RhP}$ = 5 Hz) is observed at 107 ppm. In contrast, $CDCl_3$ solutions of **2-3b** exhibit a single sharp $^{31}P\{^1H\}$ NMR resonance at 115 ppm over this temperature range. Notably, the shift to high frequency of the phosphorus NMR resonance on going from **2-3a** (73 ppm) to either **2-6a** or **2-6b**, along with the magnitude of the observed Rh-P coupling constant in **2-6a**, provide evidence for the existence of an M-S linkage in **2-6a,b**.



Scheme 2-4. Proposed mechanism for the dynamic interconversion of the NMe_2 environments in **2-6a** or **2-6b**.

The rearrangement pathway outlined in Scheme 2-4 implies that the κ^2-*N,S* ligand in **2-6a** and **2-6b** can be described as hemilabile,[32] with the S-donor serving as an anchor to the Group 9 metal. In an effort to obtain further experimental support for such a proposal, **2-6a** and **2-6b** were separately treated with one equivalent of PPh_3 (eq 2-1). However, instead of obtaining the anticipated $[(COD)M(\kappa^1\text{-N,}S\text{-}\mathbf{2\text{-}3a})(PPh_3)]^+BF_4^-$

product, an equimolar mixture of $[(COD)M(PPh_3)_2]^+BF_4^-$,[2] **2-3a**, and unreacted **2-6a** or **2-6b** was generated (^{31}P NMR).

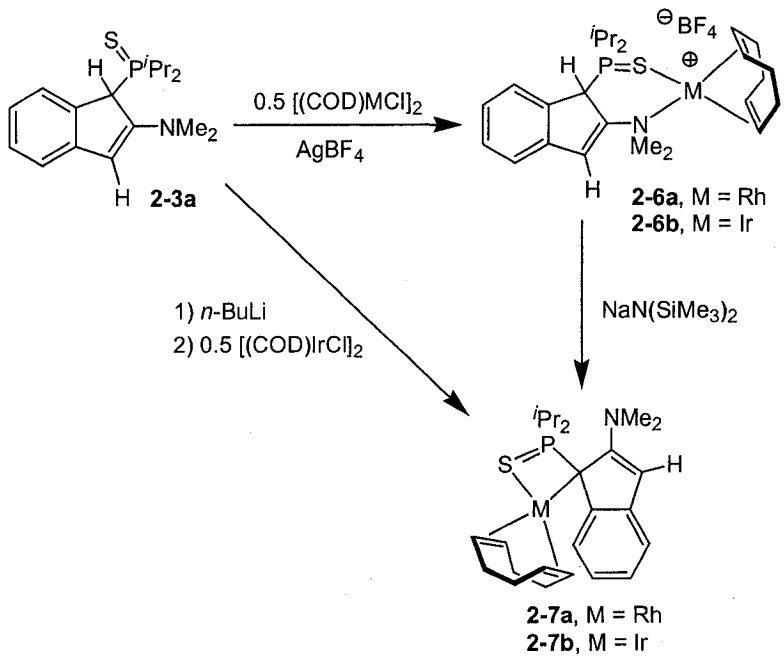


(2-1)

2.3.3 Neutral κ^2-*C,S* Complexes Derived from 2-3a

In the pursuit of neutral κ^2-*N,S* relatives of the formally zwitterionic complexes **2-2a,b** (Scheme 2-1), the κ^2-*N,S* cations **2-6a,b** were separately treated with $NaN(SiMe_3)_2$ (Scheme 2-5). In each case clean conversion to a single new phosphorus-containing compound was detected by use of ^{31}P NMR techniques, and these products were isolated as analytically pure yellow (**2-7a**) and orange (**2-7b**) solids in 70 % and 86 % yield, respectively. Both complexes yielded combustion analysis data consistent with the anticipated zwitterionic (κ^2-1-P(*S*)^{i}Pr$_2$-2-*N*Me$_2$-indenide)M(COD) product, and for the reaction involving **2-6a**, the observation of Rh-P coupling ($^2J_{RhP}$ = 15 Hz) provided evidence for Rh-S bonding in **2-7a**. However, the existence of Rh-C1 coupling ($^1J_{RhC}$ = 11 Hz) seemed to rule out κ^2-*N,S* connectivity in **2-7a**. The identity of **2-7a** and **2-7b** as κ^2-*C,S* isomers of the targeted κ^2-*N,S* compounds was confirmed based on the analysis of X-ray diffraction data. The crystallographically determined structures of **2-7a** and **2-7b** are given in Figure 2-4 and X-ray details are provided in Tables 2-1 and 2-2. Complex **2-7a** is the first reported complex featuring a Rh-C-P-S ring system,[33-39] as well as the first η^1-indenylrhodium species to be crystallographically characterized,[14] while **2-7b**

represents the first crystallographically characterized complex containing an Ir-C-P-S ring.[40] The metrical parameters associated with **2-7a** and **2-7b** are nearly identical and will be discussed collectively. Complexes **2-7a,b** feature Group 9 metals that exist within nearly planar M-C-P-S rings (mean deviation < 0.2 Å), and which exhibit equidistant M-COD linkages. As well, the P-C1 distances in **2-7a,b** are contracted significantly relative to **2-3a**, whereas the P-S distances are elongated, suggesting partial delocalization of the anionic charge along the C-P-S unit in **2-7a,b** as has been observed in some other structurally related complexes featuring anionic phosphine sulphide ligands.[41-43] Complex **2-7b** can also be prepared cleanly via lithiation of **2-3a** with *n*-BuLi followed by the addition of 0.5 equiv of $[(COD)IrCl]_2$. In using a similar protocol employing $[(COD)RhCl]_2$, **2-7a** was formed as the major product, along with varying amounts (≤ 20 %) of an as-yet unisolated new product which gave rise to a singlet ^{31}P NMR shift at 61 ppm.



Scheme 2-5. Synthesis of neutral κ^2-*C,S* (**2-7a,b**) Rh(I) and Ir(I) derivatives of **2-3a**.

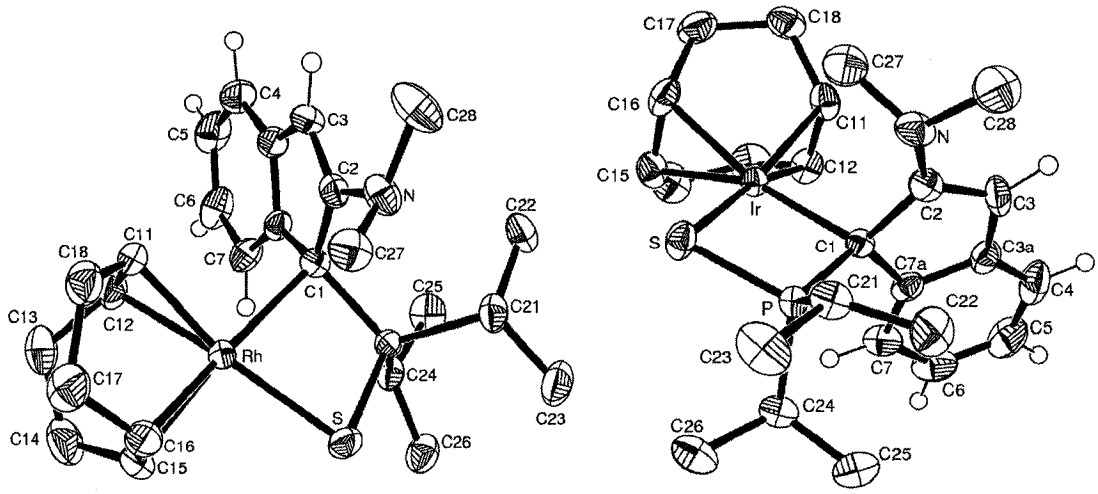
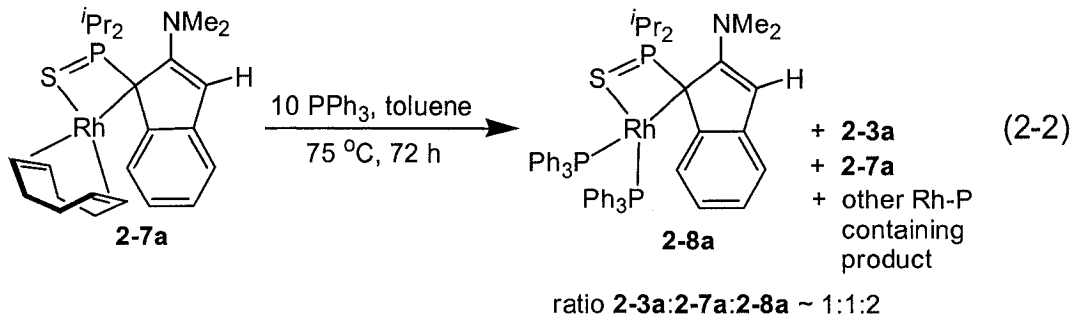


Figure 2-4. ORTEP diagram for **2-7a** (left) and **2-7b** (right), shown with 50 % displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity.



(2-2)

The reactivity of complexes **2-7a,b** with PPh_3 was compared with that of **2-6a,b**. Unlike **2-6a,b**, no reaction was observed (^{31}P NMR) for either of **2-7a** or **2-7b** upon exposure to ten equivalents of PPh_3 at 22 °C over the course of one week, suggesting that the anionic κ^2-*C,S* ligand in **2-7a,b** is coordinated more strongly than the neutral κ^2-*N,S*-**2-3a** ligand in the cations **2-6a,b**. Whereas a similar experiment involving **2-7b** conducted at 75 °C generated a complex mixture of products over 72 h, under analogous conditions **2-7a** reacted with excess PPh_3 to generate a mixture containing **2-3a**, unreacted **2-7a**, and **2-8a** as the major phosphorus-containing species (eq 2-2, Figure 2-

5). Thus far, **2-8a** has not been obtained in pure form and full characterization data for this complex are lacking. The connectivity of **2-8a** is proposed on the basis of ^{1}H and $^{31}P\{^{1}H\}$ NMR data: $^{31}P\{^{1}H\}$ NMR (toluene) for **2-8a**: δ 81.3 (d of d, P_a, $^{2}J_{RhPa}$ = 18.6 Hz, $^{3}J_{PaPb}$ = 7.4 Hz), 46.4 (d of d of d, P_b, $^{1}J_{RhPb}$ = 202.9 Hz, $^{2}J_{PbPc}$ = 39.1 Hz, $^{3}J_{PaPb}$ = 7.4 Hz), 43.2 (d of d, P_c, $^{1}J_{RhPc}$ = 156.4 Hz, $^{2}J_{PcPb}$ = 39.1 Hz).

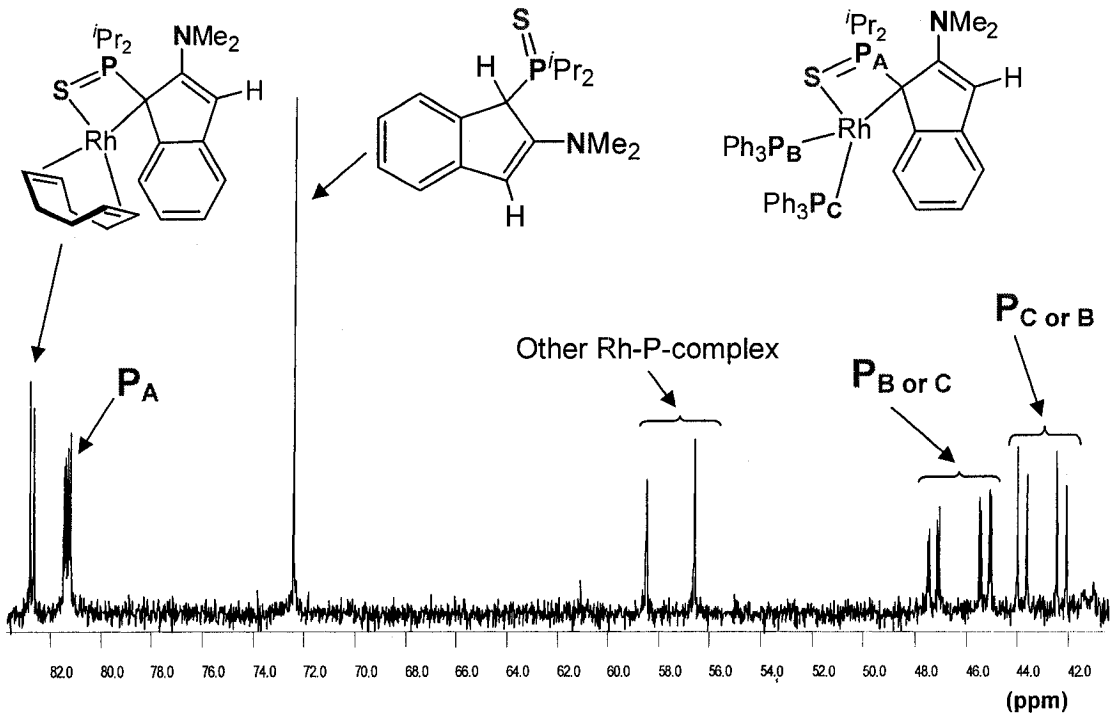
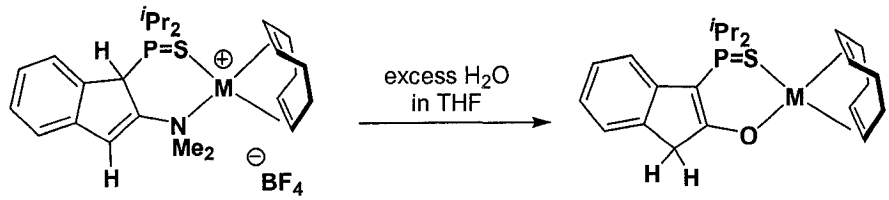


Figure 2-5. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture of **2-7a** reacted with 10 equiv of PPh_3 at 75 °C after 72 h.

2.3.4 Synthesis and Characterization of Neutral κ^2-P(*S*),*O* Complexes

During reactivity explorations of the κ^2-P(*S*),*N* complexes **2-6a,b** it was discovered that in solution, **2-6a,b** are cleanly transformed into the corresponding (κ^2-P(*S*),*O*) species (**2-9a**, M = Rh; **2-9b**, M = Ir) upon heating in the presence of water (Scheme 2-6). Complexes **2-9a,b** were isolated in analytically pure form (91 % and 90 %,

respectively) and in turn were characterized by use of NMR spectroscopic and X-ray crystallographic techniques (Figure 2-6). The X-ray experimental data and metrical parameters for the crystallographically characterized complexes **2-9a** and **2-9b** are collected in Tables 2-2 and 2-3, respectively. The overall structural features found in **2-9a,b** can be compared with other indenylphosphine sulfide complexes of Rh and Ir discussed above. While the $^{i}Pr_2(S)P\text{-}C_{ind}$ distances in both **2-9a** (1.763(3) Å) and **2-9b** (1.766(4) Å) are contracted relative to **2-3a** (1.873(2) Å), the corresponding P-S linkages in **2-9a** (2.020(1) Å) and **2-9b** (2.027(1) Å) are elongated relative to **2-3a** (1.9665(6) Å). These metrical data, when considered along with the relatively short O-C2 distances observed in **2-9a,b** (1.277(4) Å and 1.290(5) Å, respectively), indicate that a resonance contributor featuring $^{i}Pr_2(S)P{=}C(3)$ and O=C(2) linkages and a formal anionic charge on sulfur contributes significantly in these κ^2-P(*S*),*O* complexes. In addition, the equidistant M-COD linkages point to a similar *trans*-influence for the O- and S-donors in **2-9a,b**. Notably, complexes **2-9a,b** proved stable to heating in toluene for at least one week at 100 °C.



2-6a, M = Rh
2-6b, M = Ir

2-9a, M = Rh
2-9b, M = Ir

Scheme 2-6. Synthesis of κ^2-P(*S*),*O* Rh and Ir complexes, **2-9a,b**.

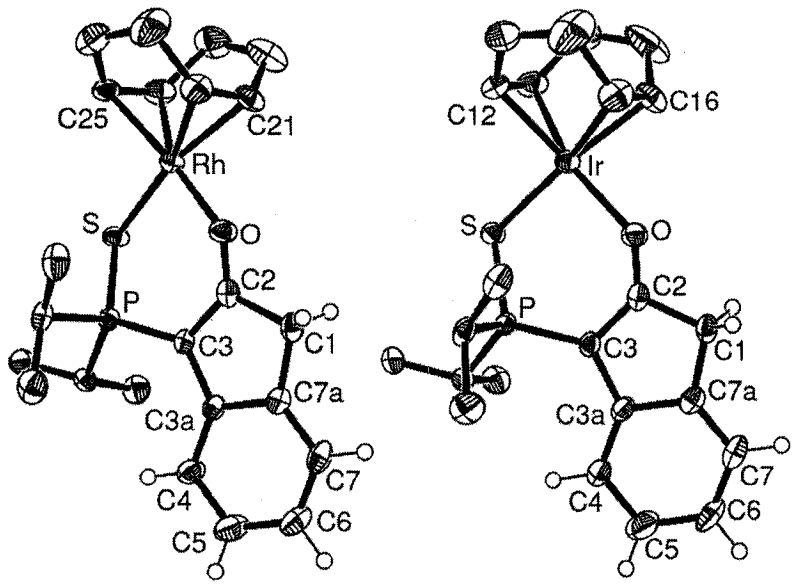


Figure 2-6. The crystallographically determined structures of **2-9a** (left) and **2-9b** (right), shown with 50 % displacement ellipsoids; selected H-atoms have been omitted for clarity.

Table 2-3. Selected Interatomic Distances (Å) for **2-9a** and **2-9b**.

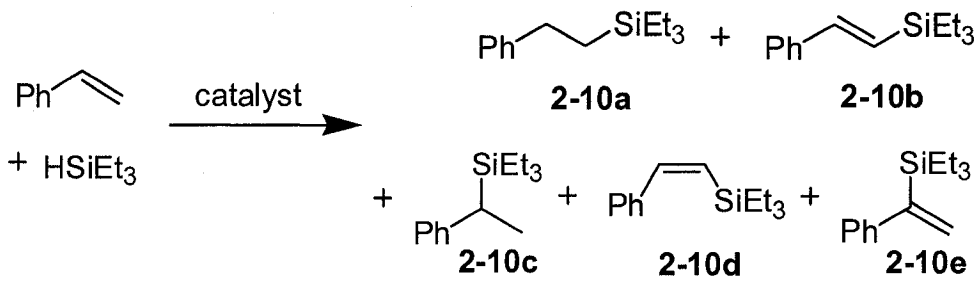
	2-9a	**2-9b**
M-S	2.3571(9)	2.335(1)
M-O	2.057(2)	2.053(3)
M-$C_{alkene1}$ [a]	2.112(3)	2.111(4)
M-$C_{alkene2}$ [a]	2.119(4)	2.111(4)
M-$C_{alkene3}$ [b]	2.103(3)	2.102(4)
M-$C_{alkene4}$ [b]	2.104(4)	2.094(4)
$^{i}Pr_2P$-*C*	1.763(3)	1.766(4)
P-S	2.020(1)	2.027(1)
O-C	1.277(4)	1.290(5)
C1-C2	1.513(4)	1.509(5)
C2-C3	1.397(5)	1.378(5)

[a]The metal-cyclooctadiene distances *trans* to S.
[b]The metal-cyclooctadiene distances *trans* to O.

2.3.5 Catalytic Addition of Triethylsilane to Styrene

Vinylsilanes represent useful organic synthons that can be prepared directly via the hydrosilylation of alkynes, although achieving high regioselectivity in such addition reactions can be challenging.[44-47] The selective dehydrogenative silylation of olefins provides an alternative route to vinysilanes,[45-48] and Group 9 catalysts including Wilkinson's catalyst, **1-1,** have proven capable of mediating such transformations.[10, 49-52] In this context, the metal-mediated addition of triethylsilane to styrene was selected as a prototypical E-H bond activation reaction for use in benchmarking the catalytic abilities of **2-6a,b** and **2-7a,b** against those of **1-1**, as well as Crabtree's catalyst, **1-2**. The predominant silicon-containing products of this reaction are given in eq 2-3, and include the addition products **2-10a** and **2-10c**, as well as the vinylsilanes **2-10b**, **2-10d**, and **2-10e**. The results of catalytic experiments conducted at 60 °C using a 5.5 mol% catalyst loading are collected in Table 2-4. Reactions mediated by the cations **2-6a,b** were restricted to 1,2-dichloroethane, due to the poor solubility of these complexes in alternative media. In the presence of either an equimolar (Table 2-4, entry 1) or an excess (Table 2-4, entry 2) amount of styrene relative to triethylsilane, **2-6a** performed poorly as a catalyst, with only ~20 % silane conversion noted after 24 h. This contrasts the efficient and selective transformation of these substrates into **2-10b** mediated by the $[Rh(COD)_2]^+BF_4^-$/2 PPh_3 catalyst system in diethyl ketone under similar conditions.[49] Low conversion was also obtained for the 1:1 reaction of styrene with triethylsilane in the presence of a catalytic amount of **2-6b** (Table 2-4, entry 3). However, 70 % conversion was achieved after 24 h by use of **2-6b** and a 5:1 ratio of these substrates, albeit with very poor selectivity (Table 2-4, entry 4). Under similar conditions employing **1-2** as a

catalyst, >99 % silane conversion was obtained with similarly poor product selectivity (Table 2-4, entry 5). Throughout, an equimolar amount of ethylbenzene compared to **2-10b** was detected, which confirms that the excess styrene employed acts as a dihydrogen acceptor in this catalytic system.

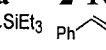


(2-3)

Improved catalytic performance was noted for the neutral κ^2-*C*,*S*-Rh complex, **2-7a**, relative to the cations **2-6a,b**. For reactions conducted in 1,2-dichloroethane, 78 % silane conversion was observed after 24 h when using a 1:1 ratio of styrene and triethylsilane (Table 2-4, entry 6). Further increases in the silane conversion (96 %), as well as improved selectivity for the dehydrogenative silylation product **2-10b**, were achieved after only 4 h when a 5:1 substrate ratio was employed (Table 2-4, entry 7), and after 24 h the triethylsilane was completely consumed (Table 2-4, entry 8). In switching to benzene as the reaction medium, additional gains in conversion and selectivity were achieved when employing **2-7a** in combination with either a 1:1 (Table 2-4, entry 10) or 5:1 (Table 2-4, entries 11 and 12) ratio of styrene and triethylsilane. While the performance of complex **1-1** in 1,2-dichloroethane is superior to that of **2-7a** under similar reaction conditions (Table 2-4, entry 9), the difference in selectivity is somewhat less pronounced for reactions conducted in benzene (Table 2-4, entry 13). By comparision, the catalytic abilities of the κ^2-*C*,*S*-Ir complex **2-7b** proved to be vastly

inferior to those of **2-7a** in both 1,2-dichloroethane (Table 2-4, entries 14 and 15) and benzene (Table 2-4, entries 16 and 17).[53, 54]

Table 2-4. Addition of Triethylsilane to Styrene[a]

Entry	Catalyst	styrene: Et_3SiH	solvent	yield [%][b]	**2-10a**[c] 	**2-10b**[c] 	**2-10c**[c] 	other[c]
1	**2-6a**	1:1	DCE	21	4	2	15	<1
2	**2-6a**	5:1	DCE	19	5	8	6	<1
3	**2-6b**	1:1	DCE	22	9	11	2	<1
4	**2-6b**	5:1	DCE	70	29	36	3	2
5	**1-2**	5:1	DCE	>99	7	41	52	<1
6	**2-7a**	1:1	DCE	78	29	40	9	<1
7	**2-7a**	5:1	DCE	96[d]	15	81	<1	<1
8	**2-7a**	5:1	DCE	>99	15	83	2	<1
9	**1-1**	5:1	DCE	>99[d]	3	93	4	<1
10	**2-7a**	1:1	C_6H_6	94	27	61	6	<1
11	**2-7a**	5:1	C_6H_6	98[d]	8	90	<1	<1
12	**2-7a**	5:1	C_6H_6	>99	8	91	1	<1
13	**1-1**	5:1	C_6H_6	>99[d]	1	94	5	<1
14	**2-7b**	1:1	DCE	34	9	18	7	<1
15	**2-7b**	5:1	DCE	64	24	33	6	1
16	**2-7b**	1:1	C_6H_6	26	5	11	7	3
17	**2-7b**	5:1	C_6H_6	36	9	14	8	5
18	**2-9a**	5:1	DCE	>99	14	84	2	<1
19	**2-9a**	5:1	C_6H_6	94	12	79	3	<1
20	**2-9b**	5:1	DCE	95	29	53	5	8
21	**2-9b**	5:1	C_6H_6	6	2	4	<1	<1

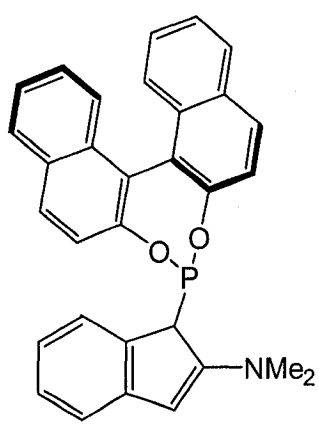
[a]Reactions employing 5.5 mol% catalyst at 60 °C; DCE = 1,2-dichloroethane; control experiments confirmed that solutions of **2-6a,b** and **2-7a,b** are stable upon heating at 60 °C for a minimum of 24 h (^{31}P NMR). [b]Based on the consumption of triethylsilane at 24 h, except where noted. [c]Product distribution based on GC-MS and GC-FID data, rounded to the nearest percent; other silicon-containing products include **2-10d** and **2-10e**. [d]Yield quoted at 4 h.

The catalytic utility of **2-9a,b** in the addition of triethylsilane to styrene was also examined (60 °C, 5.0 mol% **2-9a** or **2-9b**, 24 h; Table 2-4). The Rh complex **2-9a** proved to be an effective catalyst for this transformation, affording quantitative substrate

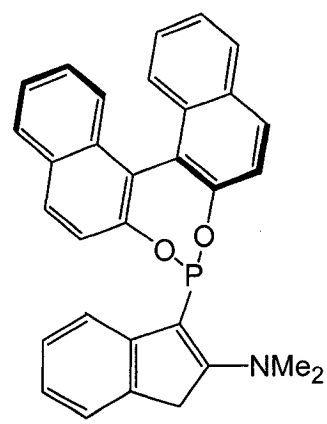
conversion and good selectivity (84 % **2-10b**; Table 2-4, entry 18) for reactions conducted in 1,2-dichloroethane. The activity and selectivity of **2-9a** was diminished only modestly in changing the solvent to benzene (Table 2-4, entry 19). By comparison, the Ir complex **2-9b** proved inferior to **2-9a** both in terms of activity and selectivity, especially for reactions conducted in benzene (Table 2-4, entries 20 and 21).

2.3.6 Synthesis of a Chiral Version of Ligand 1-3

As mentioned previously, the Group 9 metal complexes **2-1a,b** and **2-2a,b** (Scheme 2-1) have displayed interesting structural features and high catalytic reactivity for a range of E-H bond activation catalysis (E = main group element), such as hydrosilylation, hydroboration, and hydrogenation of alkenes.[9-11, 26, 55-57] Due to the ability of **1-3** to support different binding motifs and to facilitate different E-H bond reactions with high efficiency, it became of interest to modify the ligand design by incorporating a chiral moiety and in turn to explore the metal chemistry and its potential activity in asymmetric transformations. In initial efforts it was decided to incorporate chirality into the phosphine donor by use of *R*-(+)-1,1'-bi-2-naphthol (*R*-BINOL) as a source of chirality to give **2-11**.

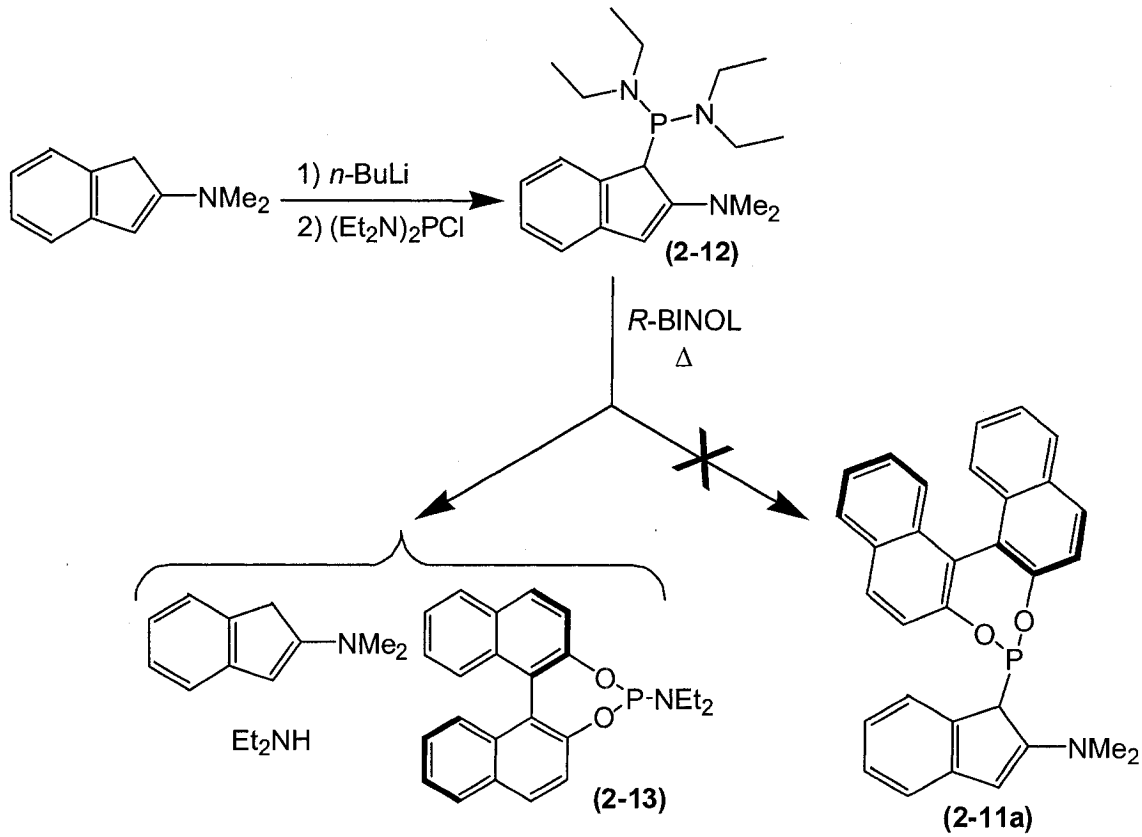


(2-11a)



(2-11b)

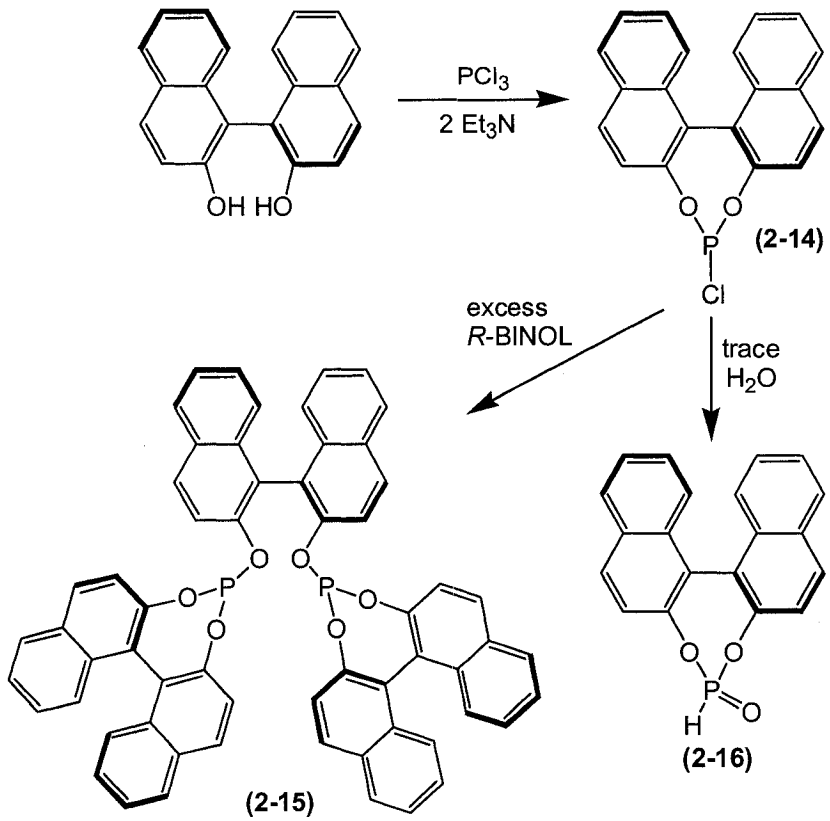
The first attempt in the synthesis of **2-11** was based on the displacement of diethylamino groups on the phosphorus center in **2-12** using *R*-BINOL, a method that had been employed previously in the preparation of related ligands (Scheme 2-7).[58-61] 2-Dimethylaminoindene was deprotonated with *n*-BuLi at -35 °C and subsequent reaction with $(NEt_2)_2PCl$ gave the intermediate **2-12**, and no indication of the C3 isomer of **2-12** was observed by the use of ^{31}P NMR spectroscopy. R-BINOL in toluene was then added to the intermediate **2-12** and the reaction mixture was heated at 115 °C for 24 h. The reaction mixture was then checked by use of ^{1}H and ^{31}P NMR techniques and careful examination of the NMR spectra revealed that instead of the desired displacement of the two diethylamino groups on the phosphorus center to give **2-11**, the C – P bond in **2-12** was broken, resulting in a mixture of 2-dimethylaminoindene, diethylamine, and **2-13**. This result was not entirely unexpected as the phosphorus-bound carbon in **2-12** is sp^3 hybridized (C1 isomer), while in the literature examples the carbon atom has sp^2 hybridization.[58-61] Attempts to isomerize **2-12** to the C3 isomer were unfruitful and therefore a new synthetic route for the synthesis of **2-11** was required.



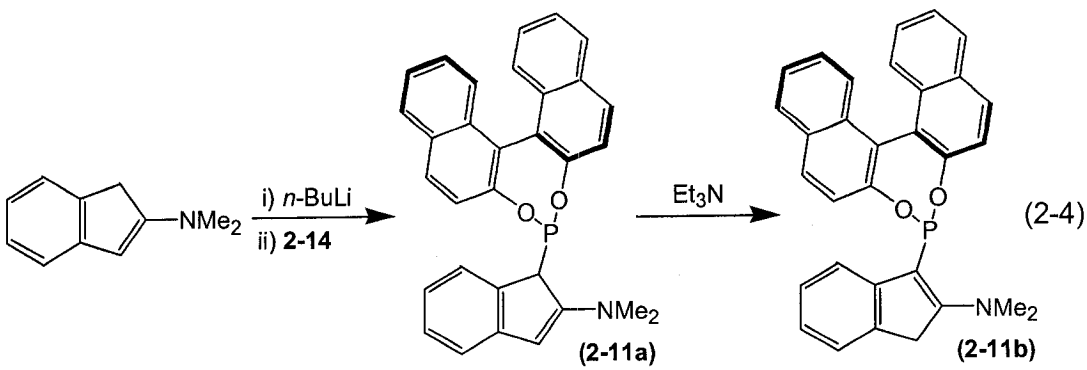
Scheme 2-7. Attempted synthesis of **2-11**.

The alternative synthesis for **2-11** was based on the preparation of the known chloro phosphine (**2-14**), followed by its addition to the lithium salt of 2-dimethylaminoindene, as in the successful synthesis for **1-3**.[10] The precursor **2-14** was prepared based on literature methods.[62-71] Notably, great care needed to be taken in terms of the reaction stoichiometry[71] and ambient moisture levels[69] to prevent the formation of the known diphosphite **2-15** and the hydrolyzed product **2-16** (Scheme 2-8). Schlenk techniques were not rigorous enough during days of high humidity to allow the clean synthesis of **2-14**. However, when high vacuum line techniques[72] were implemented, **2-14** was isolated in up to 93 % yield in small scale reactions. On scale-up

the isolated yield was lower at 82 %. Scherer and co-workers have reported isolated yields of 90-93 % for compound **2-14**.[69]



Scheme 2-8. The synthesis of **2-14** and potential by-products **2-15** and **2-16** in the presence of excess reagent or moisture.



With **2-14** in hand, dimethylaminoindene was deprotonated with *n*-BuLi at -35 °C and subsequent reaction with **2-14** led to the desired product **2-11** as a mixture of C1 (**2-11a**) and C3 (**2-11b**) isomers (eq 2-4). Several isomerization methods such as heating, passing through alumina or silica, and addition of a weak base (e.g. potassium carbonate or triethylamine) were explored. The only method aiding in the isomerization was the addition of triethylamine to a THF solution of **2-11**. Upon addition of the base, **2-11b** slowly precipitated out of solution making the isolation possible. Complex **2-11b** was isolated in analytically pure form (65 %) and in turn was characterized by use of NMR spectroscopic and X-ray crystallographic techniques (Figure 2-7).

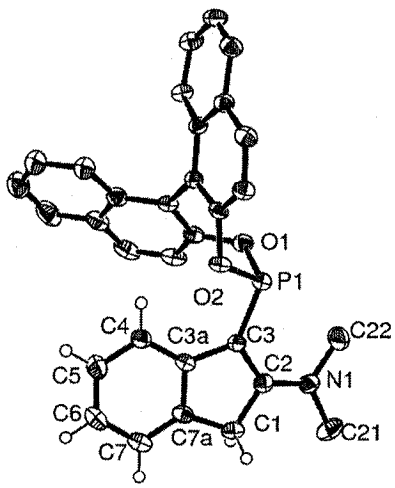


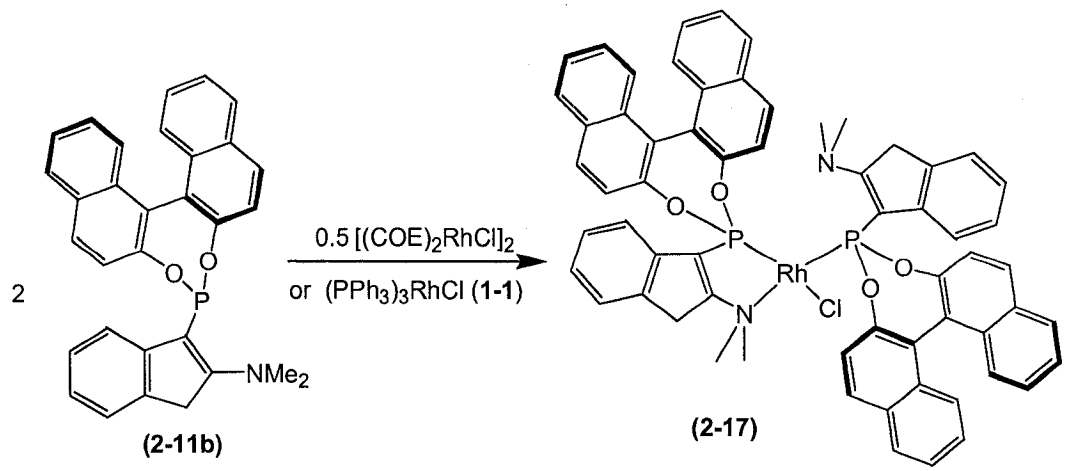
Figure 2-7. The crystallographically determined structure of **2-11b** is shown with 50 % displacement ellipsoids; selected H-atoms have been omitted for clarity.

2.3.7 Transition Metal Chemistry of 2-11b

Some coordination chemistry has been explored with **2-11b**. However, unlike in the clean coordination observed with the achiral P,N-indene **1-3**,[10, 11] when **2-11b** was reacted with $[(COD)MCl]_2$ or $[(COD)M(THF)_2]^+BF_4^-$ (M = Rh, Ir), a mixture of products was generated. When $[(COE)_2RhCl]_2$ was employed, a 2:1 ligand-to-metal complex (**2-**

17; Scheme 2-9), was formed, regardless of the ligand stoichiometry used. When **2-11b** was reacted with $(PPh_3)_3RhCl$ **1-1**, the 2:1 metal complex **2-17** was observed as the only product, along with free triphenylphosphine (Scheme 2-9). The addition of a halide abstraction reagent (e.g. $AgBF_4$) to **2-17** resulted in the formation of a multitude of products, and so different synthetic routes were explored in the aim to prepare a cationic complex. When a THF solution of $[(COE)_2Rh(THF)_2]^+BF_4^-$ (prepared *in situ* from $[(COE)_2RhCl]_2$ and $AgBF_4$) was added slowly to two equiv of **2-11b**, a mixture of phosphorus containing products (one major and some minor) was observed by use of ^{31}P NMR spectroscopy. The major observed phosphorus containing product can be attributed to a 2:1 ligand-to-metal complex (δ ^{31}P 199.1 (d of d, $^2J_{PP}$ = 36.4 Hz, $^1J_{RhP}$ = 260.2 Hz), 171.2 (d of d, $^2J_{PP}$ = 36.4 Hz, $^1J_{RhP}$ = 290.6 Hz); resembling the connectivity as seen in **2-17**). Further characterization of the 2:1 ligand-to-metal complex is warranted. These results demonstrate that **2-11b** prefers to bind in a 2:1 ratio to rhodium metal fragments.

In an effort to prepare a 1:1 metal-to-ligand complex with **2-11b**, some Group 10 coordination chemistry was attempted using $[(allyl)PdCl]_2$. Whenever **2-11b** was reacted with $[(allyl)PdCl]_2$, two major and one minor products were observed by use of ^{31}P NMR spectroscopy, and attempts to isolate pure material were met with limited success. In the case of $[(allyl)PdCl]_2/AgBF_4$, a range of new phosphorus-containing compounds was produced.

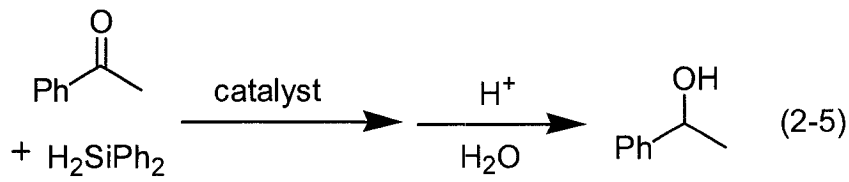


Scheme 2-9. Synthesis of the 2:1 ligand-to-metal complex **2-17** via the addition of $[(COE)_2RhCl]_2$ or $(PPh_3)_3RhCl$ (**1-1**).

Due to the limited success of isolating clean metal complexes of **2-11b**, *in situ* prepared rhodium complexes of **2-11b** were employed in catalytic studies. In a preliminary effort to assess the catalytic utility of these complexes in E-H bond addition reactions, the addition of diphenylsilane to acetophenone (Table 2-5) and the hydrogenation of methyl 2-acetamidoacrylate (Table 2-6) were examined.

2.3.8 Hydrosilylation Catalysis Mediated by *in situ* Prepared Rhodium Complexes of 2-11b

When neutral or cationic Rh precursors were used in THF (Table 2-5; entries 1 to 7) modest conversions were achieved in ketone hydrosilylation (eq 2-5). Comparing the results when 1.2 equiv or 2.4 equiv of ligand were used demonstrated that in the presence of 2.4 equiv of ligand there is significant inhibition of catalyst activity. On changing the reaction medium from THF to CH_2Cl_2 (Table 2-5, entries 8 to 11), an increase in activity was observed. However, in terms of catalyst enantioselectivity, there was no combination of metal precursor and ligand that afforded product selectivity of greater than 11 % *ee*.



(2-5)

Table 2-5. Addition of Diphenylsilane to Acetophenone.[a]

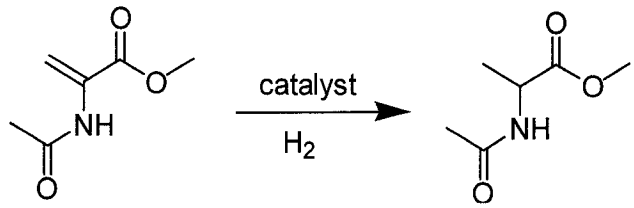
Entry	Metal precursor	Equiv of **2-11b**	Solvent	% conversion[b]	% *ee*[c]
1	$[(COE)_2RhCl]_2$	1.2	THF	63	4 (R)
2	$[(COE)_2RhCl]_2$	2.4	THF	55	7 (R)
3	$[(COE)_2Rh(THF)_2]^+BF_4^-$	1.2	THF	50	3 (R)
4	$[(COE)_2Rh(THF)_2]^+BF_4^-$	2.4	THF	30	3 (S)
5	$[(COD)Rh(THF)_2]^+BF_4^-$	1.2	THF	66	7 (S)
6	$[(COD)Rh(THF)_2]^+BF_4^-$	2.4	THF	52	0
7	$[(COD)RhCl]_2$	1.2	THF	74	2 (S)
8	$[(COE)_2RhCl]_2$	1.2	CH_2Cl_2	57	0
9	$[(COD)RhCl]_2$	1.2	CH_2Cl_2	84	1 (R)
10	$[(COE)_2Rh(THF)_2]^+BF_4^-$	1.2	CH_2Cl_2	90	4 (R)
11	$[(COD)Rh(THF)_2]^+BF_4^-$	1.2	CH_2Cl_2	93	11 (R)

[a]Conditions: 24 °C, 5.0 mol% Rh. [b]Percent conversion based on the consumption of ketone at 18 h. [c]Product distribution determined on the basis of chiral GC-FID data, rounded to the nearest percent; the major isomer is indicated in parentheses. Isomer assignment was based on literature data.[73]

2.3.9 Hydrogenation Catalysis Mediated by *in situ* Prepared Rhodium Complexes of 2-11b

In exploring the hydrogenation of methyl-2-acetamidoacrylate (eq 2-6), initial test reactions employing a cationic Rh precursor without added ligand **2-11b** in THF provided full conversion, with the expected zero enantioselectivity (Table 2-6, entry 1); in CH_2Cl_2 no conversion was achieved (Table 2-6, entry 4). Comparing entries 2 and 3 in Table 2-6 reveals that in the presence of 1.2 equiv of **2-11b**, full conversion and 40 % *ee* was achieved, whereas when the amount of **2-11b** was increased to 2.4 equiv, a reduction in

activity was observed, but product enantioselectivity increased to 67 % *ee*. Speculatively, the formation of a catalytically less active 2:1 ligand-to-metal rhodium complex might be the cause of this decrease in activity, while the selectivity might be attributed to a catalytically active coordinatively unsaturated rhodium complex present in very small amounts. The high conversion observed in entry 2 might be attributed to the presence of catalytically active coordinatively unsaturated rhodium complex as well as uncoordinated metal precursor. The presence of even a small amount of the metal precursor would reduce the enantioselectivity dramatically. In the case of entry 5 in Table 2-6, the addition of ligand improved the catalyst activity in CH_2Cl_2 relative to entry 4, but conversion and product selectivity were still very meager. Similar attempts with the analogous iridium metal precursor resulted in no detectable catalytic activity.



(2-6)

Table 2-6. Hydrogenation of Methyl 2-acetamidoacrylate.[a]

Entry	Metal precursor	Equiv of **2-11b**	Solvent	% conversion[b]	% *ee*[c]
1	$[(COD)Rh(THF)_2]^+BF_4^-$	0	THF	>99	0
2	$[(COD)Rh(THF)_2]^+BF_4^-$	1.2	THF	>99	40 (S)
3	$[(COD)Rh(THF)_2]^+BF_4^-$	2.4	THF	32	67 (S)
4	$[(COD)Rh(THF)_2]^+BF_4^-$	0	CH_2Cl_2	n/d[d]	n/d[d]
5	$[(COD)Rh(THF)_2]^+BF_4^-$	1	CH_2Cl_2	26	3 (S)

[a]Conditions: RT, 5.0 mol% catalyst, 1 atm H_2. [b]Percent conversion based on the consumption of methyl 2-acetamidoacrylate at 24 h. [c]Product distribution determined on the basis of chiral GC-FID data, rounded to the nearest percent; the major isomer is indicated in parentheses. Isomer assignment was based on literature data.[74] [d]No hydrogenated product detected.

2.4 Summary and Conclusions

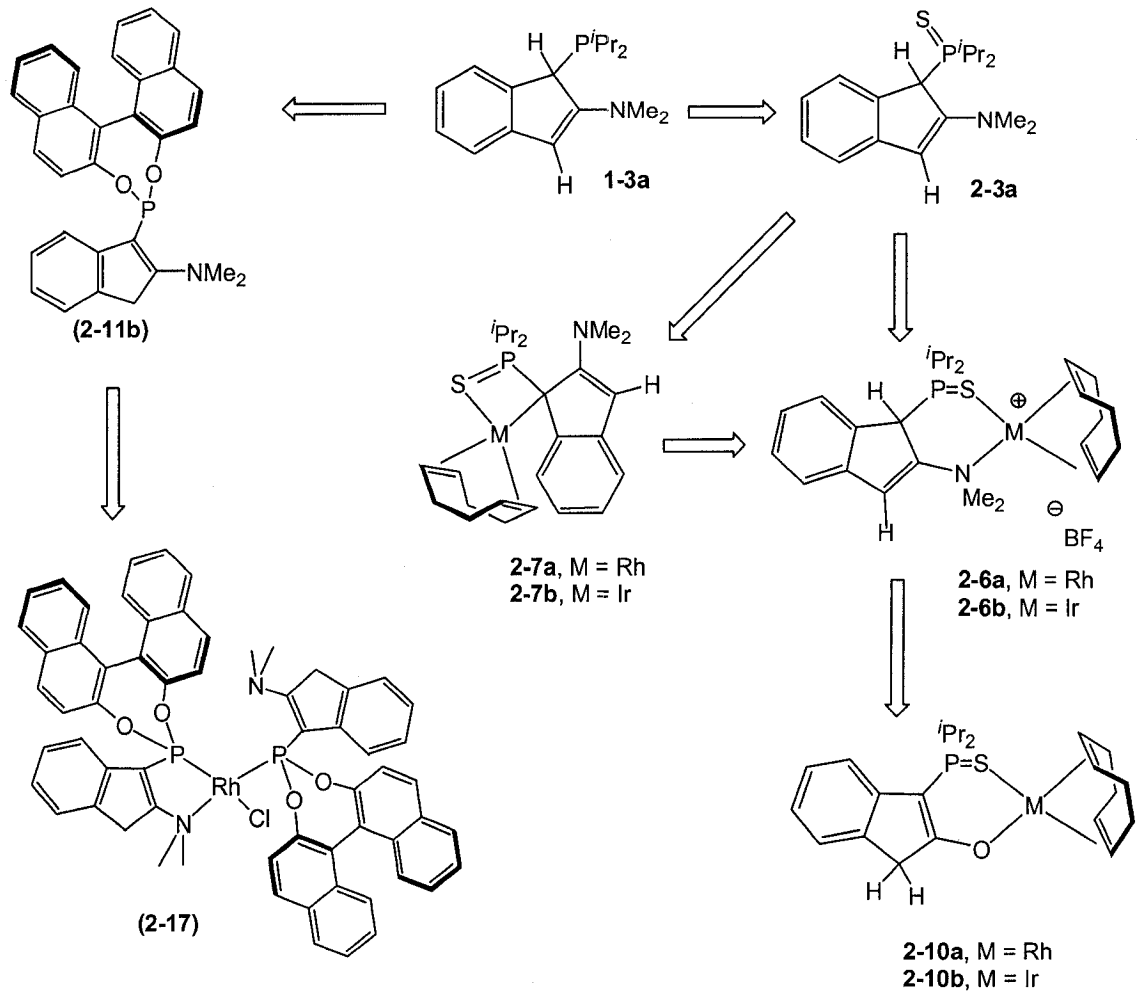
Despite the apparent structural similarities between 1-P^{i}Pr$_2$-2-NMe$_2$-indene (**1-3**) and its oxidized relative 1-^{i}Pr$_2$P(S)-2-NMe$_2$-indene (**2-3a**), the observations described herein reveal that these species, as well as their monoanionic derivatives, can differ considerably in their coordination chemistry. Although it has be shown previously that **1-3a** rapidly isomerizes to **1-3b** upon κ^2-*P,N* coordination to [(COD)M]$^+$ fragments, the indene **2-3a** is not transformed into **2-4b** within the coordination sphere of the analogous κ^2-*N,S* cations, **2-6a,b** (Scheme 2-10). It is possible that the relief of steric strain associated with the five-membered chelate ring in [(COD)M(κ^2-*P,N*-**1-3a**)]$^+$ is somehow achieved upon isomerization to [(COD)M(κ^2-*P,N*-**1-3b**)]$^+$ (i.e. **2-1a,b**), whereas the six-membered chelate ring in **2-6a,b** lacks such a driving force to promote a similar rearrangement. It was reported previously that upon deprotonation complexes **2-1a,b** are cleanly converted into the formally zwitterionic κ^2-*P,N* species, **2-2a,b**. In contrast, it is demonstrated herein that κ^2-*N,S* binding is not retained upon treatment of **2-6a,b** with NaN(SiMe$_3$)$_2$; instead, the putative (κ^2-*N,S*-1-P(*S*)^{i}Pr$_2$-2-*N*Me$_2$-indenide)M(COD) intermediate rearranges to the corresponding κ^2-*C,S* complex, **2-7a,b** (Scheme 2-10). These observations appear to underscore the importance of maintaining a rigid five-membered chelate ring as a means of enforcing κ^2-coordination in **2-2a,b** and related formally zwitterionic complexes of this type. It has been shown that heating **2-6a,b** in the presence of water can afford the (COD)M(κ^2-P(*S*),*O*) complexes **2-9a,b** (Scheme 2-10). In a preliminary catalytic survey, the ability of **2-6a,b**, **2-7a,b** and **2-9a,b** to mediate the addition of triethylsilane to styrene was evaluated. While the cationic complexes **2-6a,b** and the neutral complex **2-7b** exhibited rather poor catalytic performance, the activity

and regioselectivity exhibited by **2-7a** approached that of Wilkinson's catalyst **1-1** under some conditions. The (COD)M(κ^2-P(*S*),*O*) complex **2-9a** exhibited similar catalyst activity and regioselectivity to **2-7a** in DCE, but in C_6H_6 reduced activity and regioselectivity was observed. Compound **2-9b** has shown good catalytic activity in DCE with lower regioselectivity while in C_6H_6 very minimal conversion is observed.

By introducing chirality to the phosphine donor in **1-3**, it was hoped that a new family of effective neutral, cationic, and zwitterionic asymmetric catalyst analogues to **2-1** and **2-2** would be preparable. Unfortunately, the geometry of the chelate site has apparently changed enough that the same coordination chemistry as seen for **1-3** is not accessible for **2-11b** with $[(COD)MCl]_2$ (M = Rh, Ir). Additional coordination chemistry with $[(COE)_2RhCl]_2$ has shown that clean metal complexes of **2-11b** can be achieved, but only in a 2:1 ligand-to-metal ratio (Scheme 2-10). Preliminary catalytic studies using *in situ* prepared metal complexes of **2-11b** have exhibited relatively poor catalyst activity in the addition of diphenylsilane to acetophenone, and the catalytic activity was dramatically reduced whenever two or more equivalents of ligand were used. Furthermore, no significant enantioselectivity was achieved with any of the metal ligand combinations explored for the hydrosilylation of acetophenone. For the hydrogenation of methyl 2-acetamidoacrylate (Table 2-6) it has been shown that modest selectivity can be achieved in the presence of excess ligand, but unfortunately the metal activity is greatly reduced.

Further exploration of the above mentioned compounds in other catalytic studies will be part of future studies by other members of the Stradiotto group. Additionally, examinations of similar complexes featuring other transition metal fragments and their

catalytic activity will be part of further explorations to increase the understanding of how ancillary ligands influence the reactivity properties of associated metals.



Scheme 2-10. Summary of ligands derived from **1-3a**, and their corresponding metal complexes prepared in this chapter.

2.5 Experimental Section

2.5.1 General Considerations

Except where noted, all manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130

°C) and evacuated while hot. Celite® (Aldrich), Al_2O_3 (Aldrich), and silica gel, 230-400 Mesh (SiliCycle) were oven-dried (130 °C) for a minimum of 5 d and then evacuated for at least 24 h. The non-deuterated solvents tetrahydrofuran, dichloromethane, diethyl ether, toluene, benzene, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system purchased from mBraun Inc. Tetrahydrofuran, dichloromethane, and diethyl ether were purified over two alumina-packed columns, while toluene, benzene, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. The solvents used within the glovebox were stored over activated 4 Å molecular sieves. 1,2-Dichloroethane (Aldrich), C_6D_6 (Aldrich or Cambridge Isotopes), styrene (Aldrich, containing 10-15 ppm 4-*tert*-butylcatechol as inhibitor), and Et_3SiH (Aldrich) were each degassed by using three freeze-pump-thaw cycles and then dried over 4 Å molecular sieves for 24 h. $CDCl_3$ (Aldrich) was degassed in a similar manner, dried over CaH_2 for 7 days, distilled *in vacuo* and stored over 4 Å molecular sieves for 24 h. Et_3N (Aldrich) was stirred over KOH for 7 d, followed by distillation; the distilled Et_3N was then refluxed over CaH_2 for 3 d under dinitrogen, followed by distillation. $AgBF_4$ (Aldrich) was dried *in vacuo* for 48 h prior to use, while sulfur powder, *n*-BuLi (1.6 M in hexanes), $NaN(SiMe_3)_2$, $(Et_2N)_2PCl$ were obtained from Aldrich and were used as received. *n*-BuLi (2.9 M in hexanes), *R*-BINOL, and methyl 2-acetamidoacrylate were obtained from Alfa Aeser and were used as received. Hydrogen gas (99.999 %, UHP Grade) was obtained from Air Liquide and used as received. Compounds **1-3**,[10] 3-P^iPr_2-indene,[26] $[(COD)RhCl]_2$,[75] $[(COD)IrCl]_2$,[76] $(PPh_3)_3RhCl$ (**1-1**),[77] and $[(COE)_2RhCl]_2$[78] were prepared using literature methods and dried *in vacuo* for 24 h,

while $[(COD)Ir(PCy_3)(Py)]^+PF_6^-$ (**1-2**) and $[(allyl)PdCl]_2$ were obtained from Strem (COD = η^4-1,5-cyclooctadiene). Unless otherwise stated, ^1H, ^{13}C, and ^{31}P NMR data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^1H and ^{13}C) or 85 % H_3PO_4 in D_2O (for ^{31}P). In some cases, slightly fewer than expected independent ^1H and/or ^{13}C NMR resonances were observed, despite prolonged data acquisition times. ^1H and ^{13}C NMR chemical shift assignments are based on data obtained from ^1H-^{13}C HSQC and ^1H-^{13}C HMBC or 1D ^1H nOe NMR experiments. Variable-temperature NMR studies involving **2-6a** and **2-6b** were conducted on a Bruker AC-250 spectrometer, with temperature calibrations carried out using an external MeOH/MeOD standard.[79] The $\Delta G^{\ddagger}$ values quoted for the dynamic processes involving **2-6a** and **2-6b** were determined at 279 K and 284 K, respectively, by use of the Gutowsky-Holm approximation.[31] GC-MS and GC-FID were performed on a Perkin Elmer AutoSystem XL gas chromatograph equipped with a TurboMass mass spectrometer. GC-MS analyses were performed using a Supelco 30 m x 0.25 mm MDN-5S 5 % phenyl methylsiloxane, film thickness 0.50 μm column (temperature program: 60 °C, 1 min; 20 °C/min to 200 °C; 200 °C, 7 min). GC-FID analyses were done in a similar way except on a Supelco DB200 column. Chiral GC-FID analysis were performed on a Perkin Elmer AutoSystem XL gas chromatograph using a Varian 25 m x 0.25 mm Coating CHIRASIL-L-VAL, film thickness 0.12 μm, temperature program: 120 °C isocratic or Supelco 30 m x 0.25 mm BETA-DEX 120, film thickness 0.25 μm, temperature program: 80 °C, 15 min; 10 °C/min to 180 °C; 180 °C, 5 min. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British

Columbia, Canada. Single crystal X-ray diffraction experiments and structure solutions were performed by Dr. R. McDonald and Dr. M. J. Ferguson at the X-Ray Crystallography Laboratory, University of Alberta, Department of Chemistry, Edmonton, Alberta, and Dr. G. Schatte at the Saskatchewan Structural Science Centre, University of Saskatchewan, Saskatoon, Saskatchewan.

2.5.2 Preparation of 2-3a

A Schlenk flask containing a magnetic stir bar was charged with **1-3** (0.73 g, 2.7 mmol) and then was sealed with a septum. Magnetic stirring was initiated and then a suspension of sulfur (0.12 g, 3.8 mmol) in dichloromethane (20 mL) was transferred via cannula to the Schlenk flask containing **1-3**. Upon completion of the slurry transfer, the resulting mixture was stirred for 1 h; at this stage, ^{31}P NMR data obtained from an aliquot of the reaction mixture indicated clean conversion to **2-3a**. The dichloromethane and other volatile materials were then removed *in vacuo*. Within the glovebox, the residual solid was dissolved in toluene (15 mL) and passed down an alumina column (0.5 cm x 5 cm). Removal of the toluene and other volatile materials *in vacuo* yielded **2-3a** as an analytically pure yellow solid (0.71 g, 2.3 mmol, 85 %). Anal. Calcd. for $C_{17}H_{26}PSN$: C 66.44; H 8.52; N 4.56. Found: C 66.46; H 8.59; N 4.72. ^{1}H NMR (C_6D_6): δ 7.61 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C4-H), 7.19 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5-H), 7.06 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C7-H), 6.92 (t, $^3J_{HH}$ = 7.7 Hz, 1H, C6-H), 5.44 (s, 1H, C3-H), 4.19 (d, $^2J_{PH}$ = 17.6 Hz, 1H, C1-H), 2.49 (s, 6H, NMe_2), 2.28-2.16 (m, 2H, 2 P(C*H*Me_2)), 1.19 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 0.99 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me*$_c$Me$_d$)), 0.93 (d of d, $^3J_{PH}$ = 16.7 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CHMe$_a$*Me*$_b$)), 0.79 (d of d, $^3J_{PH}$ = 16.6 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me*$_d$)); ^{13}C{^{1}H} NMR (C_6D_6): δ 158.6

(d, $^2J_{PC}$ = 5.0 Hz, C2), 146.5 (d, $^3J_{PC}$ = 3.8 Hz, C3a), 135.4 (d, $^2J_{PC}$ = 4.6 Hz, C7a), 127.5 (C5), 125.2 (d, $^4J_{PC}$ = 2.7 Hz, C4), 121.3 (d, $^4J_{PC}$ = 1.9 Hz, C6), 118.5 (C7), 105.7 (d, $^3J_{PC}$ = 3.8 Hz, C3), 50.6 (d, $^1J_{PC}$ = 30.2 Hz, C1), 43.5 (NMe_2), 26.4 (d, $^1J_{PC}$ = 45.5 Hz, P(*C*HMe$_2$)), 26.3 (d, $^1J_{PC}$ = 47.4 Hz, P(*C*HMe$_2$)), 18.4 (d, $^2J_{PC}$ = 1.9 Hz, P(CH*Me*$_c$Me$_d$)), 17.2 (d, $^2J_{PC}$ = 2.3 Hz, P(CH*Me*$_a$Me$_b$)), 16.8 (d, $^2J_{PC}$ = 2.7 Hz, P(CHMe$_c$*Me*$_d$)), 16.5 (d, $^2J_{PC}$ = 1.9 Hz, P(CHMe$_a$*Me*$_b$)); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 72.8. Crystals of **2-3a** suitable for single-crystal X-ray diffraction analysis were grown from toluene at -35 °C. A crystal of **2-3b** suitable for single-crystal X-ray diffraction analysis was grown from a diethyl ether solution of **2-3a** stored at -35 °C.

2.5.3 Preparation of 3-^{i}Pr$_2$P(S)-indene (2-5b)

A Schlenk flask containing a magnetic stir bar was charged with elemental sulfur (0.14 g, 4.5 mmol) and dried under vacuum for 2.5 h. To this flask was then added a solution of 1-P^{i}Pr$_2$-indene (1.0 g, 4.3 mmol) in 15 mL of diethyl ether. Upon completion of transfer, the resulting mixture was stirred for 1 h, after which the diethyl ether and other volatile materials were removed *in vacuo*. The resulting solid was found to be a mixture of 1- and 3-^{i}Pr$_2$P(S)-indene (~5:95 respectively; ^1H and ^{31}P NMR) corresponding to a crude yield of 97 %. Selective crystallization from diethyl ether afforded pure 3-^{i}Pr$_2$P(S)-indene as a light yellow solid (0.82 g, 3.5 mmol, 81 %). Anal. Calcd. for $C_{15}H_{21}PS$: C 68.15; H 8.00; N 0.00. Found: C 68.05; H 8.13; N <0.3. ^1H NMR (C_6D_6): δ 7.74 (d, $^3J_{HH}$ = 7.9 Hz, 1H, C4-H), 7.30 (d, $^3J_{HH}$ = 9.8 Hz, 1H, C2-H), 7.18 (m, 2H, C7-H, and C5-H or C6-H), 7.09 (t, $^3J_{HH}$ = 7.1 Hz, 1H, C6-H or C5-H), 2.93 (br t, J = 2 Hz, 2H, CH_2), 2.17 (m, 2H, P(C*H*Me$_2$)$_2$), 3.09 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 6.8 Hz, 6H, P(CH*Me*Me)$_2$), 0.94 (d of d, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe*Me*)$_2$); $^{13}C\{^1H\}$

NMR (C_6D_6): δ 150.3 (d, $^2J_{PC}$ = 8.3 Hz, C2), 145.0 (d, J_{PC} = 8.8 Hz, C3a or C7a), 142.9 (d, J_{PC} = 10.5 Hz, C7a or C3a), 136.1 (d, $^1J_{PC}$ = 68.1 Hz, C3), 126.5 (aryl C-H), 125.4 (aryl C-H), 124.3 (aryl C-H), 122.3 (C7), 39.0 (d, $^3J_{PC}$ = 12.0 Hz, C1), 28.4 (d, $^1J_{PC}$ = 52.3 Hz, P(*C*HMe$_2$)), 17.0 (d, $^2J_{PC}$ = 2.0 Hz, P(CH*Me*Me)$_2$), 16.4 (d, $^2J_{PC}$ = 1.4 Hz, P(CHMe*Me*)$_2$); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 60.3.

2.5.4 Preparation of 2-6a

To a glass vial containing a magnetically stirred suspension of [(COD)RhCl]$_2$ (0.094 g, 0.19 mmol) in THF (2 mL) was added a suspension of $AgBF_4$ (0.075 g, 0.38 mmol) in THF (3 mL); a yellow solution was generated immediately along with a white precipitate. The supernatant solution was separated from the precipitate by filtration through Celite, and the solution was transferred to a glass vial containing a magnetically stirred solution of **2-3a** (0.12 g, 0.38 mmol) in THF (3 mL). After 30 s, a dark orange-red precipitate started to form, and after 3 additional hours the reaction supernatant solution was decanted and the remaining solid (**2-6a**) was washed with pentane (3 mL). Any remaining solvent or other volatile materials were then removed *in vacuo*, yielding **2-6a** as an analytically pure orange-red solid (0.18 g, 0.29 mmol, 76 %). Anal. Calcd. for $C_{25}H_{38}PSNRhBF_4$: C 49.61; H 6.33; N 2.31. Found: C 49.78; H 6.54; N 2.34. ^1H NMR ($CDCl_3$): δ 7.20-7.15 (m, 2H, aryl C-Hs), 7.10 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C4-H or C7-H), 6.96 (m, 1H, C5-H or C6-H), 5.21 (d, $^2J_{PH}$ = 8.6 Hz, 1H, C1-H), 4.37 (m, 2H, COD), 4.08 (m, 2H, COD), 3.31 (br s, 6H, NMe$_2$), 2.82 (m, 1H, P(C*H*Me$_2$)), 2.53 (m, 1H, P(C*H*Me$_2$) or COD), 2.41 (m, 2H, P(C*H*Me$_2$) and/or COD), 2.18 (br m, 2H, COD), 1.98 (br m, 2H, COD), 1.70 (br m, 2H, COD), 1.44 (d of d, $^3J_{PH}$ = 18.4 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*Me)), 1.39-1.32 (m, 6H, P(CH*Me*$_2$)), 0.96 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz,

3H, P(CH*Me*Me)); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.8 (C3a or C7a or C2), 131.0 (C7a or C3a or C2), 129.4 (aryl C-H), 124.6 (aryl C-H), 123.7 (aryl C-H), 119.8 (aryl C-H), 84.6 (m, COD), 82.2 (m, COD), 47.8 (d, $^1J_{PC}$ = 26.8 Hz, C1), 44.6 (br m, NMe_2), 32.6 (br m, COD), 30.8, (d, J = 40.0 Hz, P(*C*HMe_2)), 30.0 (d, J = 36.1 Hz, P(*C*HMe_2)), 29.9-29.5 (br m COD), 17.8 (P(CH*Me*Me)), 17.5 (P(CH*Me*Me)), 17.4 (P(CH*Me*Me)), 16.5 (P(CH*Me*Me)); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 103.5 (br s).

2.5.5 Preparation of 2-6b

This complex was prepared using a synthetic method analogous to that described for **2-6a**. Using $[(COD)IrCl]_2$ (0.17 g, 0.49 mmol), $AgBF_4$ (0.097 g, 0.49 mmol), and **2-3a** (0.15 g, 0.49 mmol) afforded **2-6b** as an analytically pure orange-red solid (0.20 g, 0.29 mmol, 59 %). Anal. Calcd. for $C_{25}H_{38}PSNIrBF_4$: C 43.23; H 5.51; N 2.02. Found: C 43.23; H 5.31; N 1.96. ^1H NMR ($CDCl_3$): δ 7.36-7.29 (m, 2H, C4-H or C7-H and C6-H or C5-H), 7.22 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C4-H or C7-H), 7.11 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5-H or C6-H), 5.58 (d, $^2J_{PH}$ = 7.4 Hz, 1H, C1-H), 4.69 (s, 1H, C3-H), 4.35 (m, 2H, COD), 4.20 (m, 2H, COD), 3.75-3.55 (m, 4H, COD), 3.53 (s, 6H, NMe_2), 2.84-2.77 (m, 2H, P(C*H*Me_2)$_2$), 2.36-2.22 (br m, 2H, COD), 2.03-1.86 (br m, 2H, COD), 1.68 (d of d, $^3J_{PH}$ = 18.1 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, P(CH*Me*Me)), 1.59 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)), 1.43 (d of d, $^3J_{PH}$ = 17.9 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*Me)), 1.22 (d of d, $^3J_{PH}$ = 17.4 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CH*Me*Me)); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.6 (s, C3a or C7a or C2), 129.7 (C7a or C3a or C2), 129.5 (aryl C-H), 124. 9 (m, aryl C-H), 124.1 (aryl C-H), 120.3 (aryl C-H), 70.2 (COD), 69.7 (COD), 67.7 (COD), 65.5 (COD), 58.4 (m), 47.2 (d, $^1J_{CH}$ = 23.98 Hz, C1), 44.4 (NMe_2), 34.8 (COD), 34.1 (d, $^1J_{PC}$ = 36.5 Hz, P(*C*HMe_2)), 33.5 (COD), 30.6 (COD), 29.9 (d, $^1J_{PC}$ = 34.0 Hz, P(*C*HMe_2)), 28.5

(COD), 18.5 (P(CH*Me*Me)), 18.3 (P(CH*Me*Me)), 16.9 (P(CH*Me*Me)), 15.9 (P(CH*Me*Me)); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 115.3.

2.5.6 Preparation of 2-7a

To a magnetically stirred suspension of **2-6a** (0.069 g, 0.11 mmol) in THF (3 mL) was added a suspension of $NaN(SiMe_3)_2$ (0.021 g, 0.11 mmol) in THF (3 mL) via Pasteur pipette. A precipitate formed upon addition, and the reaction mixture was stirred for 3 h. A ^{31}P NMR spectrum taken of an aliquot of the reaction solution revealed the presence of a single phosphorus-containing product with a signal at 82.9 ppm (**2-7a**). After the solvent and other volatile materials were removed *in vacuo*, the residue was extracted into pentane (3 mL) and the pentane solution containing **2-7a** was filtered through Celite and then dried *in vacuo*. The residue was taken up in toluene (3 mL) and crystallized at -35 °C, giving **2-7a** as an analytically pure yellow solid (0.040 g, 0.077 mmol, 70 %). Anal. Calcd. for $C_{25}H_{37}PSNRh$: C 58.02; H 7.21; N 2.71. Found: C 57.88; H 6.94; N 2.63. ^{1}H NMR (C_6D_6): δ 8.26 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, C4-H or C7-H), 7.44 (d, $^{3}J_{HH}$ = 7.0 Hz, 1H, C7-H or C4-H), 7.23-7.15 (m, 2H, C5-H and C6-H), 6.16 (s, 1H, C3-H), 4.50 (br m, 2H, COD), 4.30 (br s, 2H, COD), 3.35 (m, 1H, P(C*H*Me_2)), 3.13 (s, 6H, NMe_2), 2.73 (m, 1H, P(C*H*Me_2)), 2.50-1.15 (m, 11H, COD and P(CH*Me*Me)), 1.07 (d of d, $^{3}J_{PH}$ = 16.9 Hz, $^{3}J_{HH}$ = 7.1 Hz, 3H, P(CH*Me*Me)), 0.82 (d of d, $^{3}J_{PH}$ = 17.1 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H, P(CH*Me*Me)), 0.67 (d of d, $^{3}J_{PH}$ = 16.9 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H, P(CH*Me*Me)); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 161.9 (d, *J* = 1.8 Hz, C2), 138.2 (d, *J* = 9.5 Hz, C3a or C7a), 137.1 (d, *J* = 4.1 Hz, C7a or C3a), 120.8 (C4 or C7), 120.1 (C5 or C6), 117.4 (C7 or C4), 117.3 (C6 or C5), 103.6 (d, $^{3}J_{PC}$ = 8.2 Hz, C3), 80.4-77.3 (m, COD), 76.5 (d, $^{1}J_{RhC}$ = 13.9 Hz, COD), 45.9 (NMe_2), 31.4 (d, $^{1}J_{PC}$ = 31.9 Hz, P(*C*HMe_2)), 29.2-28.2 (m, COD and

P(CHMe$_2$)), 26.5 (d of d, $^1J_{PC}$ = 47.4 Hz, $^1J_{RhC}$ = 11.2 Hz, C1), 15.1 (2 P(CH*Me*Me)), 14.9 (P(CH*Me*Me)), 14.4 (P(CH*Me*Me)); $^{31}P\{^1H\}$ NMR (101.3 MHz, C_6D_6): δ 82.9 (d, $^2J_{RhP}$ = 14.9 Hz). Crystals of **2-7a** suitable for single-crystal X-ray diffraction analysis were grown from diethyl ether at -35 °C.

2.5.7 Preparation of 2-7b

A 1.6 M hexanes solution of *n*-BuLi (0.31 mL, 0.49 mmol; pre-cooled to -35 °C) was added dropwise via syringe to a glass vial containing a magnetically stirred solution (pre-cooled to -35 °C) of **2-3a** (0.15 g, 0.49 mmol) in toluene (5 mL) over 2 min, producing a faint yellow solution. The vial containing the reaction mixture was then sealed with a PTFE-lined cap and stirred for 1 h at ambient temperature; ^{31}P NMR data obtained from an aliquot of the reaction mixture at this stage confirmed the consumption of **2-3a**, along with the formation of a single new phosphorus-containing product with a signal at 54 ppm. A mixture of $[CODIrCl]_2$ (0.17 g, 0.49 mmol) in toluene (2 mL) was then transferred to the reaction mixture via Pasteur pipette, and the reaction vial was re-sealed. A dark solution formed immediately, and, after stirring for 1 h, the solution changed to a yellow-orange color and a white precipitate formed. The reaction mixture was then filtered through Celite and the supernatant was dried *in vacuo*, yielding **2-7b** as an analytically pure orange solid (0.25 g, 0.42 mmol, 86 %). Alternatively, a protocol analogous to that described for the preparation of **2-7a** can be employed, in which **2-6b** is quantitatively deprotonated with $NaN(SiMe_3)_2$ to give **2-7b** (^{31}P NMR); upon purification, **2-7b** is obtained in similar yield to that reported above. Anal. Calcd. for $C_{25}H_{37}PSNIr$: C 49.48; H 6.15; N 2.31. Found: C 49.62; H 6.36; N 2.31. ^1H NMR (C_6D_6): δ 8.20 (d, $^3J_{HH}$ = 7.1 Hz, 1H, C7-H), 7.40 (d, $^3J_{HH}$ = 6.9 Hz, 1H, C4-H), 7.20-7.15

(m, 2H, C5-H and C6-H), 5.91 (s, 1H, C3-H), 4.34 (m, 1H, COD), 4.15 (m, 1H, COD), 3.28 (m, 1H, P(C*H*Me$_2$)), 3.12 (s, 6H, NMe$_2$), 2.83 (m, 1H, COD), 2.77 (m, 1H, P(C*H*Me$_2$)), 2.43 (m, 1H, COD), 2.15-2.00 (m, 2H, COD), 1.81 (m, 2H, COD), 1.41 (m, 2H, COD), 1.23 (m, 2H, COD), 1.14 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.4 Hz, 3H, P(CH*Me*Me)), 0.83 (m, 6H, 2 P(CH*Me*Me)), 0.57 (d of d, $^3J_{PH}$ = 16.6 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, P(CH*Me*Me)); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 163.5 (C2), 141.6 (d, J = 8.3 Hz, C3a or C7a), 141.2 (C7a or C3a), 124.6 (C7), 123.2 (C5 or C6), 119.2 (C6 or C5), 118.4 (C4), 105.6 (d, $^3J_{PC}$ = 7.6 Hz, C3), 64.9 (COD), 64.2 (COD) 60.7 (COD), 46.6 (NMe$_2$), 36.0 (d, $^1J_{PC}$ = 24.6 Hz, P(*C*HMe$_2$)), 32.5 (d, $^1J_{PC}$ = 26.0 Hz, P(*C*HMe$_2$)), 31.9 (COD), 31.8 (COD), 31.4 (COD), 31.3 (COD), 23.5 (d, $^1J_{PC}$ = 105.0 Hz, C1), 16.4 (P(CH*Me*Me)), 16.4 (P(CH*Me*Me)), 16.3 (P(CH*Me*Me)), 15.5 (P(CH*Me*Me)); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 98.5. Crystals of **2-7b** suitable for single-crystal X-ray diffraction analysis were grown from diethyl ether at -35 °C.

2.5.8 Preparation of 2-9a

Complex **2-6a** (0.22 g, 0.37 mmol) was dissolved in dichloromethane (8 mL). The resulting orange solution was transferred to a re-sealable reaction flask that was sealed under nitrogen with a PTFE valve. The reaction flask was transferred to the Schlenk line and distilled water (1 mL; pre-sparged 30 minutes with nitrogen) was added to the mixture via syringe. The headspace of the reaction flask was partially evacuated, and the vessel was sealed and placed into a 60 °C oil bath. After 14 h of heating, the flask was removed from the oil bath and cooled to room temperature, at which time all solvent and other volatile materials were removed *in vacuo*. The flask was transferred to the glovebox and the solid yellow residue was extracted with pentane (3 x 10 mL). The pentane

fractions were combined and filtered through Celite to remove any insoluble material. Removal of the pentane solvent and other volatile materials *in vacuo* yielded **2-9a** as an analytically pure, yellow solid (0.16 g, 0.33 mmol, 91 %). Anal. Calcd. for $C_{23}H_{32}PSORh$: C 56.33; H 6.58. Found: C 56.64; H 6.58. ^1H NMR (C_6D_6): δ 7.15 (t, $^3J_{HH}$ = 7.7 Hz, 1H, C6-H), 7.00 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C7-H), 6.92 (t, $^3J_{HH}$ = 7.3 Hz, 1H, C5-H), 6.83 (d, $^3J_{HH}$ = 7.7 Hz, 1H, C4-H), 4.64 (m, 2H, COD), 4.10 (m, 2H, COD), 3.37 (s, 2H, C1-H), 2.32-2.24 (m, 6H, COD and P(C*H*Me$_2$)$_2$), 1.71-1.63 (m, 4H, COD), 1.30 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, P(CHMe*Me*)$_2$), 1.04 (d of d, $^3J_{PH}$ = 18.1 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe*Me*)$_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 191.7 (d, J = 5.0 Hz, C2), 147.4 (d, J = 12.1 Hz, C7a), 134.4 (d, J = 13.3 Hz, C3a), 126.6 (C6), 123.5 (C7), 120.7 (C5), 116.3 (C4), 86.6 (d, J = 12.2 Hz, COD), 81.3 (d, J = 42.3 Hz, C3), 71.0 (d, J = 13.7 Hz, COD), 43.9 (d, J = 9.8 Hz, C1), 32.2 (COD), 30.0 (COD), 27.8 (d, J = 50.7 Hz, P(*C*HMe$_2$)$_2$), 16.9 (P(CHMe*Me*)$_2$), 16.4 (P(CHMe*Me*)$_2$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 50.8. Crystals of **2-9a** suitable for single-crystal X-ray diffraction analysis were grown from pentane at -35 °C.

2.5.9 Preparation of 2-9b

A procedure analogous to that described for the synthesis of **2-9a** was employed, using **2-6b** (0.18 g, 0.26 mmol) in place of **2-6a**. Complex **2-9b** was isolated as an analytically pure, bright yellow solid (0.14 g, 0.24 mmol, 90 %). Anal. Calcd. for $C_{23}H_{32}PSOIr$: C 47.65; H 5.56; N 0.0. Found: C 47.92; H 5.67; N < 0.3. ^1H NMR (C_6D_6): δ 7.12 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C6-H), 6.98 (d, $^3J_{HH}$ = 7.2 Hz, 1H, C7-H), 6.92 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C5-H), 6.78 (d, $^3J_{HH}$ = 7.7 Hz, 1H, C4-H), 4.33 (m, 2H, COD), 3.98 (m, 2H, COD), 3.37 (s, 2H, C1-H), 2.29-2.22 (m, 6H, COD and P(C*H*Me$_2$)$_2$), 1.64-1.61 (m, 2H,

COD), 1.52-1.47 (m, 2H, COD), 1.15 (d of d, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, P(CHMe*Me*)$_2$), 0.97 (d of d, $^3J_{PH}$ = 18.2 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe*Me*)$_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 190.4 (C2), 146.7 (d, J = 11.4 Hz, C7a), 134.1 (d, J = 13.1 Hz, C3a), 126.5 (C6), 123.4 (C7), 121.1 (C5), 116.5 (C4), 81.9 (d, J = 82.4 Hz, C3), 70.1 (COD), 53.6 (COD), 43.6 (d, J = 9.7 Hz, C1), 32.8 (COD), 30.4 (COD), 27.7 (d, J = 49.5 Hz, P(*C*HMe$_2$)$_2$), 16.6 (P(CHMe*Me*)$_2$), 15.9 (P(CHMe*Me*)$_2$); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 46.6. Crystals of **2-9b** suitable for single-crystal X-ray diffraction analysis were grown from pentane at -35 °C.

2.5.10 Preparation of 2-11b

A vial containing a magnetic stir bar was charged with 2-dimethylaminoindene (0.14 g, 0.88 mmol) and 4 mL of toluene. The solution was cooled to -35 °C followed by the addition of *n*-BuLi (1.6 M in hexanes, pre-cooled to -35 °C, 0.55 mL, 0.88 mmol). The mixture was stirred for 1 h at ambient temperature. Meanwhile, a second vial was charged with **2-14** (0.31 g, 0.88 mmol) and 3 mL toluene. The solution of **2-14** was added dropwise to the indenyl lithium salt, followed by 2 h of stirring. An *in situ* ^{31}P NMR spectrum of the reaction showed a mixture of C1 and C3 isomers. The addition of four equivalents of triethylamine (0.49 mL, 3.5 mmol) facilitated the isomerization of the C1 isomer **2-11a** to the C3 isomer **2-11b**. The mixture was stirred overnight, during which time most of the C3 isomer **2-11b** precipitated out of solution. The mixture was then concentrated to near dryness followed by the addition of benzene to extract any unreacted C1 isomer **2-11a**, triethylamine and other products. The precipitate was then dried *in vacuo* yielding **2-11b** as an analytically pure white solid (0.30 g, 0.63 mmol, 71 %). Anal. Calcd. for $C_{31}H_{24}PNO_2$: C 78.63; H 5.11; N 2.96. Found: C 78.40; H 4.95; N 2.51. ^1H

NMR (CD_2Cl_2): δ 8.07 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C-H Naph.), 8.02 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C-H Naph.), 7.91 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C-H Naph.), 7.73 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C-H Naph.), 7.59 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C-H Naph.), 7.55-7.45 (m, 4H, C-Hs Naph.), 7.39-7.31 (m, 2H, C-Hs Naph.), 7.22 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C-H Naph.), 7.11 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C7-H), 6.59 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5-H or C6-H), 6.10 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4-H), 6.02 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C6-H or C5-H), 3.63 (s, CH_2), 3.38 (d, $^5J_{PH}$ = 3.5 Hz, NMe_2); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 170.9 (d, $^2J_{PC}$ = 27.7 Hz, C2), 152.6 (quat Naph.), 151.6 (quat Naph.), 146.3 (C3a or C7a), 133.9 (C7a or C3a), 133.1 (quat Naph.), 133.0 (quat Naph.), 131.5 (quat Naph.), 131.1 (quat Naph.), 130.6 (C-H Naph.), 130.1 (C-H Naph.), 128.4 (C-H Naph.), 128.4 (C-H Naph.), 128.2 (C-H Naph.), 126.8 (C-H Naph.), 126.5 (C-H Naph.), 126.1 (C-H Naph.), 125.9 (C-H Naph.), 125.5 (C6 or C5), 124.7 (C-H Naph.), 124.3 (C-H Naph.), 123.0 (quat), 122.2 (C-H Naph.), 121.8 (C7 and C-H Naph.), 121.5 (C4), 120.3 (C5 or C6), 70.6 (quat), 45.5 (d, $^4J_{PC}$ = 23.0 Hz, NMe_2), 41.1 (d, $^3J_{PC}$ = 4.4 Hz, C1); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 197.4.

2.5.11 Preparation of 2-12

A vial containing a magnetic stir bar was charged with 2-dimethylaminoindene (0.40 g, 0.25 mmol) and 2 mL of THF. The mixture was cooled to -35 °C, and magnetic stirring was initiated followed by the dropwise addition of *n*-BuLi (0.16 mL, 0.25 mmol). Following addition, the resulting mixture was stirred for 1 h. To the reaction mixture was then added cold $(Et_2N)_2PCl$ via a Eppendorf pipette, followed by stirring for 3.5 h. ^{31}P NMR data obtained from the reaction mixture indicated clean conversion to **2-12**. The THF and other volatile materials were then removed *in vacuo,* and the residue was taken up in toluene. The solution was then filtered through Celite followed by removal of the

toluene and other volatiles *in vacuo* and the solid was used without further purification. ^{1}H NMR (C_6D_6): δ 7.50 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H, C7-H), 7.27-7.20 (m, 2H, C4-H and C6-H), 7.03 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, C5-H), 5.54 (s, 1H, C3-H), 4.02 (d, $^{2}J_{PH}$ = 8.0 Hz, 1H, C1-H), 3.04-2.91 (m, 4H, 2 CH_2CH_3), 2.86-2.74 (m, 4H, 2 CH_2CH_3), 2.61 (s, 6H, NMe_2), 1.03 (t, 6H, 2 CH_2CH_3), 0.84 (t, 6H, 2 CH_2CH_3); ^{13}C{^{1}H} NMR (C_6D_6): δ 160.0 (d, $^{2}J_{PC}$ = 6.7 Hz, C2), 146.8 (C7a), 138.8 (C3a), 126.1 (C6), 123.9 (d, $^{3}J_{PC}$ = 2.3 Hz, C7), 119.8 (C5), 117.7 (C4), 101.6 (C3), 53.0 (d, $^{1}J_{PC}$ = 42.6 Hz, C1), 43.4 (d, $^{2}J_{PC}$ = 19.2 Hz, 2 CH_2CH_3), 42.9 (d, $^{2}J_{PC}$ = 18.9 Hz, 2 CH_2CH_3), 41.9 (s, NMe_2), 14.7 (2 CH_2CH_3), 14.1 (2 CH_2CH_3); ^{31}P{^{1}H} NMR (C_6D_6): δ 113.6.

2.5.12 Preparation of 2-14

Special glassware developed by Burford and co-workers[72] was used in this reaction. A 100 mL reaction bulb containing a magnetic stir bar was charged with (*R*)-BINOL (2.67 g, 9.32 mmol) and 20 mL of diethyl ether. A second reaction bulb containing a magnetic stirbar was charged with Et_3N (2.60 mL, 18.7 mmol) and 15 mL of diethyl ether. The bulbs were fitted with glass-frit filter sticks and connected through a two-compartment bridge. Each flask was freeze-pump-thawed three times. At the same time, PCl_3 (1.4 mL, 16 mmol) was vacuum transferred to a flame-dried 10 mL graduated vacuum flask. The two compartment bridge and the graduated vacuum flask were connected, and all areas exposed to air were flame dried. The PCl_3 was added to the *R*-BINOL solution (frozen) by vacuum transfer, and the mixture was allowed to warm to room temperature, followed by stirring for 1 h. The Et_3N solution was then transferred to the *R*-BINOL/PCl_3 mixture, at which point a white precipitate (NH_4Cl) formed. After stirring for 30 min, the supernatant was filtered into an empty bulb. Some precipitate was

still present after filtration, and therefore, the bulb containing the bulk precipitate (NH_4Cl) was replaced with a clean glass frit and reaction bulb and flame dried. The reaction mixture was then filtered again, and the diethyl ether and other volatile materials were removed *in vacuo* yielding **2-14** as a white solid (2.7 g, 7.7 mmol, 82 %). $^{31}P\{^1H\}$ and ^1H NMR data coincided with those found in the literature.[69]

2.5.13 Preparation of 2-17

A vial containing a magnetic stir bar was charged with **2-11b** (0.044 g, 0.094 mmol) and 3 mL of THF. To a separate vial, $[(COE)_2RhCl]_2$ (0.017 g, 0.024 mmol) and THF (2 mL) were added. The rhodium solution was added to the THF slurry of **2-11b** and magnetically stirred for 2 h. The solvent was removed *in vacuo*, and the residue washed with pentane. Any residual solvent and other volatiles were removed *in vacuo*, leaving behind **2-17** as a light brown solid (0.041 g, 0.038 mmol, 81 %). Anal. Calcd. for $C_{62}H_{48}P_2N_2O_4RhCl$: C 68.59; H 4.46; N 2.58. Found: C 66.55; H 4.03; N 2.50. ^1H NMR (C_6D_6): δ 9.52 (d, $^3J_{HH}$ = 7.4 Hz, 1H, aryl C-H), 8.61 (d, $^3J_{HH}$ = 8.7 Hz, 1H, aryl C-H), 7.89 (d, $^3J_{HH}$ = 8.8 Hz, 1H, aryl C-H), 7.80 (d, $^3J_{HH}$ = 8.1 Hz, 1H, aryl C-H), 7.63-7.69 (m, 2H, aryl C-Hs), 7.59 (t, $^3J_{HH}$ = 7.3 Hz, 1H, aryl C-H), 7.41-7.52 (m, 4H, aryl C-Hs), 7.25 (d, $^3J_{HH}$ = 8.7 Hz, 1H, aryl C-H), 7.13-7.17 (m, 1H, aryl C-H), 7.03-7.07 (m, 2H, aryl C-Hs), 6.98-7.02 (m, 2H, aryl C-Hs), 6.97 (d, $^3J_{HH}$ = 8.8 Hz, 1H, aryl C-H), 6.66-6.83 (m, 5H, aryl C-Hs), 6.51 (m, 1H, aryl C-H), 6.43 (m, 1H, aryl C-H), 6.11 (t, $^3J_{HH}$ = 7.4 Hz, 1H, aryl C-H), 6.06 (d, $^3J_{HH}$ = 6.0 Hz, 1H, aryl C-H), 5.67 (d, $^3J_{HH}$ = 8.9 Hz, 1H, aryl C-H), 5.42 (d, $^3J_{HH}$ = 8.9 Hz, 1H, aryl C-H), 5.23 (d, $^3J_{HH}$ = 7.8 Hz, 1H, aryl C-H), 5.21 (s, 1H, aryl C-H), 3.10 (s, 3H, bound NMe), 2.86 (s, 3H, bound NMe), 2.48-2.34 (m, 4H, CH_2), 1.98 (s, 6H, unbound NMe_2); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 176.4 (bound C2),

156.8 (unbound C2), 156.7 (quat), 151.4 (quat), 151.3 (quat), 151.1 (quat), 150.7 (quat), 150.2 (quat), 149.8 (quat), 149.7 (quat), 148.0 (quat), 147.9 (quat), 142.3 (C3a or C7a), 137.2 (quat), 134.8 (quat), 133.6 (quat), 133.2 (quat), 132.3 (quat), 131.9 (quat), 131.8 (quat), 131.4 (quat), 131.0 (quat), 130.3 (aryl C-H), 130.0 (quat), 129.1 (aryl C-H), 128.4 (aryl C-H), 128.2 (aryl C-H), 128.0 (aryl C-H), 127.3 (aryl C-H), 127.2 (aryl C-H), 127.1 (2 aryl C-Hs), 126.8 (aryl C-H), 126.7 (aryl C-H), 126.0 (aryl C-H), 125.8 (aryl C-H), 125.5 (aryl C-H), 125.3 (aryl C-H), 125.1 (2 aryl C-Hs), 125.0 (aryl C-H), 124.6 (aryl C-H), 124.5 (2 aryl C-Hs), 123.9 (aryl C-H), 123.7 (aryl C-H), 123.5 (aryl C-H), 122.7 (aryl C-H), 122.4 (aryl C-H), 121.6 (aryl C-H), 120.2 (aryl C-H), 117.2 (aryl C-H), 103.4 (aryl C-H), 55.7 (aryl C-H), 55.6 (aryl C-H), 50.7 (bound NMe), 48.5 (bound NMe), 40.8 (unbound NMe_2), 29.7 (CH_2), 29.6 (CH_2); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 199.4 (d of d, $^2J_{PP}$ = 36.4 Hz, $^1J_{RhP}$ = 261.2 Hz), 170.3 (d of d, $^2J_{PP}$ = 36.4 Hz, $^1J_{RhP}$ = 291.6 Hz).

2.5.14 General Protocol for Alkene Hydrosilylation Experiments

A solution of catalyst compound in the desired solvent (0.023 mmol in 4.5 mL to give a 0.0050 M solution) was allowed to equilibrate for 5 min, at which time the alkene (2.3 mmol) was added by use of an Eppendorf pipette. The vial was then sealed and shaken vigorously. Subsequently, Et_3SiH (0.45 mmol) was added by use of an Eppendorf pipette to the reaction mixture, and the vial was then sealed and shaken as before. Aliquots (1 mL) of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line, submersed in a temperature-controlled oil bath, and magnetic stirring of the solutions was initiated. At the desired sampling time, the reactor cell was opened to air and ~1 mL of pentane was added via Pasteur pipette.

The resultant mixtures were then filtered through a short Al_2O_3 column (2 cm) from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS by comparison with standard solutions of isolated products prepared by use of literature methods,[80, 81] while quantitative data were obtained from GC-FID analyses.

2.5.15 General Protocol for Ketone Hydrosilylation Experiments

Protocol was based on literature methods.[73, 82] A solution of metal precursor (0.045 mmol in 0.75 mL) and the ligand (1.2 equiv; 0.054 mmol in 0.75 mL) in the desired solvent were combined to give a 0.030 M solution of the catalyst (based on the metal). The solution was allowed to equilibrate for 45 min, at which point the ketone (0.90 mmol) was added by use of an Eppendorf pipette. The vial was then sealed, shaken vigorously and cooled to -35 °C. Subsequently, pre-cooled Ph_2SiH_2 (1.6 mmol) was added dropwise by use of an Eppendorf pipette to the reaction mixture, and the vial was then sealed and magnetically stirred for 18 h at ambient temperature. The reaction mixture was then cooled to 0 °C, and 1 M HCl (5 mL) and acetone (5 mL) were added. The mixture was stirred for 90 min at 0 °C followed by 30 min at ambient temperature. A solution of saturated sodium bicarbonate was added, and the reaction mixture was stirred until no more gas evolution was observed (approx. 15 min). The reaction mixture was extracted with Et_2O (2 x 5 mL). The combined organic layers were dried over Na_2SO_4, and the catalyst was removed by passing the solution through a plug of alumina (0.6 cm x 2 cm) from which a clear, colorless solution eluted. This solution was transferred to a GC vial and sealed. Products were identified by use of GC-MS while quantitative data were obtained from chiral GC-FID analysis using a Supelco BETA-DEX 120 column.

2.5.16 General Protocol for Hydrogenation of Amino Acid Derivative

A solution of metal precursor (0.025 mmol in 0.5 mL) and the ligand (1.2 equiv; 0.030 mmol in 0.5 mL) in the desired solvent were combined to give a 0.025 M solution of the catalyst (based on the metal). The solution was allowed to equilibrate for 45 min, at which point the alkene (0.50 mmol in 0.5 mL) was added by use of an Eppendorf pipette. The mixture was placed in glass reactor cell, which was equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cell was transferred to a Schlenk line, and the mixture was degassed by use of three freeze-pump-thaw cycles, followed by the addition of 1 atm of H_2, and magnetic stirring of the solution. At the desired sampling time, the reaction mixture was concentrated *in vacuo* and extracted with Et_2O (2 mL). The catalyst was removed by passing the Et_2O extract through a plug of silica (0.6 cm x 2 cm) from which a clear, colorless solution eluted. This solution was transferred to a GC vial and sealed. Quantitative data were obtained from chiral GC-FID analysis using a Varian CHIRAL-L-VAL column.

2.5.17 Crystallographic Solution and Refinement Details for 2-3a,b, 2-7a,b and 2-9a,b

Crystallographic data for each of these complexes were obtained by Dr. R. McDonald and Dr. M. J. Ferguson at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and absorption correction (including SAINT and SADABS) were supplied by Bruker. The structures were solved by use of direct methods (except in the case of **2-7a** and **2-9b**,

where a Patterson search/structure expansion was employed), and refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and all hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Crystal structure diagrams were generated by use of the ORTEP-3 for Windows program.[83]

2.5.18 Crystallographic Solution and Refinement Details for 2-11b

Crystallographic data for this compound was obtained by Dr. G. Schatte at 173(±2) K on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Cell parameters were initially retrieved using the COLLECT software (Nonius), and refined with the HKL DENZO and SCALEPACK software.[84] Data reduction and absorption correction (multi-scan) were also performed with the HKL DENZO and SCALEPACK software. The structure was solved by using the direct methods package in SIR-97,[85] and refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and all H-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Crystal structure diagrams were generated by use of the ORTEP-3 for Windows program.[83]

2.6 References

1. Braunstein, P. *J. Organomet. Chem.* **2004**, *689*, 3953.

2. Elsevier, C. J.; Kowall, B.; Kragten, H. *Inorg. Chem.* **1995**, *34*, 4836.

3. Comba, P.; Schiek, W. *Coord. Chem. Rev.* **2003**, *238*, 21.

4. Kamer, P. C. J.; van Leeuwen, P. W. N.; Reek, J. N. H. *Acc. Chem. Res.* **2001**, *34*, 895.

5. Fryzuk, M. D. *Nature* **2004**, *427*, 498.

6. Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527.

7. Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 4981.

8. Wile, B. M.; Burford, R. J.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2006**, *25*, 1028.

9. Cipot, J.; McDonald, R.; Stradiotto, M. *Chem. Commun.* **2005**, 4932.

10. Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618.

11. Cipot, J.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Organometallics* **2007**, *26*, 594.

12. Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 10291.

13. Zargarian, D. *Coord. Chem. Rev.* **2002**, *233*, 157.

14. Stradiotto, M.; McGlinchey, M. J. *Coord. Chem. Rev.* **2001**, *219*, 311.

15. Lobanova, I. A.; Zdanovich, V. I. *Russ. Chem. Rev.* **1988**, *57*, 967.

16. Birmingham, J. M. *Adv. Organomet. Chem.* **1964**, *2*, 365.

17. Santi, S.; Ceccon, A.; Crociani, L.; Gambaro, A.; Ganis, P.; Tiso, M.; Venzo, A.; Bacchi, A. *Organometallics* **2002**, *21*, 565.

18. Santi, S.; Ceccon, A.; Carli, F.; Crociani, L.; Bisello, A.; Tiso, M.; Venzo, A. *Organometallics* **2002**, *21*, 2679.

19. Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Blum, J.; Gelman, D.; Halterman, R. L. *Eur. J. Inorg. Chem.* **2002**, 211.

20. Rupert, K. C.; Liu, C. C.; Nguyen, T. T.; Whitener, M. A.; Sowa, J. R. *Organometallics* **2002**, *21*, 144.

21. Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Halterman, R. L. *Organometallics* **2001**, *20*, 5360.

22. Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Halterman, R. L. *Organometallics* **2001**, *20*, 2215.

23. Westcott, S. A.; Kakkar, A. K.; Taylor, N. J.; Roe, D. C.; Marder, T. B. *Can. J. Chem.* **1999**, *77*, 205.

24. Bayon, J. C.; Claver, C.; Masdeu-Bulto, A. M. *Coord. Chem. Rev.* **1999**, *195*, 73.

25. Lobana, T. S. *Prog. Inorganic Chem.* **1989**, *37*, 495.

26. Cipot, J.; Wechsler, D.; Stradiotto, M.; McDonald, R.; Ferguson, M. J. *Organometallics* **2003**, *22*, 5185.

27. Stradiotto, M.; Kozak, C. M.; McGlinchey, M. J. *J. Organomet. Chem.* **1998**, *564*, 101.

28. Lensink, C.; Gainsford, G. J. *Aust. J. Chem.* **1998**, *51*, 667.

29. Adams, J. J.; Berry, D. E.; Curnow, O. J.; Fern, G. M.; Hamilton, M. L.; Kitto, H. J.; Pipal, J. R. *Aust. J. Chem.* **2003**, *56*, 1153.

30. Fallis, K. A.; Anderson, G. K.; Rath, N. P. *Organometallics* **1992**, *11*, 885.

31. The Gutowsky-Holm approximation was employed in the calculation of ΔG_{Tc}: Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

32. Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.

33. Avis, M. W.; Goosen, M.; Elsevier, C. J.; Veldman, N.; Kooijman, H.; Spek, A. L. *Inorg. Chim. Acta* **1997**, *264*, 43.

34. Fernandez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Lopez de Luzuriaga, J. M.; Olmos, E. *J. Chem. Soc., Dalton Trans.* **1997**, 3515.

35. Berry, D. E.; Browning, J.; Dixon, K. R.; Hilts, R. W.; Pidcock, A. *Inorg. Chem.* **1992**, *31*, 1479.

36. Browning, J.; Dixon, K. R.; Hilts, R. W. *Organometallics* **1989**, *8*, 552.

37. Murray, H. H.; Garzon, G.; Raptis, R. G.; Mazany, A. M.; Porter, L. C.; Fackler, J. P. *Inorg. Chem.* **1988**, *27*, 836.

38. Browning, J.; Bushnell, G. W.; Dixon, K. R.; Pidcock, A. *Inorg. Chem.* **1983**, *22*, 2226.

39. Mazany, A. M.; Fackler, J. P. *Organometallics* **1982**, *1*, 752.

40. One Ir(III) complex featuring an Ir-C-P-S ring has been characterized spectroscopically: Valderrama, M.; Contretas, R. *J. Organomet. Chem.* **1996**, *513*, 7.

41. Browning, J.; Bushnell, G. W.; Dixon, K. R.; Hilts, R. W. *J. Organomet. Chem.* **1992**, *434*, 241.

42. Browning, J.; Dixon, K. R.; Meanwell, N. J.; Wang, F. *J. Organomet. Chem.* **1993**, *460*, 117.

43. Browning, J.; Bushnell, G. W.; Dixon, K. R.; Hilts, R. W. *J. Organomet. Chem.* **1993**, *452*, 205.

44. Field, L. D.; Ward, A. J. *J. Organomet. Chem.* **2003**, *681*, 91.

45. Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1993**, *446*, 15.

46. Speier, J. L. *Adv. Organomet. Chem.* **1979**, *681*, 91.

47. Hiyama, T.; Kusumoto, T., in *Comprehensive Organic Synthesis*, Trost, B.M. and Fleming, I., Editors. 1991, Pergamon Press: Oxford. p. 763.

48. Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374.

49. Takeuchi, R.; Yasue, H. *Organometallics* **1996**, *15*, 2098.

50. Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748.

51. Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389.

52. Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101.

53. Oro, L. A.; Fernandez, M. J.; Esteruelas, M. A.; Jimenez, M. S. *J. Mol. Catal.* **1986**, *37*, 151.

54. Apple, D. C.; Brady, K. A.; Chance, J. M.; Heard, N. E.; Nile, T. A. *J. Mol. Catal.* **1985**, *29*, 55.

55. Cipot, J.; Vogels, C. M.; McDonald, R.; Westcott, S. A.; Stradiotto, M. *Organometallics* **2006**, *25*, 5965.

56. Cipot, J.; McDonald, R.; Stradiotto, M. *Organometallics* **2006**, *25*, 29.

57. Cipot, J.; Wechsler, D.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 1737.

58. Sirbu, D.; Consiglio, G.; Gischig, S. *J. Organomet. Chem.* **2006**, *691*, 1143.

59. Kostas, I. D.; Vallianatou, K. A.; Holz, J.; Borner, A. *Appl. Organomet. Chem.* **2005**, *19*, 1090.

60. Brauer, D. J.; Kottsieper, K. W.; Rossenbach, S.; Stelzer, O. *Eur. J. Inorg. Chem.* **2003**, 1748.

61. Francio, G.; Drommi, D.; Graiff, C.; Faraone, F.; Tiripicchio, A. *Inorg. Chim. Acta* **2002**, *338*, 59.

62. Cramer, N.; Laschat, S.; Baro, A. *Organometallics* **2006**, *25*, 2284.

63. Wallner, O. A.; Olsson, V. J.; Eriksson, L.; Szabo, K. J. *Inorg. Chim. Acta* **2006**, *359*, 1767.

64. Swamy, K. C. K.; Kumaraswamy, S.; Kumar, K. S.; Muthiah, C. *Tetrahedron Lett.* **2005**, *46*, 3347.

65. Huttenloch, O.; Laxman, E.; Waldmann, H. *Chem. Eur. J.* **2002**, *8*, 4767.

66. Ini, S.; Oliver, A. G.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2001**, *20*, 3839.

67. Huttenloch, O.; Spieler, J.; Waldmann, H. *Chem. Eur. J.* **2001**, *7*, 671.

68. Kadyrov, R.; Heller, D.; Selke, R. *Tetrahedron: Asymmetry* **1998**, *9*, 329.

69. Scherer, J.; Huttner, G.; Buchner, M.; Bakos, J. *J. Organomet. Chem.* **1996**, *520*, 45.

70. Sablong, R.; Newton, C.; Dierkes, P.; Osborn, J. A. *Tetrahedron Lett.* **1996**, *37*, 4933.

71. Baker, M. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1292.

72. Burford, N.; Müller, J.; Parks, T. M. *J. Chem. Ed.* **1994**, *71*, 807.

73. Tao, B. T.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 3892.

74. Evans, D. A.; Michael, F. E.; Tedrow, J. S.; Campos, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3534.

75. Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.

76. Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

77. Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 77.

78. Vanderent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1990**, *28*, 90.

79. Braun, S.; Kalinowski, H.-O.; Berger, S., *150 and More Basic NMR Experiments*. 1998, Toronto: Wiley-VCH. p. 136.

80. Aneetha, H.; Wu, W.; Verkade, J. G. *Organometallics* **2005**, *24*, 2590.

81. Rubin, M.; Schwier, T.; Gevorgyan, N. *J. Org. Chem.* **2002**, *67*, 1936.

82. Gade, L. H.; Cesar, V.; Bellemin-Laponnaz, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 1014.

83. Farrugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

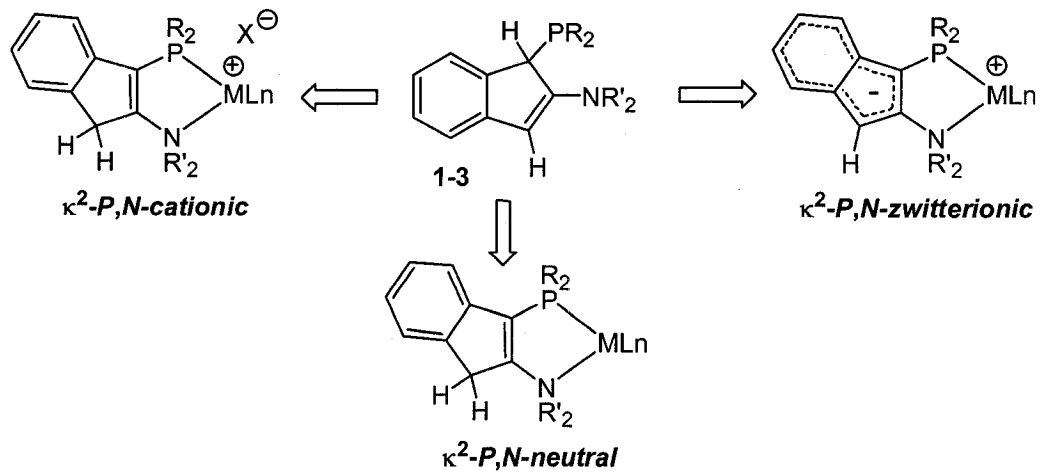
84. Otwinowski, Z.; Minor, W., *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, in *Macromolecular Crystallography, Pt A*. 1997, Academic Press Inc: San Diego. p. 307.

85. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

Chapter Three: Racemic Planar-Chiral Metalloligands Derived from Donor-Substituted Indenes: Synthetic, Structural, and Catalytic Studies

3.1 Introduction

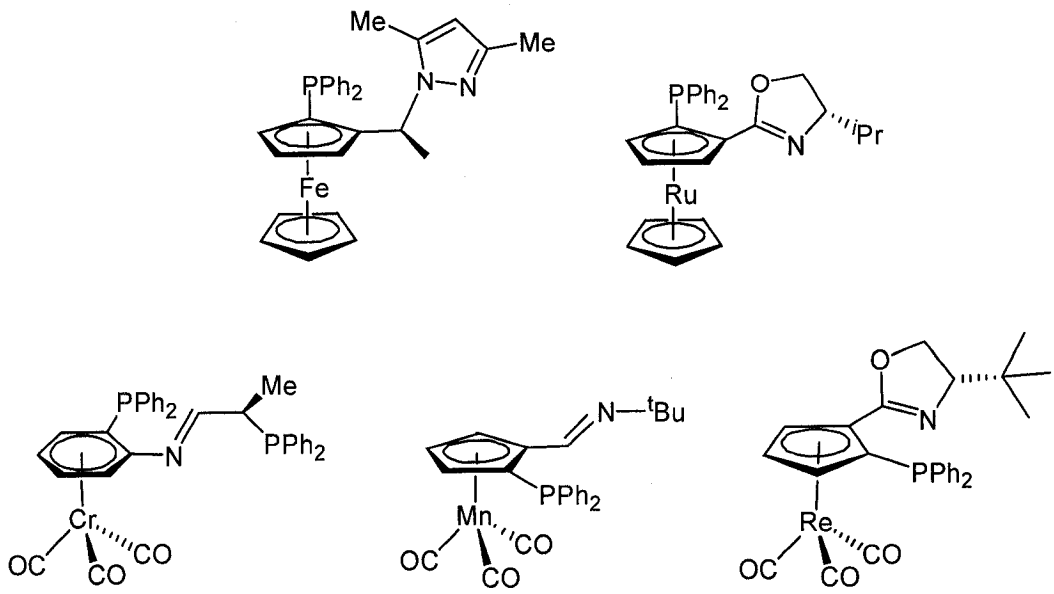
In the quest to identify new classes of metal complexes that are capable of mediating synthetically useful substrate transformations involving the activation of E-H bonds (E = main group fragment),[1-6] the Stradiotto group has explored the coordination chemistry of various donor-substituted indene ligands, as discussed previously in Chapter Two. Thus far, the coordination chemistry of ligand **1-3** has been explored by other group members with late transition metals (from Groups 8-11).[7-13] This research has demonstrated ligand **1-3** to be remarkably versatile, providing access to a range of neutral, cationic, and formally zwitterionic κ^2-*P*,*N* late metal complexes (Scheme 3-1) that exhibit interesting stoichiometric and catalytic reactivity with E-H bonds.[7-13] The zwitterionic complexes are unusual in that the indenide unit functions as an uncoordinated anionic charge reservoir to counterbalance the κ^2-*P*,*N*-coordinated cationic ML_n fragment, rather than as a locale for metal binding as is usually seen in indenyl metal chemistry.[14-18]



Scheme 3-1. Coordination complexes derived from the P,N substituted indene ligand **1-3**.

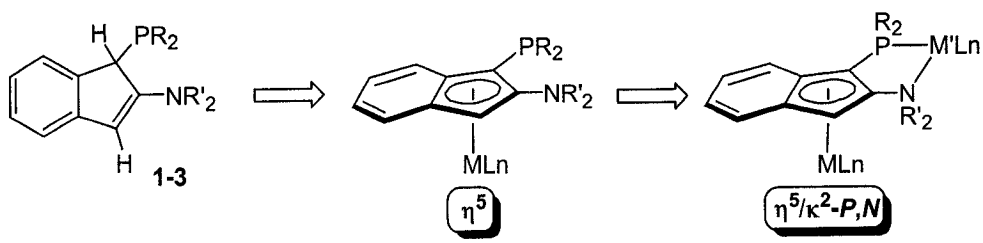
Given the unusual coordination chemistry exhibited by **1-3** in the formation of zwitterionic κ^2-*P,N* complexes, it became of interest to survey the feasibility of preparing more conventional η^5-indenyl metal derivatives of **1-3**. From a fundamental perspective, the successful synthesis of analogous η^5-ML_n and κ^2-*P,N*-ML_n derivatives of **1-3** would allow for the relative stability of such linkage isomers to be evaluated. Furthermore, it was envisioned that η^5-ML_n species derived from **1-3**, once resolved, could be employed as a new class of enantiopure planar-chiral metalloligands (PCMs) for use in the construction of chiral dinuclear η^5/κ^2-*P,N* catalyst complexes. While PCMs featuring P,N-donors built upon a ferrocenyl core have proven to be effective in promoting high activity and enantioselectivity in a range of metal-mediated asymmetric transformations,[19-24] the development of alternative planar chiral P,N-ligands based on metals such as chromium,[25-27] cobalt,[28, 29] manganese,[30-33] rhenium[34, 35] and ruthenium[36-38] have received comparatively little attention.[39] Some representative examples of alternative PCMs are shown in Scheme 3-2. However, comparative studies reported so far suggest that such alternative PCMs can in some

catalytic applications offer performance that is on par with, and even superior to,[31, 36, 37] more traditional ferrocenyl-based PCMs.



Scheme 3-2. Representative examples of PCMs featuring various 'spectator' metal fragments.

In this context, it was anticipated that the successful preparation of structurally diverse η^5-ML_n derivatives of **1-3** would enable the facially bound metal 'spectator' ML_n fragment in such complexes to serve as a control element in tuning the steric and electronic properties of the κ^2-*P*,*N*-coordinated 'reactive' $M'L_n$ fragment (Scheme 3-3).



Scheme 3-3. Generic structure of tunable PCM based on ligand **1-3**.

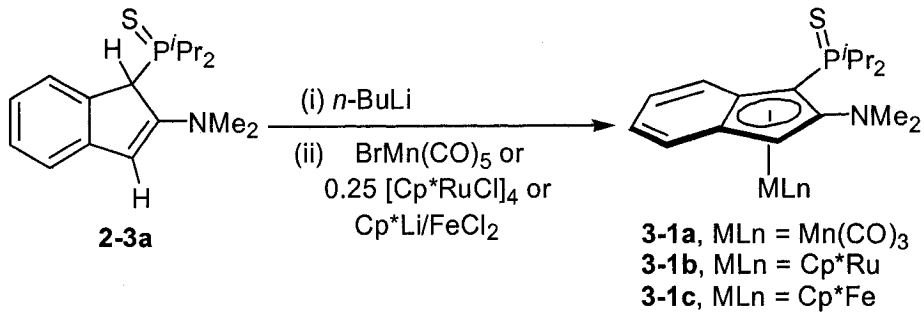
In this Chapter, the synthesis and characterization of a new family of η^5-ML_n complexes (ML_n = Cp*Fe, Cp*Ru, or $Mn(CO)_3$; Cp* = η^5-C_5Me_5) derived from 3-P^{i}Pr$_2$-indene, 1-P^{i}Pr$_2$-2-NMe$_2$-indene (**1-3a**), or 1-P(S)^{i}Pr$_2$-2-NMe$_2$-indene (**2-3a**) is discussed. Also described is the use of the racemic η^5-ML_n species **3-2a-c** as κ^2-*P*,*N*-metalloligands for $[(COD)Rh]^+$ (COD = η^4-1,5-cyclooctadiene) to give the isolable dinuclear Mn/Rh, Ru/Rh, and Fe/Rh complexes (**3-3a-c**). Notably, the preliminary catalytic studies employing **3-3a-c** revealed that altering the η^5-coordinated metal fragment in such dinuclear catalysts can lead to significant changes in the regioselectivity observed in the hydroboration of alkenes.

3.2 Results and Discussion

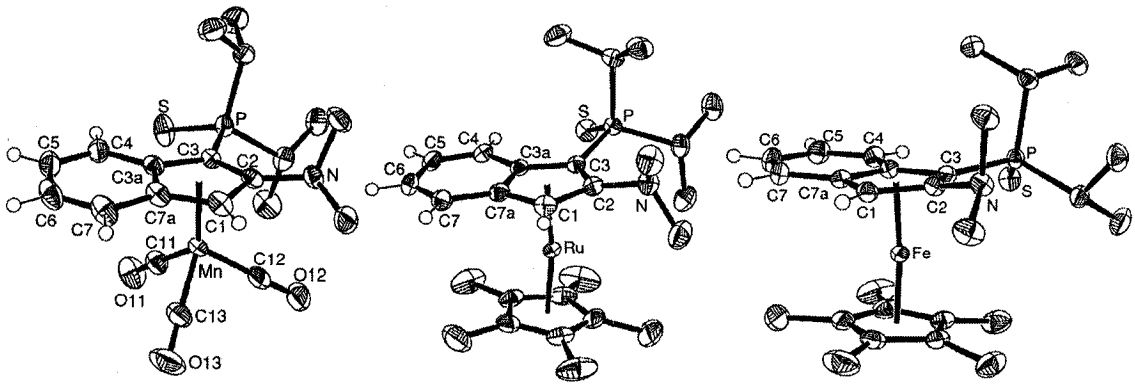
3.2.1 Preparation of Bidentate Planar Chiral Metalloligands

Initial synthetic goals have focused on the preparation of representative PCMs derived from **1-3a** featuring pentahepto $Mn(CO)_3$, Cp*Ru, and Cp*Fe metal fragments. Work done previously with the aim to preparing a η^5-$Mn(CO)_3$ complex through lithiation of **1-3a** followed by treatment with $BrMn(CO)_5$ resulted in a complex distribution of products.[40] An alternative synthetic strategy was required, therefore, starting from the corresponding phosphine sulfide **2-3a** (discussed in Chapter 2) was explored. Lithiation of **2-3a** followed by treatment with $BrMn(CO)_5$ led to the clean formation of **3-1a** (Scheme 3-4), which was isolated as an analytically pure solid in 96 % yield. Using a similar synthetic protocol, the related complexes **3-1b** and **3-1c** were obtained in 87 % and 55 % isolated yield, respectively (Scheme 3-4). Data obtained from both NMR spectroscopic and X-ray crystallographic studies involving **3-1a-c** support the

assignment of these products as η^5-ML_n species. The crystal structures for **3-1a**, **3-1b**, and **3-1c** are provided in Figure 3-1, while selected metrical parameters and X-ray experimental data for **3-1a**, **3-1b**, and **3-1c** are collected in Tables 3-1 and 3-2, respectively. In general the structures of **3-1a-c** can be compared with other η^5-indenyl Mn, Fe and Ru complexes of donor-substituted indenes.[41-48] While the structural features observed within the η^5-indenyl ligands of **3-1a-c** do not differ importantly, some significant structural differences are observed with respect to the way in which the $Mn(CO)_3$, Cp*Ru, and Cp*Fe fragments coordinate to the indenyl group in these complexes. Deviation from ideal η^5-coordination is observed in **3-1a**, with progressive lengthening of the Mn-C_{ind} distances noted as follows: Mn-C1 ≈ Mn-C3 < Mn-C2 < Mn-C3a ≈ Mn-C7a. Whereas a significant distortion from η^5-binding is also observed in the Cp*Fe complex **3-1c** (Fe-C3a ≈ Fe-C7a > Fe-C1 ≈ Fe-C2 ≈ Fe-C3), the Ru-C_{ind} distances in **3-1b** are statistically equivalent (ca. 2.23 Å), with the exception of the contracted Ru-C1 contact (2.181(2) Å).



Scheme 3-4. Synthesis of the (η^5-**1-3a**)ML_n Complexes **3-1a**, **3-1b**, and **3-1c**.



3-1a **3-1b** **3-1c**

Figure 3-1. ORTEP diagrams for **3-1a-c** shown with 50 % displacement ellipsoids and with the atomic numbering scheme depicted. Selected hydrogen atoms have been omitted for clarity.

Table 3-1. Selected Interatomic Distances (Å) for **3-1a**, **3-1b** and **3-1c**.

	3-1a	**3-1b**	**3-1c**
P-S	1.9575(6)	1.9651(7)	1.9659(6)
P-C3	1.828(1)	1.808(2)	1.813(2)
N-C2	1.417(2)	1.432(3)	1.434(2)
C1-C2	1.415(2)	1.420(3)	1.421(2)
C2-C3	1.460(2)	1.457(3)	1.452(2)
C3-C3a	1.466(2)	1.455(3)	1.458(2)
C3a-C4	1.429(2)	1.433(3)	1.434(2)
C4-C5	1.370(2)	1.358(3)	1.362(2)
C5-C6	1.416(3)	1.429(3)	1.423(3)
C6-C7	1.356(3)	1.351(3)	1.358(3)
C7-C7a	1.432(2)	1.426(3)	1.432(2)
C1-C7a	1.429(2)	1.424(3)	1.425(2)
C3a-C7a	1.431(2)	1.446(3)	1.440(2)
M-C1	2.138(2)	2.181(2)	2.059(2)
M-C2	2.158(1)	2.225(2)	2.068(2)
M-C3	2.131(2)	2.228(2)	2.063(2)
M-C3a	2.203(2)	2.229(2)	2.106(2)
M-C7a	2.190(2)	2.222(2)	2.118(2)

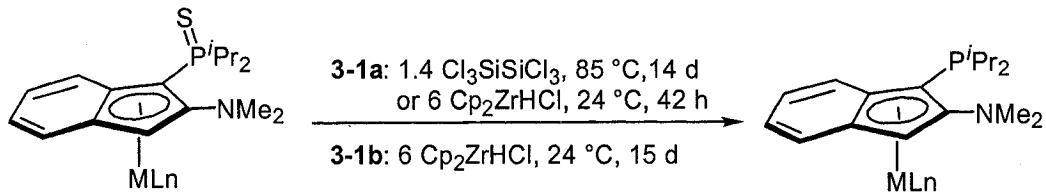
Table 3-2. Crystallographic Data for **3-1a**, **3-1b**, **3-1c**, **3-2a**, **3-2b**, **3-3c** and **3-6**.

	3-1a	**3-1b**	**3-1c**
Empirical formula	$C_{20}H_{25}Mn_1N_1O_3P_1S_1$	$C_{27}H_{40}Ru_1N_1P_1S_1$	$C_{27}H_{40}Fe_1N_1P_1S_1$
Formula weight	445.38	542.70	497.48
Crystal dimensions	0.46 × 0.39 × 0.32	0.35 × 0.32 × 0.11	0.60 × 0.29 × 0.29
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.688(2)	15.0636(7)	11.599(1)
b (Å)	15.570(4)	10.1395(5)	9.824(1)
c (Å)	13.898(3)	17.1950(8)	22.447(2)
α (deg)	90	90	90
β (deg)	91.494(4)	96.1692(8)	102.364(2)
γ (deg)	90	90	90
V (Å^3)	2095.8(8)	2611.1(2)	2498.7(4)
Z	4	4	4
ρcalcd (g cm^{-3})	1.412	1.381	1.322
μ (mm^{-1})	0.825	0.756	0.766
2θ limit (deg)	52.78	52.76	52.82
	$-12 \le h \le 12$	$-18 \le h \le 18$	$-14 \le h \le 14$
	$-19 \le k \le 19$	$-12 \le k \le 12$	$-12 \le k \le 12$
	$-17 \le l \le 17$	$-21 \le l \le 21$	$-28 \le l \le 28$
Total data collected	16327	17659	18496
Independent reflections	4273	5333	5112
R_{int}	0.0252	0.0290	0.0225
Observed reflections	3966	4696	4506
Range of transmission	0.7781–0.7027	0.9214–0.7777	0.8083–0.6563
Data/restraints/parameters	4273 / 0 / 244	5333 / 0 / 285	5112 / 0 / 285
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0273	0.0244	0.0314
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0764	0.0657	0.0865
Goodness-of-fit	1.043	1.071	1.032

	3-2a	3-2b	3-3c	3-6
Empirical formula	$C_{20}H_{25}MnNO_3P$	$C_{27}H_{40}Ru_1N_1P_1$	$C_{35}H_{52}B_1F_4Fe_1N_1P_1Rh_1$	$C_{33}H_{47}Cl_1P_1Rh_1Ru_1$
Formula weight	413.32	510.64	763.32	714.11
Crystal dimensions	0.35 x 0.30 x 0.12	0.51 × 0.47 × 0.20	0.15 × 0.10 × 0.10	0.05 × 0.05 × 0.05
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
a (Å)	9.0105(5)	11.5111(8)	11.4520(3)	8.2280(7)
b (Å)	24.956(1)	9.8759(7)	14.8950(4)	18.737(2)
c (Å)	9.4436(5)	22.979(2)	19.7890(5)	20.574(2)
α (deg)	90	90	90	79.373(5)
β (deg)	108.435(1)	103.242(1)	90	88.354(4)
γ (deg)	90	90	90	79.595(5)
V (Å^3)	2014.6(2)	2542.9(3)	3375.6(2)	3066.2(5)
Z	4	4	4	4
ρcalcd (g cm^{-3})	1.363	1.334	1.502	1.547
μ (mm^{-1})	0.753	0.693	1.014	1.191
2θ limit (deg)	52.78	52.80	54.94	52.74
	$-11 \le h \le 11$	$-14 \le h \le 14$	$-14 \le h \le 14$	$-10 \le h \le 10$
	$-31 \le k \le 31$	$-12 \le k \le 12$	$-19 \le k \le 19$	$-23 \le k \le 23$
	$-9 \le l \le 11$	$-28 \le l \le 28$	$-25 \le l \le 25$	$-25 \le l \le 24$
Total data collected	13161	19661	7698	20189
Independent reflections	4123	5200	7698	12349
R_{int}	0.0228	0.0231	N/A	0.0708
Observed reflections	Multi-scan (SADABS)	4761	6635	9540
Range of transmission	0.9151–0.7785	0.8738–0.7189	0.9054–0.8628	0.9429-0.9429
Data/restraints/parameters	4123 / 0 / 237	5200 / 0 / 276	7698 / 0 / 408	12349 / 838 / 785
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0317	0.0223	0.0441	0.0603
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0873	0.0610	0.0979	0.1344
Goodness-of-fit	1.048	1.043	1.066	1.035

Compound **3-1a** is transformed into the P,N-metalloligand **3-2a** (56 % isolated yield) upon treatment with $Cl_3SiSiCl_3$ at 85 °C over the course of 14 d (Scheme 3-5). Compound **3-2a** had been unattainable through direct methods as explored in previous studies. In an effort to identify a more convenient route to **3-2a**, some alternative reduction protocols were surveyed. Whereas the use of Raney Ni resulted in the rapid decomposition of **3-1a**, Cp_2ZrHCl proved to be a more useful reducing agent for the conversion of **3-1a** to **3-2a** at ambient temperatures, thereby allowing for the isolation of **3-2a** in 83 % yield (Scheme 3-5). However, in optimizing the synthetic protocol, a total of 6 equiv of Cp_2ZrHCl delivered over the course of 42 h was found to be necessary in order to effect the complete conversion of **3-1a** to **3-2a** at ambient temperature, and efforts to accelerate the reduction by heating of the reaction mixture (60 °C) resulted in the formation of multiple phosphorus-containing by-products. While the clean reduction of **3-1b** to **3-2b** (^{31}P NMR) was also achieved by use of excess Cp_2ZrHCl over the course of 15 d at ambient temperature (Scheme 3-5), a mixture of products (including **1-3a**) was observed in the attempted reduction of **3-1c** with Cp_2ZrHCl under similar conditions. In contrast to the complex reactivity observed between lithiated **1-3a** and $BrMn(CO)_5$,[40] compounds **3-2b** and **3-2c** were prepared conveniently from lithiated **1-3a** and 0.25 equiv $[Cp^*RuCl]_4$ or $Cp^*Li/FeCl_2$ in 74 % and 62 % isolated yield, respectively (Scheme 3-6). Solution NMR spectroscopic data support fully the formulation of **3-2a**, **3-2b** and **3-2c** as facially bound η^5-ML_n complexes, including the observation of relatively low-frequency ^{31}P NMR chemical shifts in comparison to related κ^2-*P,N* metal derivatives of **1-3a**,[7, 9-13] and the observation of a single ^1H NMR and a single ^{13}C NMR resonance attributable to the NMe_2 unit in **3-2a**, **3-2b** or **3-2c**, resulting from a rotation/inversion process

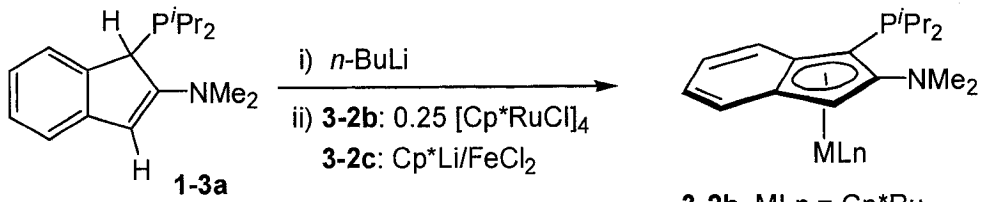
involving the uncoordinated N-donor fragment that is rapid on the NMR timescale at 300 K. Furthermore, the connectivity in **3-2a** and **3-2b** was confirmed by use of single crystal X-ray diffraction methods. Crystal structures for **3-2a** and **3-2b** are provided in Figure 3-2, while selected X-ray experimental data and metrical parameters for **3-2a** and **3-2b** are collected in Tables 3-2 and 3-3, respectively. The overall structural characteristics of **3-2a,b** compare well with those found in the related phosphine sulfides **3-1a,b** (vide supra). The reactivity of the formally zwitterionic Cp*Ru(κ^2-*P,N*) linkage isomer of **3-2b** that rearranges rapidly to a hydridocarbene complex via double geminal C-H bond activation was previously reported.[10] In monitoring the stability of **3-2b** in solution over the course of 96 h at 65 °C, no evidence for the rearrangement of **3-2b** to this Cp*Ru(κ^2-*P,N*) isomer, or the derived hydridocarbene, was observed (^{31}P NMR).



3-1a, MLn = $Mn(CO)_3$
3-1b, MLn = Cp*Ru

3-2a, MLn = $Mn(CO)_3$
3-2b, MLn = Cp*Ru

Scheme 3-5. Synthesis of complexes **3-2a** and **3-2b** via phosphine sulfide deprotection.



1-3a

3-2b, MLn = Cp*Ru
3-2c, MLn = Cp*Fe

Scheme 3-6. Synthesis of complexes **3-2b** and **3-2c** directly from ligand **1-3a**.

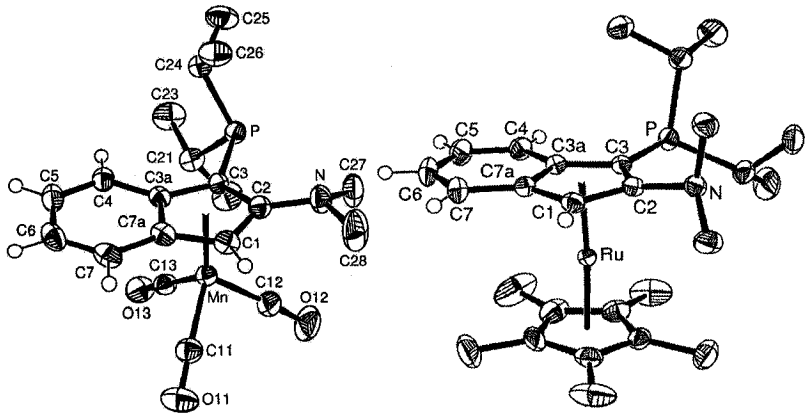


Figure 3-2. ORTEP diagrams for **3-2a** (left) and **3-2b** (right), shown with 50 % displacement ellipsoids and with the atomic numbering scheme depicted. Selected hydrogen atoms have been omitted for clarity.

Table 3-3. Selected Interatomic Distances (Å) for **3-2a** and **3-2b**.

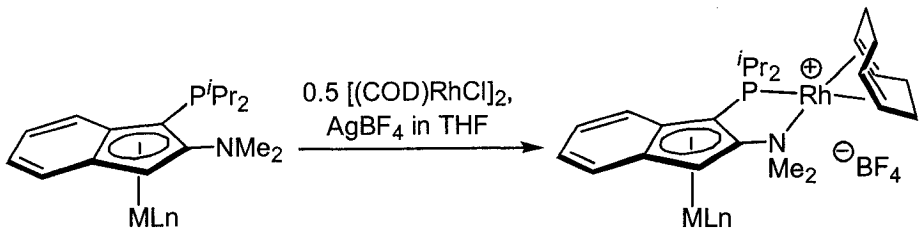
	3-2a	**3-2b**
P-C3	1.837(2)	1.824(2)
N-C2	1.377(2)	1.428(2)
C1-C2	1.428(2)	1.430(2)
C2-C3	1.454(2)	1.447(2)
C3-C3a	1.456(2)	1.452(2)
C3a-C4	1.433(2)	1.432(2)
C4-C5	1.360(2)	1.360(3)
C5-C6	1.421(3)	1.426(3)
C6-C7	1.361(3)	1.359(3)
C7-C7a	1.423(2)	1.432(2)
C1-C7a	1.432(2)	1.429(2)
C3a-C7a	1.430(2)	1.444(2)
M-C1	2.135(2)	2.189(2)
M-C2	2.238(2)	2.204(2)
M-C3	2.181(2)	2.206(2)
M-C3a	2.192(2)	2.217(2)
M-C7a	2.170(2)	2.228(2)

3.2.2 Rhodium Chemistry of Racemic Planar Chiral Metalloligands

After having established viable synthetic routes to **3-2a-c**, the Rh(I) coordination chemistry of these racemic PCMs was explored. Compounds **3-2a-c** reacted cleanly with

$[(COD)Rh(THF)_2]^+BF_4^-$ (prepared *in situ*) to give the corresponding $[(COD)Rh(\kappa^2\text{-}P,N\text{-}$ **3-2a-c**$)]^+BF_4^-$ complexes (**3-3a-c**) in 87 %, 96 % and 89 % isolated yield, respectively (Scheme 3-7). The observation of a single downfield-shifted ^{31}P NMR resonance (versus **3-2a-c**) that exhibits coupling to Rh provided support for the existence of a Rh-P linkage in **3-3a-c**. In addition, while a single ^1H NMR resonance and a single ^{13}C NMR resonance attributable to the NMe_2 unit is observed for each of **3-2a-c** (vide supra), coordination of the amino moiety to Rh in **3-3a-c** results in the observation of two distinct NMe signals in each of the ^1H NMR and ^{13}C NMR spectra, in keeping with the C_1-symmetric nature of these dinuclear complexes. For **3-3c**, the connectivity was confirmed by use of X-ray diffraction techniques. A crystal structure for **3-3c** is provided in Figure 3-3. The X-ray experimental data and selected metrical parameters for **3-3c** are collected in Tables 3-2 and 3-4, respectively. The structural features observed in the indenyl fragment of **3-3c** mirror those found within the Ru-metalloligand **3-2b**, with the exception of a modest shortening of the P-C3 distance and a lengthening of the N-C2 distance in **3-3c**. As was noted in **3-1c**, the Cp*Fe unit is not bound in a symmetrical fashion to the C_5-ring of the indenyl unit in **3-3c**, and instead exhibits a tendency toward η^3-coordination. The interatomic distances found within the Rh coordination sphere of **3-3c** are strikingly similar to those observed in the related mononuclear complex $[(COD)Rh(\kappa^2\text{-}3\text{-}P^i Pr_2\text{-}2\text{-}NMe_2\text{-indene})]^+BF_4^-$,[13] including the observation of Rh-alkene distances *trans* to P that are significantly longer than those *trans* to N, in keeping with established structural trends in coordination chemistry. Whereas the restricted conformational flexibility associated with the P,N chelate in **3-3c** holds the Cp*Fe and

$[(COD)Rh]^+$ fragments in relatively close proximity, the Rh···Fe distance (4.24 Å) precludes any significant metal-metal bonding interations.



3-2a, MLn = $Mn(CO)_3$
3-2b, MLn = Cp*Ru
3-2c, MLn = Cp*Fe

3-3a, MLn = $Mn(CO)_3$
3-3b, MLn = Cp*Ru
3-3c, MLn = Cp*Fe

Scheme 3-7. Synthesis of the $[(\kappa^2\text{-}P,N\text{-}$**3-2a-c**$)Rh(COD)]^+BF_4^-$ Complexes (**3-3a-c**).

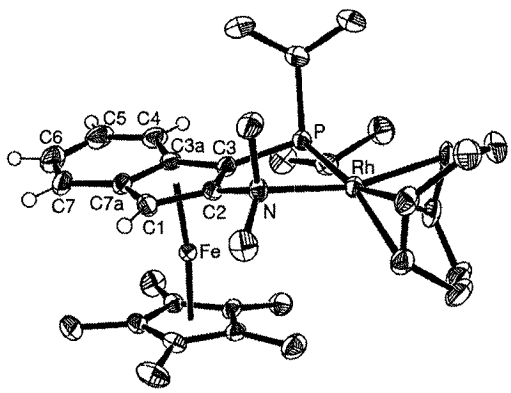


Figure 3-3. ORTEP diagram for **3-3c**, shown with 50 % displacement ellipsoids and with the atomic numbering scheme depicted. Selected hydrogen atoms, as well as the tetrafluoroborate counter anion have been omitted for clarity.

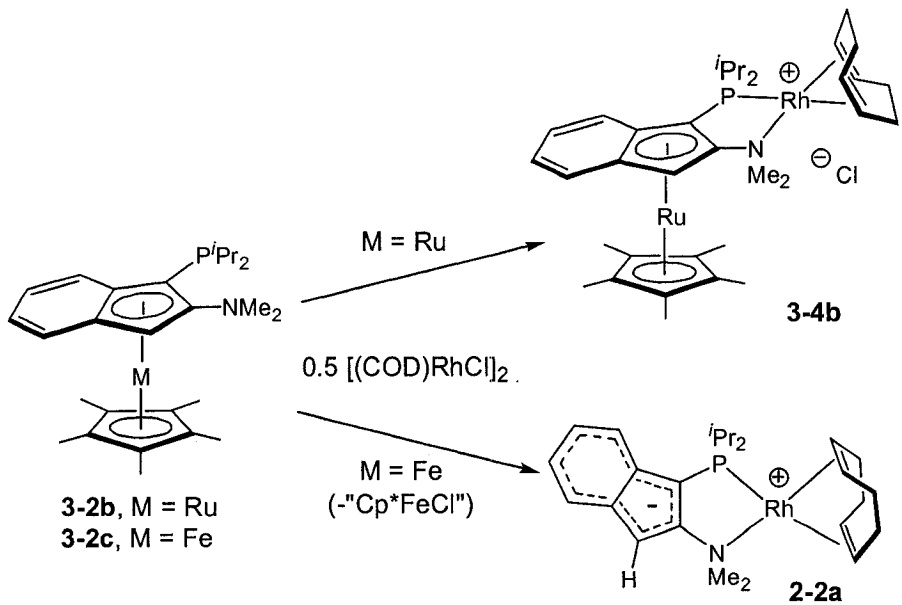
Table 3-4. Selected Interatomic Distances (Å) for **3-3c** and **3-6**.

	3-3c[a]	**3-6**[b]	**3-6**[c]
P-C3	1.802(5)	1.807(6)	1.822(6)
N-C2	1.460(6)	–	–
C1-C2	1.433(5)	1.410(9)	1.405(9)
C2-C3	1.447(6)	1.444(9)	1.444(8)
C3-C3a	1.449(6)	1.471(8)	1.453(8)
C3a-C4	1.428(6)	1.437(9)	1.426(9)
C4-C5	1.364(8)	1.36(1)	1.373(9)
C5-C6	1.425(9)	1.44(1)	1.42(1)
C6-C7	1.362(8)	1.34(1)	1.36(1)
C7-C7a	1.419(7)	1.426(9)	1.430(9)
C1-C7a	1.425(7)	1.433(9)	1.422(9)
C3a-C7a	1.463(7)	1.423(9)	1.455(8)
M-C1	2.056(5)	2.186(6)	2.185(6)
M-C2	2.058(5)	2.198(6)	2.202(6)
M-C3	2.078(5)	2.252(6)	2.243(6)
M-C3a	2.134(4)	2.259(6)	2.243(6)
M-C7a	2.121(5)	2.224(6)	2.221(6)
Rh-P	2.350(1)	2.339(2)	2.351(2)
Rh-N or Cl	2.186(3)	2.373(2)	2.380(2)
$Rh\text{-}C_{alkene1}$[d]	2.229(5)	2.218(7)	2.198(7)
$Rh\text{-}C_{alkene2}$[d]	2.270(4)	2.251(7)	2.215(7)
$Rh\text{-}C_{alkene3}$[e]	2.141(5)	2.116(6)	2.118(6)
$Rh\text{-}C_{alkene4}$[e]	2.148(5)	2.143(6)	2.148(6)

[a]The Fe-Rh distance in the final refined structure is 4.24 Å. [b,c]Within the first and second independent molecules of **3-6**, respectively. [d]The Rh-cyclooctadiene distances *trans* to phosphorus. [e]The Rh-cyclooctadiene distances *trans* to nitrogen or chloride.

In contrast to the clean coordination chemistry observed with **3-2a-c** and $[(COD)Rh(THF)_2]^+BF_4^-$ (prepared *in situ*), divergent reactivity behavior was observed for the structurally related Ru (**3-2b**) and Fe (**3-2c**) metalloligands when $[(COD)RhCl]_2$ was implemented (Scheme 3-8). Treatment of **3-2b** with 0.5 equiv $[(COD)RhCl]_2$ in THF resulted in the formation of a yellow precipitate, which was isolated in 49 % yield and identified as $[(COD)Rh(\kappa^2\text{-}P,N\text{-}$**3-2b**$)]^+Cl^-$ (**3-4b**). Under similar conditions **3-2c** was

transformed cleanly into the known zwitterionic Rh species, **2-2a**.[13] The apparent ability of **3-2c** to serve as a transfer agent for the indenyl fragment, when placed in the context of the facile *rac/meso* isomerization of $(3\text{-}PPh_2\text{-}\eta^5\text{-}C_9H_6)_2Fe$ at ambient temperature in THF solution that has been reported by Curnow and co-workers,[43] suggests that such Cp*Fe-based metalloligands may be less well-suited for some catalytic applications. However, a report by Fang and co-workers,[41] in which resolved Cp*Fe(4-$PR_2\text{-}\eta^5\text{-}C_9H_6$) complexes are shown to resist racemization, highlights the fact that the substitution pattern in such donor-substituted η^5-indenyl species can influence the overall stability of the metalloligand topology.

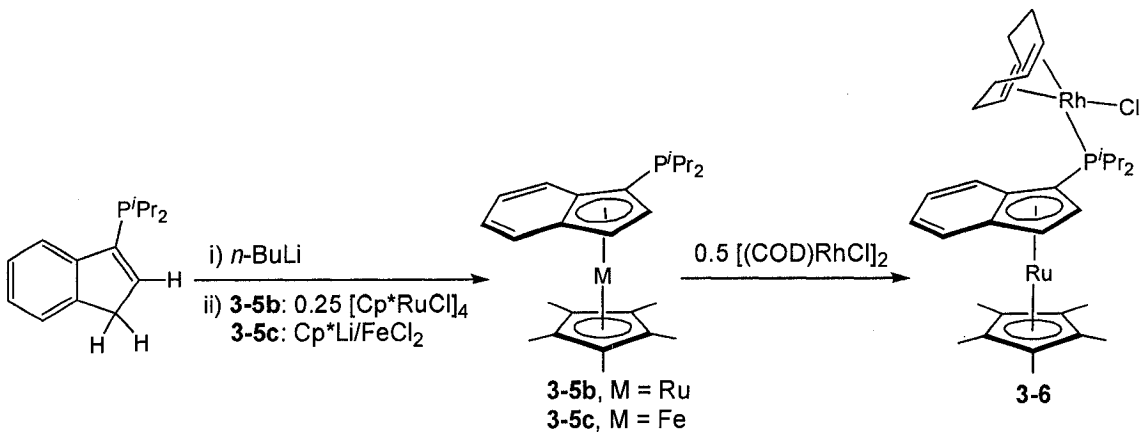


Scheme 3-8. Divergent Reactivity of **3-2b** and **3-2c** with $[(COD)RhCl]_2$.

3.2.3 Preparation of Monodentate Planar Chiral Metalloligands

In light of the increasing utility of bulky monodentate phosphine ligands in asymmetric catalysis,[49-53] it was sought to extend the synthetic efforts to the

preparation of η^5-ML_n derivatives of 3-P^{i}Pr$_2$-indene.[54] Lithiation of 3-P^{i}Pr$_2$-indene followed by the addition of $BrMn(CO)_5$ generated a complex mixture of products, from which the desired complex (3-P^{i}Pr$_2$-η^5-C_9H_6)$Mn(CO)_3$ (**3-5a**) could not be isolated. However, similar reactions employing 0.25 equiv $[Cp^*RuCl]_4$ or $Cp^*Li/FeCl_2$ in place of $BrMn(CO)_5$ afforded **3-5b** or **3-5c** in 98 % and 43 % yield, respectively (Scheme 3-9). The ability of **3-5b** to function as a monophosphine ligand was demonstrated upon treatment with 0.5 equiv of $[(COD)RhCl]_2$, thereby allowing for the isolation of (COD)RhCl(κ^1-*P*-**3-5b**) **3-6** in 96 % yield. Each of **3-5b,c** and **3-6** were characterized spectroscopically, and in the case of **3-6**, data from crystallographic studies provided confirmation of the atomic connectivity; a crystal structure for **3-6** is provided in Figure 3-4. Selected X-ray experimental data and metrical parameters for **3-6** are collected in Tables 3-2 and 3-4, respectively. The metrical features found in **3-6** can be compared with those of **3-1b**, **3-2b**, and the related complex (COD)RhCl(3-*P*^{i}Pr$_2$-indene).[54]



Scheme 3-9. Synthesis of the PCMs **3-5b,c** and the dinuclear Rh/Ru complex, **3-6**.

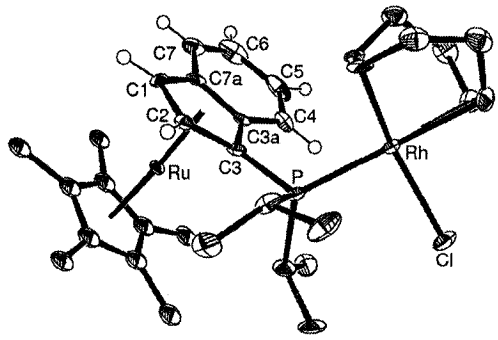
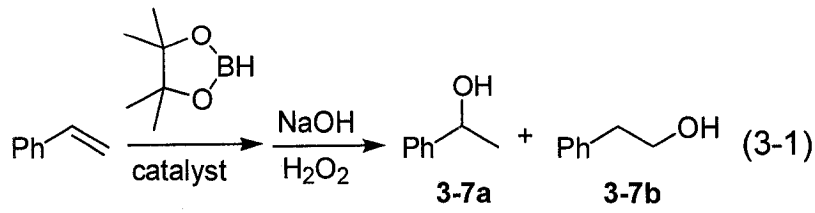


Figure 3-4. ORTEP diagram for **3-6**, shown with 50 % displacement ellipsoids and with the atomic numbering scheme depicted. Selected hydrogen atoms have been omitted for clarity. Only one of the two crystallographically independent molecules of **3-6** is shown.

3.2.4 Hydroboration Catalysis Mediated by Complexes 3-3a-c

The addition of pinacolborane (HBpin) to styrene mediated by **3-3a-c** was chosen as a test reaction with which to survey the potential influence of the η^5-coordinated organometallic moiety on the catalytic properties of the associated (κ^2-*P*,*N*)-Rh fragment in these dinuclear complexes.[6, 55, 56] Whereas catecholborane (HBcat) has traditionally been employed in such hydroboration reactivity surveys, HBpin was chosen specifically for the studies herein because HBpin is significantly more stable to air and nucleophiles than HBcat, and the greater steric bulk of HBpin provides an increased challenge in terms of attaining branched selectivity.[56, 57] Selected reports where the regioselectivity and enantioselectivity in alkene hydroboration employing HBcat is used in the evaluation of PCM designs can be found in the literature.[38, 58-61] As well as representing a widely employed chemical transformation that provides access to organoboron synthons, metal-catalyzed alkene hydroboration can serve as a prototype for E-H addition reactions in which product selectivity can be a challenge.[6, 55, 56] In addition to the possible branched and linear regioisomers that can arise from simple B-H

addition (**3-7a** and **3-7b**, eq 3-1), unsaturated species formed via dehydrogenative borylation, and products of net diboration, are also observed commonly.



(3-1)

The preliminary results of the alkene hydroboration survey are collected in Table 3-5. Notably, each of **3-3a-c** proved to be an active catalyst for this transformation, with the observed regioselectivity, albeit modest, being dependent on the nature of the η^5-coordinated metal fragment, as well as the solvent employed. In comparison, Crudden and co-workers have demonstrated that $[(COD)_2Rh]^+BF_4^-$/bisphosphine mixtures can provide > 96 % branched selectivity.[57] While the Mn/Rh complex **3-3a** demonstrated selectivity for the branched product **3-7a** in both THF (Table 3-5, entry 1) and 1,2-dichloroethane (Table 3-5, entry 2), the related Ru/Rh species **3-3b** exhibited linear selectivity in THF (Table 3-5, entry 3), but almost no selectivity in 1,2-dichloroethane (Table 3-5, entry 4). As well, the Fe/Rh complex **3-3c** exhibited poor selectivity in both of these solvents (Table 3-5, entries 5 and 6).

Table 3-5. Rhodium-Catalyzed Addition of Pinacolborane to Styrene.[a]

Entry	Catalyst	Solvent	Branched : Linear[b] (**3-7a** : **3-7b**)
1	**3-3a**	THF	66 : 34
2	**3-3a**	DCE	68 : 32
3	**3-3b**	THF	34 : 66
4	**3-3b**	DCE	56 : 44
5	**3-3c**	THF	45 : 55
6	**3-3c**	DCE	52 : 48

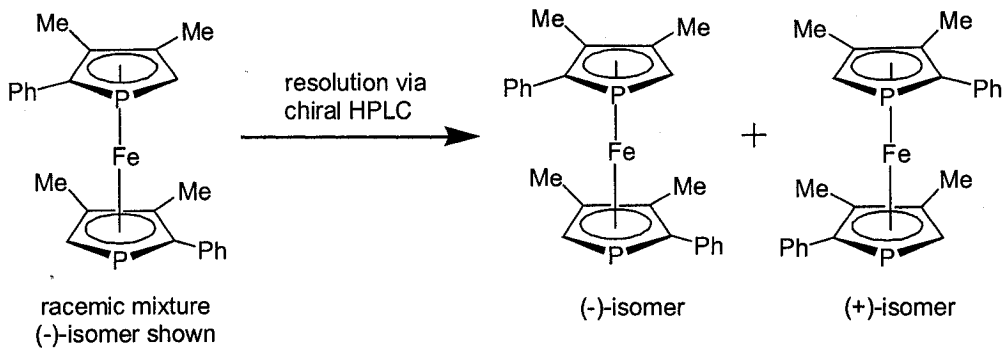
[a]Conditions: 24 °C; 5.0 mol% catalyst; 24 h; pinacolborane-to-styrene ratio of 1.2:1; DCE = 1,2-dichloroethane. In all experiments listed, > 95 % conversion of the styrene starting material was achieved. [b]Product ratio on the basis of GC-FID data, rounded to the nearest percent. In all cases, alternative boron-containing products represented < 3 % of the total product distribution.

3.3 Summary and Conclusions

In summary, the modular synthetic pathways to new η^5-ML_n derivatives of the donor-substituted indene ligands 3-P^{i}Pr$_2$-indene, **1-3a**, and **2-3a** has been established. Comparative reactivity studies featuring three examples of these η^5-ML_n complexes (i.e. ML_n = $Mn(CO)_3$, Cp*Ru, or Cp*Fe; **3-2a-c**) underscored some important differences in the behavior of such metalloligands. Whereas **3-2b** reacted cleanly with $[(COD)RhCl]_2$ to give the Ru/Rh species **3-4b**, the congeneric Fe complex **3-2c** decomposed, leading to the generation of the mononuclear zwitterionic Rh complex **2-2a**. In contrast, each of **3-2a-c** was observed to react cleanly with $[(COD)Rh(THF)_2]^+BF_4^-$, thereby allowing for the isolation of the corresponding planar-chiral (racemic) dinuclear η^5/κ^2-*P,N* catalyst complexes **3-3a-c** in high isolated yield. The preliminary alkene hydroboration results described herein establish the viability of **3-3a-c** as catalysts for the addition of E-H bonds to unsaturated substrates, although whether the source of the differing

regioselectivity displayed by **3-3a-c** is primarily steric or electronic in origin is presently unknown. However, the observation of divergent selectivity in transformations mediated by **3-3a-c** suggests that the introduction of structural changes to the η^5-coordinated metal fragment may provide a systematic way in which to modify the steric and electronic properties of the κ^2-*P*,*N*-ligated metal fragment in these and related complexes.

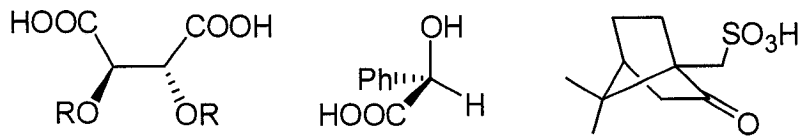
Future work will involve the resolution of such racemic PCMs, and their application as enantiopure ligands in a range of metal-mediated asymmetric catalytic transformations. Different methods can be applied to achieve the resolution of the racemic PCMs. The use of preparative chiral high pressure liquid chromatography (HPLC) has been used successfully by Fu and co-workers for the resolution of selected racemic PCMs (Scheme 3-10).[62, 63] In order for HPLC to be a viable method, the compounds in question need to have enough stability towards the stationary phase of the chiral HPLC column, and must be fully soluble in the solvent system.



Scheme 3-10. Resolution of a racemic PCM mixture via chiral HPLC.

An alternative method for the resolution of racemic chiral ligands is the protonation of the racemic ligand with an enantiopure chiral acid, thereby transforming the enantiomers into diastereomers that can be separated more easily. The isolated ligand-

acid complexes are in turn deprotected, leaving behind enantiopure ligand. Examples of some commercially available chiral acids that might be used are (*R*,*R*)-(–)-di-O,O-benzoyltartaric acid (DBTA) (**3-8a**), (*R*,*R*)-(2,3-di-[(phenylamino)carbonyl]tartaric acid (**3-8b**), *R*-(–)-mandelic acid (**3-8c**), and (1*R*)-(–)-camphorsulfonic acid (CSA) (**3-8d**) (Figure 3-5).



3-8a, R = COPh
3-8b, R = CONHPh

3-8c

3-8d

Figure 3-5. Examples of commercially available chiral acids.

3.4 Experimental Section

3.4.1 General Considerations

See Section 2.5 for a description of general experimental conditions. Any changes or additions to those procedures are described herein. Florisil® was oven-dried for 5 d and then evacuated for 24 h. CD_2Cl_2 (Cambridge Isotopes) was stirred over CaH_2 for 7 days followed by three freeze-pump-thaw cycles and distilled *in vacuo* and stored over 4 Å molecular sieves for 24 h. Pinacolborane (Aldrich) was degassed by using three repeated freeze-pump-thaw cycles and then dried over 4 Å molecular sieves for 24 h. All purchased and prepared solid reagents were dried *in vacuo* for 24 h. $[Cp^*RuCl]_4$ (Cp^* = C_5Me_5)[64] was prepared employing literature procedures, while Cp_2ZrHCl (Cp = C_5H_5), $BrMn(CO)_5$, $FeCl_2$ and $Cl_3SiSiCl_3$ were obtained from Aldrich. The lithiation of **1-3a** was

carried out by treatment with an equivalent of *n*-BuLi, using literature methods.[65] IR data were collected on a Bruker VECTOR 22 FT-IR instrument.

3.4.2 Synthesis of 3-1a

A 1.6 M hexanes solution (pre-cooled to -35 °C) of *n*-BuLi (0.20 mL, 0.32 mmol) was added dropwise via syringe to a glass vial containing a magnetically stirred solution (pre-cooled to -35 °C) of **2-3a** (0.099 g, 0.32 mmol) in toluene (5 mL) over 2 min, producing a faint yellow solution. The vial containing the reaction mixture was then sealed with a PTFE-lined cap, and the mixture was stirred for 1.5 h at ambient temperature. The clean lithiation of **2-3a** was monitored *in situ* by the disappearance of the ^{31}P NMR signal corresponding to **2-3a**, and the appearance of a single new resonance at 54 ppm. A mixture of $BrMn(CO)_5$ (0.089 g, 0.32 mmol) in toluene (5 mL) was then transferred to the reaction mixture via Pasteur pipette, and the reaction vial was re-sealed. A dark solution formed immediately, and, after stirring for 3 d, the solution changed to a yellow-orange color and a white precipitate formed. The reaction mixture was filtered through Celite, and the supernatant was dried *in vacuo*, yielding **3-1a** as an analytically pure, orange solid (0.14 g, 0.31 mmol, 96%). Anal. Calcd. for $C_{20}H_{25}PSNO_3Mn$: C 53.93; H 5.66; N 3.14. Found: C 53.61; H 5.72; N 3.26. ^{1}H NMR (C_6D_6): δ 9.42 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4-H or C7-H), 7.06 (d, $^3J_{HH}$ = 8.1 Hz, 1H, C7-H or C4-H), 6.80-6.72 (m, 2H, C5-H and C6-H), 4.46 (s, 1H, C1-H), 3.16 (m, 1H, P(C*H*Me$_2$)), 2.18 (m, 1H, P(C*H*Me$_2$)), 2.09 (s, 6H, NMe$_2$), 1.77 (d of d, $^3J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 6.0 Hz, 3H, P(CHMe*Me*)), 1.31 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 5.7 Hz, 3H, P(CHMe*Me*)), 1.08 (d of d, $^3J_{PH}$ = 17.9 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CHMe*Me*)), 1.77 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, P(CHMe*Me*)); ^{13}C{^{1}H} NMR (C_6D_6): δ 223.7 (CO), 138.7 (C2), 129.0 (C4 or C7), 127.1

(C5 or C6), 126.1 (C6 or C5), 124.7 (C7 or C4), 105.5 (d, J = 7.3 Hz, C7a or C3a), 100.0 (d, J = 7.6 Hz, C3a or C7a), 61.5 (C1), 46.2 (NMe_2), 30.7 (m, P(*C*HMe_2)), 28.0 (m, P(*C*HMe_2)), 19.6 (P(CHMe*Me*)), 19.2 (P(CHMe*Me*)), 18.5 (P(CHMe*Me*)), 17.2 (P(CHMe*Me*)); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 64.4. FTIR (cm^{-1}) ν(CO): 2014, 1945, 1931. Crystals of **3-1a** suitable for single-crystal X-ray diffraction analysis were grown from diethyl ether at -35 °C.

3.4.3 Synthesis of 3-1b

A glass vial charged with a stirbar, **2-3a** (0.28 g, 0.91 mmol), and diethyl ether (2 mL) was cooled to -35 °C. To the vial was added dropwise a 1.6 M hexanes solution of *n*-BuLi (0.57 mL, 0.91 mmol; pre-cooled to -35 °C) via Eppendorf pipette, and the mixture was stirred for 1 h. The resulting slurry was cooled to -35 °C, to which a suspension of $[Cp^*RuCl]_4$ (0.25 g, 0.23 mmol) in diethyl ether (2 mL) (pre-cooled to -35 °C) was added slowly. The reaction mixture was stirred for an additional 1.5 h at ambient temperature, and subsequently filtered through a plug of Celite. The filtrate was collected, and the solvent and other volatile materials were removed *in vacuo* to leave **3-1b** as an analytically pure, dark yellow solid (0.43 g, 0.79 mmol, 87 %). Anal. Calcd. for $C_{27}H_{40}PSNRu$: C 59.75; H 7.43; N 2.58. Found: C 59.71; H 7.49; N 2.48. ^1H NMR (C_6D_6): δ 8.40 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C7-H or C4-H), 7.13-7.18 (m, 2H, aryl CHs), 7.05-7.08 (m, 1H, aryl CH), 5.23 (s, 1H, C1-H), 3.35 (m, 1H, P(C*H*Me_cMe_d)), 2.76 (s, 6H, NMe_2), 2.45 (m, 1H, P(C*H*Me_aMe_b)), 1.73 (d of d, $^3J_{PH}$ = 18.3 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_c$$Me_d$)), 1.70 (s, 15H, C_5*Me*$_5$), 1.46 (d of d, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_d$$Me_c$)), 1.32 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*$_b$$Me_a$)), 1.05 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me*$_a$$Me_b$)); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 129.3

(aryl C), 124.0 (aryl C), 123.1 (aryl C), 122.6 (d, $^2J_{PC}$ = 9.3 Hz, C2), 120.6 (aryl C), 92.1 (d, J_{PC} = 8.3 Hz, C3a or C7a), 91.8 (d, J_{PC} = 10.2 Hz, C7a or C3a), 83.5 (C_5Me_5), 67.8 (d, $^1J_{PC}$ = 77.2 Hz, C3), 64.7 (d, $^3J_{PC}$ = 7.2 Hz, C1), 49.1 (NMe_2), 31.6 (d, $^1J_{PC}$ = 50.5 Hz, P(*C*HMe$_a$Me$_b$)), 27.8 (d, $^1J_{PC}$ = 51.5 Hz, P(*C*HMe$_c$Me$_d$)), 19.8 (P(CH*Me*Me)), 17.6 (P(CH*Me*Me)), 17.6 (P(CH*Me*Me)), 16.1 (P(CH*Me*Me)), 9.9 (C_5*Me*$_5$); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 65.3. Crystals of **3-1b** suitable for single-crystal X-ray diffraction analysis were grown from pentane at -35 °C.

3.4.4 Synthesis of 3-1c

A vial was charged with a stir bar, Cp*H (0.049 mL, 0.31 mmol), and THF (2 mL). To the vial was added a pre-cooled (-35 °C) solution of *n*-BuLi (0.11 mL of a 2.9 M hexanes solution, 0.31 mmol) via Eppendorf pipette, at which point a white precipitate formed immediately. The suspension was stirred magnetically at ambient temperature for 2 h, and then cooled to -35 °C. This suspension was then added dropwise to a suspension of $FeCl_2$ (0.039 g, 0.31 mmol) in THF (1.5 mL) that had been pre-cooled to -35 °C. The resulting lime-green mixture (**A**, containing "Cp*FeCl") was stirred magnetically for 2 h. A separate vial was charged with a stir bar, **2-3a** (0.095 g, 0.31 mmol), and THF (2 mL). The mixture was cooled to -35 °C, at which point a pre-cooled 2.9 M hexanes solution of *n*-BuLi (0.11 mL, 0.31 mmol) was added dropwise via Eppendorf pipette. The mixture was stirred magnetically at ambient temperature for 2 h, after which the solvent and other volatile materials were removed *in vacuo*. The residue was washed with hexane dried in vacuo. To the remaining solid was added THF (2 mL), and this mixture (**B**) was cooled to -35 °C. Mixture (**A**) was also cooled to -35 °C, at which point mixture **B** was added slowly to mixture **A**, giving a burgundy-colored mixture. This combined reaction mixture

was allowed to react for 18 h at ambient temperature under the influence of magnetic stirring, after which the reaction mixture was filtered through Celite, and the filtrate was dried *in vacuo*. The residue was then extracted with pentane (5 mL), and the resulting pentane mixture was filtered through a short plug of Celite. The filtrate was collected and the solvent and other volatile materials were removed *in vacuo*. Any decamethylferrocene that was produced during the synthesis was then removed by sublimation to leave **3-1c** as an analytically pure, purple solid (0.085 g, 0.17 mmol, 55 %). Anal. Calcd. for $C_{27}H_{40}PSNFe$: C 65.18; H 8.11; N 2.82. Found: C 65.07; H 8.06; N 2.75. ^{1}H NMR (C_6D_6): δ 9.33 (d, $^3J_{HH}$ = 8.3 Hz, 1H, C7-H), 7.12 (d of d, $^3J_{HH}$ = 8.3 Hz, J = 1.1 Hz, 1H, C4-H), 6.96-7.06 (m, 2H, C5-H and C6-H), 4.26 (s, 1H, C1-H), 3.13 (m, 1H, P(C*H*Me$_c$Me$_d$)), 2.34 (s, 6H, NMe$_2$), 2.06 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.90 (d of d, $^3J_{PH}$ = 18.2 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.54 (s, 15H, C$_5$*Me$_5$*), 1.37 (d of d, $^3J_{PH}$ = 16.7 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_d$*Me$_c$)), 1.16 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, P(CH*Me$_b$*Me$_a$)), 0.63 (d of d, $^3J_{PH}$ = 16.8 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me$_a$*Me$_b$)); ^{13}C{^{1}H} NMR (C_6D_6): δ 132.5 (C7), 126.8 (C4), 125.0 (C5 or C6), 123.1 (C6 or C5), 118.9 (d, $^2J_{PC}$ = 8.4 Hz, C2), 89.3 (C3a or C7a), 89.2 (C7a or C3a), 78.2 (*C*$_5$Me$_5$), 63.6 (d, $^1J_{PC}$ = 77.2 Hz, C3), 58.8 (d, $^3J_{PC}$ = 7.0 Hz, C1), 48.2 (NMe$_2$), 30.5 (d, $^1J_{PC}$ = 50.3 Hz, P(*C*HMe$_c$Me$_d$)), 29.5 (d, $^1J_{PC}$ = 24.6 Hz, P(*C*HMe$_a$Me$_b$)), 20.8 (P(CH*Me*Me)), 17.8 (P(CH*Me*Me)), 17.4 (P(CH*Me*Me)), 17.3 (P(CH*Me*Me)), 10.1 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (C_6D_6): δ 65.2. Crystals of **3-1c** suitable for single-crystal X-ray diffraction analysis were grown from pentane at -35 °C.

3.4.5 Protocol for the Reduction of 3-1a to 3-2a Using $Cl_3SiSiCl_3$

Employing a modification of a literature procedure for the reduction of phosphine sulfides,[66, 67] within the glovebox a solution of **3-1a** (0.063 g, 0.14 mmol) in toluene (3 mL) was transferred to a re-sealable reaction vessel charged with a stir bar. A solution of hexachlorodisilane (0.053 g, 0.20 mmol) in toluene (2 mL) was then transferred to the reaction vessel via Pasteur pipette and the vessel was sealed. The reaction vessel was then transferred from the glovebox to a Schlenk line, covered with aluminum foil, and heated at 85 °C in an oil bath. The progress of the reaction was monitored (^{31}P NMR), and complete conversion to a single phosphorus-containing product with a signal at -1.9 ppm was achieved after 14 d. The resulting reaction mixture was then filtered through Celite, and the solvent of the filtrate was removed *in vacuo*. The residue was extracted into pentane (3 mL) and filtered through Celite. Storage of the filtrate at -35 °C resulted in the crystallization of **3-2a** as an analytically pure orange-yellow solid (0.033 g, 0.080 mmol, 56 %). Crystals suitable for single crystal X-ray diffraction analysis were grown from a concentrated pentane solution at -35 °C. Anal. Calcd. for $C_{20}H_{25}PNO_3Mn$: C: 58.12, H: 6.10, N: 3.39; Found: 57.95, H: 6.47, N: 3.33. ^{1}H NMR (C_6D_6): δ 7.59 (d, $^3J_{HH}$ = 6.5 Hz, 1H, C4-H or C7-7), 7.23 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C7-H or C4-H), 6.77 (m, 2H, C5-H and C6-H), 4.49 (s, 1H, C1-H), 2.92 (br m, 1H, C*H*Me$_2$), 2.61 (s, 6H, NMe$_2$), 2.29 (br m, 1H, C*H*Me$_2$), 1.69 (br d, J = 16.0 Hz, 3H, CH*Me*$_2$), 1.25 (br s, 3H, CH*Me*$_2$), 1.09 (br d, J = 15.5 Hz, 3H, CH*Me*$_2$), 0.56 (br s, 3H, CH*Me*$_2$); ^{13}C{^{1}H} NMR (C_6D_6): δ 225.1 (CO), 140.0 (C2), 126.2, 126.0, 125.4, 125.0 (C4, C5, C6, C7), 105.0 (C3a or C7a), 98.8 (C7a or C3a), 67.4 (d, $^1J_{PC}$ = 44.2 Hz, C3), 61.8 (C1), 43.9 (d, $^4J_{PC}$ = 15.7 Hz, NMe$_2$), 25.5 (d, $^1J_{PC}$ = 12.3 Hz, *C*HMe$_2$), 23.4 (d, $^2J_{PC}$ = 24.8 Hz, CH*Me*$_2$), 22.9-22.5 (m, CH*Me*$_2$ and

$CHMe_2$), 20.9-20.4 (m, 2 $CHMe_2$); $^{31}P\{^1H\}$ NMR (C_6D_6): δ -1.9; FTIR (cm^{-1}) ν(CO): 2010, 1926, 1905.

3.4.6 Protocol for the Reduction of 3-1a to 3-2a Using Cp_2ZrHCl

Employing a modification of a literature procedure for the reduction of phosphine sulfides,[68, 69] within the glove-box, to a solution of **3-1a** (0.13 g, 0.29 mmol) in THF (5 mL) was added 3 equiv of Cp_2ZrHCl, followed by stirring for 18 h. Analysis of the reaction mixture (^{31}P NMR) revealed the incomplete conversion of **3-1a** to **3-2a**. The reaction mixture was filtered through Celite, an additional 3 equiv of Cp_2ZrHCl was added to the fitrate, and the mixture was stirred magnetically for an additional 24 h. Analysis of the reaction mixture (^{31}P NMR) at this stage revealed the quantitative conversion to **3-2a**. The reaction mixture was filtered through Celite, and the solvent was removed *in vacuo*. The residue was taken up in pentane or hexanes (10 mL) and filtered through Celite, followed by removal of the solvent *in vacuo*, affording **3-2a** (0.10 g, 0.24 mmol, 83 %).

3.4.7 Synthesis of 3-2b

A glass vial charged with a stirbar, excess lithiated **1-3a** (1.1 mmol), and THF (2 mL) was cooled to -35 °C. A separate vial charged with $[Cp^*RuCl]_4$ (0.24 g, 0.22 mmol) and diethyl ether (2 mL) was cooled to -35 °C, and subsequently was added slowly to the indenyl lithium. The resulting mixture was stirred magnetically at ambient temperature for 18 h. The solvent and other volatile materials were removed *in vacuo*, and the residue was taken up in a mixture of pentane (5 mL) and diethyl ether (2 mL) and passed through a Florisil column and eluted with pentane. The filtrate was then concentrated and dried *in*

vacuo affording analytically pure **3-2b** as a yellow solid (0.33 g, 0.65 mmol, 74 %). Anal. Calcd. for $C_{27}H_{40}PNRu$: C 63.50; H 7.89; N 2.74. Found: C 63.25; H 7.99; N 2.74. ^1H NMR (C_6D_6): δ 7.55 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7-H or C4-H), 6.94 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C4-H or C7-H), 6.86-6.81 (m, 2H, C5-H and C6-H), 4.67 (s, 1H, C1-H), 2.58 (s, 6H, NMe_2), 2.57-2.43 (m, 2H, P(C*H*$Me_c$$Me_d$) and P(C*H*$Me_a$$Me_b$)), 1.57 (s, 15H, C_5*Me*$_5$), 1.36 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_c$$Me_d$)), 1.33-1.25 (m, 6H, P(CH*Me*$_a$*Me*$_b$)), 1.18 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me*$_d$$Me_c$)); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 128.0 (C4 or C7), 127.3 (d, $^2J_{PC}$ = 6.5 Hz, C2), 124.7 (C7 or C4), 121.9 (C5 or C6), 120.6 (C6 or C5), 94.0 (d, J_{PC} = 10.1 Hz, C3a or C7a), 91.3 (C7a or C3a), 82.1 (C_5Me_5), 70.6 (d, $^1J_{PC}$ = 31.8 Hz, C3), 63.3 (C1), 46.8 (d, $^4J_{PC}$ = 6.7 Hz, NMe_2), 24.3 (d, $^1J_{PC}$ = 13.1 Hz, P(*C*H$Me_c$$Me_d$)), 23.7 (d, $^1J_{PC}$ = 13.1 Hz, P(*C*H$Me_a$$Me_b$)), 23.3 (d, $^2J_{PC}$ = 23.1 Hz, P(CH*Me*$_d$$Me_c$)), 22.9 (d, $^2J_{PC}$ = 20.8 Hz, P(CHMe_a*Me*$_b$)), 21.5 (d, $^2J_{PC}$ = 18.9 Hz, P(CH*Me*$_a$$Me_b$)), 20.7 (d, $^2J_{PC}$ = 11.1 Hz, P(CHMe_d*Me*$_c$)), 10.8 (C_5*Me*$_5$); $^{31}P\{^1H\}$ NMR (C_6D_6): δ -0.3. Crystals of **3b** suitable for single-crystal X-ray diffraction analysis were grown from pentane at -35 °C.

3.4.8 Synthesis of 3-2c

A vial charged with a stirbar, and a solution of Cp*FeCl (1.10 mmol) in THF (2 mL) (prepared in a manner analogous to that described for the synthesis of **3-1c**), was cooled to -35 °C. To this solution was added slowly a solution of lithiated **1-3a** (1.1 mmol) and THF (2 mL) (pre-cooled to -35 °C), and the mixture was stirred magnetically at ambient temperature for 2 h. The solvent and other volatile materials were removed *in vacuo* and the residue was taken up in pentane (5 mL) followed by filtration through a short plug of Celite. The filtrate was collected, and the solvent and other volatile materials were

removed *in vacuo*. Any decamethylferrocene that was produced during the synthesis was then removed by sublimation to leave **3-2c** as an analytically pure, purple solid (0.31 g, 0.68 mmol, 62 %). Anal. Calcd. for $C_{27}H_{40}PNFe$: C 69.57; H 8.66; N 3.01. Found: C 69.57; H 8.50; N 2.96. ^{1}H NMR (C_6D_6): δ 7.77 (d, $^3J_{HH}$ = 8.4 Hz, 1H, C7-H or C4-H), 7.22 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4-H or C7-H), 6.95-7.02 (m, 2H, C5-H and C6-H), 4.24 (s, 1H, C1-H), 2.63 (s, 6H, NMe_2), 2.53-2.62 (m, 2H, P(C*H*$Me_c$$Me_d$) and P(C*H*$Me_a$$Me_b$)), 1.58 (s, 15H, C_5*Me_5*), 1.58 (d of d, $^3J_{PH}$ = 10.3 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me_a*Me_b)), 1.30 (d of d, $^3J_{PH}$ = 13.7 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me_b*Me_a)), 1.19 (d of d, $^3J_{PH}$ = 11.3 Hz, $^3J_{HH}$ = 7.4 Hz, 3H, P(CH*Me_c*Me_d)), 1.15 (d of d, $^3J_{PH}$ = 7.1 Hz, $^3J_{HH}$ = 2.6 Hz, 3H, P(CH*Me_d*Me_c)); ^{13}C{^{1}H} NMR (C_6D_6): δ 130.1 (C4 or C7), 123.5 (C5 or C6), 122.3 (C6 or C5), 120.6 (d, $^2J_{PC}$ = 4.4 Hz, C2), 89.8 (d, J_{PC} = 12.2 Hz, C3a or C7a), 87.8 (C7a or C3a), 76.8 (C_5Me_5), 63.3 (d, $^1J_{PC}$ = 31.1 Hz, C3), 75.7 (C1), 46.3 (d, $^4J_{PC}$ = 6.4 Hz, NMe_2), 23.6 (d, $^1J_{PC}$= 25.7 Hz, P(CH*Me_c*Me_d) or P(CHMe_c*Me_d*)), 23.3 (d, $^1J_{PC}$= 13.8 Hz, P(*C*H$Me_a$$Me_b$) or P(*C*H$Me_c$$Me_d$)), 22.9 (d, $^1J_{PC}$= 11.9 Hz, (P(*C*H$Me_d$$Me_c$) or P(*C*H$Me_a$$Me_b$)), 22.7 (d, $^2J_{PC}$= 4.0 Hz, P(CHMe_c*Me_d*) or P(CH*Me_c*Me_d)), 21.5 (d, $^2J_{PC}$= 19.1 Hz, P(CH*Me_b*Me_a)), 20.2 (d, $^2J_{PC}$= 8.0 Hz, P(CHMe_b*Me_a*)), 10.2 (C_5Me_5); ^{31}P{^{1}H} NMR (C_6D_6): δ -2.5.

3.4.9 Synthesis of 3-3b

To a glass vial containing a magnetically stirred suspension of $[(COD)RhCl]_2$ (0.025 g, 0.050 mmol) in THF (2 mL) was added a suspension of $AgBF_4$ (0.020 g, 0.10 mmol) in THF (2 mL). A yellow solution was generated immediately along with a white precipitate. The supernatant solution was separated from the precipitate by filtration through Celite, and the solution was transferred to a glass vial containing a magnetically

stirred solution of **3-2b** (0.051 g, 0.10 mmol) in THF (3 mL). The reaction mixture was stirred for an additional 3 h at ambient temperature, during which time the solution developed a yellow-orange coloration. The reaction mixture was then filtered through a plug of Celite, followed by removal of the solvent and other volatiles *in vacuo* yielding **3-3b** as an analytically pure orange solid (0.078 g, 0.096 mmol, 96 %). Anal. Calcd. for $C_{35}H_{52}PNRuRhBF_4$: C 51.96; H 6.48; N 1.73. Found: C 51.84; H 6.45; N 1.75. ^{1}H NMR (CD_2Cl_2): δ 7.19 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7-H or C4-H), 7.14-7.05 (m, 3H, aryl CHs), 5.42 (br s, 1H, COD), 5.19 (s, 1H, C1-H), 4.87 (m, 1H, COD), 4.53 (m, 1H, COD), 3.90 (m, 1H, COD), 3.21 (s, 3H, NMe), 2.80 (s, 3H, NMe), 2.75-2.20 (m, 9H, P(C*H*Me$_c$Me$_d$), P(C*H*Me$_a$Me$_b$), and COD), 2.01 (d of d, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.95 (m, 1H, COD), 1.63 (d of d, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 1.59 (s, 15H, C$_5$*Me$_5$*), 1.19 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.99 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 131.1 (d, $^2J_{PC}$ = 24.3 Hz, C2), 125.5 (C4 or C7), 125.0 (aryl CH), 124.6 (aryl CH), 124.0 (aryl CH), 106.7 (m, COD), 101.7 (m, COD), 97.0 (C3a or C7a), 88.2 (C7a or C3a), 84.9 (*C*$_5$Me$_5$), 76.1 (d, *J* = 12.7 Hz, COD), 69.7 (d, *J* = 12.0 Hz, COD), 69.2 (d, $^1J_{PC}$ = 32.5 Hz, C3), 60.8 (d, *J* = 8.8 Hz, C1) 55.1 (NMe), 54.0 (NMe), 34.4 (COD), 30.4 (COD), 26.2 (d, $^1J_{PC}$ = 23.0 Hz, P(*C*HMe$_c$Me$_d$)), 26.1 (COD), 25.5 (d, $^1J_{PC}$ = 25.8 Hz, P(*C*HMe$_a$Me$_b$)), 20.8 (P(CH*Me$_c$*Me$_d$)), 20.1 (P(CHMe$_a$*Me$_b$*)), 19.4 (P(CHMe$_c$*Me$_d$*)), 18.2 (P(CH*Me$_a$*Me$_b$)), 10.0 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 42.5 (d, $^1J_{PRh}$= 150.4 Hz).

3.4.10 Synthesis of 3-3a

A procedure analogous to that described for the synthesis of **3-3b** was employed, using **3-2a** (0.015 g, 0.037 mmol) in THF (1 mL). Complex **3-3a** was isolated as an analytically pure dark yellow solid (0.023 g, 0.032 mmol, 87 %). Anal. Calcd. for $C_{28}H_{37}PNMnO_3RhBF_4$: C 47.25; H 5.24; N 1.97. Found: C 47.41; H 5.62; N 1.83. ^{1}H NMR (CD_2Cl_2): δ 7.72 (d, $^3J_{HH}$ = 8.3 Hz, 1H, C7-H or C4-H), 7.49-7.42 (m, 2H, aryl CHs), 7.29 (t, $^3J_{HH}$ = 7.4 Hz, C6-H or C5-H), 6.05 (s, 1H, C1-H), 5.60 (br s, 1H, COD), 4.94 (br s, 1H, COD), 4.66 (br s, 1H, COD), 3.94 (br s, 1H, COD), 3.39 (s, 3H, NMe), 2.81 (s, 3H, NMe), 2.81-2.68 (m, 4H, P(C*H*Me$_c$Me$_d$), P(C*H*Me$_b$Me$_a$), and COD), 2.47 (m, 1H, COD), 2.39-2.31 (m, 2H, COD), 2.01-1.93 (m, 5H, COD and P(CHMe$_c$*Me$_d$*)), 1.89-1.85 (m, 4H, P(CH*Me$_c$*Me$_d$) and COD), 1.34 (d of d, $^3J_{PH}$ = 15.3 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 1.22 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me$_a$*Me$_d$)); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 223.2 (CO), 141.5 (d, $^2J_{PC}$ = 21.4 Hz, C2), 130.5 (aryl C), 129.1 (C4 or C7), 127.3 (C5 or C6), 122.8 (aryl C), 108.0 (t, J = 7.4 Hz, COD), 102.5 (COD), 100.9 (m, aryl C), 77.4 (d, J = 12.5 Hz, COD), 71.3 (d, J = 12.5 Hz, COD), 68.3 (d, $^3J_{PC}$ = 11.7 Hz, C1), 56.6 (NMe), 50.6 (NMe), 35.1 (COD), 30.6 (COD), 29.6 (COD), 27.6 (d, $^1J_{PC}$ = 22.6 Hz, P(*C*HMe$_c$Me$_d$) or P(*C*HMe$_a$Me$_b$)), 25.8 (P(*C*HMe$_a$Me$_b$) or P(*C*HMe$_c$Me$_d$)), 25.6 (COD), 22.7 (P(CH*Me$_a$*Me$_b$)), 20.1 (d, $^2J_{PC}$ = 3.2 Hz, (P(CHMe$_c$*Me$_d$*)), 19.3 (d, $^2J_{PC}$ = 3.5 Hz, P(CH*Me$_c$*Me$_d$)), 18.8 (P(CHMe$_a$*Me$_b$*)); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 44.5 (d, $^1J_{PRh}$= 151.8 Hz). FTIR (cm^{-1}) ν(CO): 2025, 1953, 1933.

3.4.11 Synthesis of 3-3c

A procedure analogous to that described for the synthesis of **3-3b** was employed, using **3-2c** (0.044 g, 0.095 mmol) in THF (2 mL). Complex **3-3c** was isolated as an

analytically pure dark purple solid (0.068 g, 0.089 mmol, 89 %). Anal. Calcd. for $C_{35}H_{52}PNFeRhBF_4$: C 55.04; H 6.87; N 1.83. Found: C 54.83; H 7.06; N 1.52. ^{1}H NMR (CD_2Cl_2): δ 7.50 (d, $^3J_{HH}$ = 5.3 Hz, 1H, C7-H or C4-H), 7.34 (m, 1H, aryl CH), 7.31-7.27 (m, 2H, aryl CHs), 5.42 (br s, 1H, COD), 4.93 (s, 1H, C1-H), 4.80 (m, 1H, COD), 4.62 (m, 1H, COD), 4.07 (m, 1H, COD), 3.06 (s, 3H, NMe), 2.98-2.91 (m, 4H, NMe and P(C*H*Me$_c$Me$_d$)), 2.67 (m, 1H, COD), 2.52 (m, 3H, COD), 2.36 (m, 2H, COD and P(C*H*Me$_b$Me$_a$)), 2.26 (m, 2H, COD), 2.11 (d of d, $^3J_{PH}$ = 15.9 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 2.04 (m, 1H, COD), 1.74 (d of d, $^3J_{PH}$ = 23.4 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.60 (s, 15H, C_5Me_5), 1.21 (d of d, $^3J_{PH}$ = 15.1 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.78 (d of d, $^3J_{PH}$ = 16.1 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CH*Me$_a$*Me$_b$)); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 128.5 (C4 or C7), 127.3 (aryl C), 126.1 (aryl C), 125.9 (aryl C), 105.5 (t, *J* = 8.4 Hz, COD), 102.2 (t, *J* = 10.0 Hz, COD), 94.2 (quat), 83.6 (quat), 79.3 (*C*$_5$Me$_5$), 75.5 (d, *J* = 12.4 Hz, COD), 71.8 (d, *J* = 12.3 Hz, COD), 55.8 (d, *J* = 8.9 Hz, C1), 55.6 (NMe), 52.1 (NMe), 33.6 (COD), 31.0 (COD), 29.7 (COD), 27.1-26.6 (P(*C*HMe$_c$Me$_d$), P(*C*HMe$_a$Me$_b$), and COD), 22.0 (P(CHMe$_c$*Me$_d$*)), 20.6 (P(CH*Me$_a$*Me$_b$)), 19.9 (P(CH*Me$_c$*Me$_d$)), 19.5 (P(CHMe$_a$*Me$_b$*)), 9.9 (C$_5$*Me$_5$*); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 43.8 (d, $^1J_{PRh}$ = 150.0 Hz). Crystals of **3-3c** suitable for single-crystal X-ray diffraction analysis were grown from THF at -35 °C.

3.4.12 Synthesis of 3-4b

To a glass vial charged with a stirbar, **3-2b** (0.12 g, 0.24 mmol), and THF (2 mL), was added a solution of [(COD)RhCl]$_2$ (0.059 g, 0.12 mmol) in THF (4 mL). The mixture was stirred for 4 h at ambient temperature, and during this time a precipitate formed. The supernatant was decanted, and the precipitate washed with THF (5 mL). The residue was

then dried *in vacuo*, affording **3-4b** as an analytically pure yellow solid (0.088 g, 0.12 mmol, 49 %). Anal. Calcd. for $C_{35}H_{52}PNRuRhCl$: C 55.50; H 6.92; N 1.85. Found: C 55.22; H 6.77; N 1.53. ^{1}H NMR (CD_2Cl_2): δ 7.17 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7-H or C4-H), 7.12-7.00 (m, 3H, aryl CHs), 5.38 (br s, 1H, COD), 5.24 (s, 1H, C1-H), 4.82 (br s, 1H, COD), 4.55 (br s, 1H, COD), 3.84 (br s, 1H, COD), 3.20-2.80 (br. m, 6H, NMe_2), 2.69-2.45 (m, 4H, P(C*H*Me_cMe_d), P(C*H*Me_aMe_b) and COD), 2.40-2.21 (m, 4H, COD), 1.96 (d of d, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 17.5 Hz, 3H, P(CH*Me*$_d$Me$_c$)), 1.99-1.82 (m, 2H, COD), 1.59 (d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 14.0 Hz, 3H, P(CHMe$_d$*Me*$_c$)), 1.55 (s, 15H, C_5Me_5), 1.15 (d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 15.0 Hz, 3H, P(CH*Me*$_b$Me$_a$)), 0.94 (d of d, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 17.5 Hz, 3H, P(CHMe$_b$*Me*$_a$)); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 131.2 (d, $^2J_{PC}$ = 24.3 Hz, C2), 125.4 (C7 or C4), 125.0 (aryl C), 124.5 (aryl C), 123.9 (aryl C), 106.6 (br s, COD), 101.8 (br s, COD), 96.9 (d, J_{PC} = 3.9 Hz, C3a or C7a), 88.1 (C7a or C3a), 84.8 (*C*$_5$Me$_5$), 76.2 (m, COD), 69.6 (COD), 69.2 (d, $^1J_{PC}$ = 52.5 Hz, C3), 61.1 (d, $^3J_{PC}$ = 8.8 Hz, C1), 54.8 (br s, NMe_2) 34.4 (br s, COD), 30.4 (br s, COD), 26.2-26.1 (P(*C*HMe_aMe_b) and COD), 25.5 (d, $^1J_{PC}$ = 26.0 Hz, P(*C*HMe_cMe_d)), 20.8 (P(CH*Me*$_d$Me$_c$)), 20.1 (d, $^2J_{PC}$ = 4.0 Hz, P(CH*Me*$_a$Me$_b$)), 19.4 (d, $^2J_{PC}$ = 3.7 Hz, P(CHMe$_d$*Me*$_c$)), 18.2 (P(CHMe$_a$*Me*$_b$)), 10.1 (C_5*Me*$_5$); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 42.4 (d, $^1J_{PRh}$= 150.6 Hz).

3.4.13 Synthesis of 3-5b

A glass vial charged with a stirbar, 3-P^{i}Pr$_2$-indene (0.30 g, 1.29 mmol), and THF (3 mL) was cooled to -35 °C. To this vial was added dropwise by Eppendorf pipette a 1.6 M hexanes solution of *n*-BuLi (0.81 mL, 1.29 mmol; pre-cooled to -35 °C), after which the mixture was stirred magnetically for 1 h at ambient temperature. The reaction mixture was then cooled to -35 °C. A solution of $[Cp^*RuCl]_4$ (0.35 g, 0.32 mmol) in THF (2 mL)

(pre-cooled to -35 °C) was added. The mixture was stirred magnetically at ambient temperature for 18 h, after which the solvent was removed *in vacuo*, and the residue was taken up in diethyl ether (5 mL) followed by filtration through a plug of Celite. The filtrate was then concentrated and dried *in vacuo*, affording **3-5b** as an analytically pure, dark yellow solid (0.59 g, 1.26 mmol, 98 %). Anal. Calcd. for $C_{25}H_{35}PRu$: C 64.20; H 7.55; N 0.00. Found: 64.19; H 7.35; N < 0.3. ^{1}H NMR (C_6D_6): δ 7.52 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C4-H or C7-H), 6.95 (d, $^3J_{HH}$ = 8.2 Hz, 1H, C7-H or C4-H), 6.80-6.75 (m, 2H, C5-H and C6-H), 4.69 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C1-H), 4.44 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C2-H), 2.25 (m, 1H, P(C*H*MeMe)), 1.85 (m, 1H, P(C*H*MeMe)), 1.53 (s, 15H, C_5Me_5), 1.42 (d of d, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me*Me)), 1.23 (apparent t, J = 7.3 Hz, 3H, P(CH*Me*Me)), 1.08 (d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)), 1.08 (d of d, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)); ^{13}C{^{1}H} NMR (C_6D_6): δ 126.2 (d, J_{PC} = 8.0 Hz, aryl C), 124.7 (aryl C), 121.8 (aryl C), 120.3 (aryl C), 96.4 (d, J = 23.2 Hz, C3a or C7a), 94.0 (d, J = 2.9 Hz, C7a or C3a), 82.3 (C_5Me$_5$), 77.7 (d, $^2J_{PC}$ = 4.6 Hz, C2), 76.5 (d, $^1J_{PC}$ = 21.3 Hz, C3), 70.5 (C1), 25.3 (d, $^1J_{PC}$ = 15.7 Hz, P(*C*HMeMe)), 24.0 (d, $^2J_{PC}$ = 28.6 Hz, P(CH*Me*Me)), 23.4 (d, $^1J_{PC}$ = 11.2 Hz, P(*C*HMeMe)), 21.1 (d, $^2J_{PC}$ = 20.8 Hz, P(CHMe*Me*)), 20.4 (d, $^2J_{PC}$ = 12.0 Hz, P(CHMe*Me*)), 19.5 (P(CHMe*Me*)), 10.3 (C_5Me_5); ^{31}P{^{1}H} NMR (C_6D_6): δ -10.4.

3.4.14 Synthesis of 3-5c

A glass vial charged with a stirbar, 3-P^{i}Pr$_2$-indene (0.13 g, 0.56 mmol), and THF (2 mL) was cooled to -35 °C. To this vial was added dropwise by Eppendorf pipette a 1.6 M hexanes solution of *n*-BuLi (0.35 mL, 0.56 mmol; pre-cooled to -35 °C), after which the mixture was stirred magnetically for 1 h at ambient temperature. This mixture was

cooled to -35 °C, and then was transferred slowly to a vial containing a solution of Cp*FeCl (0.56 mmol) in THF (2 mL) (prepared in a manner analogous to that described for the synthesis of **3-1c**), that had been pre-cooled to -35 °C. After the mixture had been stirred magnetically at ambient temperature for 2 h, the solvent and other volatile materials were removed *in vacuo*, and the residue was taken up in pentane (5 mL) followed by filtration through a short plug of Celite. The filtrate was then passed through a short Florisil plug, and the plug was washed with additional pentane (10 mL). The combined pentane eluents were then concentrated and dried *in vacuo*. Any decamethylferrocene that was produced during the synthesis was then removed by sublimation to leave **3-5c** as an analytically pure, purple-brown (0.10 g, 0.24 mmol, 43 %). Anal. Calcd. for $C_{25}H_{35}PFe$: C 71.07; H 8.36; N 0.00. Found: 71.29; H 8.21; N < 0.3. ^{1}H NMR (CD_2Cl_2): δ 7.73 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C4-H), 7.22 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7), 6.98-6.88 (m, 2H, C5-H and C6-H), 4.35 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C1-H), 3.74 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C2-H), 2.55 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.83 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.59 (s, 15H, C_5Me_5), 1.53 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 1.29 (apparent t, *J* = 6.5 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.13 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_b$*Me$_a$)), 0.80 (d of d, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_b$*Me$_a$*)); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 126.8 (d, $^3J_{PC}$ = 7.6 Hz, C4), 125.4 (C7), 121.4 (C6), 119.8 (C5), 90.6 (d, $^2J_{PC}$ = 20.5 Hz, C3a), 89.1 (d, $^4J_{PC}$ = 3.1 Hz, C7a), 75.5 (C_5Me$_5$), 73.6 (d, $^2J_{PC}$ = 3.7 Hz, C2), 69.9 (d, $^1J_{PC}$ = 20.5 Hz, C3), 66.6 (C1), 22.9 (d, $^1J_{PC}$ = 16.6 Hz, P(*C*HMeMe)), 22.1 (d, $^2J_{PC}$ = 30.4 Hz, P(CH*Me$_d$*Me$_c$)), 21.1 (d, $^1J_{PC}$ = 12.1 Hz, P(*C*HMeMe)), 19.9 (d, $^2J_{PC}$ = 22.2 Hz, P(CH*Me$_b$*Me$_a$)), 19.2 (d, $^2J_{PC}$ = 12.2 Hz, P(CHMe$_b$*Me$_a$*)), 17.3 (P(CH*Me$_c$*Me$_d$)), 8.0 (C_5Me_5); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ -12.4.

3.4.15 Synthesis of 3-6

A glass vial was charged with a stirbar, **3-5b** (0.10 g, 0.22 mmol), and THF (2 mL). To this vial was added a solution of $[(COD)RhCl]_2$ (0.054 g, 0.11 mmol) in THF (4 mL). The mixture was stirred for 2 h at ambient temperature, after which the solvent and other volatile materials were removed *in vacuo*. To the residual solid was added pentane (5 mL), and the mixture was filtered though a plug of Celite. The filtrate was collected and dried *in vacuo*, affording **3-6** as an analytically pure, yellow-orange solid (0.15 g, 0.21 mmol, 96 %). Anal. Calcd. for $C_{33}H_{47}PRuRhCl$: C 55.48; H 6.64; N 0.00. Found: 55.66; H 6.39; N < 0.3. ^{1}H NMR (C_6D_6): δ 8.36 (br s, 1H, C4-H or C7-H), 6.88-6.83 (m, 3H, aryl CHs), 5.77 (br s, 1H, COD), 5.71 (m, 1H, COD), 4.46 (d, $^3J_{HH}$ = 2.4 Hz, 1H, C2-H), 4.31 (br s, 1H, C1-H), 3.87 (br s, 1H, COD), 3.75 (br s, 1H, COD), 2.94 (m, 1H, P(C*H*Me_aMe_b)), 2.64 (m, 1H, P(C*H*Me_cMe_d)), 2.25-2.20 (m, 3H, COD), 2.09 (m, 1H, COD), 1.74-1.58 (m, 9H, COD and P(CH*Me_cMe_d*)), 1.44 (s, 15H, C_5*Me_5*), 1.40 (d of d, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me_a*Me_b)), 1.33 (m, 1H, COD), 0.95 (m, 3H, P(CHMe_a*Me_b*)); ^{13}C{^{1}H} NMR (C_6D_6): δ 128.0 (C4 or C7), 124.5 (aryl C), 122.7 (aryl C), 120.9 (aryl C), 102.3-101.9 (m, COD), 95.0 (d, $^2J_{PC}$ = 11.6 Hz, C3a), 94.6 (d, $^3J_{PC}$ = 5.6 Hz, C7a), 82.9 (*C*$_5$Me$_5$), 80.9 (C1), 71.6 (d, $^2J_{PC}$ = 4.2 Hz, C2), 68.9 (d, $^1J_{RhC}$ = 13.5 Hz, COD), 68.6 (d, , $^1J_{RhC}$ = 13.1 Hz, COD), 33.6 (COD), 32.9 (COD), 28.9 (COD), 27.9 (COD), 27.0 (m, P(*C*HMe_aMe_b) and P(*C*HMe_cMe_d)), 21.4 (P(CH*Me_cMe_d*)), 20.8 (P(CHMe_a*Me_b*)), 20.1 (P(CHMe_c*Me_d*)), 19.0 (br s, P(CH*Me_a*Me_b)), 10.3 (C_5*Me_5*); ^{31}P{^{1}H} NMR (C_6D_6): δ 28.2 (d, $^1J_{RhP}$ = 142.1 Hz).

3.4.16 General Protocol for Hydroboration Experiments

The protocols employed are based on those described by Crudden and co-workers.[57] A solution of catalyst compound in the desired solvent (0.019 mmol in 0.95 mL to give a 0.02 M solution) was allowed to equilibrate for 5 min within a reaction vial containing a stirbar, at which point styrene (0.38 mmol) was added to the vial using an Eppendorf pipette. The vial was then sealed with a PTFE-lined cap and stirred for 10 min. Subsequently, pinacolborane (0.46 mmol) was added to the reaction mixture using an Eppendorf pipette, the vial was re-sealed. The reaction mixture was stirred magnetically at 24 °C for 24 h. After this time, the reaction mixture was concentrated *in vacuo*, and hexanes (1 mL) was added to the residue. The resultant mixture was then filtered through a short silica gel column (0.6 cm x 5 cm) and eluted with 5 mL of a 20:1 hexanes:ethyl acetate solution. The eluted colorless solution was concentrated, and the residue was taken up in diethyl ether (4 mL). To convert the boronate ester products to the corresponding alcohols, the diethyl ether solution was cooled to 0 °C and NaOH (1 mL of a 3 N aqueous solution) was added, followed by H_2O_2 (1 mL of a 30 % aqueous solution). After stirring at 0 °C for 1 h, then at ambient temperature for 1-2 h, the reaction mixture was diluted with diethyl ether (~ 4 mL) and distilled water (~ 5 mL). The organic layer was separated and retained, and the aqueous layer extracted with diethyl ether (2 x 4 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and partially concentrated. This resulting solution was then transferred to a GC vial and sealed. Quantitative data for the derived alcohols were obtained from GC-FID analysis. Tabulated data represent the average of at least two runs. GC-FID method: temperature

control, 80 °C for 15 min., then increased by 10 °C/min. to 180 °C, 180 °C for 5 min. Column: Supelco 30 m x 0.25 mm BETA-DEX 120, film thickness 0.25 μm. He flowrate: 15 psi.

3.4.17 Crystallographic Characterization of 3-1a, 3-1b, 3-1c, 3-2a, and 3-2b

Crystallographic data for each of these complexes was obtained by Dr. R. McDonald and Dr. M. J. Ferguson at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and multi-scan absorption correction (including SAINT and SADABS) were supplied by Bruker. The structures were solved by use of direct methods in the case of **3-1c**, **3-2a** and **3-2b**, or a Patterson search/structure expansion in the case of **3-1a** and **3-1b**, and refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-H atoms, and all H-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional crystallographic information is provided in the accompanying CIF. Crystal structure diagrams were generated by use of the ORTEP-3 for Windows program.[70]

3.4.18 Crystallographic Characterization of 3-3c and 3-6

Crystallographic data for each of these complexes was obtained by Dr. G. Schatte

at 173(±2) K on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Cell parameters were retrieved initially by using the COLLECT software (Nonius), and refined with the HKL DENZO and SCALEPACK software.[71] Data reduction and absorption correction were also performed with the HKL DENZO and SCALEPACK software. The structures were solved by using the direct methods package in SIR-97,[72] and refined by use of the SHELXL97-2 program,[73] employing full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms. All H-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Crystal structure diagrams were generated by use of the ORTEP-3 for Windows program.[70]

3.5 References

1. Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320.
2. Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079.
3. Tanaka, M. *Top. Curr. Chem.* **2004**, *232*, 25.
4. Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1999**, *43*, 197.
5. Han, L. B.; Tanaka, M. *Chem. Commun.* **1999**, 395.
6. Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957.
7. Cipot, J.; Vogels, C. M.; McDonald, R.; Westcott, S. A.; Stradiotto, M. *Organometallics* **2006**, *25*, 5965.

8. Cipot, J.; McDonald, R.; Stradiotto, M. *Organometallics* **2006**, *25*, 29.

9. Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Schatte, G.; Stradiotto, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 4732.

10. Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 4981.

11. Wile, B. M.; Burford, R. J.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2006**, *25*, 1028.

12. Wile, B. M.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2007**, *26*, 1069.

13. Cipot, J.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Organometallics* **2007**, *26*, 594.

14. Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 10291.

15. Bradley, C. A.; Keresztes, I.; Lobkovsky, E.; Young, V. G.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 16937.

16. Zargarian, D. *Coord. Chem. Rev.* **2002**, *233*, 157.

17. Stradiotto, M.; McGlinchey, M. J. *Coord. Chem. Rev.* **2001**, *219*, 311.

18. Lobanova, I. A.; Zdanovich, V. I. *Russ. Chem. Rev.* **1988**, *57*, 967.

19. Arrayas, R. G.; Adrio, J.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 7674.

20. Barbaro, P.; Bianchini, C.; Giambastiani, G.; Parisel, S. L. *Coord. Chem. Rev.* **2004**, *248*, 2131.

21. Atkinson, R. C. J.; Gibson, V. C.; Long, N. J. *Chem. Soc. Rev.* **2004**, *33*, 313.

22. Dai, L. X.; Tu, T.; You, S. L.; Deng, W. P.; Hou, X. L. *Acc. Chem. Res.* **2003**, *36*, 659.

23. Colacot, T. J. *Chem. Rev.* **2003**, *103*, 3101.

24. Togni, A. *Angew. Chem. Int. Ed.* **1996**, *35*, 1475.

25. Englert, U.; Hu, C.; Salzer, A.; Alberico, E. *Organometallics* **2004**, *23*, 5419.

26. Gibson, S. E.; Ibrahim, H. *Chem. Commun.* **2002**, 2465.

27. Bolm, C.; Muniz, K. *Chem. Soc. Rev.* **1999**, *28*, 51.

28. Arrayas, R. G.; Mancheno, O. G.; Carretero, J. C. *Chem. Commun.* **2004**, 1654.

29. Jones, G.; Butler, D. C. D.; Richards, C. J. *Tetrahedron Lett.* **2000**, *41*, 9351.

30. Gavrilov, K. N.; Tsarev, V. N.; Konkin, S. I.; Loim, N. M.; Petrovskii, P. V.; Kelbyscheva, E. S.; Korlyukov, A. A.; Antipin, M. Y.; Davankov, V. A. *Tetrahedron: Asymmetry* **2005**, *16*, 3224.

31. Lee, J. H.; Son, S. U.; Chung, Y. K. *Tetrahedron: Asymmetry* **2003**, *14*, 2109.

32. Son, S. U. K.; Park, K. H.; Lee, S. J.; Chung, Y. K.; Sweigart, D. A. *Chem. Commun.* **2001**, 1290.

33. Kudis, S.; Helmchen, G. *Angew. Chem. Int. Ed.* **1998**, *37*, 3047.
34. Bolm, C.; Xiao, L.; Kesselgruber, M. *Org. Biomol. Chem.* **2003**, *1*, 145.

35. Bolm, C.; Xiao, L.; Hintermann, L.; Focken, T.; Raabe, G. *Organometallics* **2004**, *23*, 2362.

36. Liu, D. L.; Xie, F.; Zhang, W. B. *Tetrahedron Lett.* **2007**, *48*, 585.

37. Hayashi, T.; Ohno, A.; Lu, S. J.; Matsumoto, Y.; Fukuyo, E.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 4221.

38. Abbenhuis, H. C. L.; Burckhardt, U.; Gramlich, V.; Martelletti, A.; Spencer, J.; Steiner, I.; Togni, A. *Organometallics* **1996**, *15*, 1614.

39. Delacroix, O.; Gladysz, J. A. *Chem. Commun.* **2003**, 665.

40. Cipot, J.; Wechsler, D.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 1737.

41. Thimmaiah, M.; Luck, R. L.; Fang, S. Y. *J. Organomet. Chem.* **2007**, *692*, 1956.

42. Adams, J. J.; Curnow, O. J.; Fern, G. M. *Inorg. Chim. Acta* **2006**, *359*, 3596.

43. Curnow, O. J.; Fern, G. M.; Hamilton, M. L.; Jenkins, E. M. *J. Organomet. Chem.* **2004**, *689*, 1897.

44. Kamigaito, M.; Watanabe, Y.; Ando, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2002**, *124*, 9994.

45. Adams, J. J.; Curnow, O. J.; Huttner, G.; Smail, S. J.; Turnbull, M. M. *J. Organomet. Chem.* **1999**, *577*, 44.

46. Stradiotto, M.; Kozak, C. M.; McGlinchey, M. J. *J. Organomet. Chem.* **1998**, *564*, 101.

47. Plenio, H.; Burth, D. *Z. Anorg. Allg. Chem.* **1996**, *622*, 225.

48. Plenio, H.; Burth, D. *Organometallics* **1996**, *15*, 1151.

49. Corbet, J. P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651.

50. de Vries, J. G.; Lefort, L. *Chem. Eur. J.* **2006**, *12*, 4722.

51. Jerphagnon, T.; Renaud, J. L.; Bruneau, C. *Tetrahedron: Asymmetry* **2004**, *15*, 2101.

52. Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131.
53. Komarov, I. V.; Borner, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 1197.

54. Cipot, J.; Wechsler, D.; Stradiotto, M.; McDonald, R.; Ferguson, M. J. *Organometallics* **2003**, *22*, 5185.

55. Carroll, A. M.; O'Sullivan, T. P.; Guiry, P. J. *Adv. Synth. Catal.* **2005**, *347*, 609.

56. Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695.

57. Crudden, C. M.; Hleba, Y. B.; Chen, A. C. *J. Am. Chem. Soc.* **2004**, *126*, 9200.

58. Kloetzing, R. J.; Lotz, M.; Knochel, P. *Tetrahedron: Asymmetry* **2003**, *14*, 255.

59. Reetz, M. T.; Beuttenmuller, E. W.; Goddard, R.; Pasto, M. *Tetrahedron Lett.* **1999**, *40*, 4977.

60. Schnyder, A.; Hintermann, L.; Togni, A. *Angew. Chem. Int. Ed.* **1995**, *34*, 931.

61. Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.

62. Liu, S. Y.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 15352.

63. Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1998**, *17*, 773.

64. Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

65. Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618.

66. Zon, G.; DeBruin, K. E.; Naumann, K.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7023.

67. Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.

68. Yun, H. D. *Aust. J. Chem.* **2004**, *57*, 383.

69. Saito, M.; Nishibayashi, Y.; Uemura, S. *Organometallics* **2004**, *23*, 4012.

70. Farrugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

71. Otwinowski, Z.; Minor, W., *Processing of X-ray diffraction data collected in oscillation mode*, in *Macromolecular Crystallography, Pt A*. 1997, Academic Press Inc: San Diego. p. 307.

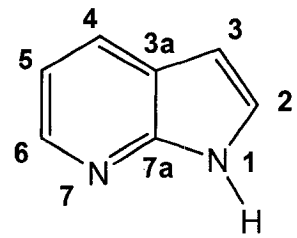
72. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

73. Sheldrick, G. M., *SHELXL97-2, Program for the Solution of Crystal Structures*. 1997: University of Göttingen, Göttingen, Germany.

Chapter Four: A New Chiral P,N-Ligand Derived from 7-Azaindole: Synthetic, Structural, and Catalytic Studies

4.1 Preamble: 7-Azaindole Numbering Convention

7-Azaindole ($C_7H_6N_2$) is a bicyclic organic molecule featuring a pyridine unit fused to a pyrrole ring (Figure 4-1). The numbering convention used in indole chemistry is very similar to that of indene (Section 2.1), whereby the one position is always assigned to the N atom in the five-membered ring.



7-Azaindole, $C_7H_6N_2$

Figure 4-1. Numbering convention used for 7-azaindole chemistry

4.2 Introduction

The pursuit of synthetic pathways producing enantiomerically pure products is a continual challenge. As described in Chapter One, the chemical community thought initially that man-made catalytic systems would be very ligand-to-substrate specific, but as it turns out, certain ligand sets can be useful for a range of applications, and several of these ligand families can be considered privileged structures (Figure 1-2).[1] Nevertheless, the development of new asymmetric catalysts is of great importance to improve processes that currently produce racemic mixtures and require a separation step to yield enantiomerically pure products. Heteroatomic bidentate ligands have been shown

to be a large contributor to the field of asymmetric catalysis;[2-8] in the context of late metal chemistry, the P,N ligand class is receiving a large amount of attention (P,N ligands containing planar chirality have been the subject of discussion in Chapter Three). These chiral bidentate ligands have proven effective in a multitude of enantioselective catalytic reactions, such as the hydroformylation, hydrogenation, and hydroboration of alkenes, as well as in palladium-catalyzed allylic alkylation.[2-8] One goal in the synthesis of catalytically active metal complexes is to prepare sets of versatile and modular ligands that can be applied to different transition metal-catalyzed processes. Examples of new classes of easily prepared, modular P,N-ligands include chiral phosphinooxazolines (PHOX)[8] and phosphinopyrrolyl-oxazolines (PyrPHOX)[8] (Figure 4-2). The latter class of ligands has been shown to be effective in palladium-catalyzed allylic alkylation with moderate to good enantioselectivity for certain substrates, while the iridium complexes of this ligand are highly efficient catalysts for the hydrogenation of olefins.[8]

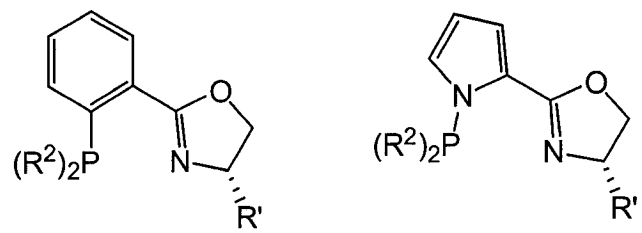


Figure 4-2. Generic structures of phosphinooxazoline (PHOX) and phosphinopyrrolyl-oxazoline (PyrPHOX) ligands.

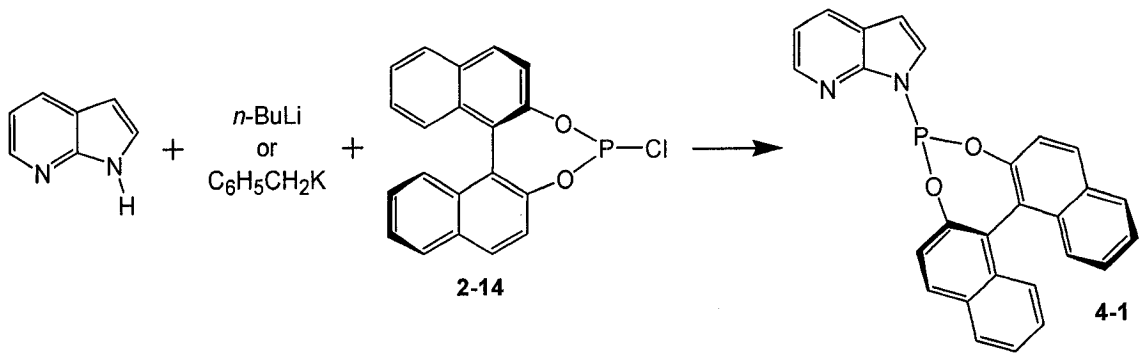
Within this chapter the synthesis of a new chiral P,N ligand derived from 7-azaindole is described. Also described is the use of this new ligand in the preparation of transition metal complexes (Rh, Ir, and Pd), and the application of these chiral complexes

as catalysts for the hydrosilylation of acetophenone with diphenylsilane (Rh), the hydrogenation of methyl-2-acetamidoacrylate (Rh and Ir), the hydroboration of styrene (Rh), and the allylic alkylation of 1,3-diphenylprop-2-enyl acetate (Pd). Notably, in the literature only two achiral P,N ligands based on 7-azaindole are reported,[9, 10] while no reports of such chiral P,N ligands exist.

4.3 Results and Discussion

4.3.1 Synthesis and Characterization of 4-1

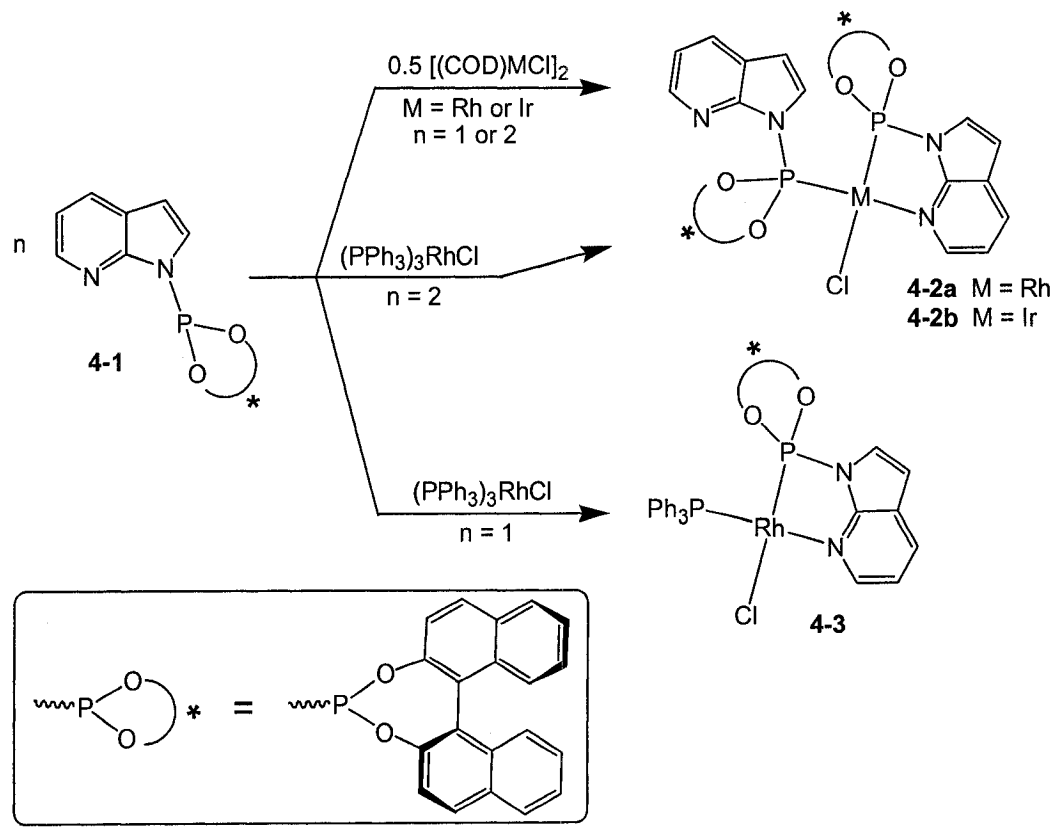
Treatment of 7-azaindole with *n*-BuLi or benzyl potassium followed by the slow addition of **2-14** resulted in the clean formation of **4-1**, which was obtained as an analytically pure white solid in 92 % yield (Scheme 4-1). The slow addition of **2-14** is required to prevent the formation of unwanted by-products such as the trimeric product **2-15** (Scheme 2-8). The stability of **4-1** in solution was monitored over the course of several weeks by use of ^{31}P NMR spectroscopic techniques. In C_6D_6 at ambient temperature no new phosphorus-containing products were observed after several weeks. However, at elevated temperatures (50 °C) in THF a new phosphorus-containing product (δ ^{31}P 137.4) was detected after 4 d, and heating of **4-1** for 11 d resulted in a 50:50 mixture of **4-1** and this as-yet-unidentified product.



Scheme 4-1. Synthesis of ligand **4-1**.

4.3.2 Synthesis and Characterization of Neutral Group 9 κ^2-*P,N* Complexes

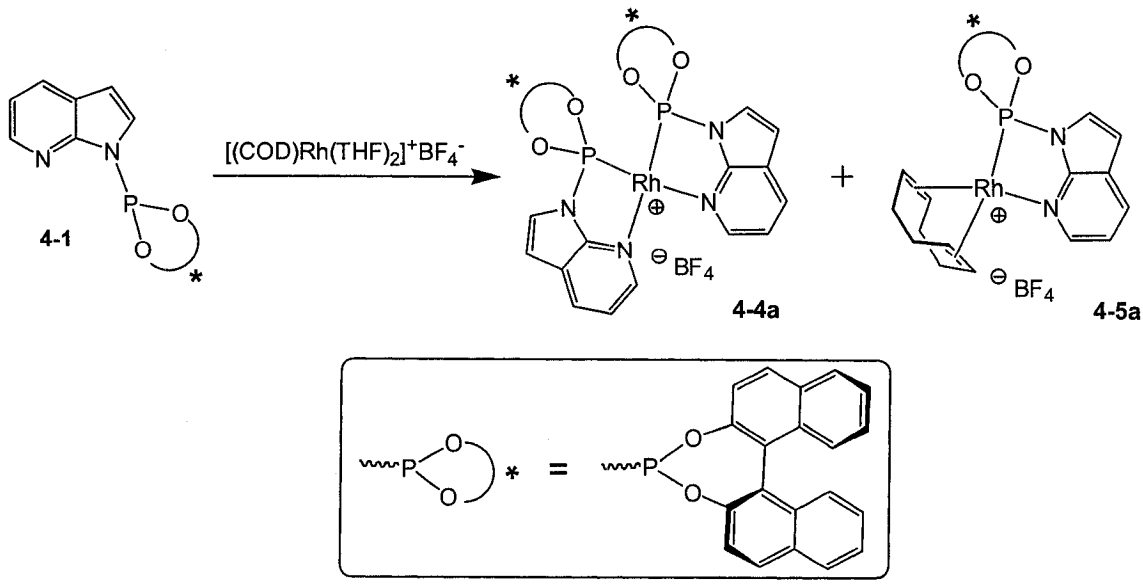
When **4-1** was treated with 0.5 equiv of $[(COD)MCl]_2$ (M = Rh or Ir), the formation of 2:1 ligand-to-metal complexes, **4-2a** and **4-2b** respectively, were observed (Scheme 4-2). The formation of **4-2a** and **4-2b** was confirmed experimentally by treating **4-1** with 0.25 equiv of $[(COD)MCl]_2$ (M = Rh or Ir), resulting in identical ^{31}P NMR chemical shifts. The complexes were isolated as pale yellow (**4-2a**) and light brown (**4-2b**) solids in 68 % and 72 % yield, respectively. In an attempt to prepare a 1:1 ligand-to-metal complex, **4-1** was treated with Wilkinson's catalyst **1-1**, which led to the formation of **4-3**; this product was obtained as a tan solid in 74 % yield. The 2:1 ligand-to-metal complex **4-2a** was also prepared by the addition of two equiv of **4-1** to **1-1** (Scheme 4-2).



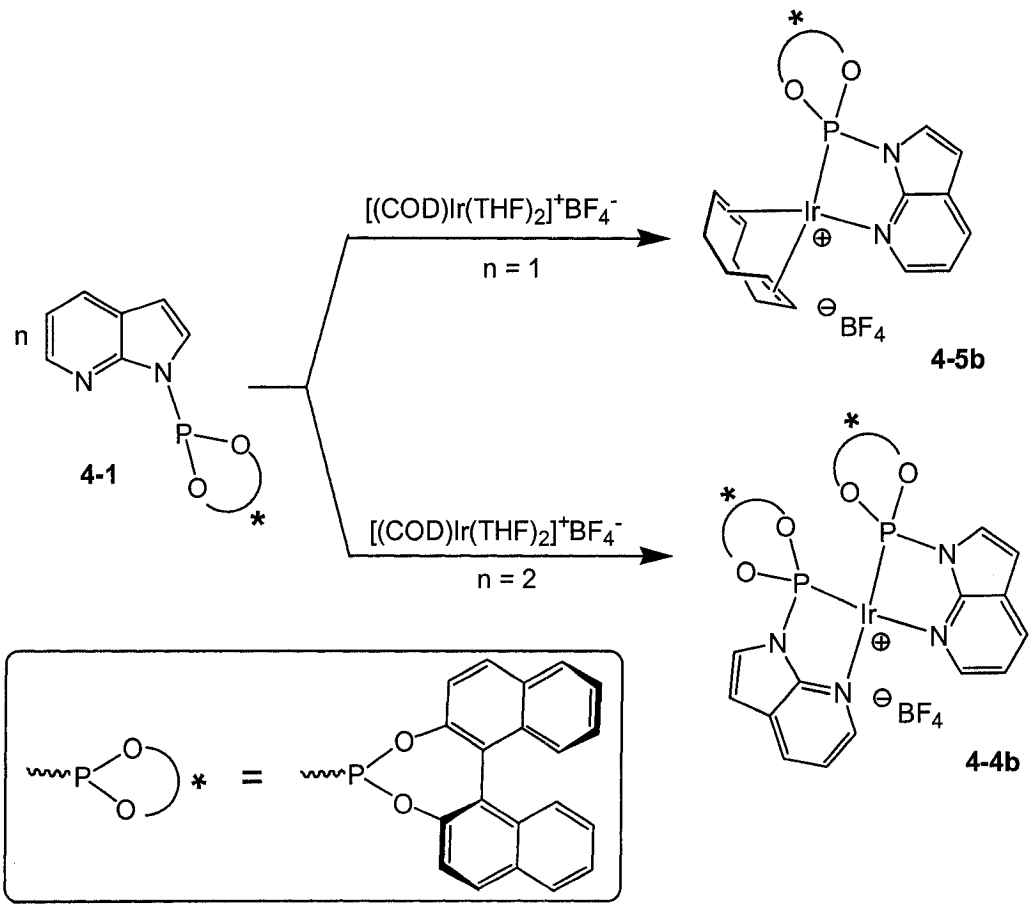
Scheme 4-2. The formation of neutral 2:1 and 1:1 ligand-to-metal complexes of **4-1**.

4.3.3 Synthesis and Characterization of Group 9 Cationic κ^2-*P,N* Complexes

In the pursuit of $[(COD)M(\kappa^2\text{-}P,N\text{-}\mathbf{4\text{-}1})]^+X^-$ complexes (M = Rh, Ir), treatment of **4-1** with $[(COD)Rh(THF)_2]^+BF_4^-$ (prepared *in situ*) resulted in the observation of two phosphorus-containing products on the basis of ^{31}P NMR spectroscopy. Further exploration revealed the two products to be 2:1 (**4-4a**) and 1:1 (**4-5a**) ligand-to-metal complexes (δ ^{31}P 148.9, d, $^1J_{RhP}$ = 277.5 Hz [2:1 complex] and δ ^{31}P 130.7, d, $^1J_{RhP}$ = 270.4 Hz [1:1 complex]) (Scheme 4-3). So far, compound **4-5a** cannot be prepared reproducibly, with yields of > 90 % rarely achieved according to ^{31}P NMR data, even in instances when a deficit in ligand is implemented. When **4-1** was treated with $[(COD)Ir(THF)_2]^+BF_4^-$ (prepared *in situ*) a single new phosphorus-containing product (**4-5b**) was observed by use of ^{31}P NMR techniques, and this was isolated as a bright red-orange solid in 86 % yield (Scheme 4-4). When two equiv of **4-1** were added to $[(COD)Ir(THF)_2]^+BF_4^-$ (prepared *in situ*) a new phosphorus containing product (**4-4b**) was obtained instead of **4-5b** (Scheme 4-4). Given the poor catalytic performance of the 2:1 ligand-to-metal complexes of **2-11b** (Section 2.3), the isolation and characterization of **4-4a,b** was not pursued.



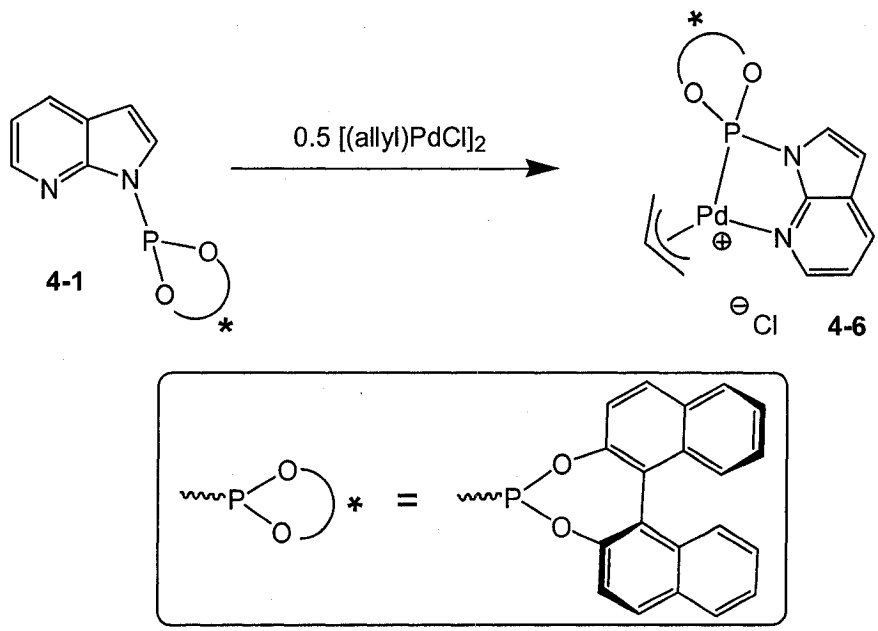
Scheme 4-3. Formation of cationic rhodium complexes of **4-1**.



Scheme 4-4. Formation of cationic iridium complexes **4-4b** and **4-5b**.

4.3.4 Synthesis and Characterization of a Palladium κ^2-*P,N* Complex

Treating **4-1** with 0.5 equiv of $[(allyl)PdCl]_2$ afforded **4-6** as a yellow solid in 86 % isolated yield (Scheme 4-5). When **4-6** is first produced it exhibits a ^{31}P NMR chemical shift of 133.1 ppm. However, over the course of 3 h, a new phosphorus containing product exhibiting a resonance at 129.4 ppm appears. This change can most likely be attributed to dynamic processes observed in palladium allyl complexes such as the *syn-anti* isomerization and/or apparent rotation of the allyl group (Scheme 4-6) to produce a closely related isomeric complex. Such an isomerization process has been reported in the literature for other palladium allyl complexes.[3, 11]



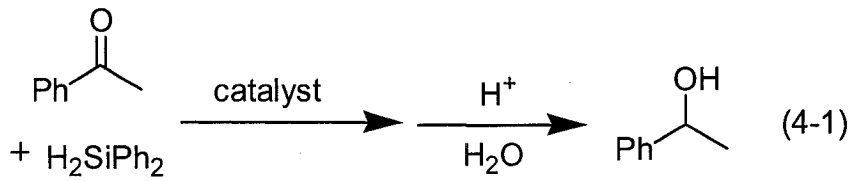
Scheme 4-5. Synthesis of complex **4-6**.

Having briefly explored the coordination chemistry of **4-1** with Rh, Ir and Pd, the catalytic utility of such complexes was examined. The results of these studies are described in the following sections. For convenience, catalyst complexes were prepared

in situ by using an appropriate metal precursor in combination with **4-1** (except where noted).

4.3.5 Asymmetric Hydrosilylation Catalysis Mediated by Rhodium Complexes of 4-1

When a neutral Rh precursor was treated with 1.2 equiv of **4-1** in THF (Table 4-1, entry 1), modest conversion of 50 % was achieved in ketone hydrosilylation (eq 4-1) with 32 % enantioselectivity. In the case when 2.4 equiv of **4-1** was used (Table 4-1, entry 2), significant inhibition on the catalyst activity was observed with ketone conversion of < 1 %. Changing to a cationic metal precursor, slightly higher conversions were observed relative to the neutral precursors when 1.2 equiv or 2.4 equiv of **4-1** was employed (Table 4-1, entries 3 and 4, respectively). Catalyst enantioselectivity in entry 3 remained similar to that observed in entry 1, while decreased selectivity was achieved in the case of 2.4 equiv (Table 4-1, entry 4).



(4-1)

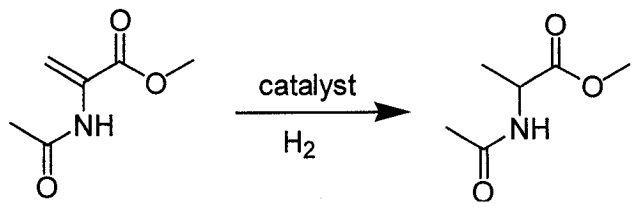
Table 4-1. Addition of Diphenylsilane to Acetophenone.[a]

Entry	Metal precursor	Equiv of **4-1**	Solvent	%[b]	% *ee*[c]
1	$[(COD)RhCl]_2$	1.2	THF	50	32 (S)
2	$[(COD)RhCl]_2$	2.4	THF	< 1	n/a
3	$[(COD)Rh(THF)_2]^+BF_4^-$	1.2	THF	69	28 (S)
4	$[(COD)Rh(THF)_2]^+BF_4^-$	2.4	THF	24	19 (S)

[a]Conditions: 24 °C, 5.0 mol% Rh. [b]Percent conversion based on the consumption of ketone at 18 h. [c]Product distribution determined on the basis of chiral GC-FID data, rounded to the nearest percent; the major isomer is indicated in parentheses. Isomer assignment was based on literature data.[12]

4.3.6 Asymmetric Hydrogenation Catalysis Mediated by Rhodium and Iridium Complexes of 4-1

In a preliminary exploration of the hydrogenation of methyl 2-acetamidoacrylate (eq 4-2), initial test reactions employing a cationic Rh precursor without added **4-1** in THF provided full conversion, with no enantioselectivity as anticipated for this achiral catalyst (Table 4-2, entry 1). Altering the solvent to CH_2Cl_2 resulted in no conversion (Table 4-2, entry 6). Comparing entries 2 and 3 in Table 4-2 reveals that in the presence of 1.2 equiv of **4-1**, full conversion and 65 % *ee* is achieved, whereas when the amount of **4-1** was increased to 2.4 equiv, a reduction in activity and product enantioselectivity to 50 % *ee* was observed. This decrease in activity when employing excess ligand follows the same trend described in Chapter Two for the study of related catalysts employing **2-11b** (Sections 2.3.8 and 2.3.9). In attempts to reduce the amount of the catalytically less active 2:1 ligand-to-metal rhodium complex formed *in situ*, the amount of **4-1** used was reduced to 1.0 equiv (Table 4-2, entry 4). In this case, a slight decrease in activity was observed while the enantioselectivity was reduced dramatically to 13 % from 65 % seen in entry 2. This speaks to the difficulty of generating the active catalyst (**4-5a**) in a reproducible manner, as described in Section 4.3.3. In the case of entry 5 in Table 4-2, when neutral **4-3** (isolated) was implemented, very low conversion with no enantioselectivity was observed. When a cationic Ir precursor without added ligand **4-1** in CH_2Cl_2 was employed, full conversion with no enantioselectivity (Table 4-2, entry 7) was achieved. Unfortunately, the addition of **4-1** to this cationic Ir precursor (Table 4-2, entry 8) completely shuts down the catalytic activity. The same trend was found when THF was used in place of CH_2Cl_2.



(4-2)

Table 4-2. Hydrogenation of Methyl 2-acetamidoacrylate.[a]

Entry	Metal precursor	Equiv of **4-1**	Solvent	%[b]	% ee[c]
1	$[(COD)Rh(THF)_2]^+BF_4^-$	0	THF	>99	0
2	$[(COD)Rh(THF)_2]^+BF_4^-$	1.2	THF	>99	65 (S)
3	$[(COD)Rh(THF)_2]^+BF_4^-$	2.4	THF	78	50 (S)
4	$[(COD)Rh(THF)_2]^+BF_4^-$	1	THF	94	13 (S)
5[d]	$(PPh_3)_3RhCl$	1	THF	3	1 (S)
6	$[(COD)Rh(THF)_2]^+BF_4^-$	0	CH_2Cl_2	n/d[e]	n/d[e]
7	$[(COD)Ir(THF)_2]^+BF_4^-$	0	CH_2Cl_2	>99	0
8	$[(COD)Ir(THF)_2]^+BF_4^-$	1	CH_2Cl_2	n/d[e]	n/d[e]

[a]Conditions: 24 °C, 5.0 mol% Rh or Ir, 1 atm H_2. [b]Percent conversion based on the consumption of methyl-2-acetamidoacrylate at 24 h. [c]Product distribution determined on the basis of chiral GC-FID data, rounded to the nearest percent; the major isomer is indicated in parentheses. Isomer assignment was based on literature data.[13] [d]Isolated compound **4-3** was used as catalyst. [e]No hydrogenated products detected.

4.3.7 Asymmetric Hydroboration Catalysis Mediated by Rhodium Complexes of 4-1

The hydroboration of styrene has been examined previously in Chapter Three, and was employed in testing the catalytic utility of **4-1**. In this regard, $[(COD)_2Rh]^+BF_4^-$/**4-1** mixtures (1.1:1) were examined as a catalyst for the hydroboration of styrene using pinacolborane (HBpin) and catecholborane (HBcat). When HBpin was implemented the catalyst demonstrated selectivity towards the branched product **3-8a** at both substrate concentrations of 0.19 M (Table 4-3, entry 1) and 0.046 M (Table 4-3, entry 2) with better selectivity at 0.046 M. In the case of HBcat no selectivity was observed at either

concentrations (Table 4-3, entries 3 and 4). Surprisingly, no enantioselectivity was observed in any of these catalytic runs.

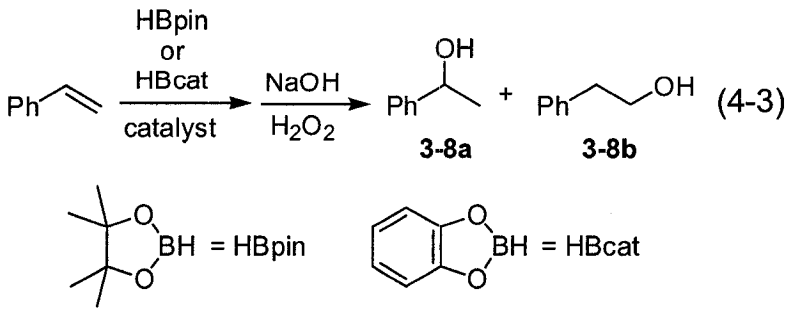


Table 4-3. Rhodium-Catalyzed Addition of HBpin and HBcat to Styrene.[a]

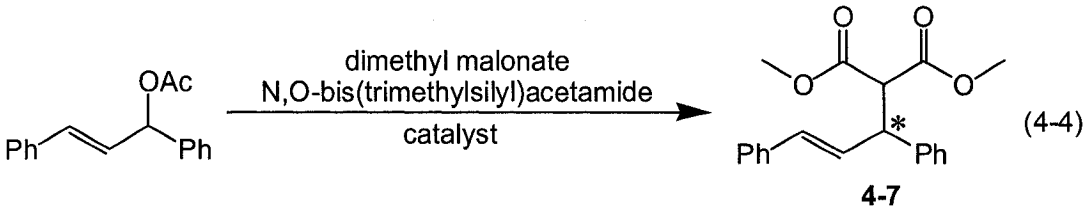
Entry	Borane[b]	Substrate Conc. (M)	Branched : Linear[c] (**3-8a** : **3-8b**)	% *ee*[d]
1	**HBpin**	0.19	59 : 41	0
2	**HBpin**	0.046	71 : 29	0
3	**HBcat**	0.19	50 : 50	0
4	**HBcat**	0.046	50 : 50	0

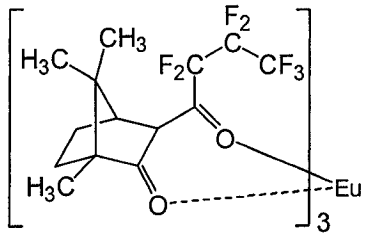
[a]Conditions: -30 °C; 5.0 mol% Rh; 1 equiv of **4-1**; 24 h; borane-to-styrene ratio of 1.2:1; THF. In all experiments listed, > 95 % conversion of the styrene starting material was achieved. [b]HBpin = pinacolborane; HBcat = catecholborane. [c]Product ratio on the basis of GC-FID data, rounded to the nearest percent. In all cases, alternative boron-containing products represented < 3 % of the total product distribution. [d]Enantioselectivity determined on the basis of chiral GC-FID data, rounded to the nearest percent.

4.3.8 Asymmetric Allylic Alkylation Catalysis Mediated by Palladium Complexes of 4-1

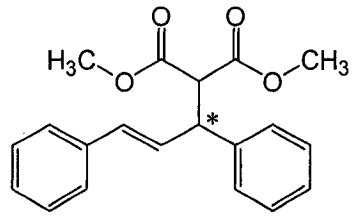
In an alternative catalytic test reaction, the new chiral P,N ligand **4-1** was examined in the enantioselective palladium-catalyzed allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate (eq 4-4). Reaction conditions were altered in a systematic manner in an effort to obtain the best enantioselectivities. In this study, enantioselectivities were determined through the integration of the ^{1}H NMR

signals of the methyl groups of the diastereomeric products formed after the addition of a chiral shift reagent, europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (Figure 4-3).[14-16] A representative plot of the influence of added $Eu(hfc)_3$ on the appearance of the ^1H NMR spectrum of the reaction product (**4-7**) is given in Figure 4-4.





Europium shift reagent
$Eu(hfc)_3$



Palladium-catalyzed allylic alkylation product **4-7**

Figure 4-3. Structures of the chiral shift reagent and the alkylation product **4-7**.

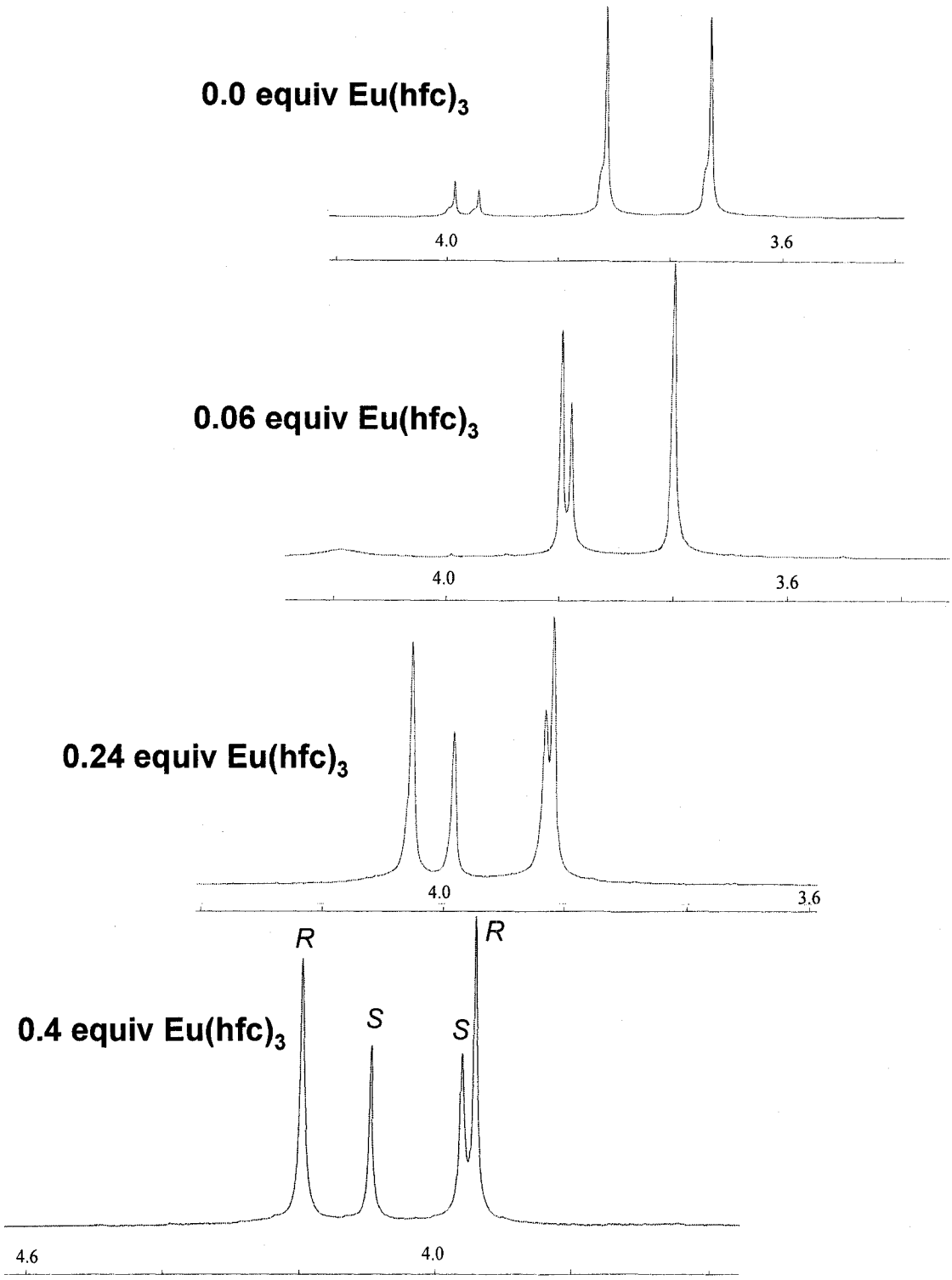


Figure 4-4. The effects of chiral shift reagent on the ^{1}H NMR signals of **4-7**. The enantioselectivity is determined on the basis of the ratio of peaks '*R*' and '*S*' corresponding to the two enantiomers of **4-7**.

Initial comparisons (Table 4-4) were made between substrate concentrations of 0.2 M vs. 0.04 M and the presence of a large excess of nucleophile. The effect of solvents was also examined in Table 4-4 and Table 4-5. The results collected in Table 4-4 demonstrate that at ambient temperature after 24 h there is a notable effect on % conversion and enantioselectivity arising due to substrate concentration. Comparing the pairs of entries 1 and 2, 3 and 4, 5 and 6, and 7 and 8, demonstrates a trend that higher conversions are achieved with 0.2 M concentrations than with 0.04 M while increased enantioselectivities are observed for the more dilute experiments (entries 2, 4, 6, and 8). This observation is in agreement with those reported by Ellman and co-workers,[17] where the highest values of *ee* were obtained at low substrate concentration of 0.03 M, but a prolonged reaction time of > 168 h was required. Comparing all of the results summarized in Table 4-4, the conditions giving the highest enantioselectivity of 57 % (Table 4-4, entry 6) feature: i) substrate concentration of 0.04 M; ii) substrate-to-nucleophile ratio of 1 : 1.1; and iii) THF as the solvent. In Table 4-5, the effects of lowering the reaction temperature to -30 °C was explored. The effect on the enantioselectivity is reversed for substrate concentration when CH_2Cl_2 was implemented (Table 4-5, entries 1 and 2) while in THF (Table 4-5, entries 3 and 4) the same trend as in Table 4-4 is noted. Although similar conversions were achieved after 48 h, no increase in enantioselectivity was observed suggesting that lowering the temperature has minimal effect on enantioselectivity in this system. In light of the increase in enantioselectivity observed for experiments employing concentrations at 0.04 M vs. 0.2 M, a ten-fold dilution was examined to determine if product enantioselectivity would increase (Table 4-6, entry 1). When a substrate concentration of 0.004 M in THF at 24 °C with a

substrate-to-nucleophile ratio of 1 : 1.1 was used, after 72 h, substrate conversion of 97 % with a % *ee* of 67 % was observed.

Table 4-4. Palladium-catalyzed allylic alkylation at 24 °C.[a]

Entry	Substrate Conc. (M)	Solvent	Ratio[b]	Time (h)	%[c]	% *ee*[d]
1	0.2	CH_2Cl_2	1 : 1.1	24	>99	24 (R)
2	0.04	CH_2Cl_2	1 : 1.1	24	85	43 (R)
3	0.2	CH_2Cl_2	1 : 3	24	>99	22 (R)
4	0.04	CH_2Cl_2	1 : 3	24	>99	40 (R)
5	0.2	THF	1 : 1.1	24	96	40 (R)
6	0.04	THF	1 : 1.1	24	93	57 (R)
7	0.2	THF	1 : 3	24	>99	15 (R)
8	0.04	THF	1 : 3	24	81	38 (R)

[a]Conditions: 5.0 mol% Pd. [b]Substrate-to-nucleophile ratio. [c]Percent conversion to **4-7** based on the consumption of 1,3-diphenylprop-2-enyl acetate. [d]Product distribution determined on the basis of ^{1}H NMR integration of the methyl groups of the product after the addition of chiral shift reagent [Eu(hfc)$_3$], rounded to the nearest percent (error $\pm$ 5 %); the major isomer is indicated in parentheses. Isomer assignment was based on literature data.[14]

Table 4-5. Palladium-catalyzed allylic alkylation at -30 °C.[a]

Entry	Substrate Conc. (M)	Solvent	Ratio[b]	Time (h)	%[c]	% *ee*[d]
1	0.2	CH_2Cl_2	1 : 1.1	48	99	41 (R)
2	0.04	CH_2Cl_2	1 : 1.1	48	33	32 (R)
3	0.2	THF	1 : 1.1	48	95	40 (R)
4	0.04	THF	1 : 1.1	48	9	57 (R)

[a]Conditions: 5.0 mol% Pd. [b]Substrate-to-nucleophile ratio. [c]Percent conversion to **4-7** based on the consumption of 1,3-diphenylprop-2-enyl acetate. [d]Product distribution determined on the basis of ^{1}H NMR integration of the methyl groups of the product after the addition of chiral shift reagent [Eu(hfc)$_3$], rounded to the nearest percent (error $\pm$ 5 %); the major isomer is indicated in parentheses. Isomer assignment was based on literature data.[14]

Table 4-6. Palladium-catalyzed allylic alkylation at 24 °C and 0.004 M substrate in THF.[a]

Entry	Equiv **4-1**	Ratio[b]	Time (h)	%[c]	% *ee*[d]
1	1	1 : 1.1	72	97	67 (R)
2	1	1 : 1.1	100	99	66 (R)
3	1	1 : 1.1	148	>99	73 (R)
4	2	1 : 1.1	72	27	7 (S)
5	2	1 : 1.1	100	61	17 (S)
6	2	1 : 1.1	148	52	19 (S)
7	3	1 : 1.1	72	6	4 (S)
8	3	1 : 1.1	100	10	7 (S)
9	3	1 : 1.1	148	8	17 (S)
10	0.5	1 : 1.1	100	49	70 (R)
11	0.5	1 : 1.1	148	46	75 (R)
12[e]	1	1 : 1.1	72	98	52 (R)
13[e]	1	1 : 1.1	100	99	56 (R)
14[e]	1	1 : 1.1	148	99	56 (R)

[a]Conditions: 5.0 mol% Pd. [b]Substrate-to-nucleophile ratio. [c]Percent conversion based on the consumption of 1,3-diphenylprop-2-enyl acetate. [d]Product distribution determined on the basis of ^{1}H NMR integration of the methyl groups of the product after the addition of chiral shift reagent [Eu(hfc)$_3$], rounded to the nearest percent (error $\pm$ 5 %); the major isomer is indicated in parentheses. Isomer assignment was based on literature data.[14] [e]Ligand was prepared several weeks prior to execution of the experiment.

Due to the observed reduction in catalytic activity for the other catalytic reactions discussed in Sections 4.3.5 – 4.3.7 when an excess of ligand was employed, it was of interest to see if a similar effect would be observed for the palladium-catalyzed allylic alkylation. The additions of one, two and three equiv of **4-1** were explored, and % conversion and % *ee* were determined after 72, 100, and 148 h. When two equiv of **4-1** was used, a dramatic decrease in yield of **4-7** and enantioselectivity was observed (Table 4-6, entries 4 to 6) compared to one equiv (Table 4-6, entries 1 to 3), where a % *ee* of 73 was achieved after 148 h (entry 3). The addition of three equiv of **4-1** (Table 4-6, entries 7 to 9) inhibited catalytic performance even more than when two equiv of **4-1** (Table 4-6,

entries 4 to 6) was added. Surprisingly, with two or three equiv of **4-1** the product **4-7** is formed such that the S-enantiomer predominates, while with one equiv the R-enantiomer is favoured. Clearly the presence of excess ligand produces a different type of catalyst mixture. Reducing the amount of **4-1** to 0.5 equiv (Table 4-6, entries 10 and 11) had minimal effect on the % *ee* (cf Table 4-6, entries 2 and 3), while the % conversion was reduced by half. This observation suggests that the metal precursor $[(allyl)PdCl]_2$ is catalytically inactive in this case and the active catalyst is a 1:1 ligand-to-metal complex. Notably, when the best conditions (Table 4-6, entries 2 to 4) were repeated with **4-1** that had been prepared several weeks earlier (Table 4-6, entries 13 to 15) an obvious decrease in enantioselectivity without a reduction in % conversion was observed.

When catalytic reaction conditions from Table 4-6, entry 1 (1,3-diphenylprop-2-enyl acetate several attempts. This demonstrates that such conditions for this catalytic system are very sensitive. Therefore, reaction conditions from Table 4-4, entry 6 (1,3-diphenylprop-2-enyl acetate: 0.04 M) were repeated with freshly made ligand **4-1** and ligand **4-1** that had been prepared approximately ten month before , see Table 4-7.

When freshly prepared ligand was employed (Table 4-7, entry 1), a conversion of 76 % with an % *ee* of 37 % was observed after 24 h. Extending the reaction time to 72 h (Table 4-7, entry 2), conversion of 93 % was achieved with a similar % *ee* of 34 % compared to entry 1. On the other hand when ligand **4-1**, which had been prepared several months prior to the execution of the experiment, was employed under the same conditions (Table 4-7, entries 3 and 4) resulted in similar conversions while a decrease in % *ee* is observed. This demonstrates that ligand **4-1** should always be freshly prepared in order to receive the best possible enantioselectivities.

Table 4-7. Palladium-catalyzed allylic alkylation at 24 °C and 0.04 M substrate.[a]

Entry	Solvent	Ratio[b]	Time (h)	%[c]	% *ee*[d]
1	THF	1 : 1.1	24	76	37 (R)
2[e]	THF	1 : 1.1	72	93	34 (R)
3[f]	THF	1 : 1.1	24	77	26 (R)
4[e,f]	THF	1 : 1.1	72	97	20 (R)

[a]Conditions: 5.0 mol% Pd. [b]Substrate-to-nucleophile ratio. [c]Percent conversion to **4-7** based on the consumption of 1,3-diphenylprop-2-enyl acetate. [d]Product distribution determined on the basis of ^{1}H NMR integration of the methyl groups of the product after the addition of chiral shift reagent [Eu(hfc)$_3$], rounded to the nearest percent (error ± 5 %); the major isomer is indicated in parentheses. Isomer assignment was based on literature data.[14] [e]Duplicate data. [f]Ligand was prepared several weeks prior to use.

4.4 Summary and Conclusions

The synthesis of **4-1** represents the first example of a modular new class of a chiral P,N ligands prepared easily from 7-azaindole. The coordination chemistry of ligand **4-1** was explored with Rh, Ir and Pd. When a neutral metal precursor [(COD)MCl]$_2$ (M = Rh or Ir) was reacted with **4-1**, only the 2:1 ligand-to-metal complexes **4-2a,b** were produced (Scheme 4-2). In attempts to make 1:1 ligand-to-metal complexes, [(COD)M(THF)$_2$]$^+$BF$_4^-$ (M = Rh or Ir) was added to **4-1**; in the case of Rh, a mixture of cationic 1:1 and 2:1 ligand-to-metal complexes (**4-5a** and **4-4a**, respectively; Scheme 4-3) was formed and attempts to produce **4-5a** in a reproducible manner were met with limit success. A neutral 1:1 ligand-to-metal Rh complex **4-3** was synthesized (Scheme 4-2) by selecting Wilkinson's catalyst **1-1** as the metal precursor. When Ir was implemented, the cationic 1:1 and 2:1 ligand-to-metal complexes (**4-5b** and **4-4b**, respectively; Scheme 4-4) could be synthesized independently. The Pd compound **4-6** was synthesized in a clean and simple manner. This coordination chemistry survey has shown that ligand **4-1** prefers to bind in a 2:1 ligand-to-metal fashion with Group 9

metals (in most cases); 1:1 ligand-to-metal complexes can only be achieved in certain situations.

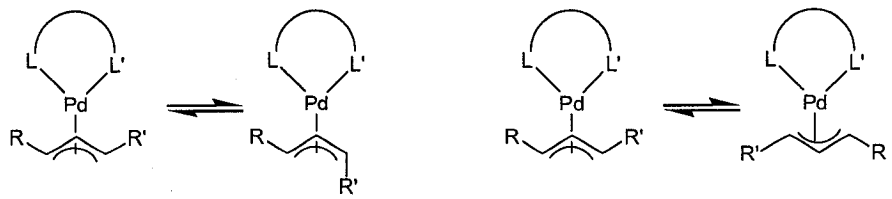
The catalytic utility of **4-1** in the hydrosilylation of acetophenone with diphenylsilane (Rh), the hydrogenation of methyl-2-acetamidoacrylate (Rh and Ir), the hydroboration of styrene (Rh), and the allylic alkylation of 1,3-diphenylprop-2-enyl acetate (Pd) has been explored using catalysts prepared *in situ* from **4-1** and an appropriate metal reagent. Rh catalysts have exhibited low activity in the addition of diphenylsilane to acetophenone (yields of < 70 %), and the catalytic activity was dramatically reduced whenever two or more equivalents of ligand were used, while the enantioselectivity remained relatively low (20-30 %). In the addition of borane to styrene, full conversion was always achieved while branched selectivity was observed with HBpin and no selectivity was noted when HBcat was added. In all hydroboration reactions, there was an unexpected lack of enantioselectivity, despite the use of the enantiomerically pure ligand **4-1**. The hydrogenation of methyl 2-acetamidoacrylate has been catalyzed by *in situ* prepared cationic Rh complexes. When using 1.2 equiv of **4-1**, full consumption of starting material was observed with product enantioselectivity of 69 %. When two or more equiv of ligand were added, a reduction in yield and enantioselectivity was observed, confirming the trends seen in Chapter Two with ligand **2-11b**. Repeating this reaction with one equiv of ligand resulted in a dramatic reduction in *ee* emphasizing the difficulty to synthesize the 1:1 ligand-to-metal Rh complex in a reproducible manner. The Ir analogue proved to be inactive for the hydrogenation of methyl 2-acetamidoacrylate. These results demonstrate that the Rh complexes featuring **4-1** are catalytically active and have the potential of providing good enantioselectivity,

although more work needs to be undertaken to find a reproducible synthetic route for the preparation of compound **4-5a** (1:1 ligand-to-metal Rh complex). Future work would also involve the hydrogenation of imines at 1 atm as well as examination of all hydrogenations at increased hydrogen pressure. A spectroscopic study of the aging of **4-1** is warranted.

In the palladium-catalyzed allylic alkylation of 1,3-diphenylprop-2-enyl acetate, ligand **4-1** has shown potential to facilitate this reaction with good enantioselectivity. Surveying different reaction conditions from substrate concentration, substrate-to-nucleophile ratio, temperature, solvent, and equiv of ligand resulted in optimized reaction conditions: one equiv of **4-1** in THF with a substrate concentration of 0.004 M and the addition of 1.1 equiv of nucleophile (to substrate) at 24 °C. Notably, the best results of % *ee* were obtained when freshly prepared ligand was implemented, suggesting that **4-1** may suffer from instability in the solid state. The thermal instability of **4-1** in solution was outlined in Section 4.3.1.

Future work will involve further optimization of the catalytic conditions in the hope to achieve higher *ee*'s in this Pd-catalyzed reaction. One way of improving the *ee*'s could be through the addition of a spectator halide ligand to facilitate *syn-anti* isomerization (Scheme 4-6). Usually halide ligands within the coordination sphere are considered to be of limited importance and are replaced by weakly coordinating anions such as triflate, tetrafluoroborate, or hexafluorophosphate.[18] Dynamic processes such as *syn-anti* isomerization and apparent rotations (Scheme 4-6) are a common phenomenon for allyl palladium complexes. Studies of these processes in the literature have shown that the type of counterion present has a dramatic influence on the rate of

isomerization. An increased rate of isomerization is observed in the presence of halide ions vs. non-halide ions.[18]



Scheme 4-6. Dynamic process observed in palladium allyl complexes.

4.5 Experimental Section

4.5.1 General Considerations

See Sections 2.5 and 3.4 for a description of general experimental conditions. Any changes or additions to those procedures are described herein. Europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate], dimethyl malonate, and acetic anhydride were obtained from Aldrich and used as received. 7-Azaindole, potassium acetate, and pinacol were obtained from Aldrich and dried *in vacuo* for 24 h prior to use. Catecholborane (Aldrich) was degassed by using three freeze-pump-thaw cycles and then dried over 4 Å molecular sieves for 24 h. 1,3-Diphenyl allyl alcohol and N,O-bis(trimethylsilyl)acetamide were obtained from Fluka and used as received. $[(allyl)PdCl]_2$ was obtained from Strem Chemicals and dried *in vacuo* for 24 h. Benzyl potassium[19] and 1,3-diphenyl-2-acetylpropene[20] were prepared via literature methods.

4.5.2 Preparation of 4-1

A 1.6 M hexanes solution (pre-cooled to -35 °C) of *n*-BuLi (0.51 mL, 0.82 mmol) or a pre-cooled (-35 °C) THF solution (4 mL) of benzyl potassium (0.11 g, 0.82 mmol)

was added dropwise to a vial containing a magnetically stirred solution (pre-cooled to -35 C) of 7-azaindole (0.097 g, 0.82 mmol) in THF (4 mL), producing a colorless solution. The reaction mixture was stirred for 45 min at ambient temperature followed by cooling to -35 °C. A pre-cooled (-35 °C) mixture of **2-14** and THF (5 mL) was then transferred slowly to the reaction mixture via Pasteur pipette. Note: if the addition is completed too quickly, the reaction mixture will turn yellow; otherwise it is colorless. Upon completion of transfer, the resulting mixture was stirred for 2 h, after which the THF and other volatile materials were removed *in vacuo*. The residue was dissolved in a mixture of diethyl ether (4 mL) and benzene (2 mL) and filtered through Celite. The filtrate was dried *in vacuo* yielding **4-1** as an analytically pure, white solid (0.33 g, 0.76 mmol, 92 %). Anal. Calcd. for $C_{27}H_{17}PN_2O_2$: C 74.98; H 3.97; N 6.48. Found: C 74.58; H 3.93; N 6.26. ^{1}H NMR (C_6D_6): δ 8.42 (d of d, $^3J_{HH}$ = 4.5 Hz, J = 1.5 Hz, 1H, C4-H or C6-H Aza.), 7.61 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C-H Naph.), 7.57 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C-H Naph.), 7.55 (d, $^3J_{HH}$ = 4.0 Hz, 1H, C-H Naph.), 7.53 (d, $^3J_{HH}$ = 4.5 Hz, 1H, C-H Naph.), 7.45 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C6-H or C4-H Aza.), 7.41 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C-H Naph.), 7.32 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C-H Naph.), 7.30 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C-H Naph.), 7.17-7.10 (m, 2H, C-H Naph.), 6.97 (m, 1H, C-H Naph.), 6.93 (m, 1H, C-H Naph.), 6.81 (d of d, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, C5-H Aza.), 6.76 (d, $^3J_{HH}$ = 4.0 Hz, 1H, C2-H or C3-H Aza.), 6.65 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C-H Naph.), 5.92 (d of d, $^3J_{HH}$ = 4.0 Hz, J = 1.0 Hz, C3-H or C2-H Aza.); ^{13}C{^{1}H} NMR (C_6D_6): δ 152.8 (d, J = 16.0 Hz, quat Aza.), 148.4 (quat Naph.), 148.0 (d, J = 4.2 Hz, quat Naph.), 143.7 (C4 or C6 Aza.), 133.0 (quat Naph.), 132.6 (quat Naph.), 131.7 (quat Naph.), 131.4 (quat Naph.), 131.1 (C-H Naph.), 130.1 (C-H Naph.), 128.5 (C-H Naph.), 128.4 (C-H Naph.), 128.2 (C6 or C4 Aza.), 127.0 (C-H Naph.), 126.9

(C-H Naph.), 126.5 (C-H Naph.), 126.4 (C-H Naph.), 126.2 (d, J = 4.3 Hz, C2 or C3 Aza.), 125.2 (C-H Naph.), 125.1 (C-H Naph.), 124.5 (d, J = 5.4 Hz, quat Aza.), 123.6 (quat Naph.), 122.3 (quat Naph.), 121.5 (C-H Naph.), 121.3 (C-H Naph.), 117.7 (C5 Aza.), 104.2 (C3 or C2 Aza.); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 133.8.

4.5.3 Preparation of 4-2a

To a vial containing a magnetically stirred solution of **4-1** (0.056 g, 0.13 mmol) in THF (2 mL) was added dropwise a solution of $[(COD)RhCl]_2$ (0.016 g, 0.032 mmol) in THF (2 mL). The reaction mixture was stirred for 1 h, after which the solvent and other volatiles were removed *in vacuo*. The residue was washed with pentane (2 mL) and dried *in vacuo*, yielding **4-2a** as a pale yellow solid (0.044 g, 0.044 mmol, 68 %). ^{1}H NMR (C_6D_6): δ 9.34 (1H, C-H), 8.50-8.45 (m, 2H, C-Hs), 8.40 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H, C-H), 7.68-7.63 (m, 2H, C-Hs), 7.60 (d, J = 8.75 Hz, 1H, C-H), 7.55-7.45 (m, 3H, C-Hs), 7.41 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, C-H), 7.35 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, C-H), 7.30-7.26 (m, 2H, C-Hs), 7.23 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, C-H), 7.13 (m, 1H, C-H), 7.07-6.98 (m, 3H, C-Hs), 6.97-6.82 (m, 4H, C-Hs), 6.81-6.75 (m, 2H, C-Hs), 6.71 (m, 1H, C-H), 6.57-6.50 (m, 2H, C-Hs), 6.41 (m, 1H, C-H), 6.21 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H, C-H), 6.11 (d, $^{3}J_{HH}$ = 3.5 Hz, 1H, C-H), 5.96 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, C-H), 5.80-5.75 (m, 2H, C-H); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 151.8 (quat), 148.8 (quat), 148.4 (quat), 147.9 (quat), 143.1 (C-H), 142.9 (C-H), 132.8 (quat), 132.2 (quat), 132.1 (quat), 132.1 (quat), 131.9 (quat), 131.8 (quat), 131.0 (quat), 130.7 (quat), 130.6 (C-H), 130.2 (C-H), 129.8 (C-H), 129.4 (C-H), 129.3 (C-H), 129.0 (C-H), 128.8 (C-H), 128.2 (C-H), 128.2 (C-H), 128.1 (C-H), 128.0 (C-H), 127.2 (C-H), 127.0 (C-H), 126.9 (C-H), 126.8 (C-H), 126.3 (C-H), 125.8 (C-H), 125.8 (C-H), 125.4 (C-H), 125.3 (C-H), 124.7 (C-H), 124.5 (C-H), 123.6 (C-H), 123.6 (quat), 123.1 (quat), 122.3

(quat), 121.9 (quat), 121.3 (quat), 120.8 (C-H), 120.3 (C-H), 118.5 (quat), 117.5 (C-H), 117.3 (C-H), 108.0 (C-H), 103.6 (C-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 146.6 (d of d, $^{1}J_{PRh}$ = 275.2 Hz, $^{2}J_{PP}$ = 64.5 Hz), 140.0 (d of d, $^{1}J_{PRh}$ = 309.3 Hz, $^{2}J_{PP}$ = 64.2 Hz).

4.5.4 Preparation of 4-2b

A procedure analogous to that described for the synthesis of **4-2a** was employed, using $[(COD)IrCl]_2$ (0.048 g, 0.072 mmol) in THF (2 mL). Complex **4-2b** was isolated as a light brown solid (0.11 g, 0.10 mmol, 72 %). ^{1}H NMR (C_6D_6): δ 9.51 (br s, 1H, C-H), 8.42 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, C-H), 8.37-8.34 (m, 2H, C-H), 7.89 (br s, 1H, C-H), 7.67 (d, J = 8.75 Hz, 1H, C-H), 7.62 (d, J = 8.75 Hz, 1H, C-H), 7.55-7.49 (m, 3H, C-H), 7.42 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H, C-H), 7.36 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, C-H), 7.32-7.28 (m, 2H, C-H), 7.25 (d, $^{3}J_{HH}$ = 8.6 Hz, 1H, C-H), 7.06-7.02 (m, 2H, C-H), 6.98-6.89 (m, 4H, C-H), 6.88-6.83 (m, 2H, C-H), 6.82-6.78 (m, 2H, C-H), 6.71 (m, 1H, C-H), 6.59-6.52 (m, 2H, C-H), 6.39 (m, 1H, C-H), 6.27 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H, C-H), 6.15 (d, $^{3}J_{HH}$ = 3.3 Hz, 1H, C-H), 5.96 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H, C-H), 5.93 (d, $^{3}J_{HH}$ = 3.5 Hz, 1H, C-H), 5.75 (d, $^{3}J_{HH}$ = 2.9 Hz, 1H, C-H); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 151.4 (quat), 148.7 (quat), 148.5 (quat), 147.7 (quat), 142.8 (C-H), 141.0 (C-H), 132.8 (quat), 132.3 (quat), 132.2 (quat), 132.0 (quat), 131.7 (quat), 130.9 (quat), 130.7 (quat), 130.6 (C-H), 130.4 (C-H), 129.9 (C-H), 129.4 (C-H), 128.7 (C-H), 128.1 (C-H), 128.1 (C-H), 127.3 (C-H), 127.1 (C-H), 127.0 (C-H), 126.9 (C-H), 126.3 (C-H), 125.7 (C-H), 125.4 (C-H), 125.2 (C-H), 125.1 (C-H), 124.6 (C-H), 124.5 (C-H), 124.3 (quat), 123.6 (C-H), 123.1 (quat), 122.2 (quat), 121.8 (quat), 121.2 (quat), 120.9 (C-H), 120.6 (C-H), 118.6 (quat), 118.6 (quat), 117.4 (C-H), 117.1 (C-H), 107.8 (C-H), 103.3 (C-H); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 146.6 (d of d, $^{1}J_{PRh}$ = 275.2 Hz, $^{2}J_{PP}$ = 64.5 Hz), 140.0 (d of d, $^{1}J_{PRh}$ = 309.3 Hz, $^{2}J_{PP}$ = 64.2 Hz).

4.5.5 Preparation of 4-3

To a vial containing a magnetically stirred solution of **4-1** (0.047 g, 0.11 mmol) in THF (2 mL) was added dropwise a solution of $(PPh_3)_3RhCl$ (0.10 g, 0.11 mmol) in THF (2 mL), and the reaction mixture was stirred for 2 h. Pentane (10 mL) was added to the reaction mixture, causing the product to precipitate. The supernatant was decanted away and the precipitate washed with pentane (2 mL). The solid was dried *in vacuo*, yielding **4-3** as a yellow-brown solid (0.065 g, 0.081 mmol, 74 %). ^{1}H NMR (C_6D_6): δ 9.97 (d, $^3J_{HH}$ = 5.3 Hz, 1H, C-H), 7.99-7.91 (m, 6H, C-Hs), 7.79 (br s, 1H, C-H), 7.57 (d, $^3J_{HH}$ = 8.2 Hz, 1H, C-H), 7.44 (d, $^3J_{HH}$ = 8.85 Hz, 1H, C-H), 7.42 (d, $^3J_{HH}$ = 8.2 Hz, 1H, C-H), 7.31 (d, $^3J_{HH}$ = 8.6 Hz, 1H, C-H), 7.26 (d, $^3J_{HH}$ = 8.8 Hz, 1H, C-H), 7.08-7.20 (m, 3H, C-Hs), 7.03 (m, 1H C-H), 6.93 (d, $^3J_{HH}$ = 8.8 Hz, 1H, C-H), 6.91-6.83 (m, 3H, C-Hs), 6.80-6.76 (m, 8H, C-Hs), 6.58 (m, 1H, C-H), 5.91 (d, $^3J_{HH}$ = 3.7 Hz, 1H, C-H), 5.80 (d, $^3J_{HH}$ = 3.6 Hz, 1H, C-H); ^{13}C{^{1}H} NMR (C_6D_6): δ 154.3 (d, J = 24.3 Hz, quat), 148.5 (d, J = 14.6 Hz, quat), 147.8 (d, J = 7.2 Hz, quat), 143.7 (C-H), 136.1 (quat), 135.7 (quat), 135.3 (C-H), 135.2 (C-H), 132.7 (quat), 132.5 (quat), 131.6 (quat), 131.3 (quat), 130.4 (C-H), 130.2 (C-H), 129.5 (C-H), 128.9 (C-H), 128.4 (C-H), 128.2 (C-H), 127.4 (C-H), 126.9 (C-H), 126.9 (C-H), 126.5 (C-H), 125.8 (C-H), 125.4 (C-H), 124.9 (C-H), 124.8 (C-H), 124.8 (C-H), 122.3 (C-H), 122.3 (quat), 122.1 (C-H), 121.8 (C-H), 118.2 (d, J = 6.3 Hz, quat), 117.4 (C-H), 107.8 (C-H); ^{31}P{^{1}H} NMR (C_6D_6): δ 135.4 (d of d, $^1J_{PRh}$ = 322.0 Hz, $^2J_{PP}$ = 64.7 Hz, 1P, azaindolePBinol), 43.4 (d of d, $^1J_{PRh}$ = 159.8 Hz, $^2J_{PP}$ = 64.7 Hz, PPh_3).

4.5.6 Preparation of 4-5b

To a vial containing a magnetically stirred suspension of $[(COD)IrCl]_2$ (0.074, 0.11 mmol) in THF (2 mL) was added a suspension of $AgBF_4$ (0.043, 0.22 mmol) in THF (2 mL). An orange solution was generated immediately along with a white precipitate. The supernatant solution was separated from the precipitate by filtration through Celite, and the solution was transferred to a vial containing a magnetically stirred solution of **4-1** (0.095 g, 0.22 mmol) in THF (2 mL). The reaction mixture was stirred for an additional 3 h at ambient temperature, during which time the solution developed a red-orange coloration. The reaction mixture was then filtered through a plug of Celite, followed by removal of the solvent and other volatiles *in vacuo* to yield **4-5b** as a bright red-orange solid (0.16 g, 0.19 mmol, 86 %). ^{1}H NMR (CD_2Cl_2): δ 8.43 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C-H), 8.31 (d, $^3J_{HH}$ = 5.5 Hz, 1H, C-H), 8.24 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C-H), 8.21 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C-H), 8.15-8.10 (m, 2H, C-Hs), 7.76 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C-H), 7.68-7.60 (m, 3H, C-Hs), 7.47-7.39 (m, 5H, C-Hs), 7.14 (d, $^3J_{HH}$ = 4.0 Hz, 1H, C-H), 6.43 (d of d, J = 2.0 Hz, J = 3.5 Hz, 1H, C-H), 6.04 (br s, 1H, COD), 5.98 (br s, 1H, COD), 4.19 (br s, 1H, COD), 4.13 (br s, 1H, COD), 2.52-2.18 (m, 8H, COD); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.9 (quat), 146.8 (d, J = 13.7 Hz, quat), 145.8 (d, J = 7.0 Hz, quat), 142.4 (C-H), 135.1 (C-H), 132.4 (quat), 132.2 (quat), 132.1 (C-H), 132.0 (C-H), 128.8 (C-H), 128.8 (C-H), 127.5 (2 C-Hs), 127.0 (C-H), 127.0 (C-H), 126.7 (C-H), 126.6 (C-H), 124.6 (d, J = 6.0 Hz, C-H), 122.3 (quat), 122.0 (quat), 121.1 (d, J = 8.3 Hz, quat), 120.0 (C-H), 119.8 (C-H), 119.7 (C-H), 111.9 (C-H), 70.3 (m, C-H), 62.2 (C-H), 33.2 (CH_2), 33.0 (CH_2), 29.0 (CH_2), 28.8 (CH_2); ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 115.3.

4.5.7 Preparation of 4-6

To a vial containing a magnetically stirred solution of **4-1** (0.078 g, 0.18 mmol) in THF (1 mL) was added dropwise a solution of $[(allyl)PdCl]_2$ (0.033 g, 0.090 mmol) in THF (2 mL). The reaction mixture was stirred for 1 h, and the solvent and other volatiles were removed *in vacuo* yielding **4-6** as a yellow solid (0.092 g, 0.15 mmol, 86 %). Note: No correlations were observed for the allyl CH_2 groups in the 2D NMR experiments (HSQC and HMBC). ^1H NMR (CD_2Cl_2): δ 8.60 (d of d, $^3J_{HH}$ = 5.0 Hz, J = 1.4 Hz, 1H, C4-H or C6-H Aza.), 8.19 (d, $^3J_{HH}$ = 8.9 Hz, 1H, C-H Naph.), 8.09 (d, $^3J_{HH}$ = 8.3 Hz, 1H, C-H Naph.), 8.06-8.03 (m, 2H, C6-H or C4-H Aza. and C-H Naph.), 7.98 (d, $^3J_{HH}$ = 8.9 Hz, 2H, C-Hs Naph.), 7.62-7.57 (m, 2H, C-Hs Naph.), 7.51-7.45 (m, 2H, C-Hs Naph.), 7.44-7.39 (m, 2H, C-Hs Naph.), 7.34 (d of d, 1H, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 7.9 Hz, C5-H Aza.), 7.15 (d of d, 1H, $^3J_{HH}$ = 8.80 Hz, J = 0.7 Hz, C-H Naph.), 6.71 (d of d, 1H, $^3J_{HH}$ = 3.8 Hz, J = 1.6 Hz, C2-H or C3-H Aza.), 6.55 (d, $^3J_{HH}$ = 3.8 Hz, 1H, C3-H or C2-H Aza.), 5.83 (m, 1H, allyl), 3.94 (br s, 4H, allyl); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 152.5 (C3a or C7a Aza.), 152.3 (C7a or C3a Aza.), 147.5 (quat Naph.), 147.4 (quat Naph.), 146.9 (d, J = 4.9 Hz, quat Naph.), 143.3 (C4 or C6 Aza.), 132.4 (d, J = 4.5 Hz, quat Naph.), 132.2 (quat Naph.), 131.9 (quat Naph.), 131.5 (C-H Naph.), 131.1 (C-H Naph.), 130.4 (C-H Naph. or C6 or C4 Aza.), 128.7-128.6 (m, C-H Naph. and/or C6 or C4 Aza. and allyl C-H), 127.0 (C-H Naph.), 127.0 (C-H Naph.), 127.0 (C-H Naph.), 126.9 (C-H Naph.), 126.1 (C-H Naph. and C2 or C3 Aza.), 123.0 (quat Naph.), 122.6 (quat Naph.), 121.7 (d, J = 2.0 Hz, C-H Naph.), 120.3 (C-H Naph.), 118.8 (C5 Aza.), 107.5 (C3 or C2 Aza.); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 133.1.

4.5.8 General Protocol for Ketone Hydrosilylation Experiments

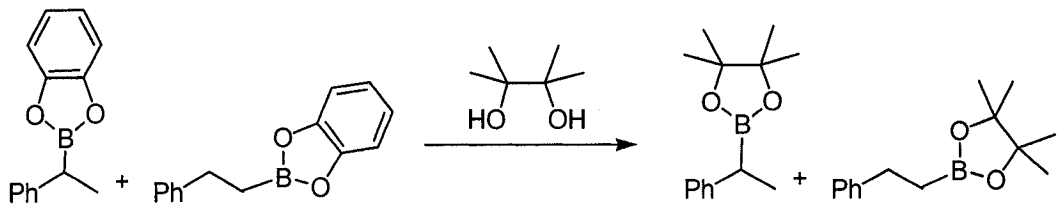
See Section 2.5.15 for the general protocol of the hydrosilylation of acetophenone with diphenylsilane.

4.5.9 General Protocol for Hydrogenation of Amino Acid Derivative

See Section 2.5.16 for the general protocol of the hydrogenation of methyl 2-acetamidoacrylate.

4.5.10 General Protocol for Hydroboration Experiments

See Section 3.4.16 for the general protocol of the hydroboration of styrene with HBpin. In the case when HBcat was employed, pinacol (2.1 equiv) was added to the reaction mixture after 24 h followed by stirring for an additional 24 h to replace catechol with pinacol (eq 4-5). The work up procedure of the hydroboration products was the same as that undertaken for HBpin, Section 3.4.16.



(4-5)

4.5.11 General Protocol for Pd-catalyzed Allylic Alkylation Experiments

A 0.020 M stock solution of catalyst was prepared by adding $[(allyl)PdCl]_2$ (0.0073 g, 0.020 mmol) in THF (1 mL) to ligand **4-1** (0.017 g, 0.040 mmol) in THF (1 mL) followed by stirring for 30 min. A 0.40 M stock solution of the substrate was prepared by dissolving 1,3-diphenylprop-2-enyl acetate (0.27 g, 1.1 mmol) in THF (2.7

mL). A 0.12 mL aliquot was taken from each of the two stock solutions and combined, this reaction mixture was stirred for 20 min and was then diluted with THF to a total volume of 12 mL to produce a final substrate concentration of 0.004 M. Dimethyl malonate (6.6 μL, 0.058 mmol; 1.1 equiv), N,O-bis(trimethylsilyl)acetamide (14.1 μL, 0.058 mmol, 1.1 equiv), and KOAc (catalytic amount) were added to the reaction mixture, and the resulting suspension was stirred at 24 °C for 72-148 h. The reaction mixture was then concentrated *in vacuo*, passed through a short silica gel column (0.6 cm x 5 cm) and eluted with diethyl ether/hexanes (2:1). A portion of the eluent was transferred to a GC vial and sealed, while the remaining eluent was concentrated *in vacuo*. The reaction products were identified by use of GC-MS, while quantitative data were obtained from GC-FID analysis. The enantiomeric excess of **4-7** was determined by the addition of $Eu(hfc)_3$ (8-10 mg) in $CDCl_3$ (0.6 mL) to the reaction sample. The mixture was vigorously shaken and transferred into an NMR tube. The ^1H NMR spectrum of the sample showed a set of four signals around 4 ppm (depending on the amount of shift-reagent used, Figure 4-3). The two signals at higher frequency correspond to one of the methyl groups of each of the two enantiomers of **4-7**, and integration of these signals could be used to give the enantiomeric excess. The sum of the integral of the two signals provided a similar value to the integration of the partially resolved peaks. Isomer assignment was based on literature data.[14]

4.6 References

1. Yoon, T. P.; Jacobsen, E. N. *Science* **2003**, *299*, 1691.

2. Fuchs, N.; d'Augustin, M.; Humam, M.; Alexakis, A.; Taras, R.; Gladiali, S. *Tetrahedron: Asymmetry* **2005**, *16*, 3143.

3. Franco, D.; Gomez, M.; Jimenez, F.; Muller, G.; Rocamora, M.; Maestro, M. A.; Mahia, J. *Organometallics* **2004**, *23*, 3197.

4. Gladiali, S.; Loriga, G.; Medici, S.; Taras, R. *J. Mol. Catal. A-Chem.* **2003**, *196*, 27.

5. Kilroy, T. G.; Hennessy, A. J.; Connolly, D. J.; Malone, Y. M.; Farrell, A.; Guiry, P. J. *J. Mol. Catal. A-Chem.* **2003**, *196*, 65.

6. Gladiali, S.; Grepioni, F.; Medici, S.; Zucca, A.; Berente, Z.; Kollar, L. *Eur. J. Inorg. Chem.* **2003**556.

7. Gladiali, S.; Dore, A.; Fabbri, D. *Tetrahedron: Asymmetry* **1994**, *5*, 1143.

8. Cozzi, P. G.; Zimmermann, N.; Hilgraf, R.; Schaffner, S.; Pfaltz, A. *Adv. Synth. Catal.* **2001**, *343*, 450.

9. Milton, H. L.; Wheatley, M. V.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chem. Commun.* **2004**, *7*, 1106.

10. Burrows, A. D.; Mahon, M. F.; Varrone, M. *Dalton Trans.* **2003**4718.

11. Camus, J. M.; Andrieu, J.; Richard, P.; Poli, R. *Eur. J. Inorg. Chem.* **2004**1081.

12. Tao, B. T.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 3892.

13. Evans, D. A.; Michael, F. E.; Tedrow, J. S.; Campos, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3534.

14. Brenchley, G.; Fedouloff, M.; Mahon, M. F.; Molloy, K. C.; Wills, M. *Tetrahedron* **1995**, *51*, 10581.

15. von Matt, P.; Pfaltz, A. *Angew. Chem. Int. Ed.* **1993**, *32*, 566.

16. Leutenegger, U.; Umbricht, G.; Fahrni, C.; von Matt, P.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143.

17. Schenkel, L. B.; Ellman, J. A. *Org. Lett.* **2003**, *5*, 545.

18. Fagnou, K.; Lautens, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 26.

19. Schlosser, M.; Hartmann, J. *Angew. Chem. Int. Ed.* **1973**, *12*, 508.

20. Watson, L. D. G.; Yudin, A. K. *J. Am. Chem. Soc.* **2005**, *127*, 17516.

Chapter Five: Conclusion

5.1 Summary of Key Thesis Results

Over the past five decades, homogeneous transition metal catalysts have been developed into useful and versatile tools for the synthesis of fine and bulk chemicals that are used in our everyday lives.[1] These homogeneous catalysts are commonly made up of transition metals bound to one or more ligand sets, where the electronic and steric contributions of the ligands can have a significant impact upon the reactivity and selectivity of the catalyst in mediating various substrate transformations. In the area of Group 9 transition metal chemistry, the synthetic utility of neutral and cationic Rh and Ir catalyst complexes stabilized by mixed donor bidentate ancillary ligands has been demonstrated for many transformations involving the activation of E-H bonds (E = main group element) in small molecule substrates. As described in Chapter One, the development of new catalyst structural motifs through the design of new ancillary ligands is a persistent challenge in organometallic chemistry. Although, conclusions and future work have been discussed within each chapter, some significant points and directions for future work are summarized here.

In this thesis, the development of new ancillary ligands derived from a P,N substituted indene backbone (**1-3a**) was discussed. 1-P(S)^{i}Pr$_2$-2-NMe$_2$-indene **2-3a** can be prepared via a one-step synthetic pathway from **1-3a**, and this ligand can support neutral and cationic Rh(I) and Ir(I) fragments, including neutral complexes that bind the metal in an unusual κ^2-*C,S* fashion. The neutral κ^2-*C,S* Rh complex **2-7a** has shown similar catalytic activity and regioselectivity to that of Wilkinson's catalyst **1-1** under some conditions. Reactivity studies in the presence of water have shown clean conversion of

complexes **2-6a,b** to the (COD)M(κ^2-P(*S*),*O*) complexes **2-9a,b**; under some conditions **2-9a,b** have shown similar catalytic activity and regioselectivity to those observed with **2-7a** in the addition of triethylsilane to styrene. Incorporation of chirality into the P,N binding site of ligand **1-3a** afforded ligand **2-11b**; the metal coordination chemistry of **2-11b** and catalytic activity is quite different than that observed with **1-3a**.

The ability of the P,N ligand (**1-3a**) to support two metal fragments was described in Chapter Three, showing that this ligand can be considered ambidentate. The catalytic ability of the racemic bimetallic complexes **3-3a-c** has been explored in the hydroboration of styrene with pinacolborane. The divergent selectivity was observed suggests that the introduction of structural changes to the η^5-coordinated metal fragment (MLn = $Mn(CO)_3$ **3-3a**, Cp*Ru **3-3b** or Cp*Fe **3-3c**) may provide a systematic way in which to modify the steric and electronic properties of the κ^2-*P,N*-ligated metal fragment in these complexes.

While the ligands discussed in Chapters Two and Three are based on an indenyl backbone, the development of a new chiral P,N ligand based on 7-azaindole was described in Chapter Four. Ligand **4-1** was prepared in a facile and modular manner and shows divergent metal coordination chemistry with transition metals such as Rh, Ir and Pd. In certain catalytic asymmetric transformations some of these metal complexes have shown to promote good catalytic activity and enantioselectivity.

5.2 Future Directions

Currently, the origin of the reactivity differences observed between related Group 9 complexes presented in this thesis are not known. However, the observation that slight binding differences can provide a difference in complex stability, such as in the clean

conversion of **2-6a,b** to **2-9a,b** in the presence of water while **2-7a,b** simply decompose, shows that small changes can have a large impact on complex reactivity. The survey of other catalytic reactions with the metal complexes from Chapter Two should provide information from which a structure-activity relationship can be drawn and further modifications to the ligand can be undertaken. The exploration of the ligands discussed in Chapter Two (**2-3a** and **2-11b**) with other transition metal fragments should also increase the understanding of how these ancillary ligands influence the reactivity properties of associated metals.

The different regioselectivity displayed by **3-3a-c** provides insight that the η^5-bound spectator metal influences the κ^2-*P,N* ligated metal fragment in different ways. Given this observation, the resolution of the racemic bimetallic complex would provide a new class of PCMs where the η^5-bound spectator metal can be modified in a modular manner. Potential resolution methods such as chiral HPLC and protonation with a chiral acid to form diastereomers are discussed in Chapter Three. The exploration of these PCMs in different chemical transformations should give insight on how the structure-activity relationship is influenced by the η^5-bound spectator metal.

In Chapter Four the simple synthesis of **4-1** has been demonstrated while the synthesis of certain metal complexes has proven more difficult than expected. The explorations of the *in situ* prepared cationic Rh complexes have shown promise to provide good enantioselectivity in the hydrogenation of methyl-2-acetamidoacrylate, but repeatability issues were observed; further studies to determine a reproducible synthetic route for **4-5a** need to be undertaken. Future catalytic studies to be explored would involve using the Group 9 complexes **4-5a,b** in the hydrogenation of imines at 1 atm, as

well as employing increased hydrogen pressure for the hydrogenation reactions explored at 1 atm. Clean coordination chemistry has been observed with $[(allyl)PdCl]_2$ providing **4-6** as well as good catalytic activity and enantioselectivity. Further optimization of the palladium catalyzed allylic alkylation will be part of future endeavors by exploring the effect of the addition of a halide ion such as tetrabutylammonium chloride, bromide, iodide or borohydride.[2] Good enantioselectivities have been observed when freshly prepared **4-1** was employed, while earlier prepared **4-1** showed diminished selectivity in catalytic reactions, therefore, a spectroscopy study of the aging of **4-1** is warranted.

Finally, as has been alluded to in Chapter One, the electronic and steric contributions by ancillary ligands can have a significant impact upon the activity and selectivity of the catalyst in a variety of chemical transformations. To this end, it has been demonstrated that the ancillary ligands in this thesis serve as an effective tool in influencing the metal center during catalytic applications.

5.3 References

1. Kettler, P. B. *Org. Process Res. Dev.* **2003**, *7*, 342.
2. Fagnou, K.; Lautens, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 26.

Bibliography

Abbenhuis, H. C. L.; Burckhardt, U.; Gramlich, V.; Martelletti, A.; Spencer, J.; Steiner, I.; Togni, A. *Organometallics* **1996**, *15*, 1614.

Adams, J. J.; Curnow, O. J.; Huttner, G.; Smail, S. J.; Turnbull, M. M. *J. Organomet. Chem.* **1999**, *577*, 44.

Adams, J. J.; Berry, D. E.; Curnow, O. J.; Fern, G. M.; Hamilton, M. L.; Kitto, H. J.; Pipal, J. R. *Aust. J. Chem.* **2003**, *56*, 1153.

Adams, J. J.; Curnow, O. J.; Fern, G. M. *Inorg. Chim. Acta* **2006**, *359*, 3596.

Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079.

Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

Aneetha, H.; Wu, W.; Verkade, J. G. *Organometallics* **2005**, *24*, 2590.

Apple, D. C.; Brady, K. A.; Chance, J. M.; Heard, N. E.; Nile, T. A. *J. Mol. Catal.* **1985**, *29*, 55.

Arrayas, R. G.; Mancheno, O. G.; Carretero, J. C. *Chem. Commun.* **2004**, 1654.

Arrayas, R. G.; Adrio, J.; Carretero, J. C. *Angew. Chem. Int. Ed.* **2006**, *45*, 7674.

Atkinson, R. C. J.; Gibson, V. C.; Long, N. J. *Chem. Soc. Rev.* **2004**, *33*, 313.

Avis, M. W.; Goosen, M.; Elsevier, C. J.; Veldman, N.; Kooijman, H.; Spek, A. L. *Inorg. Chim. Acta* **1997**, *264*, 43.

Baker, M. J.; Pringle, P. G. *J. Chem. Soc. Chem. Commun.* **1991**, 1292.

Barbaro, P.; Bianchini, C.; Giambastiani, G.; Parisel, S. L. *Coord. Chem. Rev.* **2004**, *248*, 2131.

Bartok, M. *Curr. Org. Chem.* **2006**, *10*, 1533.

Bayon, J. C.; Claver, C.; Masdeu-Bulto, A. M. *Coord. Chem. Rev.* **1999**, *195*, 73.

Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320.

Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957.

Berry, D. E.; Browning, J.; Dixon, K. R.; Hilts, R. W.; Pidcock, A. *Inorg. Chem.* **1992**, *31*, 1479.

Betley, T. A.; Peters, J. C. *Inorg. Chem.* **2002**, *41*, 6541.

Betley, T. A.; Peters, J. C. *Angew. Chem. Int. Ed.* **2003**, *42*, 2385.

Birmingham, J. M. *Adv. Organomet. Chem.* **1964**, *2*, 365.

Blaser, H. U.; Buser, H. P.; Coers, K.; Hanreich, R.; Jalett, H. P.; Jelsch, E.; Pugin, B.; Schneider, H. D.; Spindler, F.; Wegmann, A. *Chimia* **1999**, *53*, 275.

Blaser, H. U.; Pugin, B.; Spindler, F. *J. Mol. Catal. A-Chem.* **2005**, *231*, 1.

Blaser, H. U.; Schmidt, E., *Asymmetric Catalysis on Industrial Scale: Challenges, Approaches and Solutions*. 1st ed. 2004, Weinheim: Wiley-VCH Verlag GmbH & Co.

Blaser, H. U.; Spindler, F.; Studer, A. *Appl. Catal. A-Gen.* **2001**, *221*, 119.

Bolm, C.; Muniz, K. *Chem. Soc. Rev.* **1999**, *28*, 51.

Bolm, C.; Xiao, L.; Hintermann, L.; Focken, T.; Raabe, G. *Organometallics* **2004**, *23*, 2362.

Bolm, C.; Xiao, L.; Kesselgruber, M. *Org. Biomol. Chem.* **2003**, *1*, 145.

Bradley, C. A.; Keresztes, I.; Lobkovsky, E.; Young, V. G.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 16937.

Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 10291.

Brauer, D. J.; Kottsieper, K. W.; Rossenbach, S.; Stelzer, O. *Eur. J. Inorg. Chem.* **2003**, 1748.

Braun, S.; Kalinowski, H.-O.; Berger, S., *150 and More Basic NMR Experiments*. 1998, Toronto: Wiley-VCH. 136.

Braunstein, P. *J. Organomet. Chem.* **2004**, *689*, 3953.

Brenchley, G.; Fedouloff, M.; Mahon, M. F.; Molloy, K. C.; Wills, M. *Tetrahedron* **1995**, *51*, 10581.

Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem. Int. Ed.* **1990**, *29*, 977.

Brock, W. H.; Jensen, K. A.; Jorgensen, C. K.; Kauffman, G. B. *Polyhedron* **1983**, *2*, 1.

Browning, J.; Bushnell, G. W.; Dixon, K. R.; Hilts, R. W. *J. Organomet. Chem.* **1992**, *434*, 241.

Browning, J.; Bushnell, G. W.; Dixon, K. R.; Hilts, R. W. *J. Organomet. Chem.* **1993**, *452*, 205.

Browning, J.; Bushnell, G. W.; Dixon, K. R.; Pidcock, A. *Inorg. Chem.* **1983**, *22*, 2226.

Browning, J.; Dixon, K. R.; Hilts, R. W. *Organometallics* **1989**, *8*, 552.

Browning, J.; Dixon, K. R.; Meanwell, N. J.; Wang, F. *J. Organomet. Chem.* **1993**, *460*, 117.

Burford, N.; Müller, J.; Parks, T. M. *J. Chem. Ed.* **1994**, *71*, 807.

Burrows, A. D.; Mahon, M. F.; Varrone, M. *Dalton Trans.* **2003**, 4718.

Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem. Int. Ed.* **1966**, *5*, 385.

Cai, D. W.; Payack, J. F.; Bender, D. R.; Hughes, D. L.; Verhoeven, T. R.; Reider, P. J. *Org. Syn.* **1999**, *76*, 6.

Camus, J. M.; Andrieu, J.; Richard, P.; Poli, R. *Eur. J. Inorg. Chem.* **2004**, 1081.

Carroll, A. M.; O'Sullivan, T. P.; Guiry, P. J. *Adv. Synth. Catal.* **2005**, *347*, 609.

Cipot, J.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Organometallics* **2007**, *26*, 594.

Cipot, J.; McDonald, R.; Stradiotto, M. *Chem. Commun.* **2005**, 4932.

Cipot, J.; McDonald, R.; Stradiotto, M. *Organometallics* **2006**, *25*, 29.

Cipot, J.; Vogels, C. M.; McDonald, R.; Westcott, S. A.; Stradiotto, M. *Organometallics* **2006**, *25*, 5965.

Cipot, J.; Wechsler, D.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 1737.

Cipot, J.; Wechsler, D.; Stradiotto, M.; McDonald, R.; Ferguson, M. J. *Organometallics* **2003**, *22*, 5185.

Clayden, J.; Greeves, N.; Warren, S.; Wothers, P., *Organic Chemistry*. 2001, New York: Oxford University Press.

Colacot, T. J. *Chem. Rev.* **2003**, *103*, 3101.

Comba, P.; Schiek, W. *Coord. Chem. Rev.* **2003**, *238*, 21.

Corbet, J. P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651.

Cozzi, P. G.; Zimmermann, N.; Hilgraf, R.; Schaffner, S.; Pfaltz, A. *Adv. Synth. Catal.* **2001**, *343*, 450.

Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331.

Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals*. 3rd ed. 2001, New York: John Wiley & Sons.

Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205.

Crabtree, R. H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *135*, 395.

Cramer, N.; Laschat, S.; Baro, A. *Organometallics* **2006**, *25*, 2284.

Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695.

Crudden, C. M.; Hleba, Y. B.; Chen, A. C. *J. Am. Chem. Soc.* **2004**, *126*, 9200.

Curnow, O. J.; Fern, G. M.; Hamilton, M. L.; Jenkins, E. M. *J. Organomet. Chem.* **2004**, *689*, 1897.

Dai, L. X.; Tu, T.; You, S. L.; Deng, W. P.; Hou, X. L. *Acc. Chem. Res.* **2003**, *36*, 659.

de Vries, J. G.; Lefort, L. *Chem. Eur. J.* **2006**, *12*, 4722.

Delacroix, O.; Gladysz, J. A. *Chem. Commun.* **2003**, 665.

Dyker, G. *Angew. Chem. Int. Ed.* **1999**, *38*, 1699.

Elsevier, C. J.; Kowall, B.; Kragten, H. *Inorg. Chem.* **1995**, *34*, 4836.

Elsevier, C. J.; Reedijk, J.; Walton, P. H.; Ward, M. D. *Dalton Trans.* **2003**, 1869.

Englert, U.; Hu, C.; Salzer, A.; Alberico, E. *Organometallics* **2004**, *23*, 5419.

Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671.

Evans, D. A.; Michael, F. E.; Tedrow, J. S.; Campos, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3534.

Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

Fagnou, K.; Lautens, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 26.

Fallis, K. A.; Anderson, G. K.; Rath, N. P. *Organometallics* **1992**, *11*, 885.

Farrugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Fernandez, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Lopez de Luzuriaga, J. M.; Olmos, E. *J. Chem. Soc.-Dalton Trans.* **1997**, 3515.

Field, L. D.; Ward, A. J. *J. Organomet. Chem.* **2003**, *681*, 91.

Francio, G.; Drommi, D.; Graiff, C.; Faraone, F.; Tiripicchio, A. *Inorg. Chim. Acta* **2002**, *338*, 59.

Franco, D.; Gomez, M.; Jimenez, F.; Muller, G.; Rocamora, M.; Maestro, M. A.; Mahia, J. *Organometallics* **2004**, *23*, 3197.

Fryzuk, M. D. *Nature* **2004**, *427*, 498.

Fuchs, N.; d'Augustin, M.; Humam, M.; Alexakis, A.; Taras, R.; Gladiali, S. *Tetrahedron: Asymmetry* **2005**, *16*, 3143.

Gade, L. H.; Cesar, V.; Bellemin-Laponnaz, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 1014.

Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363.

Gavrilov, K. N.; Tsarev, V. N.; Konkin, S. I.; Loim, N. M.; Petrovskii, P. V.; Kelbyscheva, E. S.; Korlyukov, A. A.; Antipin, M. Y.; Davankov, V. A. *Tetrahedron: Asymmetry* **2005**, *16*, 3224.

Gibson, S. E.; Ibrahim, H. *Chem. Commun.* **2002**, 2465.

Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.

Gladiali, S.; Dore, A.; Fabbri, D. *Tetrahedron: Asymmetry* **1994**, *5*, 1143.

Gladiali, S.; Loriga, G.; Medici, S.; Taras, R. *J. Mol. Catal. A-Chem.* **2003**, *196*, 27.

Gladiali, S.; Grepioni, F.; Medici, S.; Zucca, A.; Berente, Z.; Kollar, L. *Eur. J. Inorg. Chem.* **2003**, 556.

Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

Han, L. B.; Tanaka, M. *Chem. Commun.* **1999**, 395.

Harrod, J. F. *Coord. Chem. Rev.* **2000**, *206*, 493.

Hayashi, T.; Ohno, A.; Lu, S. J.; Matsumoto, Y.; Fukuyo, E.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 4221.

Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

Hiyama, T.; Kusumoto, T., in *Comprehensive Organic Synthesis*, Trost, B.M. and Fleming, I., Editors. 1991, Pergamon Press: Oxford. p. 763.

Hutchings, G. J. *Ann. Rev. Mater. Res.* **2005**, *35*, 143.

Huttenloch, O.; Laxman, E.; Waldmann, H. *Chem. Eur. J.* **2002**, *8*, 4767.

Huttenloch, O.; Spieler, J.; Waldmann, H. *Chem. Eur. J.* **2001**, *7*, 671.

Ini, S.; Oliver, A. G.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2001**, *20*, 3839.

Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3.

Jardine, F. H.; Osborn, J. A.; Wilkinson, G.; Young, J. F. *Chem. Ind. (London)* **1965**, 560.

Jeffrey, J. C.; Rauchfuss, T. B. *Inorg. Chem.* **1979**, *18*, 2658.

Jerphagnon, T.; Renaud, J. L.; Bruneau, C. *Tetrahedron: Asymmetry* **2004**, *15*, 2101.

Jia, C. G.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633.

Jones, G.; Butler, D. C. D.; Richards, C. J. *Tetrahedron Lett.* **2000**, *41*, 9351.

Kadyrov, R.; Heller, D.; Selke, R. *Tetrahedron: Asymmetry* **1998**, *9*, 329.

Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748.

Kalsi, P. S., *Stereochemistry - Conformation and Mechanism*. 1990, New Delhi: Wiley Eastern Ltd.

Kamer, P. C. J.; van Leeuwen, P. W. N.; Reek, J. N. H. *Acc. Chem. Res.* **2001**, *34*, 895.

Kamigaito, M.; Watanabe, Y.; Ando, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2002**, *124*, 9994.

Kettler, P. B. *Org. Process Res. Dev.* **2003**, *7*, 342.

Kilroy, T. G.; Hennessy, A. J.; Connolly, D. J.; Malone, Y. M.; Farrell, A.; Guiry, P. J. *J. Mol. Catal. A-Chem.* **2003**, *196*, 65.

Kloetzing, R. J.; Lotz, M.; Knochel, P. *Tetrahedron: Asymmetry* **2003**, *14*, 255.

Knowles, W. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 1999.

Knowles, W. S., *Asymmetric Hydrogenations - Monsanto L-Dopa Process*, in *Asymmetric Catalysis on Industrial Scale: Challenges, Approaches and Solutions*, Blaser, H.U. and Schmidt, E., Eds. 2004, Wiley-VCH Verlag GmbH & Co.: Weinheim. p. 23.

Komarov, I. V.; Borner, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 1197.

Kostas, I. D.; Vallianatou, K. A.; Holz, J.; Borner, A. *Appl. Organomet. Chem.* **2005**, *19*, 1090.

Kudis, S.; Helmchen, G. *Angew. Chem. Int. Ed.* **1998**, *37*, 3047.

Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.

Lee, J. H.; Son, S. U.; Chung, Y. K. *Tetrahedron: Asymmetry* **2003**, *14*, 2109.

Lensink, C.; Gainsford, G. J. *Aust. J. Chem.* **1998**, *51*, 667.

Leutenegger, U.; Umbricht, G.; Fahrni, C.; von Matt, P.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 2143.

Liu, D. L.; Xie, F.; Zhang, W. B. *Tetrahedron Lett.* **2007**, *48*, 585.

Liu, S. Y.; Hills, I. D.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 15352.

Lobana, T. S. *Prog. Inorganic Chem.* **1989**, *37*, 495.

Lobanova, I. A.; Zdanovich, V. I. *Russ. Chem. Rev.* **1988**, *57*, 967.

Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Schatte, G.; Stradiotto, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 4732.

Marciniec, B.; Gulinski, J. *J. Organomet. Chem.* **1993**, *446*, 15.

Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374.

Mazany, A. M.; Fackler, J. P. *Organometallics* **1982**, *1*, 752.

Milton, H. L.; Wheatley, M. V.; Slawin, A. M. Z.; Woollins, J. D. *Inorg. Chem. Commun.* **2004**, *7*, 1106.

Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932.

Moss, G. P. *Pure App. Chem.* **1996**, *68*, 2193.

Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131.

Munowitz, M., *Principles of Chemistry*. 2000, New York: W. W. Norton & Company, Inc.

Murray, H. H.; Garzon, G.; Raptis, R. G.; Mazany, A. M.; Porter, L. C.; Fackler, J. P. *Inorg. Chem.* **1988**, *27*, 836.

Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.

Noyori, R. *Angew. Chem. Int. Ed.* **2002**, *41*, 2008.

Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101.

Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389.

Oro, L. A.; Fernandez, M. J.; Esteruelas, M. A.; Jimenez, M. S. *J. Mol. Catal.* **1986**, *37*, 151.

Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. (A)* **1966**, 1711.

Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 77.

Otwinowski, Z.; Minor, W., *Processing of X-ray diffraction data collected in oscillation mode*, in *Macromolecular Crystallography, Pt A*. 1997, Academic Press Inc: San Diego. p. 307.

Plenio, H.; Burth, D. *Organometallics* **1996**, *15*, 1151.

Plenio, H.; Burth, D. *Z. Anorg. Allg. Chem.* **1996**, *622*, 225.

Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *Nature* **2004**, *427*, 527.

Qiao, S.; Hoic, D. A.; Fu, G. C. *Organometallics* **1998**, *17*, 773.

Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2005**, *24*, 4981.

Reetz, M. T.; Beuttenmuller, E. W.; Goddard, R.; Pasto, M. *Tetrahedron Lett.* **1999**, *40*, 4977.

Reichl, J. A.; Berry, D. H. *Adv. Organomet. Chem.* **1999**, *43*, 197.

Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731.

Rubin, M.; Schwier, T.; Gevorgyan, N. *J. Org. Chem.* **2002**, *67*, 1936.

Rupert, K. C.; Liu, C. C.; Nguyen, T. T.; Whitener, M. A.; Sowa, J. R. *Organometallics* **2002**, *21*, 144.

Sablong, R.; Newton, C.; Dierkes, P.; Osborn, J. A. *Tetrahedron Lett.* **1996**, *37*, 4933.

Saito, M.; Nishibayashi, Y.; Uemura, S. *Organometallics* **2004**, *23*, 4012.

Santi, S.; Ceccon, A.; Carli, F.; Crociani, L.; Bisello, A.; Tiso, M.; Venzo, A. *Organometallics* **2002**, *21*, 2679.

Santi, S.; Ceccon, A.; Crociani, L.; Gambaro, A.; Ganis, P.; Tiso, M.; Venzo, A.; Bacchi, A. *Organometallics* **2002**, *21*, 565.

Schenkel, L. B.; Ellman, J. A. *Org. Lett.* **2003**, *5*, 545.

Scherer, J.; Huttner, G.; Buchner, M.; Bakos, J. *J. Organomet. Chem.* **1996**, *520*, 45.

Schlosser, M.; Hartmann, J. *Angew. Chem. Int. Ed.* **1973**, *12*, 508.

Schneider, J. J. *Angew. Chem. Int. Ed.* **1996**, *35*, 1069.

Schnyder, A.; Hintermann, L.; Togni, A. *Angew. Chem. Int. Ed.* **1995**, *34*, 931.

Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Halterman, R. L. *Organometallics* **2001**, *20*, 2215.

Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Halterman, R. L. *Organometallics* **2001**, *20*, 5360.

Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Blum, J.; Gelman, D.; Halterman, R. L. *Eur. J. Inorg. Chem.* **2002**, 211.

Sheldrick, G. M., *SHELXL97-2, Program for the Solution of Crystal Structures*. 1997: University of Göttingen, Göttingen, Germany.

Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879.

Sirbu, D.; Consiglio, G.; Gischig, S. *J. Organomet. Chem.* **2006**, *691*, 1143.

Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.
Son, S. U. K.; Park, K. H.; Lee, S. J.; Chung, Y. K.; Sweigart, D. A. *Chem. Commun.* **2001**, 1290.

Speier, J. L. *Adv. Organomet. Chem.* **1979**, *681*, 91.

Spessard, G. O.; Miessler, G. L., *Organometallic Chemistry*. 1996, Upper Saddle River, New Jersey: Prentice-Hall Inc.

Spindler, F.; Blaser, H. U. *Enantiomer* **1999**, *4*, 557.

Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618.

Stradiotto, M.; Kozak, C. M.; McGlinchey, M. J. *J. Organomet. Chem.* **1998**, *564*, 101.

Stradiotto, M.; McGlinchey, M. J. *Coord. Chem. Rev.* **2001**, *219*, 311.

Swamy, K. C. K.; Kumaraswamy, S.; Kumar, K. S.; Muthiah, C. *Tetrahedron Lett.* **2005**, *46*, 3347.

Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* **1986**, *51*, 629.

Takeuchi, R.; Yasue, H. *Organometallics* **1996**, *15*, 2098.

Tanaka, M. *Top. Curr. Chem.* **2004**, *232*, 25.

Tao, B. T.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 3892.

Thimmaiah, M.; Luck, R. L.; Fang, S. Y. *J. Organomet. Chem.* **2007**, *692*, 1956.

Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.

Togni, A. *Angew. Chem. Int. Ed.* **1996**, *35*, 1475.

Tundo, P.; Perosa, A. *Chem. Soc. Rev.* **2007**, *36*, 532.

Tungler, A.; Sipos, E.; Hada, V. *Curr. Org. Chem.* **2006**, *10*, 1569.

Valderrama, M.; Contretas, R. *J. Organomet. Chem.* **1996**, *513*, 7.

Vanderent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1990**, *28*, 90.

Vecchio, B. M.; de Maria, G. *Chim. Oggi-Chem. Today* **2006**, *24*, 3.

von Matt, P.; Pfaltz, A. *Angew. Chem. Int. Ed.* **1993**, *32*, 566.

Wallner, O. A.; Olsson, V. J.; Eriksson, L.; Szabo, K. J. *Inorg. Chim. Acta* **2006**, *359*, 1767.

Watson, L. D. G.; Yudin, A. K. *J. Am. Chem. Soc.* **2005**, *127*, 17516.

Westcott, S. A.; Kakkar, A. K.; Taylor, N. J.; Roe, D. C.; Marder, T. B. *Can. J. Chem.* **1999**, *77*, 205.

Wile, B. M.; Burford, R. J.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2006**, *25*, 1028.

Wile, B. M.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics* **2007**, *26*, 1069.

Yin, L. X.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133.

Yoon, T. P.; Jacobsen, E. N. *Science* **2003**, *299*, 1691.

Young, J. F.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1965**,131.

Yun, H. D. *Aust. J. Chem.* **2004**, *57*, 383.

Zargarian, D. *Coord. Chem. Rev.* **2002**, *233*, 157.

Zon, G.; DeBruin, K. E.; Naumann, K.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7023.