Metallated group IX and group X phosphinimine complexes.

Katie Tak-Kwan. Chan
University of Windsor

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UMI®
Metallated Group IX and Group X Phosphinimine Complexes

By
Katie T. K. Chan

A Thesis
Submitted to the Faculty of Graduate Studies and Research through the Department of Chemistry and Biochemistry in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor

Windsor, Ontario, Canada
April, 2003
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Abstract

The focus of this research has been the preparation of late transition metal phosphinimine complexes. The thesis herein describes the synthesis of a series of monomeric Group IX phosphinimine complexes. \([\text{RhCOD(o-C}_6\text{H}_5\text{PPh}_2\text{NR})]\) \(\text{R} = 2,6-\text{C}_6\text{H}_{12}(\text{CH}_3)_2\ \text{44, 2,6-}\text{C}_6\text{H}_5\text{Pr}_2\ \text{45, 3,5-}\text{C}_6\text{H}_5(\text{CH}_3)_2\ \text{46 and Ph 47}\) were prepared \textit{via} salt metathesis under mild conditions. The analogous complexes \([\text{Rh(o-C}_6\text{H}_5\text{PPh}_2\text{NPh})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]\ \text{52 and [IrCOD(o-C}_6\text{H}_5\text{PPh}_2\text{NPh})]}\ \text{53} were also readily prepared by similar methods. Reactivity studies were performed on these complexes. Unexpectedly, complexes \text{46, 47, 52 and 53} underwent oxidative addition of methylene chloride. However, when steric bulk was introduced on the 2,6-positions of the N-phenyl ring (compounds \text{44 and 45}), oxidative addition of \text{CH}_2\text{Cl}_2 was not observed.

The reaction of Group X transition metals with phosphinimine ligands was also explored. Attempts to coordinate \([\text{Li(o-C}_6\text{H}_5\text{PPh}_2\text{NR})]_2\text{Et}_2\text{O} \ (\text{R} = \text{SiMe}_3\ \text{61 and tBu 62})\) to Group X transition metals proved to be unsuccessful due to steric congestion. However, transmetallation did occur when less bulky phosphinimine ligands were used, such as, \([\text{Li(o-C}_6\text{H}_5\text{PPh}_2\text{NR})]_2\text{Et}_2\text{O} \ (\text{R} = \text{Ph 63 and 3,5-}\text{C}_6\text{H}_5(\text{CH}_3)_2\ \text{66})\). The Group X phosphinimine complexes described herein, \([\text{Ni(o-C}_6\text{H}_5\text{PPh}_2\text{NR})]_2\) \(\text{R} = \text{Ph 67 and 3,5-}\text{C}_6\text{H}_5(\text{CH}_3)_2\ \text{68}\) and \([\text{Pd(o-C}_6\text{H}_5\text{PPh}_2\text{NPh})]_2\ \text{69, were bis-ligand type complexes.} \)
"I have not failed. I have just found 10,000 ways that won't work."
— Thomas Alva Edison

If A equals success, then the formula is: \( A = X + Y + Z \),
- \( X \) is work. \( Y \) is play.
- \( Z \) is keep your mouth shut.
— Albert Einstein

"Meeting challenges and enduring them, even though such experiences are often fraught with pain, is part of the great drive in human nature to expand beyond previously accepted limits."
— Michael Murphy
Acknowledgments

Graduate study is a test of endurance. The work presented in this thesis could not have been possible without the support of many people.

I wish to begin with expressing my sincere gratitude and appreciation to my supervisor, Dr. D. W. Stephan for his excellent supervision, continuous encouragement and valuable suggestion throughout the development of this work. I would also like to thanks Dr. S. J. Loeb and Dr. R. G. Maev for their role as my committee members.

I am also obliged to all faculty members of the Department of Chemistry and Biochemistry, especially Dr. L. Lee for her encouragement since my undergraduate study. Many thanks are owed to all past and present Stephan group, Dr. Jim Kickham, Dr. Todd Graham, Dr. Denise Walsh, Emily, Chad, Sarah, Jason, Steve, Lourisa, Jenny, Nancy, Aaron, Chris, etc. for all your friendship, daily discussion and spirit throughout the year. I am also grateful to Dr. P. Wei and Mike Fuerth for their expertise on X-ray crystallography and NMR spectroscopy.

My heartfelt thanks to my family relentless support and encouragement throughout the years. Their confidences in me and continuing support have been vital to my ability in pursuing graduate studies.

Last but not least, I would like to thank a precious friend, Robert L. K. Yu for his endearing friendship, endless support and belief in me enabled me to successfully achieve a goal which at times seemed impossible to reach.
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<td>atm</td>
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<td>BIPE</td>
<td>bis((N-\text{-}p\text{-}tolylimino)diphenylphosphoranyl) ethane</td>
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<td>BIPM</td>
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<td>Bn</td>
<td>benzyl ((-\text{CH}_2\text{C}_6\text{H}_5))</td>
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<tr>
<td>J</td>
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</tr>
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<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethylsilyl</td>
</tr>
<tr>
<td>Tol</td>
<td>tolyl (C₆H₄CH₃)</td>
</tr>
<tr>
<td>µ</td>
<td>bridging</td>
</tr>
<tr>
<td>α</td>
<td>alpha</td>
</tr>
<tr>
<td>β</td>
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<td>γ</td>
<td>gamma</td>
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Chapter One
Introduction

The continued development of well-defined transition metal complexes has had a huge impact on catalysis, especially single-site olefin polymerization catalysis.\textsuperscript{1-3} Synthesis of new polymerization catalysts such as early metal metallocenes,\textsuperscript{4,5} early metal non-metallocenes,\textsuperscript{6} and recently, Schiff base-containing late metal systems\textsuperscript{7-15} have generated intense interest because of the unique reactivity from each catalyst and the potential insight gained through understanding ligand-metal effects on the catalyst behavior. Within our own research group, attention has been focused primarily on catalysts that contain phosphinimide ligands. While investigating early transition metal complexes of phosphinimide ligands, we have shown that they can act as effective catalysts for ethylene polymerization upon activation with the appropriate co-catalyst.\textsuperscript{16-22}

While early transition metal systems continue to be a fruitful area of study, recent interest has focused on late metal olefin polymerization catalysts, such as the work performed by Brookhart\textsuperscript{8,9,24-25} Gibson,\textsuperscript{10-12,26} and most recently Grubbs.\textsuperscript{14} These systems are very interesting, as they offer a unique approach to a variety of highly branched polyethylene. As part of our continuing efforts, we are exploring late metal complexes of phosphinimine and phosphinimide ligands. This introductory chapter briefly describes the historical development of the chemistry of Group IX and Group X transition metals. In addition, different types and properties of phosphinimine ligands, and previously reported phosphinimine metal complexes will be described.
1.1 **Historical Development of Rhodium Chemistry**

Rhodium is one of the least abundant elements in the earth's crust, and yet the chemistry of this metal is among the most diverse of all the transition metals and is being vigorously investigated at the present time.\(^{27-92}\) Rhodium forms organometallic compounds in oxidation states ranging from +4 to -3, although by far the most common oxidation states are Rh(I) and Rh(III).

The first compound containing a rhodium-carbon bond was synthesized by Manchot and König in 1925 by treating \([\text{RhCl}_2]\) with CO.\(^{38}\) This complex was later formulated correctly by Hieber and Lagally\(^{34}\) as the halogen bridged dimer \([\text{Rh}_2\text{Cl}_2(\text{CO})_4]^-\). A decade later, Wilkinson and co-workers\(^{85}\) reported the preparation and characterization of the rhodium cation, \([\text{Rh}(\eta^5-\text{C}_5\text{H}_5)_2]^+\). The first rhodium complex containing a rhodium-alkene bond \([\{\text{RhCl}(\eta^3-1,5-\text{COD})\}^2\text{L}_2\]}\) was prepared by Chatt and Venanzi in 1956.\(^{36}\) The same year, the first important class of rhodium carbonyl complex, which later developed into useful hydroformylation catalysts, \([\text{trans-RhCl}(\text{CO})\text{L}_2]\) (L=tertiary phosphine or arsine) was reported by Hieber and Heusinger.\(^{37}\) Three years later, Fischer's group in Germany\(^{38}\) and Wilkinson's group in England\(^{39}\) simultaneously reported the discovery of the first rhodium compound containing a coordinated conjugated diene \([\text{Rh}(\eta^5-\text{C}_5\text{H}_5)(\eta^1\text{-C}_5\text{H}_6)]\}. Later, Cramer\(^{40}\) discovered the first rhodium complex containing a monoalkene ligand \([\{\text{RhCl}(\eta^5\text{-C}_5\text{H}_5)_2\}^2\text{L}_2\]}\). This discovery was quickly followed by the report of the first compounds containing a rhodium-carbon \(\sigma\)-bond \([\text{RhBr}(1\text{-naphthyl})_2\text{L}_2]^-\) (L = tertiary phosphine) by Chatt and Underhill.\(^{41}\) Perhaps the most important discovery which led to the explosion of interest in organorhodium chemistry came in 1965 when Wilkinson
and his co-workers$^5$ reported that solutions of $[\text{RhCl(PPh}_3)_3]$ would homogeneously catalyze the hydrogenation of alkenes and alkynes. Since then, there has been intense industrial and academic interest in the synthesis and chemistry of compounds containing rhodium-carbon and rhodium-hydrogen bonds.

1.2 Oxidative Addition of Chlorinated Solvents using Late Transition Metal Complexes

Oxidative addition is perhaps one of the most important factors governing catalytic reactions, since many catalytic cycles involve this process as a key step. Oxidative addition reactions of aliphatic compounds containing a C-X bond (X=Cl, Br or I) to low-valent transition metals are well documented.$^{43-52}$ There are many examples of oxidative addition reactions involving molecules of the type CH$_2$X (X=I or Br), and especially numerous are reports with more reactive species such as CH$_2$I$_2$, CH$_2$Br$_2$ and CH$_2$ICl.$^{58-55}$ Early reports of reactions with the solvents CH$_2$Cl$_2$ and CHCl$_3$ suggested that thermal$^{56}$ or photochemical$^{54,57}$ initiation was required. Recently though, several reactions involving oxidative addition of CH$_2$Cl$_2$ with transition metal complexes under mild conditions have been documented. In general, these reactions lead to products containing halomethyl (Cl-H$_2$C-M-Cl, or Cl-H$_2$C-M$^+$ X$^-$), methylene-bridged (X-M-CH$_2$-M-X) derivatives, or even metal carbene complexes.

The activation of dihalomethane by late metal transition metal complexes has been studied as a method of generating the metal-halomethane unit, M-CH$_2$X (X = halogen).$^{46,55,54,58-60}$ Throughout the years, examples of simple
oxidative addition of CH₂Cl₂ to form chloromethyl complexes have been reported for electron-rich transition metal complexes containing mono-61-63 or poly-dentate phosphine ligands,64,65 bi- or tri-dentate nitrogen ligands,66-68 sulfur macrocycles69 and phosphorus-nitrogen hybrid ligands.70-72 Heaton et al.,60 for example, reported the synthesis of mer-[Rh(py)₃(CH₂Cl)Cl₂] 1 (Figure 1.1) from the reaction of [Rh₂(C₈H₁₆)(μ-Cl)]₂ (C₈H₁₆ = cyclooctene) with pyridine in CH₂Cl₂.

![Figure 1.1 mer-[Rh(py)₃(CH₂Cl)Cl₂]](image)

Occasionally, double activation of the dihalomethane results in the formation of bridging methylene (μ-CH₂) binuclear complexes. These reactions have been observed with the highly basic rhodium complexes [Rh₂(dppe)₂(μ-Cl)]₂,73 [Rh₂(PR₃)₄(μ-Cl)]₂(PR₃=PEt₃ or PPh₂Me) and [Rh₂(CN)₂Bu₁₂(μ-pz)]₂ (pz=pyrazolate).75 The first type of double oxidative addition reaction of CH₂Cl₂ to a metal complex was reported in 1997 by Caulton et al.,76 [RuH₂(H₂)L₂][L=P(C₆H₁₁)₃] underwent an unprecedented oxidative addition of both C-Cl bonds of CH₂Cl₂ to a single metal center, providing a convenient synthesis of the alkene metathesis catalyst [RuCl₂(CH₂){P(C₆H₁₁)₃}₂] 2 (Figure 1.2).
1.3 Development of Late Transition Metal Catalysts

In recent years, there has been increasing interest in the development of late transition metal-based catalysts for the polymerization of α-olefins and functionalized olefins under ambient conditions. The most notable catalysts thus far were reported by Brookhart and co-workers in 1995. They synthesized highly active cationic nickel (II) and palladium (II)-based catalysts of the type \([\text{ArN} = \text{C}(\text{R})\text{C}(\text{R}) = \text{NAr}]\text{M-CH}_3\). There are three key features of these α-diimine polymerization catalysts. First, the highly electrophilic cationic nickel and palladium metal centers result in rapid rates of olefin insertion. Second, the use of the sterically bulky α-diimine ligand favors insertion over chain transfer. Third, the use of noncoordinating counterions provides an accessible coordination site for the incoming olefin.

Late metal catalysts systems serve as a promising alternative to both traditional Ziegler-Natta and metalloocene catalysts. Since early transition metal catalysts are highly oxophilic, they are incompatible with functionalized vinyl monomers. Late transition metal catalysts are less oxophilic. Traditionally, however, they produced dimers or low-molecular weight oligomers due to chain termination via β-hydride elimination.
However, Brookhart's late transition metal catalyst systems demonstrated the ability to produce high molecular weight polyethylene and poly α-olefins,28 in addition to copolymerizing ethylene and functionalized olefins such as alkyl acrylates (when M = palladium).77,78 There are only a limited number of late transition metal catalysts for the polymerization of high molecular weight polymers reported in the literature.96-99 Most of them are based on either the neutral nickel (II) complexes14,80,95,100-106 (Figure 1.3) of monoanionic bidentate ligands, or cationic nickel, palladium, iron, or cobalt complexes8,9,38,77,78 (Figure 1.4) containing neutral multidentate ligands with bulky substituted nitrogen donor atoms.10,24,107.

\[ X = \text{H, SO}_4\text{Na} \]
\[ Y = \text{aryl, OR}\]^{\text{"}}\]
\[ L = \text{PR}_3, \text{subst. pyridine, CR}_2\text{PR}_3 \]

\[ X = \text{H, NO}_2 \]
\[ R = \text{H, aryl} \]
\[ R' = \text{Me; L = CH}_3\text{CN} \]
\[ R' = \text{Ph; L = PPh}_3 \]

Figure 1.3 Examples of neutral nickel (II) complexes
Figure 1.4  Examples of Ni, Pd, Fe and Co complexes

The recent discoveries of late transition metal catalysts are mostly based on the structural types shown in 4 - 6, and these systems have spurred intense research for new late transition metal olefin polymerization catalysts using different types of ligand structures.

1.4  Synthesis and Types of Phosphinimine Ligands

Staudinger first reported the preparation of phosphinimines in 1919 as the product of the redox reaction between tertiary phosphines (PR₃) with trimethylsilylazide (TMSN₃) to yield nitrogen gas and the corresponding triaryl- or trialkyl-phosphine silylimide (Figure 1.5).\(^{108}\)

\[
\text{PR}_3 + \text{TMS-N}_3 \rightarrow \text{R}_3\text{P} = \text{N-TMS} + \text{N}_2
\]

R = alkyl, aryl

Figure 1.5  General equation of Staudinger’s reaction
Monophosphazenes of the type \( R_3P=NR'(R' \neq H) \) are commonly referred to as phosphinimines, phosphoranimines or imino phosphoranes. They are useful intermediates in the synthesis of natural products\(^{100-111} \) and of nitrogen-containing organic compounds. The phosphinimine ligand can be represented as two resonance hybrids, \( R_3P^\equiv-N-R \) and \( R_3P=NR' \), and they are isoelectronic with phosphorus ylides. This kind of ligand framework is electronically very versatile, as it donates electron to the transition metal center resulting in strong MN bond character where M is a transition metal.

The nature of the highly polar P-N bond in the phosphinimine ligand makes it versatile in coordination and organometallic chemistry.\(^{112-118} \) Variation of the substituents either on the nitrogen, or on the phosphorus atoms can both affect the basicity of the imine nitrogen, as well the steric and electronic properties of the phosphorus center.\(^{119,120} \) The nitrogen atom of the phosphinimine acts as either a two-electron donor,\(^{121-128} \) for example in \( (CO)_6W(Ph_3PNPh) \) \( 8 \), or as a four-electron donor, as in the bridging mode of \( Mo_2(CO)_6(Ph_3PNH)_2 \) \( 9 \) (Figure 1.6).\(^{124} \)

![Diagram of compounds 8 and 9]

**Figure 1.6** Examples of the imine nitrogen of phosphinimine acting as a 2 or 4 e⁻ donor
As a result, the phosphinimine ligand offers a high degree of chemical flexibility that is useful when designing new organometallic compounds.

In general, there are several common approaches to synthesize phosphinimines. As was shown in Figure 1.5, the oxidation of a phosphine with the appropriate alkyl, aryl or silyl azide is the most commonly used method to generate phosphinimine compounds.\textsuperscript{108} Another alternative is using N-lithiated phosphinimides (also known as lithium phosphonium azayldiides). They were initially prepared by Schmidbaur and Jonas\textsuperscript{125} in 1967 by direct metallation of the corresponding phosphinimine\textsuperscript{126,127} with a base such as methyl lithium in ether. In an extension of this chemistry, the corresponding N-substituted phosphinimine 11 can be obtained by reacting the N-lithiated phosphinimide 10 with a phosphorus electrophile (Figure 1.7).\textsuperscript{125,128-130}

\[
\begin{align*}
R_3P=NLi & \quad + \quad R'_2PCl & \quad \rightarrow \quad R_3P=N-PR'_2 \\
10 & \quad 11
\end{align*}
\]

Figure 1.7 Reaction of a phosphorus electrophile with N-lithiated phosphinimide

Several research groups have demonstrated that introduction of a second phosphine moiety on the phosphinimine backbone to create a bidentate ligand is also possible (Figure 1.8).\textsuperscript{131} This kind of ligand system is versatile, since it provides further possibility of developing new classes of ligand simply by changing the bridging species in the backbone. Cavell and co-workers have demonstrated that the controlled oxidation of \textit{bis}(diphenylphosphino)methane (dppm) with trimethylsilyl azide produces the heterodifunctional phosphine-
phosphinimine 12 in good yield.\textsuperscript{159-154} This reaction represents the first example of the selective oxidation of an alkane diphosphine with a nitrogen base.

\[
\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2 + \text{Me}_3\text{EN}_3 \xrightarrow{-\text{N}_2} \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2 \underline{\text{NEMe}_3} \quad n = 1, 2 \quad E = \text{Ge}, \text{Si}
\]

**Figure 1.8** Formation of phosphine-phosphinimine ligand system

This synthetic route can be applied to different bridged diphosphorus compounds and provides access to substituted phosphinimine-phosphine. Ligands of the type 12 are versatile, since they combine the ligating properties of the phosphinimines with those of the traditional tertiary phosphines.

Besides changing functional groups on phosphorus, functional groups attached to the nitrogen can also be easily modified.\textsuperscript{185} Cavell and co-workers have demonstrated an alternative route to Staudinger's reaction. They attached a nitro aromatic ring to the phosphinimine nitrogen through the reaction of the nitro fluoro aromatic with an iminosilylated phosphorus compound \textit{via} the elimination of Me\textsubscript{3}SiF.\textsuperscript{(Figure 1.9)}\textsuperscript{126} This reaction provides a safe route to synthesize nitro aromatic phosphinimine-phosphine ligands, while avoiding the preparation of explosive nitro aromatic azides which would be essential for the Staudinger route.
The bidentate form of phosphinimine ligands, such as bis(phosphinimine) methane $\left[ \text{CH}_2(\text{PR}_3=\text{N-aryl})_2 \right]^{136-140}$ has also been thoroughly investigated.$^{136,137,141}$ Bis(methylene phosphoranyl)methane is analogous to 1,3-diketones. Elsevier et al.$^{142}$ proposed that it exists in two tautomeric forms although they could not establish such behaviour neither in solution nor in the solid state. (Figure 1.10).

Compound 16 is the typical representation of the ligand, whereas 17 is the tautomeric form, in which a proton migration has occurred from the central carbon atom to one of the nitrogen atoms. The two highly polarized P=N groups cause the methylene hydrogen atoms of tautomer 16 to be acidic,$^{143}$ therefore deprotonation of the methylene group readily occurs.
1.5 Metallated Phosphinimine Complexes

Since the first reports on the synthesis of phosphinimine ligands,\textsuperscript{108} many investigations of the reactivity and coordination behavior of these compounds have been performed. There are few examples of a phosphinimine ligand acting as a four electron donor as in $\text{Mo}_2(\text{CO})_6(\text{HN}≡\text{PPh}_3)\text{_3}$\textsuperscript{9}, where each $\text{P}≡\text{N}$ ligand bridges \textit{via} the nitrogen atom between the two Mo atoms. Since then, information on mono-phosphinimine complexes has been explored with metals such as: $\text{V},\text{Co},\text{Cu},\text{W},\text{Os},\text{Zn},\text{Cd},\text{Hg},\text{Al},\text{Ge}\text{128,150-152}$ and $\text{B}\text{153}$.

In 1975, Fukui and co-workers synthesized the first example of palladium(II) complexes with $p$-substituted phenyliminotriphenylphosphine $\text{18}$ and $N$-trimethylsilyliminodiphenylmethylphosphine ligands $\text{19}$ (Figure 1.11).\textsuperscript{154}

![Figure 1.11 Pd(II) complexes with $p$-substituted phenyliminotriphenylphosphine and $N$-trimethylsilyliminodiphenylmethylphosphine ligands](image)

\(R = \text{NO}_2, \text{Cl, H, CH}_3\)
In efforts to try to obtain insight into the coordination properties and behaviour of the phosphinimine ligand, $R_3P=NR'$ toward different transition metals, in 1990, Elsevier synthesized the rhodium(I) phosphinimine complexes $[\text{RhL}_2\text{Cl}(RP=NR')]$ (R = Me$_3$, Et$_3$, Me$_2$Ph, Ph$_3$ and R' = H, SiMe$_3$, 'Bu, Ph, p-tolyl). This was achieved by reacting $[\text{RhLCl}]_2$ ($L = \text{CO, COD}$) and the phosphinimine ligand in benzene or chloroform at room temperature.$^{155}$ In the same year, Cavell and co-workers synthesized the first structurally characterized example of a phosphinimine-phosphine palladium(II) complex, \(RN=PPh_2(CH_2)_nEPh_3PdCl_2\) (R = SiMe$_3$, GeMe$_3$, H ; n = 1, 2 ; E = P, As).$^{156}$ In the following year, phosphinimine complexes of platinum(II) were reported.$^{156}$ Since then, late transition metal complexes containing phosphinimine groups have been extensively studied. In 1997, the first phosphinimine gold complex was isolated from the reaction of $[\text{Au}(PPh_3)(\text{NOsO}_3)]$ with Ph$_3$PNPh to yield the N-phosphinimine complex $[\text{Au}(PPh_3)(\text{PhN=PPh}_3)]^{+}[\text{NOsO}_3]^{-}$ (Figure 1.12).$^{157}$

\[
\begin{align*}
\text{Figure 1.12} & \quad \text{Structure of } [\text{Au}(PPh_3)(\text{PhN=PPh}_3)]^{+}[\text{NOsO}_3]^{-}
\end{align*}
\]

The combination of a reactive metal species and a polarized phosphinimine ligand has demonstrated some interesting reactivity. In 1999, Nicholson et al.
discovered the first example of cyclometallation of Ph₅PNPh with PhCH₂Mn(CO)₅ in refluxing heptane (Figure 1.13).¹⁵⁸

\[
\text{Ph₅PNPh + PhCH₂Mn(CO)₅} \xrightarrow{\Delta \text{heptane}} \text{Ph₅PN} \underset{\text{Mn(CO)₄ + PhCH₂CHO}}{\text{Ph}}
\]

21

Figure 1.13 Orthomanganation of Ph₅PNPh

Recently, Stalke et al. has examined the use of the deprotonated phosphinimine \([\sigma-\text{LiC₆H₄Ph₂P=NSiMe₃}]¹⁵⁹\) (formed from the lithiation of Ph₅PNSiMe₃ with MeLi) as a ligand for the stabilization of a series of diarylstannylene and plumbylene complexes (Figure 1.14).¹⁶⁰ They also successfully synthesized the corresponding organocopper complex, \([\text{Cu}(\sigma-C₆H₄PPh₂NSiMe₃)]₂\), and the zinc complex, \([\text{Zn}(\sigma-C₆H₄PPh₂NSiMe₃)]₄\), by reacting the same deprotonated phosphinimine with CuBr and ZnCl₂ respectively.¹⁶¹

\[
\begin{align*}
\text{22} & \quad \xrightarrow{\text{MCl₃/Et₂O/ -30°C}} \quad \text{23} \\
& \quad \text{- LiCl} \\
& \text{(M = Sn, Pb)}
\end{align*}
\]

Figure 1.14 Reaction of \([\sigma-\text{LiC₆H₄Ph₂P=NSiMe₃}]\) with Sn(II) and Pb(II)
In these cases, a lithiated phosphinimine was chosen as a starting material because this complex provided the following requirements of an organometallic ligand capable of side arm donation. First, the deprotonated ortho phenyl carbon atom leads to a metal-carbon σ-bond in transmetallation reactions with metal halides. Secondly, the imine nitrogen atom donates its electron pair to the metal center for further stabilization.

Another class of phosphinimine compound, [(Ph₂P=N-R)₂CH₂] (R=aryl, tolyl), which contain two phosphorus atoms were also fully investigated. The organometallic and coordination chemistry of this bis(iminophosphoranyl)methane (BIPM) ligand towards various transition metals such as Mo,⁹⁴ Rh,¹³⁵,¹⁴²,¹⁶²,¹⁶₅ Ir,¹⁴²,¹⁶²-¹⁶⁴ Pd,¹³⁴,¹⁶⁵,¹⁶⁶ and Pt¹⁶³,¹⁶⁶,¹⁶⁷ have been published. Previous reports have shown that reaction of the N-SiMe₃-substituted BIPM ligand with d⁰ transition metals such as WX₆ (X=Cl, F)¹⁶⁸ and OsO₄¹⁶⁹ resulted in the formation of N,N’-coordinated six membered metallacycles. The key feature in all these reactions involved the cleavage of the reactive Si-N bond, where heterocyclic compounds were being synthesized in all cases instead of forming phosphinimine complexes. Conversely, N-aryl substituted BIPM ligands have proven to be more suitable in reactions with late metals like Pt, Rh and Ir¹⁷⁰ resulting in the formation of phosphinimine metal complexes. However, these reactions result in the formation of two isomers, 24 and 25. The BIPM ligand acts as a σ-N, σ-N’ chelate in isomer 24, and as a σ-N, σ-C chelated in isomer 25 (Figure 1.15). The alternative coordination mode in 25 is the result of the ability of one of the methylene protons to migrate to one
of the terminal N atoms. Due to this proton migration, the formation of the four-membered metallacycles were unavoidable.

![Chemical structures of complexes 24 and 25.](image)

Figure 1.15 Different coordination modes of the reaction of BIPM with late metals

In 1996, Elsevier et al. successfully synthesized a modified version of the BIPM ligand by substituting the bridging CH₂ group with a CHCH₃ group. This modification introduced more steric hindrance around the central carbon atom, and hence favours stabilization of the σ-N, σ-N' coordinated species. At the same time, the inductive electronic effect of the methyl group decreases the acidity of the methane proton. As a result, the reactions of Pt₂Cl₄(PR₃)₂ (PR₃ = PE₃ or PMe₂Ph) with 1,1-bis((N-p-tolylimino)diphenylphosphoranyl) ethane (1,1-BIPE) 26 afforded the σ-N monodentate complex 27. Conversion of 27 into the six membered platination cycle 28 took place after prolonged stirring in methylene chloride (Figure 1.16).
Figure 1.16 Reaction of Pt₃Cl₄(PR₃)₂ (PR₃=PEt₃ or PMe₂Ph) with 1,1-BIPE

Later, Stephan and Cavell simultaneously published their work on the mono- and di-lithiation of bis(diphenyl-N-trimethylsilylphosphinimino)methane. Since the backbone CH₂ protons are moderately acidic, the ligand can be deprotonated by strong bases to generate the mono- and di-anionic species. These compounds have proven to be convenient precursors for transmetallation reactions, forming various metal complexes (Figure 1.17).

Figure 1.17 Mono or double deprotonation of CH₂(Ph₃P=NSiMe₃)₂
While not directly related to the present thesis, it is also noteworthy that besides reacting with late transition metal, these dilithiated bis(phosphinimine)methane are proven to form Ti, Zr$^{140,175}$ and bridging Cr carbene complexes.$^{174}$ Also, reaction of compound 31 with metals such as aluminum, gallium and indium halides readily yield four coordinate complexes of the form \([\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2]\)MCl$_2$ 32 (Figure 1.18).$^{175}$

![Diagram](image)

**Figure 1.18** Reaction of LiCH(Ph$_2$PNSiMe$_3$)$_2$ with group 13 metals

Recently, Gambarotta et al. demonstrated the coordination of VCl$_5$(THF)$_5$ with the monolithium phosphinimine anion to afford the vanadium complex \([\text{Me}_3\text{SiN=PPh}_2\text{C}\text{HPPh}_3=\text{NSiMe}_3]\)VCl$_2$-toluene.$^{176}$

### 1.6 Scope of Thesis

Over the past few years, our research group has been interested in phosphinimide ligands, and we have shown that titanium phosphinimide complexes can act as effective catalysts for ethylene polymerization upon activation. In recent years, the focus has been extended to the study of late transition metal phosphinimine complexes. Phosphinimine ligands offer a high degree of chemical flexibility through modification of the substituents on the
nitrogen or on the phosphorus atom. The combination of this anionic ligand to form neutral late transition metal complexes that possess a strong metal carbon \( \sigma \)-bond, may prove to be more stable than coordination bonds, thus imparting higher thermal stability. The original goal of this project was to prepare late transition metal complexes that possess a phosphinimine ligand in order to perform ethylene polymerization studies. Work in this thesis demonstrated substantial insight on the coordination studies of Group IX and Group X late transition metal complexes with phosphinimine ligands. Nonetheless, combining an electron rich Group IX metal with the polar phosphinimine ligand has shown some interesting chemistry. The thesis herein will focus on the synthesis of Group IX (Rh, Ir) and Group X (Ni, Pd, Pt) phosphinimine complexes, in addition to a preliminary investigation of their reactivities.
Chapter Two

Synthesis of Group IX Phosphinimine Complexes

2.1 Introduction

Throughout the years, our laboratory has endeavored to discover new families of highly active catalysts for olefin polymerization when activated with activators. Based on the similarities of the electronic and steric properties between cyclopentadienide and phosphinimide ligands, we have focused our attention on the development of early transition metal complexes containing phosphinimide ligands. For example, titanium phosphinimide complexes are very active catalysts for olefin polymerization when activated with MAO, $\text{B(C}_6\text{H}_5\text{)}_3$, or $\text{[Ph}_3\text{C][B(C}_6\text{F}_5\text{)}_4]^{16,17}$. In recent years, our group has broadened our studies to include late transition metal olefin polymerization catalysts, since related systems supported by $\alpha$-diimine ligands have demonstrated the potential to effect olefin polymerization catalysts upon activation. In order to explore this area, our research has been centered around studies of Group IX and Group X late metal complexes containing phosphinimine ligands. This chapter outlines the synthesis of Group IX phosphinimine complexes, and subsequently, the intriguing chemistry of the reaction between the solvent methylene chloride and the late metal compounds.

2.2 Experimental

General Data: All preparations were performed under an atmosphere of dry, anaerobic $\text{N}_2$ gas employing either Schlenk line techniques or a MBraun inert atmosphere glove box. All glassware were oven-dried overnight prior to use.
THF, diethyl ether, toluene, and pentane were distilled from sodium benzophenone ketyl under nitrogen. CH₂Cl₂ was dried over CaH₂ and distilled under nitrogen. C₆D₆, CD₂Cl₂ and THF-d₈ were degassed by the freeze-thaw method at least three times prior to use. Ph₂PNPh and DIPPHOS were used as received from Aldrich Chemical Co. ¹H, ¹³C{¹H}, ³¹P{¹H}, ⁷Li{¹H} and ²H NMR spectra were recorded on Bruker Avance 300 MHz or 500 MHz spectrometers. Trace amounts of protonated solvents were used as references and ¹H, ³¹P{¹H} and ⁷Li{¹H} chemical shifts are reported relative to SiMe₄, 85% H₃PO₄ and LiCl respectively. Combustion analyses were performed by the Center for Catalysis and Materials Research (CCMR), Windsor, Ontario, Canada. X-ray structure solution and refinement calculations were performed by Dr. P. Wei.

**General Information on X-Ray Data Collection and Reduction**

All X-ray data collection, data reduction, solution structure and refinements obtained in this thesis were performed using the same method; thus only one general description is given. Deviation will be noted in appropriate sections of the thesis.

X-ray quality crystals were manipulated and mounted in 0.5 mm capillaries in a glove box, thus a dry, O₂-free environment for each crystal was maintained. Diffraction experiments were performed on a Siemens Smart systems CCD diffractometer employing graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) and collecting a hemisphere of data with 30-second exposure times. Data were further processed using the SHELX crystallographic
software operating on a Pentium computer. An empirical absorption correction was applied to the data using SADABS. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements.

**General Information of Structure Solution and Refinement**

Non-hydrogen atomic scattering factors were taken from literature tabulations.\(^{177}\) Atom positions were determined either by SHELXTL-93 direct methods or a Patterson routine with successive difference Fourier map calculations. Refinements were carried out by full-matrix least-squares technique on $F$ minimizing the function $\omega([F_o] - |F_c|)^2$ where the weight $\omega$ is defined as $4F_o^2/2\sigma(F_o^2)$ and $F_o$ and $F_c$ are the observed and calculated structure factor amplitudes, respectively. In the final cycles of refinements, all non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atom positions were calculated to ride on the carbon atoms to which they were bound assuming a C-H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 120% of the temperature factors of the carbon atoms to which they were bound. All hydrogen atom contributions were calculated but not refined. After final cycles of refinement, no chemically significant residual electron density was observed.

**Synthesis of arylazides:** N-2,6-C$_7$H$_5$(CH$_3$)$_2$, 33, N-2,6-C$_7$H$_5$Pr, 34 and N-3,5-C$_7$H$_5$(CH$_3$)$_2$, 35\(^{178}\)

Compounds 33-35 were prepared by similar methods, thus only one representative procedure is described. A mixture of 2,6-dimethylphenylaniline
(12.0g, 99 mmol) and NaNO₂ (7.5g, 109 mmol) were added to a cooled (-30°C) acidic (40 mL conc. HCl and 40 mL distilled H₂O) solution of NaBF₄ (21.7g, 198 mmol). After several minutes of stirring, a yellow precipitate gradually formed, and the mixture was stirred at -30°C for 30 minutes. The slightly air-sensitive tetrafluoroborate salt was filtered quickly in air and washed with cold H₂O. The yellow salt was added portion wise to a cooled (0°C) aqueous solution (100 mL) of NaN₃ (19.3g, 297 mmol). After vigorous gas evolution, the orange mixture was stirred overnight at room temperature. The product was extracted from the aqueous layer with diethyl ether (3 x 10 mL) and dried over anhydrous MgSO₄. The solution was filtered, and the solvent removed to give a red oil (7.5g, 61mmol). The oil was used without purification due to the risk of explosion. 33: 

1H NMR (500 MHz, CDCl₃) δ: 6.96 (m, 2H, C₆H₅), 6.67 (m, 1H, C₆H₅), 2.21 (s, 6H, CH₃). 34: 1H NMR (500 MHz, CDCl₃) δ: 7.07-7.21 (m, 3H, C₆H₅), 3.38 (m, 2H, 1Pr), 1.28 (m, 12H, 1Pr). 35: 1H NMR (500 MHz, CDCl₃) δ: 7.08 (s, 2H, C₆H₅), 6.42 (m, 1H, C₆H₅), 2.38 (s, 6H, CH₃). 13C{1H}NMR agreed with literature data.

**Synthesis of Ph₂P=N(2,6-C₆H₄(CH₃)₂) 36, Ph₂P=N(2,6-C₆H₄/Pr₃) 37, Ph₂P=N(3,5-C₆H₄(CH₃)₂) 38**

Compounds 36-38 were prepared by similar methods, thus only one representative procedure is described. A solution of 2,6-dimethylphenyl azide (1.2g, 9.9mmol) in CH₂Cl₂ (2 mL) was added dropwise at RT to a solution of PPh₃ (1.3g, 4.9mmol) in the same solvent (5 mL). The homogeneous solution was stirred overnight and was then concentrated to approximately 2 mL in
vacuo. Pentane (5 mL) was added, and a pale yellow solid precipitated out of solution. The product was filtered, washed with cold pentane (3 x 5 mL) and dried in vacuo. 36: Yield: 1.12 g (64%). $^1$H NMR (500 MHz, C$_6$D$_6$) δ: 7.70-7.66 (m, 6H, $^3$J$_{H-H}$=12Hz, PPh$_3$), 7.14 (m, 2H, C$_6$H$_5$(CH$_3$)$_2$), 7.05-7.02 (m, 3H, PPh$_3$), 7.00-6.96 (m, 6H, PPh$_3$), 6.89 (d, 1H, $^1$J$_{H-H}$=7Hz, C$_6$H$_5$(CH$_3$)$_2$), 2.24 (s, 6H, CH$_3$) $^{13}$C{$^1$H}NMR (75.5MHz, C$_6$D$_6$) δ: 147.9 (s, C$_6$H$_5$(CH$_3$)$_2$), 135.1 (s, C$_6$H$_5$(CH$_3$)$_2$), 133.8 (s, PPh$_3$), 132.5 (d, $^2$J$_{P-C}$=8Hz, PPh$_3$), 131.2 (s, PPh$_3$), 128.5 (s, PPh$_3$), 119.1 (s, C$_6$H$_5$(CH$_3$)$_2$), 118.5 (s, C$_6$H$_5$(CH$_3$)$_2$), 21.8 (s, CH$_3$). $^{31}$P{$^1$H}NMR (202.5 MHz, C$_6$D$_6$) δ: -9.8.

37: Yield: 1.34 g (80%). $^1$H NMR (300 MHz, C$_6$D$_6$) δ: 7.69-7.62 (m, 6H, PPh$_3$), 7.23 (d, 2H, $^1$J$_{H-H}$=8Hz, C$_6$H$_5$Pr$_2$), 6.96-7.11 (m, 10H), 3.68-3.53 (sept, 2H, $^1$J$_{H-H}$=7Hz, $^3$Pr), 1.09 (d, 12H, $^1$J$_{H-H}$=7Hz, $^3$Pr) $^{13}$C{$^1$H} NMR (75.5 MHz, C$_6$D$_6$) δ: 142.7 (d, $^2$J$_{P-C}$=7Hz, C$_6$H$_5$Pr$_2$), 134.4 (s, $^3$Pr), 133.0 (s, PPh$_3$), 123.2 (d, $^2$J$_{P-C}$=9Hz, PPh$_3$), 130.9 (s, PPh$_3$), 128.3 (d, $^3$J$_{P-C}$=12Hz, PPh$_3$), 123.1 (s, C$_6$H$_5$Pr$_2$), 119.9 (s, C$_6$H$_5$Pr$_2$), 28.9 (s, $^3$Pr), 23.8 (s, $^3$Pr). $^{31}$P{$^1$H} NMR (121.5 MHz, C$_6$D$_6$) δ: -8.9. Anal. Calc'd for C$_{30}$H$_{42}$PN: C, 82.35; H, 7.37; N, 3.20. Found: C, 82.46; H, 7.42; N, 3.19.

38: Yield: 1.02 g (70%). $^1$H NMR (500 MHz, C$_6$D$_6$) δ: 7.88-7.81 (m, 6H, PPh$_3$), 7.07-6.96 (m, 9H, PPh$_3$), 6.93 (s, 2H, C$_6$H$_5$(CH$_3$)$_2$), 6.48 (s, 1H, C$_6$H$_5$(CH$_3$)$_2$), 2.19 (s, 6H, CH$_3$). $^{13}$C{$^1$H}NMR (75.5MHz, C$_6$D$_6$) δ: 152.0 (s, PPh$_3$), 138.0 (s, C$_6$H$_5$(CH$_3$)$_2$), 133.1 (d, $^2$J$_{P-C}$=9Hz, PPh$_3$), 132.1 (s, C$_6$H$_5$(CH$_3$)$_2$), 131.5 (d, $^1$J$_{P-C}$=2Hz, PPh$_3$), 128.7 (d, $^3$J$_{P-C}$=12Hz, PPh$_3$), 122.2 (d, $^3$J$_{P-C}$=18Hz, C$_6$H$_5$(CH$_3$)$_2$), 120.2 (s, C$_6$H$_5$(CH$_3$)$_2$), 21.3 (s, CH$_3$). $^{31}$P{$^1$H}NMR (202.5 MHz, C$_6$D$_6$) δ: -1.5.
Ortho-lithiation of Ph₃P=N(2,6-C₆H₅(CH₃)₂) with LiMe 40

Ph₃P=N(2,6-C₆H₅(CH₃)₂) (0.2g, 0.52mmol) was dissolved in Et₂O (5 mL), and LiMe (0.45mL, 0.63mmol) was added dropwise at RT. The solution turned yellow immediately, and gradually changed color to light orange. The mixture was stirred overnight, after which time the solvent was removed \textit{in vacuo}. Yield: 0.18g (85%). \(^1\)H NMR (500 MHz, C₆D₆) δ: 8.51 (br, 2H, PC₆H₄), 7.54-7.51 (m, 8H, PPh₃), 7.28 (br, 2H, C₆H₅(CH₃)₂), 7.04-7.00 (m, 8H, PPh₃), 6.96-6.93 (m, 12H), 6.81-6.79 (m, 2H, PC₆H₄), 3.12-3.08 (m, 4H, CH₂), 1.96 (s, 12H, C₆H₅(CH₃)₂), 0.90-0.85 (m, 6H, CH₂CH₃). \(^{13}\)C\{\(^1\)H\}NMR (75.5MHz, C₆D₆) δ: 147.8 (s, C₆H₅(CH₃)₂), 141.9 (s, C₆H₅(CH₃)₂), 141.2 (s, PC₆H₄), 134.5 (d, \(^3\)J_C-H=7 Hz, PPh₃), 133.2 (s, PC₆H₄), 132.7 (d, \(^3\)J_C-H=8 Hz, PPh₃), 131.6 (s), 130.2 (s), 128.7 (s), 123.4 (s), 120.5 (s, PC₆H₄), 65.1 (s, CH₂), 20.7 (s, C₆H₅(CH₃)₂), 14.5 (s, CH₂CH₃). \(^7\)Li\{\(^1\)H\}NMR (194.4 MHz, C₆D₆) δ: 3.38. \(^{31}\)P\{\(^1\)H\}NMR (202.5 MHz, C₆D₆) δ: 15.2.

Ortho-lithiation of Ph₃P=N(2,6-C₆H₅Pr₂) with LiMe 41

Ph₃P=N(2,6-C₆H₅Pr₂) (0.12 g, 0.27 mmol) was dissolved in Et₂O (5mL), and LiMe (1.4M in Et₂O) (0.24 mL, 0.33 mmol) was added dropwise at RT. The homogeneous yellow solution was stirred for 12 days during which time the solution became light orange in color. The solvent was removed \textit{in vacuo}, and the residue was washed with benzene to afford a yellow solid. Yield: 0.14 g (52%). \(^1\)H NMR (500 MHz, C₆D₆) δ: 8.61 (d, 2H, \(^3\)J_H-H=7Hz, PC₆H₄), 7.54-7.48 (m, 8H, PPh₃), 7.25-7.23 (m, 4H, C₆H₅Pr₂), 7.10-6.89 (m, 20H), 3.71-3.58 (sept, 4H, \(^3\)J_H-H=7Hz, \(^1\)Pr), 3.27-3.21 (m, 4H, CH₂), 1.22 (br, 12H, \(^1\)Pr), 1.10-1.06 (m, 14H, \(^1\)Pr).
6H, CH₂CH₃), 0.57 (br, 12H, Pr). ¹³C{¹H}NMR (75.5MHz, C₆D₆) δ: 145.2 (d, ¹JPC=7Hz, PC₆H₅), 144.6 (s, C₆H₅Pr₂), 142.7 (d, ¹JPC=7Hz, PPh₃), 134.4 (s), 133.1 (d, ²JP=C=9Hz, PC₆H₅), 132.4 (d, ²JP=C=9Hz, PPh₃), 130.9 (s, PPh₃), 130.6 (s), 124.3 (s), 123.5 (s, C₆H₅Pr₂), 122.3 (s), 119.9 (s), 65.7 (s, CH₂), 28.9 (s, C₆H₅Pr₂), 23.8 (s, Pr), 15.3 (s, CH₂CH₃). ⁷Li{¹H}NMR (194.4 MHz, C₆D₆) δ: 6.73. ³¹P{¹H}NMR (202.5 MHz, C₆D₆) δ: 18.4.

Ortho-lithiation of Ph₃P=N(3,5-C₆H₃(CH₃)₂) with Li⁺Bu 42

Ph₃P=N(3,5-C₆H₃(CH₃)₂) (0.2g, 0.52mmol) was dissolved in Et₂O (5mL), and n-BuLi (2.5M in hexane), (0.25mL, 0.63mmol) was added dropwise at RT. The solution turned dark red immediately. The mixture was stirred overnight, after which time the solvent was removed in vacuo. Yield: 0.13g (63%). ¹H NMR (300 MHz, C₆D₆) δ: 8.28 (m, 2H, PC₆H₅), 7.85-7.75 (m, 8H, PPh₃), 7.32-7.26 (m, 2H, PC₆H₅), 7.18 (m, 2H, PC₆H₅), 7.08-6.93 (m, 16H), 6.36-6.35 (m, 4H, C₆H₅(CH₃)₂), 2.10-1.97 (m, 12H, C₆H₅(CH₃)₂), 2.82 (m, 4H, CH₂), 0.49 (m, 6H, CH₂CH₃). ¹³C{¹H}NMR (75.5MHz, C₆D₆) δ
Ortho-lithiation of Ph₃P=NPh with LiPh

Ph₃P=NPh (0.15g, 0.42mmol) was dissolved in Et₂O (5 mL), and LiPh (0.3mL, 0.55mmol) was added dropwise at RT. The imide dissolved slowly and a yellow precipitate formed gradually. The mixture was allowed to stir overnight. The precipitate was then filtered, washed with diethyl ether and dried in vacuo. Yield: 0.16g (47%). ¹H NMR (500 MHz, C₆D₆) δ: 8.28 (d, 2H, ³J_H-H = 7Hz, PC₆H₄), 7.89 (m, 8H, PPh₃), 7.28 (m, 4H, NPh), 7.09-6.95 (m, 14H), 6.89-6.94 (m, 8H, PPh₂), 6.61 (m, 2H, PC₆H₄), 3.35-3.31 (m, 4H, CH₂), 1.17-1.14 (m, 6H, CH₂CH₃).

¹³C {¹H} NMR (75.5MHz, C₆D₆) δ: 151.7 (s, NPh), 142.1 (s, PC₆H₄), 133.4 (d, ²J_Pc = 9Hz, PPh₂), 132.5 (s, PPh₂), 131.5 (s, PC₆H₄), 130.8 (s), 129.5-129.8 (m, NPh), 128.8-128.5 (m), 124.5-123.9 (m), 123.3 (s, PPh₂), 117.9 (s, PC₆H₄), 65.6 (s, CH₂), 14.9 (s, CH₂CH₃). ⁷Li{¹H} NMR (194.4 MHz, C₆D₆) δ: 4.2. ³¹P{¹H} NMR (202.5 MHz, C₆D₆) δ: 18.1.

Synthesis of [RhCOD(o-C₆H₄PPh₃N(2,6-C₆H₄(CH₃)₃))]

[RhCOD(o-C₆H₄PPh₃N(2,6-C₆H₄Pr)₃)]

[RhCOD(o-C₆H₄PPh₃N(3,5-C₆H₄(CH₃)₃))] 46,

[RhCOD(o-C₆H₄PPh₃NPh)] 47

Compounds 44–47 were prepared by similar methods, thus only one representative procedure is described. A mixture of [Li(o-C₆H₄PPh₃N(2,6-C₆H₄(CH₃)₃))]₂·Et₂O (0.26g, 0.31mmol) and [RhCl(COD)]₂ (0.22g, 0.44mmol) was dissolved in THF (5 mL) at RT. The homogeneous reddish solution was stirred overnight, after which time the solvent was removed in vacuo. The residue was washed with pentane and recrystallized from THF/Et₂O or THF/C₆D₆. 44: Yield: 0.08g (48%). ¹H NMR (500MHz, C₆D₆) δ: 7.60-7.56 (m,
5H, PPh₂), 7.25 (d, 1H, JRh-H=7 Hz, PC₆H₅), 6.96-6.82 (m, 11H), 4.18-4.17 (m, 2H, COD), 3.95-3.94 (m, 2H, COD), 2.56-2.54 (m, 2H, COD), 2.38-2.36 (m, 2H, COD), 2.12 (s, 6H, C₆H₃(CH₃)₄), 2.07-2.04 (m, 2H, COD), 1.94-1.91 (m, 2H, COD). ¹³C{¹H} NMR (75.5 MHz, C₆D₆) δ: 173.5 (d, JRh-C=41Hz, PC₆H₅), 145.4 (s, C₆H₃(CH₃)₄), 136.5 (s, C₆H₃(CH₃)₄), 135.5 (s, PC₆H₅), 132.8 (d, JP-C=9Hz, PPh₂), 131.1 (s), 130.9 (s, PPh₂), 129.1 (s, PPh₂), 128.2 (s) 123.9 (m), 94.4 (d, JRh-C=7Hz, COD), 68.8 (d, JRh-C=15Hz, COD), 32.3 (s, COD), 30.0 (s, COD), 20.9 (s, C₆H₃(CH₃)₄). ³¹P{¹H} NMR (202.5 MHz, C₆D₆) δ: 43.3 (d, JRh-P=11Hz). Anal. Calc'd for C₃₄H₅₃PNRh: C, 69.04; H, 5.96; N, 2.37. Found: C, 68.61; H, 5.70; N, 2.28.

45: Yield: 0.08 g (43%). ¹H NMR (500MHz, C₆D₆) δ: 7.78-7.74 (m, 4H, J₄P-C₃=9Hz, PPh₂), 7.51 (d, 1H, JRh-H=8Hz, PC₆H₅), 7.19 (s, 1H, PC₆H₅), 7.02-6.99 (m, 4H, PPh₂), 6.97-6.93 (m, 2H, C₆H₃Pr₂), 6.92-6.86 (m, 5H), 4.24-4.18 (m, 4H, JRh-H=26Hz, COD), 2.54-2.41 (m, 4H, COD), 2.01-1.96 (m, 4H, COD), 1.52 (d, 6H, JRh-H=7Hz, JPr), 0.40 (d, 6H, JRh-H=7Hz, JPr). ¹³C{¹H} NMR (75.5 MHz, C₆D₆) δ: 173.6 (d, JRh-C=40Hz, PC₆H₅), 146.5 (d, JP-C=6Hz, PPh₂), 143.0 (d, JP-C=5Hz, PC₆H₅), 140.3 (s, C₆H₃Pr₂), 135.5 (d, JRh-C=18Hz, PC₆H₅), 132.7 (d, Jp-C=8Hz, PC₆H₅), 131.4 (s, JPr), 131.3 (s, C₆H₃Pr₂), 130.3 (s, JPr), 129.6 (s, PC₆H₅), 129.4 (s), 124.1 (s), 123.8 (d, Jp-C=3Hz, PPh₂), 123.3 (s), 123.1 (s), 92.8 (d, JRh-Pr-C=7Hz, COD), 69.4 (d, JRh-C=15Hz, COD), 32.2 (s, COD), 30.0 (s, COD), 28.5 (s, JPr), 25.3 (s, JPr), 23.9 (s, JPr). ³¹P{¹H} NMR (202.5MHz, C₆D₆) δ: 39.9. Anal. Calc'd for C₃₈H₄₃PNRh: C, 70.47; H, 6.69; N, 2.16. Found: C, 69.59; H, 6.89; N, 2.25.
46: Yield: 0.09g (60%). $^1$H NMR (500MHz, C$_6$D$_6$) δ: 7.69-7.65 (m, 4H, PPh$_2$), 7.55 (d, 1H, $^3$J$_{H-H}$=7Hz, PC$_6$H$_4$), 7.23 (d, 1H, $^3$J$_{H-H}$=7Hz, PC$_6$H$_4$), 7.04 (m, 1H, $^3$J$_{H-H}$=7Hz, PC$_6$H$_4$), 7.00-6.98 (m, 2H, PPh$_2$), 6.93-6.88 (m, 5H), 6.65 (s, 2H, C$_6$H$_5$(CH$_3$)$_3$), 6.47 (s, 1H, C$_6$H$_5$(CH$_3$)$_3$), 4.47 (m, 2H, COD), 4.15 (m, 2H, COD), 2.57 (m, 2H, COD), 2.43 (m, 2H, COD), 2.07 (m, 2H, COD), 2.01 (m, 2H, COD), 1.97 (s, 6H, C$_6$H$_5$(CH$_3$)$_3$). $^{13}$C{$^1$H} NMR (75.5 MHz, C$_6$D$_6$) δ: 174.1 (d, $^1$J$_{Rh-C}=40$Hz, PC$_6$H$_4$), 147.9 (s, PC$_6$H$_4$), 141.9 (s, C$_6$H$_5$(CH$_3$)$_3$), 137.5 (s, PPh$_2$), 135.4 (d, $^2$J$_{P-C}=18$Hz, PC$_6$H$_4$), 133.5 (d, $^1$J$_{P-C}=9$Hz, PPh$_2$), 131.7 (s, PC$_6$H$_4$), 130.3 (s, C$_6$H$_5$(CH$_3$)$_3$), 130.0 (s, PC$_6$H$_4$), 128.6 (s), 128.4 (s), 127.4 (d, $^3$J$_{Rh-C}=7$Hz, C$_6$H$_5$(CH$_3$)$_3$), 125.1 (s, C$_6$H$_5$(CH$_3$)$_3$), 123.4 (s), 93.8 (d, $^1$J$_{Rh-C}=7$Hz, COD), 69.1 (d, $^1$J$_{Rh-C}=15$Hz, COD), 32.6 (s, COD), 30.1 (s, COD), 21.4 (s, C$_6$H$_5$(CH$_3$)$_3$). $^{31}$P{$^1$H} NMR (202.5MHz, C$_6$D$_6$) δ: 47.6. Anal. Calc'd for C$_{35}$H$_{65}$PNRhz: C, 69.04; H, 5.96; N, 2.37. Found: C, 69.00; H, 6.51; N, 2.24.

47: Yield: 0.24g (60%). $^1$H NMR (300MHz, C$_6$D$_6$) δ: 7.67-7.61 (m, 4H, PPh$_2$), 7.55-7.53 (m, 1H, $^3$J$_{P-H}=8$Hz, PC$_6$H$_4$), 7.24-7.18 (m, 1H, $^3$J$_{H-H}=7$Hz, PC$_6$H$_4$), 7.06-6.98 (m, 4H, PPh$_2$), 6.96-6.95 (m, 2H, NPh), 6.92-6.84 (m, 6H), 6.79-6.74 (m, 1H, PC$_6$H$_4$), 4.38-4.36 (m, 2H, COD), 4.16-4.13 (m, 2H, COD), 2.60-2.50 (m, 2H, COD), 2.46-2.36 (m, 2H, COD), 2.11-2.02 (m, 2H, COD), 1.98-1.91 (m, 2H, COD). $^{13}$C{$^1$H} NMR (75.5MHz, C$_6$D$_6$) δ: 174.5-173.5 (d, $^1$J$_{Rh-C}=40$Hz, PC$_6$H$_4$), 148.1 (d, $^2$J$_{P-C}=4$Hz, NPh), 140.1 (s, PC$_6$H$_4$), 133.1 (d, $^2$J$_{P-C}=9$Hz, PPh$_2$), 131.6 (s), 129.9 (s, PPh$_2$), 129.7 (s, PC$_6$H$_4$), 129.4 (s, PC$_6$H$_4$), 129.3 (s), 128.5 (s), 123.4 (s), 122.9 (s), 93.4 (d, $^1$J$_{Rh-C}=7$Hz, COD), 68.9 (d, $^1$J$_{Rh-C}=15$Hz, COD), 32.5 (s, COD), 30.7 (s, COD). $^{31}$P{$^1$H} NMR (202.5MHz, C$_6$D$_6$) δ: 46.4 (d, $^2$J$_{Rh-P}=10$)
Hz). Anal. Calc'd for C_{32}H_{31}PNRh: C, 68.21; H, 5.55; N, 2.49. Found: C, 68.27; H, 5.71; N, 2.67.

**Synthesis of [Rh(o-C_{6}H_{4}PPh_{2}NPh)(CH_{2}-o-C_{6}H_{4}PPh_{2}NPh)(\mu-Cl)_{2}Rh(COD)]**

[\text{RhCOD(o-C_{6}H_{4}PPh_{2}NPh)}](0.098 g, 0.17 mmol) was dissolved in CH_{2}Cl_{2} (10 mL). The yellow solution was heated at reflux for 24 h, during which time the solution became orange in colour. The solvent was removed \textit{in vacuo}, and the product was recrystallized in benzene/CH_{2}Cl_{2}. Yield: 0.18 g (94%). ^{1}H NMR (500 MHz, CD_{6}) δ: 8.42-8.38 (br, 2H, PC_{6}H_{4}), 7.97 (dd, 1H, ^{3}J_{Rh-H}=8Hz, ^{4}J_{P-H}=3Hz, PC_{6}H_{4}), 7.92-7.87 (m, 4H, PPh_{2}), 7.84-7.79 (m, 2H, PC_{6}H_{4}), 7.69-7.65 (m, 3H, PC_{6}H_{4}), 7.53-7.45 (m, 4H, PPh_{2}), 7.28 (t, 2H, ^{3}J_{H-H}=7Hz, NPh), 7.13-6.83 (m, 16H), 6.76-6.68 (m, 4H, NPh), 4.23 (dd, 2H, ^{2}J_{Rh-H}=10Hz, ^{1}J_{P-H}=4Hz, RhCH_{2}), 4.11 (m, 2H, COD), 3.79 (m, 2H, COD), 2.26-2.21 (m, 4H, COD), 1.37-1.33 (m, 4H, COD). ^{13}C{^{1}H} NMR (75.5 MHz, CD_{6}) δ: 170.7 (m, PC_{6}H_{4}), 157.9 (s, NPh), 150.9 (s, PPh_{2}), 148.9 (s, PC_{6}H_{4}), 138.1 (s), 137.9-134.8 (m, PPh_{2}), 134.7 (s, PC_{6}H_{4}), 134.1 (s, PC_{6}H_{4}), 133.1-132.9 (m, PPh_{2}), 132.7 (s), 131.6-131.5 (m, PC_{6}H_{4}), 130.8 (s), 130.5 (s, NPh), 125.0 (s), 124.6 (s), 122.9 (s), 122.1 (s), 121.6 (s), 78.3 (d, ^{1}J_{Rh-C}=14Hz, COD), 76.6-76.0 (dd, ^{1}J_{Rh-C}=32Hz, ^{3}J_{P-C}=14Hz, RhCH_{2}), 31.3 (s, COD), 30.9 (s, COD). ^{31}P{^{1}H} NMR (121.5 MHz, CD_{6}) δ: 43.8 (d, ^{2}J_{Rh-P}=12 Hz), 27.1 (d, ^{2}J_{Rh-P}=3 Hz). Anal. Calc'd for C_{37}H_{30}P_{2}N_{2}Cl_{2}Rh_{2}: C, 62.03; H, 4.75; N, 2.54. Found: C, 58.09; H, 5.35; N, 1.78.
Synthesis of [Rh(\(\sigma\)-C\(_6\)H\(_5\)PPh\(_3\)NPh)(Ph\(_3\)PCH\(_2\)CH\(_2\)PPh\(_3\))] 52

A solution of 1,2-\(\text{bis}\)(diphenylphosphino)ethane (DIPHOS) (0.04g, 0.07mmol) in THF (5 mL) was added dropwise at RT to [RhCOD(\(\sigma\)-C\(_6\)H\(_5\)PPh\(_3\)NPh)] (0.03g, 0.08mmol) in the same solvent (5 mL). The mixture was stirred overnight at RT, after which time the solvent was removed in vacuo. The resulting solid was washed with benzene to remove excess DIPHOS, and was subsequently dried in vacuo. Yield: 0.03g (51%). \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)) \(\delta\): 8.03-7.99 (m, 4H, DIPHOS-PPh\(_3\)), 7.74 (br, 1H, PC\(_6\)H\(_4\)), 7.57-7.53 (m, 4H, PPh\(_3\)), 7.51-7.48 (m, 4H, DIPHOS-PPh\(_3\)), 7.08-7.02 (m, 15H), 6.99-6.93 (m, 6H), 6.82 (t, 1H, \(^3\)J\(_{H-H}\)=7Hz, PC\(_6\)H\(_4\)), 6.70 (q, 1H, \(^3\)J\(_{P-H}\)=13Hz, \(^3\)J\(_{H-H}\)=6Hz, PC\(_6\)H\(_4\)), 6.56-6.53 (m, 2H, NPh), 6.48-6.45 (m, 1H, \(^3\)J\(_{H-H}\)=7Hz, PC\(_6\)H\(_4\)), 1.93-1.83 (m, 2H, \(^2\)J\(_{P-H}\)=26Hz, \(^3\)J\(_{H-H}\)=7Hz, DIPHOS-CH\(_2\)), 1.73-1.64 (m, 2H, \(^2\)J\(_{P-H}\)=25Hz, \(^3\)J\(_{H-H}\)=7Hz, DIPHOS-CH\(_2\)).

\(^{13}\)C\({}^1\)H NMR (75.5 MHz, C\(_6\)D\(_6\)) \(\delta\): 153.9 (s, PC\(_6\)H\(_4\)), 146.3 (s), 144.6 (s), 142.2 (m, DIPHOS-C\(_6\)H\(_5\)), 138.6 (d, \(^2\)J\(_{P-C}\)=24 Hz, DIPHOS-C\(_6\)H\(_5\)), 137.9 (d, \(^2\)J\(_{P-C}\)=23 Hz, DIPHOS-C\(_6\)H\(_5\)), 134.4 (d, \(^1\)J\(_{P-C}\)=33 Hz, PPh\(_3\)), 133.6 (d, \(^2\)J\(_{P-C}\)=11 Hz, PPh\(_3\)), 132.5 (s), 131.4 (s), 130.9 (s), 128.7 (s), 126.2 (d, \(^2\)J\(_{P-C}\)=13 Hz, PC\(_6\)H\(_4\)), 123.5 (s), 121.1 (d, \(^2\)J\(_{P-C}\)=15 Hz, NPh), 119.2 (s, NC\(_6\)H\(_5\)), 32.1 (m, DIPHOS-CH\(_2\)), 29.4 (m, DIPHOS-CH\(_2\)). \(^3\)P\({}^1\)H NMR (202.5 MHz, C\(_6\)D\(_6\)) \(\delta\): 74.9 (dd, \(^1\)J\(_{Rh-P}\)=209Hz, \(^3\)J\(_{P-P}\)=24Hz), 57.2 (ddd, \(^1\)J\(_{Rh-P}\)=121Hz, \(^3\)J\(_{P-P}\)=24Hz), 24.1 (dd, \(^2\)J\(_{Rh-P}\)=22Hz, \(^3\)J\(_{P-P}\)=11Hz). Anal. Calc'd for C\(_{48}\)H\(_{40}\)P\(_6\)NRh: C, 69.49; H, 5.22; N, 1.69. Found: C, 69.75; H, 5.38; N, 1.55.
Synthesis of $[\text{IrCOD}(\alpha\text{-C}_6\text{H}_4\text{PPh}_2\text{NPh})]$ 53

A mixture of $[\text{Li}(\alpha\text{-C}_6\text{H}_4\text{PPh}_2\text{NPh})]_2\text{Et}_2\text{O}$ (0.25 g, 0.30 mmol) and $[\text{IrCl(COD)}]_2$ (0.09 g, 0.14 mmol) was dissolved in THF (5 mL) at RT. The homogeneous reddish solution was stirred overnight, after which time the solvent was removed in vacuo. The residue was washed with pentane and recrystallized in THF. Yield: 0.06 g (67%). $^1\text{H}$ NMR (300 MHz, C$_6$D$_6$) $\delta$: 7.86 (d, 1H, $^3\text{J}_{\text{P-H}}=9$ Hz, PC$_6$H$_4$), 7.60-7.53 (m, 4H, PPh$_3$), 7.30-7.25 (m, 1H, $^5\text{J}_{\text{H-H}}=7$ Hz, PC$_6$H$_4$), 7.11-7.07 (m, 2H, NPh), 6.98-6.90 (m, 6H), 6.87-6.81 (m, 4H, PPh$_3$), 6.78-6.73 (s, 1H, PC$_6$H$_4$), 3.99-3.82 (m, 4H, COD), 2.61-2.35 (m, 4H, COD), 1.99-1.82 (m, 4H, COD). $^{13}\text{C}^1\text{H}$ NMR (75.5 MHz, C$_6$D$_6$) $\delta$: 172.9 (s, PC$_6$H$_4$), 146.3 (s, NPh), 140.9 (s), 135.5 (s, PC$_6$H$_4$), 133.2 (d, $^2\text{J}_{\text{P-C}}=9$ Hz, PPh$_3$), 133.1 (s), 130.4 (s, PC$_6$H$_4$), 130.1 (s), 129.8 (s), 129.5 (s, NPh), 124.3 (s), 123.9 (s, PC$_6$H$_4$), 77.8 (s, COD), 52.7 (s, COD), 33.3 (s, COD), 31.4 (s, COD). $^{31}\text{P}^1\text{H}$ NMR (121.5 MHz, C$_6$D$_6$) $\delta$: 57.7. Anal. Calc'd for C$_{52}$H$_{81}$PNIr: C, 58.88; H, 4.79; N, 2.15. Found: C, 58.69; H, 4.77; N, 2.05.

X-Ray Structure Determinations of 36, 44, 45, 46·C$_6$H$_5$O, 47, 48·2 C$_6$H$_5$ and 53

Data were collected at room temperature. No crystal decay was observed for any of the compounds. The resulting crystallographic values are given in Tables 2.1 and 2.2. ORTEP drawings of 36, 44, 45, 46·C$_6$H$_5$O, 47, 48·2 C$_6$H$_5$, and 53 are shown in Figures 2.3, 2.6-2.9, 2.11 and 2.15 respectively, with 30% thermal ellipsoids. Selected bond distances and angles are listed in the captions for Figure 2.3, 2.6-2.9, 2.11 and 2.15 respectively.
Table 2.1: Crystallographic Parameters for 36, 44 and 45

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\[ R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} / \sum |F_o|, \quad R_w = \frac{\sum (|F_o| - |F_c|)^2}{\sum |F_o|^2} \]
Table 2.2: Crystallographic Parameters for 46·C₆H₅O, 47, 48·2 C₆H₆ and 53

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\[^{a}R = \sum |F_{o}| - |F_{e}| / \sum |F_{o}|, \ R_{w} = \left[ \sum (|F_{o}| - |F_{e}|)^2 \right]^{0.5} / \sum |F_{o}|^2\]
2.3 Results and Discussion

The focus of this research has been the synthesis of late transition metal containing phosphinimine complexes. A series of rhodium phosphinimine (Ph₃P(NR ary) complexes with various substituents on the imine nitrogen phenyl ring (44-47) were prepared. Different substituents could be introduced on the ligand from the use of various substituted phenyl azides, which are in turn, synthesized from modification of several different literature preparations.¹⁸⁰,¹⁸¹ Most previously reported syntheses of phenyl azides suffer from low yields and the presence of impurities, however, when a diazonium tetrafluoroborate salt is generated as the intermediate, the reaction proceeds smoothly.¹⁷⁸ Subsequent nucleophilic displacement with an azide anion forms 33-35 in high yields (Figure 2.1).

![Figure 2.1 Synthesis of 2,6- or 3,5-disubstituted phenyl azide](image)

The phosphinimine ligands 36-38 were synthesized upon oxidation of triphenylphosphine with the appropriate substituted phenyl azides 33-35 (Figure 2.2). The products were obtained in high yields after recrystallization. Upon oxidation, there is a slight upfield shift in the ³¹P{¹H} NMR spectrum for
compounds 36 (-9.8 ppm) and 37 (-8.9 ppm), and a slight downfield shift for compound 38 (-1.5 ppm) compared with free PPh₃ (-5.2 ppm). ¹H and ¹³C{¹H} NMR spectroscopy showed evidence for the formation of the desired products. The X-ray structure of compound 36 is illustrated in Figure 2.3. Compound 36 was similar to triphenyl(phenylimino)phosphine 39, except two methyl groups were introduced to the 2,6-position of the N-phenyl ring. The P=N distance of compound 36 (1.552(2) Å) was shorter than the analogous distance in Ph₃PNPh (1.602(3) Å). The N-Caryl bond distance of compound 36 (1.406(3) Å) was significantly longer than the N-Caryl distance in Ph₃PNPh (1.330(5) Å). The P-N-Caryl bond angle of Ph₃PNPh (130.4(3)°) was smaller than P(1)-N(1)-C(19) angle of 36 (132.23(17)°). The elongation of the N-Caryl bond and the larger P-N-C angle in 36 is likely due to the introduction of the ortho-methyl groups in where the aryl ring was required to bent further away to compensate the steric interaction.

![Chemical Structure](image)

Figure 2.2 Synthesis of 2,6- or 3,5-disubstituted phosphinimine ligands
Figure 2.3 ORTEP drawing of 36, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: P(1)-C(1) 1.825(2) Å, P(1)-C(13) 1.823(2) Å, P(1)-N(1) 1.552(2) Å, N(1)-C(19) 1.406(3) Å; P(1)-N(1)-C(19) 132.23(17)°

Lithiation of triphenyl(phenylimino)phosphine, Ph₃PNPh 39, was achieved employing a literature method. Replacing Ph₃PNPh with LiPh generated the ortho-metallated species [Li(o-C₆H₄PPh₂NPh)]₂·Et₂O 43 in 47% yield. Lithiation of substituted aryl phosphinimines (36-38) were performed by a modified method, where LiMe or Li₆Bu was used instead of LiPh. Depending on the size of the N-aryl substituents, longer reaction times were required.
(Figure 2.4). All lithiated intermediates showed a downfield resonance in $^3$P.$^1$H spectrum, indicating the coordination of lithium metal to the phospinimimine ligand. The $^1$H NMR spectrum showed that deprotonation at the ortho position of one phenyl ring had occurred. This species likely has a structure similar to an analogous compound reported by Steiner et al., where they reacted Ph$_3$PNSiMe$_3$ with LiMe,$^{159}$ forming the dimeric organolithium complex [Li(σ-C$_6$H$_4$PPh$_2$NPh)]$_2$·Et$_2$O. Exhaustive attempts to obtain X-ray quality crystals of compounds 40–43 were unsuccessful.

![Diagram of lithiation of substituted phospinimine ligands](image)

Figure 2.4  Lithiation of substituted phospinimine ligands

The ortho-metallated species 40–43 all had the requirements of an organometallic ligand capable of side arm donation. The deprotonated ortho phenyl carbon atom is able to form a rhodium-carbon σ-bond in a transmetallation reaction with the chloro(1,5-cyclooctadiene)rhodium(I) dimer, forming the monomeric rhodium(I) organometallic complexes 44–47 (Figure 2.5). In addition, the nitrogen atom from the Ph$_3$PNR unit acts as a side-arm
donating group through donation of an electron pair to the rhodium center, thus providing further stability to the monomeric complexes.

![Reaction Scheme](image)

**Figure 2.5 Synthesis of rhodium(I) phosphinimine complexes 44-47**

Complexes 44-47 were synthesized in good yield by treating $[\text{RhCl(COD)}]_2$ with the appropriate organolithium intermediates 40-43 in THF at room temperature. All complexes were characterized by a variety of techniques, such as $^1H$, $^{13}C$,$^1H$ and $^{31}P$,$^1H$ NMR spectroscopy, elemental analyses and X-ray diffraction studies. While comparing all rhodium(I) metal complexes 44-47, there was an upfield shift in the $^{31}P$,$^1H$ spectrum when steric bulk was introduced to the 2,6-positions of the imine phenyl ring. When the N-phenyl ring was unsubstituted (compound 47), the $^{31}P$,$^1H$ NMR had a signal at 46.4 ppm. When the N-phenyl ring was substituted by two methyl groups at 2,6-positions (compound 44), the $^{31}P$,$^1H$ signal shifted further upfield to 43.3 ppm. Whereas when the N-phenyl ring was substituted by two more bulky isopropyl groups at 2,6-positions (compound 45), the $^{31}P$,$^1H$ signal shifted to 39.9 ppm. In contrast, if steric bulk was introduced to the 3,5-positions of the imine phenyl ring as in compound 46, the $^{31}P$,$^1H$ shift remained very similar to
the unsubstituted compound $47$. The rhodium-bound aryl carbon gave rise to a doublet in the $^{13}C\{^1H\}$ NMR in the range of 170–180 ppm ($^1J_{Rh-C}$ typically 40 Hz), confirming that the rhodium atom was bound directly to the aryl ring of the phosphinimine ligand. $^1H$ NMR studies unambiguously showed the formation of compounds $44$-$47$. The $^1H$ NMR spectra of all four species showed distinct methylene and methine protons of the cyclooctadiene(COD) ligand due to the dissymmetry of the metallated phosphinimine ligand. A NOESY NMR experiments unambiguously confirmed that the upfield methylene and methine signals are assigned to those trans to the aryl-carbon. Crystals of $44$-$47$ suitable for X-ray structural determination were grown from a mixture of THF/Et$_2$O or THF/C$_6$D$_6$ solvents. The X-ray structures of compounds $44$-$47$ are illustrated in Figures 2.6 – 2.9. X-ray structures of compounds $44$-$47$ were very similar. All exhibited a Rh-C $\sigma$ bond and a Rh$\leftarrow$N donor bond, in addition to a coordinated cyclooctadiene ligand, thus generating a monomeric, slightly distorted square planar, 4-coordinate Rh complex with bite angles at the Rh center (N-Rh-C) of 85.12(9)$^\circ$ (compound $44$), 85.49(9)$^\circ$ (compound $45$), 85.10(9)$^\circ$ (compound $46$), and 84.77(9)$^\circ$ (compound $47$). They also feature a five-membered metallocycle containing four different atom types incorporating the P=N bond. The metallocyclic ring was essentially planar and the phenyl ring attached to the Rh metal was almost co-planar with the metallocycle. The N-phenyl ring was twisted away from co-planarity with respect to the metallocyclic ring. This presumably arose from the steric interaction of the phosphinimine ligand with the cyclooctadiene ligand on the Rh metal center. This resulted in a lengthening of the N-C$_{\text{phenyl}}$ distance in the rhodium metallated compound $44$. 

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(1.445(3) Å) relative to the free ligand 36 (1.406(3) Å). Similar phenomenon were also observed in the structure of \( [\text{RhCOD} (\sigma-\text{C}_6\text{H}_4\text{PPh}_2\text{NPh})] \) 47 (1.450(3) Å) compared to the free ligand Ph$_3$PNPh (1.330(5) Å). When comparing the P=N distance of compound 36 (1.552(2) Å) with the rhodium coordinated compound 44 (1.614(2) Å), bond lengths are significantly different. Since two methyl groups were introduced to the 2,6-positions of the N-phenyl ring, additional steric bulk was applied between the metallacyclic ring and the N-phenyl ring. Therefore, lengthening of the P=N bond was required to reduced steric strain. Conversely, the P=N bond length did not alter observably between the free Ph$_3$PNPh (1.602(3) Å) and the rhodium complex 47 (1.609(2) Å). That the expected lengthening of the P=N bond upon coordination to the rhodium center was not observed in this case might be due to the compensation of twisting of the phenyl group out of the plane. Therefore, it was the N-C bond that lengthened, rather then the P=N bond that changed. The Rh-C(1) bond length of compound 44 (2.065(3) Å), compound 45 (2.058(3) Å), compound 46 (2.068(3) Å), and compound 47 (2.069(3) Å) were comparable to other complexes containing Rh-C$_{aryl}$ bonds. For example: 2.049(6) Å in Rh(CH$_2$PhC$_F_3$)[$C_6$H(CH$_3$)$_2$(CH$_2$PPh$_2$)$_2$]$_{1183}$ or 2.079(3) Å in RhCp*(C$_6$F$_5$)(PMe$_3$)$_2$.184
Figure 2.6  ORTEP drawing of 44, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Rh(1)-N(1) 2.125(2) Å, Rh(1)-C(1) 2.065(3) Å, P(1)-N(1) 1.614(2) Å, N(1)-C(19) 1.445(3) Å, Rh(1)-C(27) 2.233(3) Å, Rh(1)-C(28) 2.213(3) Å, Rh(1)-C(31) 2.112(3) Å, Rh(1)-C(32) 2.089(3) Å; N(1)-Rh(1)-C(1) 85.12(9)°, P(1)-N(1)-Rh(1) 115.84(10)°, C(19)-N(1)-Rh(1) 123.96(16)°, C(27)-Rh(1)-C(32) 81.06(11)°, C(28)-Rh(1)-C(31) 80.95(12)°.
Figure 2.7  ORTEP drawing of 45, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Rh(1)-N(1) 2.141(2) Å, Rh(1)-C(1) 2.058(3) Å, P(1)-N(1) 1.605(2) Å, N(1)-C(19) 1.440(3) Å, Rh(1)-C(31) 2.183(3) Å, Rh(1)-C(32) 2.220(3) Å, Rh(1)-C(35) 2.102(3) Å, Rh(1)-C(36) 2.116(3) Å; N(1)-Rh(1)-C(1) 85.49(9)°, P(1)-N(1)-Rh(1) 112.43(11)°, C(19)-N(1)-Rh(1) 124.01(17)°, C(31)-Rh(1)-C(36) 81.31(12)°, C(32)-Rh(1)-C(35) 80.96(12)°.
Figure 2.8  ORTEP drawing of 46. 30% thermal ellipsoids are shown, hydrogen atoms and the co-crystallized THF molecule have been omitted for clarity. Selected bond distances and angles: Rh(1)-N(1) 2.108(2) Å, Rh(1)-C(1) 2.068(3) Å, P(1)-N(1) 1.617(2) Å, N(1)-C(19) 1.454(3) Å, Rh(1)-C(27) 2.200(3) Å, Rh(1)-C(28) 2.235(3) Å, Rh(1)-C(31) 2.090(3) Å, Rh(1)-C(32) 2.107(3) Å; N(1)-Rh(1)-C(1) 85.10(9)°, P(1)-N(1)-Rh(1) 115.78(11)°, C(19)-N(1)-Rh(1) 124.54(17)°, C(27)-Rh(1)-C(32) 81.47(11)°, C(28)-Rh(1)-C(31) 81.02(11)°.
Figure 2.9  ORTEP drawing of 47, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Rh(1)-N(1) 2.112(2) Å, Rh(1)-C(1) 2.069(3) Å, P(1)-N(1) 1.609(2) Å, N(1)-C(19) 1.450(3) Å, Rh(1)-C(25) 2.095(3) Å, Rh(1)-C(32) 2.104(3) Å, Rh(1)-C(28) 2.225(3) Å, Rh(1)-C(29) 2.207(3) Å; N(1)-Rh(1)-C(1) 84.77(9)°, P(1)-N(1)-Rh(1) 115.33(12)°, C(19)-N(1)-Rh(1) 126.31(16)°, C(25)-Rh(1)-C(28) 80.98(11)°, C(32)-Rh(1)-C(29) 81.20(11)°.
Yellow crystals of \([\text{RhCOD(o-C}_6\text{H}_4\text{PPh}_2\text{NPh})]\) \(47\) were recrystallized from \(\text{THF/Et}_2\text{O}\). However, it was unexpected that a solution of compound \(47\) in methylene chloride slowly transformed to other compounds. These new compounds were formed in essentially quantitative yields after stirring in \(\text{CH}_2\text{Cl}_2\) for a couple of days. X-ray crystallographic study of compound \(48\) demonstrated that the orange coloured, binuclear Rh(I)-Rh(III) complex had formed (Figure 2.11). This complex consisted of two phosphininmine ligands with a methylene group inserted into one of the \(\text{Rh-C}_\text{aryl}\) bonds, generating a five as well as a six-membered metallacycle. The binuclear structure was apparent with two rhodium centers joined by two bridging chloride ligands. The geometry of the Rh(III) center was pseudo-octahedral, where both nitrogen atoms occupied the axial position with an almost linear \(\text{N}(1)\)-Rh(I)-N(2) angle of 176.90(18)°. A cyclooctadiene ligand was coordinated to the Rh(I) center, generating a slightly distorted square planar geometry with a bite angle at the rhodium (I) center of 88.58(6)°. The Rh(1)-N(2) bond length (2.153(5) Å) in the six membered metallacycle was longer than Rh(1)-N(1) bond length (2.107(5) Å) in the five membered metallacycle. In the same manner, P(2)-N(2) bond length (1.616(5) Å) in the six membered metallacycle is also longer than the P(1)-N(1) bond length (1.602(5) Å) in the five membered metallacycle. The Rh(1)-Rh(2) distance of 3.647 Å demonstrated the absence of a Rh-Rh metal bond. While reacting compound \(47\) with \(\text{CH}_2\text{Cl}_2\), two products (\(48\) and \(49\)) are present in solution. Compound \(48\) was the dominant species and compound \(49\) was the minor species (Figure 2.10). This transformation could be conveniently followed by \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopy. After compound \(47\) was stored in \(\text{CH}_2\text{Cl}_2\)
solution for a few hours, new resonances appeared in the $^{31}\text{P}\left\{^{1}\text{H}\right\}$ NMR spectrum, while peaks due to 47 slowly diminish. Within a few days, all traces of compound 47 were gone. Compound 48 showed two sets of resonances. A doublet centered at 43.7 ppm ($^{2}\text{J}_{\text{Rh-P}}=12\text{ Hz}$) was attributed to the phosphorus atom in the five-membered metallacycle, and another doublet centered at 27.1 ppm ($^{2}\text{J}_{\text{Rh-P}}=3\text{ Hz}$) was attributed to the phosphorus atom in the six-membered metallacycle. For compound 49, a doublet centered at 34.6 ppm ($^{2}\text{J}_{\text{Rh-P}}=11\text{Hz}$) was attributed to the phosphorus atom in the five-membered metallacycle, while a singlet centered at 28.1 ppm was attributed to the phosphorus atom in the six-membered metallacycle.

Figure 2.10  Reaction of 47 with methylene chloride
Figure 2.11 ORTEP drawing of 48, 30% thermal ellipsoids are shown, hydrogen atoms and the co-crystallized benzene molecule have been omitted for clarity. Selected bond distances and angles: Rh(1)-C(1) 2.005(6) Å, Rh(1)-C(49) 2.082(6) Å, Rh(1)-N(1) 2.107(5) Å, Rh(1)-N(2) 2.153(5) Å, Rh(1)-Cl(1) 2.566(2) Å, Rh(2)-C(53) 2.090(8) Å, Rh(2)-C(50) 2.090(8) Å, Rh(2)-C(54) 2.095(7) Å, Rh(2)-C(57) 2.113(9) Å, N(1)-P(1) 1.602(5) Å, N(2)-P(2) 1.616(5) Å, C(48)-C(49) 1.485(9) Å; C(1)-Rh(1)-C(49) 90.3(2)°, C(1)-Rh(1)-N(1) 84.4(2)°, C(49)-Rh(1)-N(2) 89.7(2)°, N(1)-Rh(1)-N(2) 176.90(18)°, C(53)-Rh(2)-C(50) 82.6(4)°, C(54)-Rh(2)-C(57) 83.9(4)°.
Triphenylphosphine (PPh₃) was reacted with the bi-nuclear Rh(I)-Rh(III) 48 (Figure 2.12). This reaction resulted in cleavage of the chloride bridge and coordination either to the Rh(I) or Rh(III) center, forming different mononuclear fragments. Possible reaction products are shown in Figure 2.12. Though multiple products were formed in this reaction, the $^{31}$P{$^1$H} NMR spectrum revealed that the major product was compound 49 (d at 34.6 ppm ($^2$J$_{Rh}$, $\nu$=11Hz) and s at 28.1 ppm). It is likely that the PPh₃ did not coordinate strongly to the rhodium center; instead, it rearranged and formed the more stable rhodium(III) dimer 49. Due to the very similar solubility of compounds 49-51, attempts to isolate pure compound 49 were not successful.

Figure 2.12  Reaction of compound 48 with PPh₃

Since insertion of the methylene group into the rhodium-aryl bond of compound 47 occurred, we tried to extend this chemistry to the more bulky N-
phenyl 2,6-disubstituted complexes 44 and 45, and the N-phenyl 3,5-disubstituted complex 46. For this purpose, compounds 44-46 were further purified by recrystallization or by precipitation from a saturated THF solution, then reacted with methylene chloride at room temperature. Interestingly, both N-phenyl 2,6-disubstituted complexes 44 and 45 did not react with methylene chloride even after prolonged stirring. $^{31}$P($^1$H) and $^1$H NMR spectroscopy showed no evidence for the formation of any new compound. In contrast, multiple products were formed while reacting the N-phenyl 3,5-disubstituted complex 46 with methylene chloride. $^{31}$P($^1$H) NMR showed the disappearance of the initial signal (46.8 ppm), and four new signals appeared within the range of 47–28 ppm with varied intensities. Attempts to separate these products were unsuccessful. It seemed that when steric bulk was introduced to the 2,6-position of the N-phenyl ring (compounds 44 and 45), it prevented oxidative addition of the methylene chloride to the rhodium center.

In order to further study the insertion of the methylene group into the rhodium–carbon bond, two tailor-made compounds, a rhodium and an iridium compound were synthesized. Compound 52 is analogous to compound 47, having a more bulky chelated phosphine ligand, DIPHOS (1,2-bis(diphenylphosphinoethane)) coordinated to the rhodium center instead of a cyclooctadiene moiety (Figure 2.13). Compound 53 is also analogous to compound 47, though with an iridium metal center (Figure 2.14).
Compound 52 was synthesized in moderate yield by reacting compound 47 with 1.1 equivalents of DIPHOS to displace the COD ligand on the rhodium center. Compound 52 was obtained pure by precipitating out of a saturated THF solution upon prolonged storage. Attempts to obtain X-ray quality crystals of compound 52 were unsuccessful; in fact, it was characterized by $^{31}$P{¹H}, ¹H and ¹³C{¹H} NMR spectroscopy. The $^{31}$P{¹H} NMR spectrum showed three distinct signals: a doublet of doublets centered at 74.9 ppm, and a doublet of doublet of doublets centered at 57.2 ppm, which corresponded to the phosphorus atoms on the DIPHOS ligand, as well as a doublet of doublets centered at 24.1 ppm, corresponding to the phosphorus from the phosphinimine ligand.
Elemental analysis indicated that 52 has the empirical formula of \([\text{Rh}(\sigma-\text{C}_6\text{H}_4\text{PPh}_3\text{NPh})(\text{Ph}_3\text{PCH}_2\text{CH}_2\text{PPh}_3)]\).

Compound 53 was synthesized in moderate yield by reacting compound 48 with \([\text{IrCl}(\text{COD})]_2\) in THF at room temperature (Figure 2.14). $^{31}\text{P}\{^1\text{H}\}$ spectroscopy showed a singlet centered at 57.7 ppm, whereas $^1\text{H}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy as well as elemental analysis confirmed the formulation of compound 53. Orange coloured plate-like X-ray quality crystals were obtained by slowly evaporating a concentrated THF solution of compound 53. The ORTEP view of 53 is shown in Figure 2.15. Compound 53 was isostructural to compound 47 except with an iridium metal center. The X-ray analysis demonstrated that the iridium center has a slightly distorted square planar geometry. Compound 53 exhibited an Ir-C $\sigma$-bond and a Ir$\leftrightarrow$N donor bond thereby forming a five-membered metallacycle. The metal center also contains a cyclooctadiene ligand thus forming a 4-coordinated iridium (I) complex with a bite angle of 84.77(19)$^\circ$ \([\text{C}(1)\text{-Ir}(1)\text{-N}(1)]\), which is almost identical to the analogous bite angle found in the rhodium compound 47 (84.77(9)$^\circ$). The imine phenyl ring was twisted and bent away from the COD ligand with an angle of 126.6(3)$^\circ$, which is also found in compound 47 (126.31(16)$^\circ$). The angles around the COD ligand: C(29)-Ir(1)-C(26) (80.7(2)$^\circ$) and C(30)-Ir(1)-C(25) (81.8(2)$^\circ$) were also relatively close to the analogous angles in compound 47. While comparing the M-N bond lengths of compound 47 and 53, the Rh(1)-N(1) bond length (2.112(2) Å), was longer than the analogous Ir(1)-N(1) bond length (2.081(5) Å).
Figure 2.15 ORTEP drawing of 53, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Ir(1)-N(1) 2.081(5) Å, Ir(1)-C(1) 2.084(5) Å, P(1)-N(1) 1.628(5) Å, N(1)-C(19) 1.440(7) Å, Ir(1)-C(25) 2.104(6) Å, Ir(1)-C(26) 2.106(6) Å, Ir(1)-C(29) 2.195(6) Å, Ir(1)-C(30) 2.179(5) Å; N(1)-Ir(1)-C(1) 84.77(19)°, P(1)-N(1)-Ir(1) 115.8(3)°, C(19)-N(1)-Ir(1) 126.6(3)°, C(25)-Ir(1)-C(30) 81.3(2)°, C(26)-Ir(1)-C(29) 80.7(2)°.
Both compound 52 and compound 53 reacted with methylene chloride at room temperature. The proposed products for the reaction of compound 52 with CH₂Cl₂ are shown in Figure 2.16. Compound 54 showed 3 sets of signals in $^{31}$P{¹H} NMR spectrum: a doublet of doublets of doublets centered at 57.5 ppm, and a doublet of doublets centered at 51.2 ppm which corresponded to the phosphorus atoms on the DIPHOS ligand. As well, a doublet centered at 30.0 ppm corresponding to the phosphorus atom from the phosphinimine ligand. A comparison of the $^{31}$P{¹H} NMR spectrum of compound 54 with compound 52 showed that signals are relatively similar except for the doublet of doublets centered at 74.9 ppm (compound 52), which was shifted significantly to 51.2 ppm. Due to the similarity of the $^{31}$P{¹H} NMR spectra of these complexes, we proposed that a similar species has formed via oxidative addition of the C-Cl bonds followed by insertion of the CH₂ into the Rh-Caryl bond.

Figure 2.16  Proposed reaction of compound 52 with CH₂Cl₂
To further confirm a monomeric compound was formed in the case shown in Figure 2.16, compound 48 was reacted with 1.1 equivalents of DIPHOS in order to produce the binuclear compound 55 where the COD ligand was displaced by the DIPHOS ligand. The products of the reactions shown in Figure 2.16 and Figure 2.17 were compared. The $^{31}$P$\{^1$H$\}$ NMR spectrum showed that multiple products with signals ranging from 80 – 20 ppm were formed. Signals centered at 77.1 ppm (d, $^1$J$_{Rh-P}=200$ Hz) and 73.1 ppm (d, $^1$J$_{Rh-P}=199$ Hz) indicated the formation of compounds 56 or 57. These $^{31}$P$\{^1$H$\}$ NMR signals were confirmed by reacting the [RhCl(COD)]$_2$ with excess DIPHOS ligands. Also evident were signals centered at 84.7 ppm ($^2$J$_{Rh-P}=10$ Hz) and 28.1 ppm, indicated the formation of compound 49. Another compound was present which had three signals: 74.1 ppm (d, $^1$J$_{Rh-P}=198$ Hz), 44.7 ppm (d, $^2$J$_{Rh-P}=13$ Hz) and 27.4 ppm suggesting the formation of compound 55 (Figure 2.17). Attempts to separate compounds 49, 55, 56 and 57 were unsuccessful. The different products formed in the reactions illustrated in Figure 2.16 and Figure 2.17 further suggest that compound 52 has likely underwent oxidative addition in order to form a monomeric rhodium (I) complex (compound 54). The observations indicate the displacement of COD ligand in compound 47 with the DIPHOS ligand prevented the dimerization to form a species like compound 49 from occurring. This is likely due to the stronger Rh-P $\sigma$-bond which prohibited the dissociation of the DIPHOS ligand from the rhodium center, which prevents further rearrangement of compound 52.
Figure 2.17  Ligand displacement reaction of compound 48 with DIPHOS

Similar reactions were performed with the iridium(I) compound 53. The colour of the reaction mixture changed from orange to yellow after prolonged stirring in methylene chloride. The $^{31}$P/$^1$H NMR showed the disappearance of the starting material signal and that multiple products had formed. Attempts to isolate single products were unsuccessful.

The $^1$H NMR spectrum of both compounds 52 and 53 after reaction with CH$_2$Cl$_2$ were complicated. Resonances due to the inserted CH$_2$ group into the M-C$_{aryl}$ bond were apparently obscured by other resonances. In order to confirm the insertion of the methylene group into the M-C$_{aryl}$ bond, $^2$D NMR experiments were performed. After prolonged stirring of compounds 52 and 53 in CD$_2$Cl$_2$, $^2$D NMR spectra revealed the presence of a signal centered at 4.23 ppm for compound 54, and a signal centered at 4.25 ppm in product mixture
while reacting compound 53 with CD₂Cl₂. These results unambiguously show the insertion of the CD₂ group into these two compounds.

In order to further study the reactivity of compound 47, different alkyl halide reagents were used in attempts to perform oxidative addition across the rhodium metal center. Methyl iodide, benzyl chloride, 1,2-dichloroethane, 1,3-difluoropropane and 1,4-dichlorobutane were reacted with compound 47. All reagents exhibited either multiple product formation or very low product yields. Attempts to isolate products were unsuccessful. The addition of diazomethane or (trimethylsilyl)diazomethane to compound 47 at room temperature resulted no reaction.

2.4 Summary

In summary, a series of monomeric Group IX phosphinimine complexes 44-47 were readily prepared by a salt metathesis reaction under mild conditions. The observation that a solution of [{RhCOD(o-C₆H₄PPh₂NPh)}] 47 in methylene chloride slowly transformed into compounds 48 and 49 was unexpected. It was likely that complex 47 underwent oxidative addition of methylene chloride to the rhodium metal center, followed by the ligand rearrangement to yield the binuclear complexes. It should be noted that when steric bulk was introduced to the 2,6-position of the N-phenyl ring (compounds 44 and 45), oxidative addition of CH₃Cl on the rhodium center was inhibited.
Chapter Three

Synthesis of Group X Phosphinimine Complexes

3.1 Introduction

As described in the previous chapter, early transition metal catalyst systems continue to be a fruitful area of study; however, recently, much attention has been focused on late transition metal complexes. Brookhart,\textsuperscript{8,9,23-25,185} Gibson\textsuperscript{10-15} and Grubbs\textsuperscript{19} have developed several late transition metal complexes which show high activities for the polymerization of simple olefins either in the presence or absence of co-catalyst. Our initial goal was to synthesize monomeric late metal phosphinimine complexes where steric bulk can be easily modified via typical synthetic routes for the phosphinimine ligand. Reactions involving Group X metals with phosphinimine ligands tended to form bis-ligand complexes. This chapter describes the synthesis of a series of Group X phosphinimine complexes.

3.2 Experimental

General Data: All preparations, \textsuperscript{1}H, \textsuperscript{13}C\{\textsuperscript{1}H\}, \textsuperscript{31}P\{\textsuperscript{1}H\}, \textsuperscript{7}Li\{\textsuperscript{1}H\} NMR and combustion analyses were performed under conditions similar to those described in Section 2.2. Ph\textsubscript{3}PNPh was used as received from Aldrich Chemical Co. The ligand precursors Ph\textsubscript{3}PNSiMe\textsubscript{3}\textsuperscript{125} and Ph\textsubscript{3}PN\textsuperscript{i}Bu\textsuperscript{186} were prepared as described in literature.
Synthesis of \(\left[\text{Ni}(o-\text{C}_{6}\text{H}_{4}\text{PPh}_{2}\text{NPh})_{2}\right]^{\pm}\) 67

A mixture of \(\left[\text{Li}(o-\text{C}_{6}\text{H}_{4}\text{PPh}_{2}\text{NPh})_{2}\right]^{\pm}\text{Et}_2\text{O} \) (0.13g, 0.16mmol) and \(\text{NiBr}_2(\text{PPh}_3)_2\) (0.12g, 0.16mmol) was dissolved in THF (5 mL) at -20°C. The reddish solution was stirred overnight at RT, after which time the solvent was removed in vacuo. The residue was washed with pentane and recrystallized in benzene to afford red crystals. Yield: 0.17g (74%). \(^1\text{H} \text{NMR} (300 \text{ MHz, } \text{C}_6\text{D}_6)\) \(\delta: 8.02\) (d, 2H, \(^3\text{J}_{\text{HH}}=8\text{Hz, } \text{PC}_6\text{H}_4\), \(7.65-7.59\) (m, 8H, \text{PPh}_2), \(7.05-6.92\) (m, 18H), \(6.89-6.83\) (m, 2H, \text{PC}_6\text{H}_4), \(6.77-6.71\) (m, 2H, \text{PC}_6\text{H}_4), \(6.68-6.66\) (m, 6H, NPh, \text{PC}_6\text{H}_4).

\(^{13}\text{C}\{^1\text{H}\} \text{NMR} (75.5 \text{ MHz, } \text{C}_6\text{D}_6)\) \(\delta: 170.4\) (d, \(^2\text{J}_{\text{PC}}=24\text{Hz, } \text{PC}_6\text{H}_4\), \(149.6\) (s, \text{PC}_6\text{H}_4), \(143.8\) (s, \text{PC}_6\text{H}_3), \(143.5\) (s, \text{PC}_6\text{H}_4), \(141.7\) (s, \text{PC}_6\text{H}_3), \(133.6\) (d, \(^2\text{J}_{\text{PC}}=10\text{Hz, } \text{PPh}_2\), \(132.7\) (s), \(131.5\) (s, \text{PC}_6\text{H}_4), \(131.3\) (s), \(130.4\) (s, NPh), \(121.8\) (s, \text{PC}_6\text{H}_4), \(120.1\) (s, \text{PC}_6\text{H}_4). \(^{31}\text{P}\{^1\text{H}\} \text{NMR} (202.5 \text{ MHz, } \text{C}_6\text{D}_6)\) \(\delta: 33.7\). Anal. Calc'd for C\(_{48}\)H\(_{38}\)P\(_2\)N\(_2\)Ni: C, 75.51; H, 5.02; N, 3.67. Found: C, 74.97; H, 5.27; N, 3.51.

Synthesis of \(\left[\text{Ni}(o-\text{C}_{6}\text{H}_{4}\text{PPh}_{2}\text{N}(3,5-\text{C}_{6}\text{H}_{5}(\text{CH}_3)_2))_{2}\right]^{\pm}\) 68

A mixture of \(\left[\text{Li}(o-\text{C}_{6}\text{H}_{4}\text{PPh}_{2}\text{N}(3,5-\text{C}_{6}\text{H}_{5}(\text{CH}_3)_2))_{2}\right]^{\pm}\text{Et}_2\text{O} \) (0.14g, 0.17mmol) and \(\text{NiBr}_2(\text{PPh}_3)_2\) (0.13g, 0.16mmol) was dissolved in THF (5 mL) at RT. The reddish solution was stirred overnight, after which time the solvent was removed in vacuo. The residue was washed with pentane and recrystallized in benzene/THF to afford orange crystals. Yield: 0.08g (58%). \(^1\text{H} \text{NMR} (500 \text{ MHz, } \text{C}_6\text{D}_6)\) \(\delta: 8.04\) (d, 2H, \(^3\text{J}_{\text{HH}}=8\text{Hz, } \text{PC}_6\text{H}_4\), \(7.74-7.62\) (m, 8H, \text{PPh}_2), \(7.08-6.95\) (m, 14H), \(6.92-6.83\) (m, 2H, \text{PC}_6\text{H}_4), \(6.81-6.73\) (m, 2H, \text{PC}_6\text{H}_4), \(6.64\) (s, 4H, NMe\(_3\)\text{C}_6\text{H}_3), \(6.26\) (s, 2H, NMe\(_3\)\text{C}_6\text{H}_3), \(1.90\) (s, 12H, Me). \(^{13}\text{C}\{^1\text{H}\} \text{NMR} (75.5 \text{ MHz, } \text{C}_6\text{D}_6)\) \(\delta: \ldots\).
MHz, C₆D₆) δ: 169.7 (d, ¹Jₚ-C=25Hz, PC₆H₄), 149.5 (s, PC₆H₄), 144.3 (s, PPh₂), 142.8 (s, PC₆H₄), 141.7 (s, PPh₂), 135.6 (s, PPh₂), 133.3 (d, ²Jₚ-C = 10Hz, PPh₂), 132.0 (s), 131.4 (s, PC₆H₄), 129.1 (s, NMe₂C₆H₅), 126.6 (d, ²Jₚ-C = 14Hz, PC₆H₄), 122.4 (s), 121.7 (s, NMe₂C₆H₅), 20.9 (s, Me). ³¹P{¹H}NMR (202.5 MHz, C₆D₆) δ: 35.4. Anal. Calc'd for C₅₆H₆₆P₇N₂Ni: C, 76.21; H, 5.66; N, 3.42. Found: C, 74.80; H, 5.70; N, 3.14.

Synthesis of [Pd(o-C₆H₄PPh₃NPh)₂] 69

A mixture of [Li(o-C₆H₄PPh₃NPh)]₂·Et₂O (0.23g, 0.28mmol) and PdCl₂(COD) (0.08g, 0.28mmol) was dissolved in THF (5 mL) at RT. The mixture was stirred at RT for 6h during which time a fine grayish green solid precipitated from solution. The heterogeneous mixture was stirred overnight, after which time it was filtered through Celite. The yellow filtrate was concentrated to ca. 1 mL, and a yellow powder was precipitated after storage under benzene overnight. The yellow powder was filtered, dissolved in CH₂Cl₂ and recrystallized in the absence of light at -20°C. This compound decomposed in the presence of light.

Yield: 0.12g (52%). ¹H NMR (500 MHz, C₆D₆) δ: 8.27 (d, 2H, ³Jₚ-H=8Hz, PC₆H₄), 7.72-7.67 (m, 8H, ³Jₚ-H=11Hz, ³Jₚ-H=7Hz, PPh₂), 7.25-7.22 (m, 2H, PC₆H₄), 7.02 (dt, 4H, ³Jₚ-H=7Hz, ³Jₚ-H=1Hz, NPh), 6.95 (dt, 8H, ³Jₚ-H=8Hz, ³Jₚ-H=2Hz, PPh₂), 6.81-6.79 (m, 8H), 6.73 (dd, 4H, ³Jₚ-H=8Hz, PPh₂), 6.62 (dd, 2H, ³Jₚ-H=7Hz, NPh). ¹³C{¹H}NMR (75.5 MHz, C₆D₆) δ: 171.2 (d, ²Jₚ-C=20Hz, PC₆H₄), 148.9 (s, PC₆H₄), 144.9 (s, PPh₂), 143.0 (s, PPh₂), 140.9 (s), 133.8 (d, ²Jₚ-C=10Hz, PPh₂), 131.6 (s), 131.1 (s), 130.0 (s), 129.9 (s, NPh), 127.2 (s, NPh), 125.9 (d, ²Jₚ-C=12Hz, PC₆H₄), 121.9 (s), 121.8 (s, PC₆H₄), 119.1 (s, PC₆H₄).
$^{31}$P{¹H} NMR (202.5 MHz, C₆D₆) δ: 27.8. Anal. Calc’d for C₄₄H₈₆P₂N₂Pd: C, 71.07; H, 4.72; N, 3.45. Found: C, 72.84; H, 5.36; N, 3.08.

Synthesis of [Pd(o-C₆H₄PPh₂NPh)(μ-Cl)]₂ 70

A mixture of [Li(o-C₆H₄PPh₂NPh)]₂·Et₂O (0.23g, 0.28mmol) and PdCl₂(COD) (0.08g, 0.28mmol) was dissolved in THF (5 mL) at RT. The mixture was stirred at RT for 6h during which time a fine grayish green solid precipitated from solution. The heterogeneous mixture was stirred overnight, after which time it was filtered through Celite and was subsequently dried in vacuo. The yellow residue was dissolved in CH₂Cl₂ and recrystallized at RT to afford tiny orange crystals. Yield: 0.04g (14%). ¹H NMR (500 MHz, CD₂Cl₂) δ: 7.83-7.79 (m, 8H, PPh₂), 7.61-7.59 (m, 6H, PPh₂), 7.50 (m, 2H, PC₆H₄), 7.49-7.47 (m, 8H), 7.27 (dd, 2H, JH-H=8Hz, PC₆H₄), 7.07-6.99 (m, 4H, NPh), 6.93-6.91 (m, 4H, NPh), 6.86 (d, 2H, JH-H=7Hz, PC₆H₄), 6.82-6.79 (m, 2H, NPh). ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂) δ: 149.2 (d, JPC=18Hz, PC₆H₄), 147.1 (s, PC₆H₄), 142.2 (s, PPh₂), 135.4 (s, PPh₂), 133.2 (d, JPC=10Hz, PPh₂), 133.0 (s, PPh₂), 129.9 (s, NPh), 127.9 (s, NPh), 127.5 (s, PC₆H₄), 126.9 (s, NPh), 126.3 (d, JPC=11Hz, PC₆H₄), 125.2 (s, NPh), 124.3 (s, PC₆H₄), 121.5 (s, PC₆H₄). $^{31}$P{¹H} NMR (202.5 MHz, CD₂Cl₂) δ: 45.5. Anal. Calc’d for: C, 58.82; H, 3.87; N, 2.83. Found: C, 57.12; H, 3.85; N, 2.64.
X-Ray Structure Determinations of 67, 68, 69, 70

Data were collected at room temperature. No crystal decay was observed for any of the compounds. The resulting crystallographic values are given in Table 3.1. ORTEP drawings of 67, 68, 69, 70 are shown in Figures 3.5 - 3.8 respectively, with 30% thermal ellipsoids. Selected bond distances and angles are listed in the captions for Figure 3.5 - 3.8 respectively.
Table 3.1: Crystallographic Parameters for 67·1.5C₆D₆, 68·1.5C₆D₆, 69·CH₂Cl₂, and 70

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<th>Formula</th>
<th>67·1.5C₆D₆</th>
<th>68·1.5C₆D₆</th>
<th>69·CH₂Cl₂</th>
<th>70</th>
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<td>90</td>
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*R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, \text{ R_w = [\sum (|F_o| - |F_c|^2)]/\sum |F_o|^2}^{0.5}
3.3 Results and Discussion

The initial goal of this project was to synthesize neutral monomeric late metal phosphinimine complexes. Early attempts using triphenylphosphinimine, Ph₃PNR (R = 'Bu or SiMe₃) as ligand precursors were later proven to be unsuitable for the preparation of Group X late transition metal complexes. However, the less bulky triphenylphosphinimine ligand, Ph₃PNPh, permitted Group X phosphinimine complexes to be successfully synthesized, and these complexes will be discussed herein.

Two alternative routes were examined in efforts to synthesize Group X late metal phosphinimine complexes. In the first approach, a transmetallation reaction was used. The intermediate organolithium complexes 61 or 62 were synthesized according to literature procedures,¹⁵⁹ where lithiation was performed using methyl lithium at room temperature (for R = SiMe₃), or -78°C (for R = 'Bu). These organolithium complexes were then reacted with various Ni(II), Pd(II) or Pt(II) starting materials (Figure 3.1).

![Chemical structures](image)

R = SiMe₃ 58, 'Bu 59, Ph 60  \[ \text{R = SiMe}_3, ' \text{Bu} 61, \text{Ph} 62, \text{Ph} 43 \]  M = Ni(II), Pd(II), Pt(II)

Figure 3.1 Attempt to synthesize neutral late metal phosphinimine complexes using the transmetallation reaction.
Unfortunately, regardless of solvent or reaction conditions, the late metal precursor did not appear to coordinate to the triphenylphosphinimine ligand with \( R = \text{Bu or SiMe}_3 \). \(^{31}\text{P}\{^{1}\text{H}\} \) and \(^{1}\text{H} \) NMR spectroscopy demonstrated that multiple products were formed, most of which could not be identified, with the exception of the neutral ligand. In only one case, X-ray quality crystals were obtained from the product mixture. While reacting \([\text{Li}(\text{o-C}_6\text{H}_4\text{PPh}_3\text{N}^\text{Bu})_2] \cdot \text{Et}_2\text{O} \) \( \text{62} \) with \( \text{PdCl}_2 \) and \( \text{AgBF}_4 \) at elevated temperatures, colorless crystals were obtained. An X-ray diffraction study showed the compound to be \([\text{Ph}_3\text{PNH}^\text{Bu}]\cdot[\text{BF}_4] \) and indicated that metathesis did not occur.

Since this strategy had failed to yield ortho-metallated phosphinimine complexes, another synthetic route was employed. In this second approach, ortho-bromination reaction was performed, where the organolithium intermediate was treated with bromine to yield ortho-brominated product. This intermediate was then reacted with zero valent Group X late metal complexes (such as \( \text{Ni(COD)}_2 \) or \( \text{Pd(PPh}_3)_4 \)), in attempt to effect oxidative addition across the Caryl-Br bond (Figure 3.2).
Figure 3.2  Attempt to synthesize late metal phosphinimine complexes using an ortho-brominated intermediate

However, problems occurred while performing the ortho-bromination reaction. Multiple products were formed from this step, and attempts to isolate the desired products were unsuccessful. After reacting with late transition metal starting materials, multiple unidentifiable products were formed. Changing the reaction conditions did not reduce the number of products. Attempts to purify product mixtures were unsuccessful. We propose that the steric demands of the ligand precluded the complex formation, thus a less bulky phosphinimine ligand, Ph$_3$PNPh, was used instead. The organolithium intermediate [Li($\sigma$-C$_6$H$_4$PPh$_2$NPh)$_2$]$_2$Et$_2$O was synthesized in situ as described in Chapter 2, and was then further reacted with Group X metal complexes. A red coloured Ni(II) organometallic compound [Ni($\sigma$-C$_6$H$_4$PPh$_2$NPh)$_2$]$_2$ 67 was obtained by reacting 63 with one equivalent of bis-triphenylphosphine nickel(II) bromide (Figure 3.3). It is noteworthy that attempts to synthesize monomer nickel(II) phosphinimine complexes using two equivalents of NiBr$_2$(PPh$_3$)$_2$ were also unsuccessful; unidentified green coloured paramagnetic products were formed.
Figure 3.3 Synthesis of Ni(II) phosphinimine complexes

The isostructural yellow coloured organometallic Pd(II) complex [Pd(o-C₆H₄PPh₂NPh)]₂ 69 was synthesized by reacting the organolithium intermediate 63 with dichloro(1,5-cyclooctadiene)palladium(II) complex (Figure 3.4). In this particular reaction, in addition to the formation of compound 69, an orange coloured Pd(II) chloro-bridged dimer 70 was also formed in low yield. Attempts to increase the yields of compound 70 by changing reaction conditions were unsuccessful. Decomposition of compound 69 in solution occurred gradually by precipitation of a black solid from the solvent after prolonged storage under light. The chloro-bridged compound 70 remained stable after prolonged storage under light.
Compounds 67, 69 and 70 were characterized spectroscopically by \(^1\)H, \(^{31}\)P\(^{\text{1H}}\) and \(^{13}\)C\(^{\text{1H}}\) NMR, as well as by elemental analysis and X-ray crystallography. ORTEP drawings of 67, 69 and 70 are shown in Figures 3.5, 3.6 and 3.7 respectively. Structure of compound 67 and compound 69 were found to be isostructural. Both compounds 67 and compound 69 exhibit two M–C σ-bonds and two M←N donor bonds, giving a four-coordinate metal center with slightly distorted square planar geometry. The structure of [Ni(o-C\(_6\)H\(_4\)PPh\(_2\)NPh)]\(_2\) 67 displays two Ni–C σ-bonds with distances of 1.922(5) and 1.910(5) Å, respectively, which fall within the normal range of other Ni–Caryl bonds such as 1.894(3) Å in [NiBr{o-C\(_6\)H\(_4\)B(pin)\}],\(^{187}\) 1.8850(16) Å in [NiCl(C\(_6\)H\(_4\)\{CH\(_2\)NMe\(_2\)\}_{2-2,6-SiMe\(_3\)-4})],\(^{188}\) and 1.90(2) Å in trans-(Me\(_3\)P)BrNi(η\(^2\)-C(N\(^{\text{Bu}}\)CH\(_2\)-o-C\(_6\)H\(_4\)))NiBr(PMe\(_3\))\(_2\).\(^{189}\) The structure of [Pd(o-
C₆H₄PPh₂NPh₂ 69 also displays two Pd-C σ-bonds with distances of 2.002(4) and 2.011(4) Å, respectively. These are also typical for other Pd-Caryl bonds, such as, 2.016(5) Å in [Pd(C₆H₅)Br(PMe₃)CPh(NEt₂)],²⁰⁰ 2.026(5) Å in [PdBr{o-C₆H₃B(pin)}(PCy₃)₂],¹⁸⁷ and 2.000(3) Å in trans-[PdCl{C₆H₅(CO₂H)₂-2,5}(PPh₃)₂]¹⁹¹ The average N-Caryl bond lengths of compound 67 (1.431(6) Å) are slightly longer than average N-Caryl bond lengths in compound 69 (1.412(4) Å). The P=N bond lengths of compound 67 (average of 1.616(4) Å), are also slightly longer than the P=N bond lengths of compound 69 (average of 1.604(3) Å), as well as the P=N bond distance of the parent phosphinimine Ph₃P=NPh (1.602(3) Å).¹⁸² In both compounds 67 and 69, the N-phenyl ring was twisted almost perpendicular away of the metallacyclic ring. The N(1)-Ni(1)-N(2) angle of 93.29(18)° for compound 67 which is slightly more acute then the corresponding N(1)-Pd(1)-N(2) angle of 94.87(11)° for compound 69.

As described, compound 70 was also crystallized from the same reaction mixture as compound 69 in 14% yield. X-ray crystal structure determination revealed the structure of 70 to be dimeric, with the chloride atoms acting as bridging ligands (Figure 3.7). Each palladium atom in the metallacycle is in a slightly distorted square planar coordination environment. Interatomic distances from palladium to carbon, nitrogen and both the chlorine atoms are comparable to those found for similar complexes (Table 3.2). Compound 70 was the desired complex, where the bridging ligands can be split easily using tertiary phosphines forming monomeric derivatives. Unfortunately, attempts to increase the yield of compound 70 using varied reaction conditions were unsuccessful.
Figure 3.5  ORTEP drawing of 67, 30% thermal ellipsoids are shown, hydrogen atoms and the co-crystallized benzene molecule have been omitted for clarity. Selected bond distances and angles:

Ni(1)-N(1) 1.997(4) Å, Ni(1)-C(1) 1.922(5) Å, P(1)-N(1) 1.619(4) Å;
N(2)-Ni(1)-N(1) 93.29(18)°, N(1)-Ni(1)-C(1) 90.5(2)°, N(1)-P(1)-C(6) 103.3(3)°, P(1)-N(1)-Ni(1) 114.1(2)°, C(19)-N(1)-Ni(1) 122.8(4)°.
Figure 3.6  ORTEP drawing of 69; 30% thermal ellipsoids are shown, hydrogen atoms and the co-crystallized methylene chloride molecule have been omitted for clarity. Selected bond distances and angles: Pd(1)-C(25) 2.002(4) Å, Pd(1)-N(2) 2.172(3) Å, N(2)-P(2) 1.607(3) Å, P(2)-C(26) 1.786(4) Å, N(2)-C(43) 1.405(5) Å; C(25)-Pd(1)-C(1) 94.36(15)°, C(25)-Pd(1)-N(2) 84.72(13)°, Pd(1)-N(2)-P(2) 102.74(15)°, N(2)-P(2)-C(26) 101.72(16)°, Pd(1)-N(2)-C(43) 127.5(2)°.
Figure 3.7  ORTEP drawing of 70, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Pd(1)-Cl(1) 2.3502(12) Å, Pd(1)-Cl(1A) 2.5130(13) Å, Pd(1)-N(1) 2.047(2) Å, N(1)-P(1) 1.614(2) Å, P(1)-C(1) 1.784(3) Å, Pd(1)-C(6) 1.992(2) Å; Cl(1)-Pd(1)-Cl(1)#1 84.81(4)°, Cl(1)-Pd(1)-C(6) 96.09(8)°, C(6)-Pd(1)-N(1) 85.45(10)°, Pd(1)-N(1)-C(19) 122.32(16)°, Pd(1)-N(1)-P(1) 110.84(11)°, Pd(1)-C(6)-C(1) 116.50(18)°.
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<td>2.3502(12)</td>
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<td>2.3105(14)</td>
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Table 3.2 Comparison of selected bond distances (Å) of compound 70 with similar complexes.

It was noteworthy that the bond distances between the palladium metal center and the two bridging chlorines are different. This phenomenon can be explained by using the *trans* influence of the N-donor atom vs the C<sub>aryl</sub> atom. The stronger Pd-C<sub>aryl</sub> bond causes a weakening of the Pd-Cl bond *trans* to the Pd-C<sub>aryl</sub> σ-bond, relative to the Pd-Cl bond *trans* to the Pd-N bond.

Due to the success of coordinating nickel and palladium to the triphenylphosphinimine ligand (Ph₃PNPh), [PtCl₄(COD)] was also reacted with [Li(o-C₆H₄PPh₂NPh)]₂Et₂O 63 in an attempt to synthesize a Pt(II) analogue. The organolithium intermediate 63 was synthesized *in situ* as described in Chapter 2, and was reacted with [PtCl₄(COD)] in THF at room temperature. The ³¹P{¹H} spectrum showed two sets of signals with platinum coupling satellites, centered at 36.6 ppm (²Jₚt-P = 126Hz), as well as 33.9 ppm (²Jₚt-P = 138 Hz) which indicated the presence of platinum in the complexes. ¹³C{¹H}NMR
spectroscopy showed a downfield C-Pt resonance centered at 167.4 ppm, confirming the presence of the C-Pt bond. Due to the similar solubility of the two complexes, attempts to separate them were unsuccessful. In this case, neither single crystals suitable for X-ray analysis nor a reliable elemental analysis determination could be received, very limited information could be obtained from the spectroscopic data. Though based on the similar types of bis-ligand complexes 67 and 69 were formed from the reaction of \([\text{Li}(0-C_6H_4\text{PPh}_2\text{NPh})_2]\_2\cdot\text{Et}_2\text{O}\) with \(\text{NiBr}_2(\text{PPh}_3)_2\) and \(\text{PdCl}_2(\text{COD})\) respectively, complex with the structure of \([\text{Pt}(0-C_6H_4\text{PPh}_2\text{NPh})_2]\_2\) was proposed as one of the possible products. Further investigations are necessary to confirm the exact structure of the products.

A similar synthetic approach has also been applied to the \((3,5-\text{dimethylphenylimino})\text{triphenylphosphine}\) ligand system, \(\text{Ph}_3\text{P} = \text{N}(3,5-\text{C}_6\text{H}_3(\text{CH}_3)_2)\) 26, to give the bis-ligand nickel (II) complex 68. Compound 26 was lithiated using \(\text{Li}^n\text{Bu}\) \textit{in situ} as described in previous chapter, and was then reacted with \(\text{NiBr}_2(\text{PPh}_3)_2\) in THF at room temperature. Orange X-ray quality crystals were obtained and the X-ray determination study indicated that the metal complex had a structure shown in Figure 3.9. The nickel center has a slightly distorted square planar geometry, and has similar structure with compound 67. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum shown a signal centered at 35.4 ppm, and \(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR data confirmed the formation of the complex. An ORTEP drawing of compound 68 is shown in Figure 3.8.
Figure 3.8  ORTEP drawing of 68, 30% thermal ellipsoids are shown, hydrogen atoms, the co-crystallized benzene and NiBr(PPH₃)₃ molecule and have been omitted for clarity. Selected bond distances and angles: Ni(1)-N(1) 2.016(6) Å, Ni(1)-C(1) 1.907(8) Å, P(1)-N(1) 1.606(6) Å; N(1A)-Ni(1)-N(1) 94.8(3)°, N(1)-Ni(1)-C(1) 85.9(3)°, P(1)-N(1)-Ni(1) 108.5(3)°, C(19)-N(1)-Ni(1) 125.4(5)°.
Noteworthy in the transmetallation reaction of $[\text{Li}(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{NPh})]_2\cdot\text{Et}_3\text{O}$ 63 and $[\text{Li}(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{N}(3,5\text{-C}_6\text{H}_3(\text{CH}_3)_2))]_2\cdot\text{Et}_3\text{O}$ 66 with NiBr$_2$(PPh$_3$)$_2$, a side product, NiBr(PPh$_3$)$_3$ was obtained. X-ray crystallography unambiguously showed the formation of the Ni(I) compound. Similar redox chemistry was observed by Stalke et al. in the reaction of $[\text{Li}(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{NSiMe}_3)]_2\cdot\text{Et}_3\text{O}$ with CuCl$_2$, which generated a reductive coupling product $[\langle(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{NSiMe}_3)\rangle_2]$ and an organo-copper (I) compound. Though in our case, the ligand coupling product was not isolated, we propose that a similar compound with the structure $[\langle(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{NR})\rangle_2]$ (R = Ph, or 3,5-C$_6$H$_3$(CH$_3$)$_2$) is a likely side product in the transmetallation of compound 63 and compound 66 with NiBr$_2$(PPh$_3$)$_2$.

3.4 Summary

In summary, attempts to coordinate the ortho-lithiated compound $[\text{Li}(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{NSiMe}_3)]_2\cdot\text{Et}_3\text{O}$ 61 or $[\text{Li}(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{N}^\text{tBu})]_2\cdot\text{Et}_3\text{O}$ 62 to Group X late transition metals using various approaches were unsuccessful. Conversely, transmetallation of the ortho-lithiated triphenylphosphinimine ligand, $[\text{Li}(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{NR})]_2\cdot\text{Et}_3\text{O}$ (R = Ph 43 or 3,5-C$_6$H$_3$(CH$_3$)$_2$ 66) results in a side arm N-donating chelating organometallic ligand. In all the metal complexes mentioned, the triphenylphosphinimine ligand moiety acts as a side-arm donating group, donating electron density to the metal center through the imine nitrogen atom. The reaction of 43 or 66 with NiBr$_2$(PPh$_3$)$_2$ and PdCl$_2$(COD) results in the formation of compounds $[\text{Ni}(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{NPh})]_2$ 67, $[\text{Ni}(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{N}(3,5\text{-C}_6\text{H}_3(\text{CH}_3)_2))]_2$ 68, and $[\text{Pd}(\sigma\text{-C}_6\text{H}_4\text{PPh}_2\text{NPh})]_2$ 69 as major
products. The chloro-bridged dimer, [Pd(o-C₆H₄PPh₂NPh)(μ-Cl)₂] 70 was also isolated as a minor product when PdCl₂(COD) was used as a metal precursor.
Chapter Four
Summary

The research herein has described synthetic chemistry of Group IX and Group X phosphinimine complexes. The results provide insight into the coordination chemistry of Group IX and Group X late transition metal with phosphinimine ligands.

A series of Group IX phosphinimine complexes were synthesized via salt metathesis reactions under mild conditions. The oxidative addition of dichloromethane, followed by ligand rearrangement was observed in compounds 46, 47, 52, as well as the analogous iridium compound 53. A possible mechanism for this reaction could involve the initial formation of the chloromethyl (Cl-CH₂-M-Cl) derivative, and then undergo reductive elimination to form a C-C bond. The compound will then undergo oxidative addition again to form the products. This process reacted rapidly, therefore intermediate was not observed by spectroscopic methods. It was found that the inclusion of bulky aryl substituents on the imine nitrogen inhibited the oxidative addition reaction. Steric congestion appears to be an important factor in influencing the facile addition reaction. Future research involving these complexes will be focused on the study of ligand effects upon a variety of processes that are, catalyzed by Group IX metal complexes, such as hydroformylation.

Additionally, a series of Group X phosphinimine complexes have been prepared. The first synthetic goal of this project was the preparation of monomeric Group X transition metal phosphinimine complexes. Though, we demonstrated that reacting Group X metals with phosphinimine ligands tended
to form bis-ligand complexes. These compounds are anticipated not to act as practical polymerization catalysts. However, in one case where PdCl₂(COD) was used as the metal precursor, the desired complex was formed in very low yield. Further attempts to increase the yield of compound 69 by optimizing the reaction condition is worth pursuing.

In conclusion, the research described and discussed in this thesis has established the coordination chemistry of both Group IX and Group X complexes containing phosphinimine ligands. The study of steric influences toward oxidative addition of dichloromethane in group IX phosphinimine complexes was also performed. These synthetic fundamental accomplishments described herein lay the foundation for investigation into potential catalytic reactions.
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Electronic Influences on Oxidative Addition of CH₂Cl₂. (manuscript in
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Pingrong Wei, Katie T. K. Chan and Douglas W. Stephan*
Metallated Triphenylphosphinimine Complexes. (manuscript in
preparation)