SYNTHESES AND COORDINATION CHEMISTRY OF AN N-HETEROCYCLIC CARBENE-CONTAINING TRIDENTATE LIGAND

by

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ABSTRACT

One of the most exciting advances in transition-metal-catalyzed processes has been the move toward use of N-heterocyclic carbenes (NHCs) as ancillary ligands. The variation possible in NHC design is immense with one of the most important design aspects being the incorporation of NHC donors into polydentate arrays to generate tridentate pincer ligands. However, research into this class of compounds was limited until the isolation of the first stable crystalline NHC two decades ago. Therefore, understanding of the organometallic chemistry of this class of compounds remains limited in comparison to the closely related phosphine ligands. Thus, this thesis focuses on the preparation of a di-o-phenylene-bridged tridentate PCP donor set and the reactivity of coordination complexes of late transition metals containing this new ligand system.

Incorporation of this tridentate ligand onto the group 10 triad of elements via oxidative addition proceeds smoothly to generate square-planar metal hydride complexes of the form \([(PCP)MH][PF_6]\) (where M = Ni(II), Pd(II) and Pt(II)). Initiating reactivity studies of this series of complexes exposed a new type of non-innocent ligand behaviour involving formation of a C-C bond between the carbene atom and an ethyl moiety. Isotopic labeling experiments and DFT calculations are used to provide mechanistic insight into this process that is viewed as a possible source of catalyst deactivation in similar systems.

Group 9 metal complexes of rhodium and iridium incorporating tridentate ligand arrays have achieved considerable success in the activation and functionalization of C-H bonds. To examine the reactivity of pincer complexes utilizing a central NHC donor a variety of new rhodium and iridium complexes were synthesized. A rhodium hydride
species (PCP)RhH showed catalytic activity in the dehydrogenation of ammonia borane as well as in the hydrosilylation of terminal alkynes. Complexes consisting of both metal centres also exhibited ligand rearrangement processes that challenge the presumed stability of rigid tridentate ligand frameworks.
PREFACE

Chapters two, three, four and five and six were conducted in collaboration with Professor Michael D. Fryzuk, the research supervisor for the thesis, who assisted with the development of the related work. A version of Chapter 2 has been published. Tobias Steinke, Bryan K. Shaw, Howard Jong, Brian O. Patrick, and Michael D. Fryzuk. (2009) Synthesis and Coordination Chemistry of a Tridentate \( o \)-Phenylene-Bridged Diphosphine-NHC System. Organometallics. 28:2830–2836. Dr. Tobias Steinke was responsible for the first successful synthesis of the PCP ligand. I was responsible for optimizing the synthesis of the PCP ligand and provided the majority of the analysis of the compounds as well as assisting with the manuscript preparation. Dr. Howard Jong and Dr. Brian O. Patrick assisted with X-ray structure determination.

A version of Chapter 3 has been published. Tobias Steinke, Bryan K. Shaw, Howard Jong, Brian O. Patrick, Michael D. Fryzuk, and Jennifer C. Green. (2009) Noninnocent Behavior of Ancillary Ligands: Apparent Trans Coupling of a Saturated N-Heterocyclic Carbene Unit with an Ethyl Ligand Mediated by Nickel. J. Am. Chem. Soc. 131(30):10461–10466. Dr. Tobias Steinke performed the original reaction of the \([(\text{PCP})\text{NiH}][\text{PF}_6]\) with ethylene. I was responsible for all the experiments involving the deuterium labeling studies and all the necessary analysis as well as assisting in the manuscript preparation. Dr. Howard Jong and Dr. Brian O. Patrick assisted with X-ray structure determination. Dr. Jennifer C. Green (Oxford) performed the computational analysis. All further experimental research and data analysis in Chapter 4, 5 and 6 were performed by the author of this thesis with the exception of X-ray structure assistance provided by Dr. Howard Jong and Mr. Nathan Halcovitch.
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<table>
<thead>
<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>a, b, c</td>
<td>unit cell dimensions; lengths (Å)</td>
</tr>
<tr>
<td>α, β, γ</td>
<td>unit cell dimensions, angles (°)</td>
</tr>
<tr>
<td>AB</td>
<td>ammonia borane</td>
</tr>
<tr>
<td>Anal.</td>
<td>analysis</td>
</tr>
<tr>
<td>atm</td>
<td>atmosphere</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>Bu</td>
<td>butyl group</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>carbon-13</td>
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<tr>
<td>ca.</td>
<td>approximately</td>
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<tr>
<td>calcd</td>
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<tr>
<td>COA</td>
<td>cyclooctane</td>
</tr>
<tr>
<td>COD</td>
<td>1,5-cyclooctadiene</td>
</tr>
<tr>
<td>Δ</td>
<td>heat</td>
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<tr>
<td>δ</td>
<td>chemical shift</td>
</tr>
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<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
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<td>Description</td>
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<td>-------------</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl group</td>
</tr>
<tr>
<td>$^1\text{H}$</td>
<td>proton</td>
</tr>
<tr>
<td>{ $^1\text{H}$ }</td>
<td>proton decoupled</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>HSQC</td>
<td>heteronuclear single quantum coherence</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>IMes</td>
<td>1,3-dimesitylimidazol-2-ylidene</td>
</tr>
<tr>
<td>$^a J_{AB}$</td>
<td>n-bond scalar coupling constant between nuclei A and B</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>kcal</td>
<td>kilocalories</td>
</tr>
<tr>
<td>kJ</td>
<td>kilojoules</td>
</tr>
<tr>
<td>KHMDS</td>
<td>potassium bis(trimethylsilyl)amide</td>
</tr>
<tr>
<td>Mes</td>
<td>2,4,6-trimethylphenyl, or mesityl</td>
</tr>
<tr>
<td>m</td>
<td>multiplet</td>
</tr>
<tr>
<td>$m$</td>
<td>meta</td>
</tr>
<tr>
<td>mmol</td>
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</tr>
<tr>
<td>mol</td>
<td>mole</td>
</tr>
<tr>
<td>$^{15}\text{N}$</td>
<td>nitrogen-15</td>
</tr>
<tr>
<td>NBE</td>
<td>norbornene</td>
</tr>
<tr>
<td>NHC</td>
<td>N-heterocyclic carbene</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>$o$</td>
<td>ortho</td>
</tr>
<tr>
<td>ORTEP</td>
<td>Oakridge Thermal Ellipsoid Program</td>
</tr>
</tbody>
</table>
OAc               acetate

p                para

$^{31}$P           phosphorus-31

PCP               refers to the donor atoms in a tridentate ligand array

PF$_6$            potassium hexafluorophosphate

Ph                phenyl group

ppm               parts per million

$i$Pr             isopropyl group

q                 quartet

rt                room temperature

s                 singlet

sep               septet

t$^t$              tert

t                 triplet

TBE               tert-butylethylene

THF               tetrahydrofuran

TMS               trimethylsilyl group, -Si(CH$_3$)$_3$

Tol               toluene

$V$               unit cell volume ($\text{Å}^3$)

$Z$               number of asymmetric units in unit cell

$\mu$             bridging or absorption coefficient (X-ray)
ACKNOWLEDGEMENTS

I wish to acknowledge first and foremost, my research supervisor Dr. Michael D. Fryzuk. Dr. Fryzuk’s lab was not my expected placement when I came to UBC but if I had to do it again I wouldn’t change a thing. Professor Fryzuk’s passion for academia and attention to detail is remarkable and under his supervision I have learned what it takes to become a successful chemist. I am very grateful for the lessons I have learned in the Fryzuk lab and thank Dr. Fryzuk for always finding time in his busy schedule to help with research issues and especially during the preparation of this dissertation.

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DEDICATION

This work is dedicated to my friends and family who I could not have done this without. Especially my parents Jim and Kathy, who have provided endless moral and financial support for which I cannot thank them enough. And of course Angie, who proved to me that there really is the right person for everyone.
Chapter One

Introduction

1.1 Introduction to Carbenes

A carbene is best described as a compound that contains a neutral divalent carbon atom with six electrons in its valence shell represented by the general formula :CR₂. The idea of a carbene was first proposed in 1855 when the alkaline hydrolysis of bromoform was believed to proceed through a divalent dibromocarbene intermediate.¹ The first significant contribution to the chemistry of carbenes came in 1954 when Doering and Hoffmann provided evidence for a dihalomethylene intermediate in an alkene cyclopropanation reaction.² Breslow first suggested the stabilization of a carbene by a heteroatom in a thiazolium zwitterion four years later.³ Although unaware at the time, Tschugajeff and co-workers prepared the first carbene-metal complex in 1915 by reaction of tetrakis(methylisocyanide) platinum(II) with hydrazine (Scheme 1.1).⁴⁻⁶ The heteroatom-stabilized ligand was not suggested until much later⁷ and then proven in 1973 using NMR spectroscopy and X-ray crystallography.⁸
Scheme 1.1. Interconversion of Tschugajeff’s red salt (1.1) and yellow salt (1.2). Graphic has been adapted from reference [6].

It was in the early 1960’s that Wanzlick postulated that the stability of carbenes might be enhanced by the inclusion of amino substituents and attempted to synthesize 1,3-diphenylimidazolidin-2-ylidene (1.5) by thermal elimination of chloroform from 1,3-diphenyl-2-(trichloromethyl)imidazolidine (1.3) (Scheme 1.2). However, the carbene was not observed and cross-coupling experiments between different entetraamines indicated an equilibrium between the dimer (1.4) and two carbenes was unlikely. A more recent report has since provided evidence to support the possibility that an equilibrium exists between 1.4 and 1.5. Wanzlick’s preliminary work towards the isolation of a stable carbene was a significant step for future developments in this field.

Scheme 1.2. Entetraamine resulting from the elimination of chloroform from 1.3. Graphic has been adapted from reference [6].
A few years later, in 1964, Fischer et al. reported the synthesis and characterization of the first metal-carbene complex of any kind: methoxyphenylmethylene tungsten(0) pentacarbonyl (Scheme 1.3). Then in 1968, Wanzlick et al. and Öfele independently reported the synthesis of two different, unsaturated, N-heterocyclic carbene-metal complexes (Scheme 1.4). In each case a ligand on the coordinatively unsaturated metal salt acted as a base, converting the imidazolium salt to the imidazolin-2-ylidene, which is stabilized by coordination to the metal centre.

**Scheme 1.3.** Synthesis of the first recognized metal-carbene complex.

\[
\begin{align*}
\text{W(CO)}_5 & \xrightarrow{\text{LiR, Et}_2\text{O}} \text{W(CO)}_5\text{Li} \xrightarrow{\text{Me}_4\text{NCl, H}^+} \text{W(CO)}_5\text{C} \xrightarrow{\text{CH}_2\text{N}_2} \text{W(CO)}_5
\end{align*}
\]

1.6 \( R = \text{Ph} \)
1.7 \( R = \text{CH}_3 \)

**Scheme 1.4.** Synthesis of the first recognized N-heterocyclic carbene-metal complexes by Wanzlick (1.8) and Öfele (1.9).

\[
\begin{align*}
2 \left[ \begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{Ph}
\end{array} \right] \underset{\text{ClO}_4^-}{\xrightarrow{\text{Hg(OAc)}_2, \Delta, (-2 \text{ HOAc})}} & \left[ \begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{Ph}
\end{array} \right] \\
& \overset{2\text{ClO}_4^-}{\xrightarrow{\text{Ph}}} \left[ \begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{Ph}
\end{array} \right] \\
& \overset{\text{Ph}}{\xrightarrow{\text{Ph}}} \left[ \begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{Ph}
\end{array} \right] \\
& \overset{\text{Ph}}{\xrightarrow{\text{Ph}}} \left[ \begin{array}{c}
\text{Ph} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{Ph}
\end{array} \right]
\end{align*}
\]

1.8

\[
\begin{align*}
\left[ \begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{H}_3\text{C}
\end{array} \right] & \underset{\text{HCr(CO)}_5^-}{\xrightarrow{\Delta, (-\text{H}_2)}} \left[ \begin{array}{c}
\text{H}_3\text{C} \\
\text{N} \\
\text{N} \\
\text{H} \\
\text{H}_3\text{C}
\end{array} \right]
\end{align*}
\]

1.9
Bertrand and co-workers reported the first major breakthrough towards the isolation of a carbene in 1988 through the elimination of N₂ via thermolysis (250 °C), or photolysis (300nm), from [bis(diisopropylamino)phosphino](trimethylsilyl)diazomethane (1.10). The resulting (trimethylsilyl)[bis(diisopropylamino)phosphanyl]carbene (1.11) was isolated as a red oil and found to be stable for several weeks under an inert atmosphere at ambient temperature (Scheme 1.5).¹⁶,¹⁷ However, it was the isolation of the first stable, crystalline carbene compound that ultimately began intensive research into the chemistry of carbenes. In 1991, Arduengo et al. was able to deprotonate the sterically demanding, substituted N,N’-diadamantyl imidazolium salt 1.12 leading to the first stable N-heterocyclic carbene (NHC) 1,3-bis(adamantyl)imidazolin-2-ylidene (1.13) (Scheme 1.5).¹⁸ The isolation of the first carbene showed that under the right steric and electronic conditions carbenes are not just highly reactive intermediates and in the years following a variety of substituted NHCs have been synthesized.¹⁹-²¹

Scheme 1.5. Isolation of the first stable carbenes 1.11 and 1.13.
1.2 Stabilization of Carbenes

The geometry of the carbene carbon can range from linear, which implies sp-hybridization of the frontier orbitals, to bent, which leads to sp\(^2\)-hybridization of the frontier orbitals. A linear carbene consists of two non-bonding degenerate orbitals (p\(_x\) and p\(_y\)); deviation from linearity removes the degeneracy and leaves one of these p-orbitals relatively unchanged called p\(_\pi\), while the other gains stability through an increase in s character (σ). The linear geometry is an extreme case; most carbenes are bent and their frontier orbitals will be referred to as σ and p\(_\pi\). Spin multiplicity in these bent carbenes can be envisioned in four different ways based on the electronic configuration of the non-bonding electrons (Figure 1.1). The common orientations are the triplet state I and the singlet state II, while the less stable singlet state III and an excited state IV are conceivable but not observed. Calculations show a large energy gap of at least 46 kcal/mol between σ and p\(_\pi\) favours the singlet state while an energy gap of less that 35 kcal/mol likely results in the triplet ground state.

**Figure 1.1.** Four possible electronic configurations for a six-electron carbene carbon with a bent geometry. Graphic adapted from reference [17].
It is important to understand the ground state spin multiplicity of a particular carbene as it directly influences both the stability and reactivity of the molecule.\textsuperscript{23} For example, singlet carbenes with their filled $\sigma$ and empty $p_\pi$ orbital display ambiphilic behaviour while triplet carbenes act as a diradical, because of the two unpaired electrons. The spin multiplicity is determined by both the steric and electronic effect of the $\alpha$-substituents bonded to the carbene carbon. The influence of the electronegativity of the atoms bound directly to the carbene can be described in two ways: (i) it is generally accepted that electron-withdrawing groups favour the singlet over the triplet state through stabilization of the filled non-bonding $\sigma$-orbital by increasing its $s$ character while the $p_\pi$ orbital remains relatively unchanged;\textsuperscript{24-28} (ii) substituents with $\sigma$-electron-donating properties decrease the $\sigma$-$p_\pi$ gap and thus stabilize the triplet ground state.

Aside from inductive effects electronic delocalization (mesomeric effects) play a vital role in determining both the geometry around the carbene atom as well as its stabilization.\textsuperscript{22,29} In most cases the $\alpha$-group can be classified as either X (for electron-donating groups such as F, Cl, Br, I, NR$_2$, PR$_2$, OR, SR, SR$_3$) or Z (for electron-withdrawing groups such as COR, CN, CF$_3$, BR$_2$, SiR$_3$, PR$_3^+$).\textsuperscript{17} Based on these classifications, most singlet carbenes can be placed into one of three categories according to the substituents present: the bent (X,X) type, the linear (Z,Z), or the quasi-linear (X,Z) carbenes (Figure 1.2). Although this system categorizes most singlet carbenes, a number of carbenes have been synthesized that are stabilized through only one phosphino\textsuperscript{30} or amino group,\textsuperscript{31-34} while the second $\alpha$-substituent has little electronic impact. The final category that must be considered is the case in which the carbene bears no stabilizing $\alpha$-groups. This type of singlet carbene is limited to the recent isolation of bis(diisopropy-
lamino)cyclopropenylidene 1.18 (Figure 1.3). \(^{35}\)

![Diagram of electron delocalization and resonance forms of carbenes](image)

**Figure 1.2.** Electron delocalization and representative resonance forms of A (X,X), B (X,Z) and C (Z,Z) type carbenes.

The stabilization of singlet carbenes containing two electron-donating substituents (X,X) is a result of the interaction between the \(\pi\)-electrons of the \(\alpha\)-atoms and the empty \(p_\pi\) orbital of the carbene. The overall effect is a destabilization of the \(p_\pi\) orbital, which in turn increases the \(\sigma\)-\(p_\pi\) gap. This interaction is best described as 3-centre 4-electron \(\pi\) system where the X-C bonds have partial multiple bond character. The most common carbenes of this type are the dimethoxycarbenes,\(^{36,37}\) dihalocarbenes,\(^{38-40}\) and diaminocarbenes, including NHCs which will be featured throughout this thesis.

Carbenes of the type (X,Z) are stabilized through the “push-pull” interaction between the lone pair of the electron-donating substituent to the empty carbene \(p_\gamma\)-orbital, and a simultaneous weaker donation of electron density from the \(p_\alpha\)-orbital to an empty substituent \(p\)-orbital. The net effect is a stabilization of the \(p_\alpha\) orbital and a destabilization of the \(p_\gamma\) orbital, which favours the singlet state and a polarized allene type bonding system. Good examples of this class of carbene are the phosphanyl(silyl)carbene,\(^{16}\) (phosphanyl)(phosphonio)carbenes,\(^{41}\) and trifluoroethylidynesulfur trifluoride.\(^{42,43}\)
For the third category featuring both electron-withdrawing substituents $(Z,Z)$, the degeneracy of the carbene $p_x$ and $p_y$ orbital is broken as the filled $p_y$ is stabilized through interaction with the empty $p$-orbital of the $\alpha$-groups. This increased energy gap results in a singlet carbene even though the geometry of $(Z,Z)$ carbenes is predicted to be linear.\textsuperscript{24-28} Carbenes of this type have never been isolated; however, some masked analogues such as borylmethyleneboranes have been synthesized and shown to react through transient dicarborylcarbene intermediates.\textsuperscript{44}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{carbenes.png}
\caption{Carbenes stabilized by one $\alpha$-group (1.14-1.17) and containing no $\alpha$-stabilizing groups (1.18).}
\end{figure}

Sterically bulky $\alpha$-substituents help to kinetically stabilize all types of carbenes and can also dictate the ground state multiplicity by imposing geometrical restriction around the carbene.\textsuperscript{17} This is most relevant in the stabilization of triplet carbenes as increasing the steric bulk forces the carbene-substituent bond angle to approach linearity,
which favours the triplet state.\textsuperscript{45,46} Approximately 40 years after this realization prompted the first attempted isolation of a triplet carbene,\textsuperscript{47} Tomioka et al. successfully synthesized a triplet carbene that is stable for up to one week at room temperature. The bulky substituents along with electron delocalization through the extended $\pi$ system helps to slow degradation through dimerization and reaction with oxygen\textsuperscript{48} (Scheme 1.6).

**Scheme 1.6.** A triplet carbene stabilized by bulky $\alpha$-substituents. Graphic adapted from reference [4].

1.3 **Organometallic Carbene Complexes**

In order to maximize orbital overlap when forming metal-carbene bonds a bent geometry at the carbene is required, therefore carbenes of the (X,X) type are best suited for metal coordination, while linear carbenes form weak carbene-metal bonds.\textsuperscript{4,49} Fischer type metal-carbene complexes usually involve a low oxidation state metal and are stabilized by either heteroatom or phenyl substitutents on the carbene.\textsuperscript{50} Named in honour of the discoverer of the first transition metal-carbene complex in 1964,\textsuperscript{13} Fischer carbenes follow a donor-acceptor model where the carbene donates through its sp\textsuperscript{2}-hybridized $\sigma$-orbital to an empty metal d-orbital and simultaneously accepts back-donation from a filled d-orbital on the metal via its empty p$_\pi$-orbital (Figure 1.4). The end result is an electrophilic carbene-metal bond exhibiting partial double bond character.
Figure 1.4. Fischer type metal-carbene bonding and representative resonance forms.

A second type of metal-carbene bonding was uncovered in 1974 when Schrock reported the first synthesis of a high oxidation state \((d^0)\) metal-alkylidene complex (1.20) by an intramolecular \(\alpha\)-hydride abstraction (eq. 1.1). These species differ from Fischer carbenes as they have only hydrogen or simple alkyl substituents, which lack the capability to provide stabilization of the carbene through electron delocalization into the empty \(p_\pi\)-orbital. The bonding in these latter derivatives is considered a covalent interaction between two triplet fragments with a near equal distribution between the carbon and metal resulting in a true metal-carbon double bond (Figure 1.5). Unlike Fischer carbenes, the family of Schrock carbenes possesses a carbon that is nucleophilic and found exclusively on early transition metals; however, distinguishing between Fischer and Shrock type carbenes is not always straightforward.
N-heterocyclic carbenes pose a challenge to the naming system outline above because like Fischer carbenes they benefit from stabilization through a heteroatom, but the mesomeric effect of the amino substituents reduces the need for back-donation from the metal into the empty $p\pi$-orbital. For this reason NHCs were initially considered as pure $\sigma$-donors with negligible $\pi$-back-donation from the metal.\textsuperscript{53-55} Recently the $\pi$-acceptor capabilities of NHCs have been considered more significant than originally thought, especially in the case of electron rich metal centres.\textsuperscript{56,57} Even the $\pi$-donating contribution of NHCs has been shown to play a role in their bonding with electron deficient metal complexes.\textsuperscript{58} Additional studies of an electron rich platinum centre indicate that $\pi$-back-donation is favoured in the case of saturated NHC rings over the unsaturated version.\textsuperscript{59}

![Figure 1.5. Schrock type metal-carbene bonding and representative resonance forms.](image)

The similarities between the monodentate 2-electron donor properties of NHCs and phosphine ligands along with the successes of phosphine-containing transition metal complexes in catalysis has created an interest in NHCs as a phosphine analog. In fact, N-heterocyclic carbenes have been shown to be even stronger $\sigma$-donors then even the most basic phosphines.\textsuperscript{55,60} Perhaps the most well known example of an improvement upon...
moving from a phosphine to an NHC donor is the evolution of Grubbs’ alkene metathesis catalyst (Figure 1.6).^{61} The increased catalytic activity has been attributed to a higher affinity of the alkene to coordinate and a lower activation barrier towards the product.^{62} Since the substituents are one or two bonds away from the donor atom another advantage of NHCs is the ability to tune the steric environment around the ligand with little change on its electronic properties. Likewise alterations of the NHC ring system can change the electronic effect of the carbene with very little steric impact.^{63}

![Figure 1.6](image)

**Figure 1.6.** Modification from Grubb’s first generation catalyst (1.21) to second generation catalyst (1.22) by replacement of a phosphine donor with an NHC.

### 1.4 Synthesis of N-heterocyclic Carbenes

N-heterocyclic carbenes derived from the unsaturated imidazolin-2-ylidene core are likely the most common group of stable heterocyclic carbenes. The most convenient route to access these species is through deprotonation of an imidazolium precursor (eq. 1.2) where the nitrogen substituent may be a variety of alkyl or aryl groups and R’ can range from hydrogen or halogens to multiple ring structures. Scheme 1.7 provides

\[ \begin{align*}
\text{R'} & \quad \text{R'} \\
\text{R} & \quad \text{X} \\
\text{R} & \quad \text{H} \\
\text{R} & \quad \text{N}^{+} \\
\text{N} & \quad \text{H} \\
\text{R} & \quad \text{N} \\
\text{N} & \quad \text{R} \\
\text{R} & \quad \text{X}^{−} \\
\end{align*} \]

\[ \xrightarrow{\text{Base} \ (- \ H\text{Base}^{+}\text{X}^{−})} \]

\[ \begin{align*}
\text{R'} & \quad \text{R'} \\
\text{R} & \quad \text{N}^{−} \\
\text{R} & \quad \text{N}^{−} \\
\text{R} & \quad \text{R} \\
\end{align*} \]
examples of the most reliable synthetic pathways to imidazolium salts (routes a,b,c) and one route leading directly to the imidazolin-2-ylidene (route d in Scheme 1.7). The one-pot reaction involving glyoxal, a primary amine and formaldehyde in the presence of a Brønsted acid allows for the isolation of a wide range of symmetrically substituted imidazolium salts and can be performed on the bench top.\textsuperscript{64} Isolation of the initial condensation product before cyclization allows for the incorporation of unusual or very sterically demanding nitrogen substituents.\textsuperscript{65,66} To generate asymmetrically substituted imidazolium salts one equivalent of a primary amine is used under acidic conditions during the ring closing reaction followed by nucleophilic substitution of a different primary amine at the unsubstituted site of the N-alkylimidazole.\textsuperscript{67}

**Scheme 1.7.** Common synthetic routes providing imidazolium salts or imidazolin-2-ylidenes.

![Scheme 1.7](image-url)
In the third example, an aryl substituted imidazolinium salt consisting of a saturated backbone results from the ring closure of the corresponding 1,2-diamine with triethylorthoformate in the presence of an ammonium salt. The final route in Scheme 1.7 involves the formation of an imidazolin-2-thione through condensation between α-hydroxyketones with N,N'-substituted thiourea derivatives containing the desired functionality. Reduction of the imidazolin-2-thione with potassium in boiling tetrahydrofuran leads directly to the imidazolino-2-ylidene.

1.5 Tridentate “Pincer” Ligands Containing N-Heterocyclic Carbenes

The isolation of a thermally stable NHC by Arduengo et al. in 1991, along with the relative ease of altering the functionality of the nitrogen substituents, has created an increase in research aimed at exploring the organometallic chemistry of NHCs. One important design aspect has been the incorporation of NHC donors into polydentate arrays, usually in combination with other classical donors, such as pyridine, oxazolines, and phosphines to generate tripodal and “pincer” ligands. The term pincer refers to a rigid, linear tridentate ligand, which generally coordinates in a meridional or pseudo-meridional geometry to provide a robust, thermally stable coordination complex suitable for catalysis. The first ligand of this type, (1.3-[(di-t-butylphosphino)methyl]benzene), and its coordination chemistry was reported in 1976. More recently, pincer ligand scaffolds incorporating NHC donors have been developed including, but not limited to, neutral [CNC], [PCP], and [NCN] ancillary ligands as well as monoanionic [CCC] ligand sets (Figure 1.7). The donor atoms and their substituents can control the accessibility of the metal to potential substrates and the electron density around the metal. This allows for the ability to tune the reactivity of
metal complexes bearing pincer ligands by altering the electronic and steric properties of the donor atoms.

![Chemical structures of pincer ligands](image)

**Figure 1.7.** N-heterocyclic carbene based pincer ligands relevant to this work.

### 1.5.1 NHC-Containing Pincer Complexes of Rhodium

The first report of a NHC pincer complex of rhodium came in 1995, while the chemistry of NHC ligand design was still in its infancy. The authors formed an octahedral Rh(III) complex featuring a six-membered NHC ring by stirring a number of 10-S-3 tetraazapentalene derivatives in a benzene/dichloromethane (1:1) solution of RhCl(PPh₃)₃ (Scheme 1.8). The coordination mode observed in the product was dependent upon the nature of the R group found on the nitrogen atom, with smaller alkyl groups giving the unsymmetric product (1.23-1.24) while aryl substituents preferred the symmetric product (1.25-1.26).
Scheme 1.8. Formation of the first NHC pincer complexes of rhodium from 10-S-3 tetraazapentalenes.

The first rhodium NHC pincer of the PCP type appeared in 2005, incorporating an imidazolin-2-ylidene connected to two diphenylphosphine donors through an ethylene linker. Although the alkyl linker allows for a degree of flexibility in the ligand, solid-state molecular structure data confirms the ligand coordinates in a meridional conformation. The anticipated product of the reaction between the trinuclear silver complex (1.27) and [Rh(COD)Cl]$_2$ was the Rh(I) chloride (1.28) shown in Scheme 1.9. However, the result was instead the air-stable Rh(III) complex (1.29) produced via the oxidative addition of CH$_2$Cl$_2$ to the intermediate 1.28. To avoid this unwanted product the analogous reaction was carried out in the non-halogenated solvent dimethylformamide, which yielded the unexpected rhodium trichloride complex 1.30. The source of the chloride ions is believed to be through oxidative degradation in the presence of AgCl, a process that has been studied in ruthenium NHC systems. The trivalent rhodium species formed are believed to arise through a highly reactive intermediate (1.28) and therefore the transmetallation reaction was repeated with [Rh(CO)$_2$Cl]$_2$ in order to trap the Rh(I) PCP complex (1.31).
Scheme 1.9. Synthesis of rhodium complexes bearing the PCP ligand. Graphic adapted from reference [89].

One application of late transition metal complexes in catalysis is the synthesis of vinylsilanes through the hydrosilylation of alkynes. Since many catalyst systems are plagued by regio- and stereo-control there is continual interest in catalyst systems with enhanced selectivity. As complexes of rhodium have shown excellent regio- and stereo-control during the catalytic hydrosilylation of alkynes the three new rhodium pincer species 1.29-1.31 were tested as hydrosilylation catalysts. With an optimized 1:3 alkyne/hydrosilane ratio all three complexes displayed similar activity suggesting that a common catalytic cycle is initiated upon conversion of the products back to the reactive Rh(I) intermediate (1.28). Isomer selectivity was hindered by bulkier silanes like tert-butylidimethysilane but in the case of phenyldimethylsilane the trans isomer was obtained.
in 88% yield. Although the alkyne was rapidly consumed, longer reaction times (up to 24 h) increased stereoselectivity through a slow isomerization pathway between the cis and trans isomer previously seen with a Rh(I) complex.\textsuperscript{95}

**Scheme 1.10.** Possible regio- and stereoisomers resulting during hydrosilylation.

A rhodium complex supported by a CNC pincer motif has been synthesized through deprotonation of the imidazolium proligand 1.32 with triethylamine (Scheme 1.11). Interestingly the reaction gives two products; the dinuclear rhodium(I) species 1.33 constitutes the major product while the remaining product was identified as the rhodium(III) complex 1.34.\textsuperscript{96} To confirm that 1.33 is in fact a reaction intermediate in the formation of 1.34 a second equivalent of the imidazolium salt 1.32 was added to a solution of the dinuclear species producing the Rh(III) complex in near quantitative yield. The mechanism of the reaction is not well understood although aerating the reaction solution increases overall yield suggesting oxidation of the rhodium starting material is the first step of the synthesis. Complex 1.34 demonstrated good activity in catalytic hydrogen transfer from alcohols to ketones with aromatic ketones showing the highest reactivity. The high stability imparted by the tridentate ligand allows for the catalytic properties of this class of compounds to be studied at elevated temperatures and without efforts to remove air and moisture.
Scheme 1.11. Reaction pathway leading to the mononuclear (CNC)RhBr$_3$ (1.32) complex. Graphic adapted from reference [72].

1.5.2 NHC-Containing Pincer Complexes of Iridium

Iridium complexes involving NHC pincer ligands are relatively new with the first example of the CCC coordination motif appearing in the literature in 2008.$^{97}$ The synthesis required initial activation of the C-H bonds of 1.35 through metallation onto a zirconium centre followed by transmetallation with iridium, which allowed for isolation of the iodo-bridged dimer 1.36 (Scheme 1.12). Inspired by the report of an iridium pincer complex capable of initiating N-H bond activation,$^{98}$ the authors examined the activity of the [(CCC)Ir$_2$]$_2$ dimer in the intramolecular hydroamination of secondary amines. The stability of pincer complexes was clearly evident as reactivity studies at 110 °C over periods up to 22 hours were possible in a variety of solvents, including water, with good product yields. The chemistry of 1.36 was then extended by a separate research group...
who were able to cleave the iodine bridged species with coordinating solvents to form the first mononuclear iridium NHC pincer complexes (1.37-1.38).\(^99\)

**Scheme 1.12.** Synthesis of the first NHC containing iridium pincer complexes.

A benzimidazolium salt (1.39) precursor of the CCC type of ligand has also been developed and successfully coordinated to an iridium centre in a tridendate meridional fashion (Scheme 1.13). The metallation reaction is dependant on the base selected; for example, 30 equivalents of NEt\(_3\) are required in the formation of 1.40 while slightly more that 2 equivalents of CsF are necessary to give complexes 1.41 and 1.42 in moderate yields.\(^{100}\)
Scheme 1.13. Synthesis of the benzimidazole based iridium CCC complexes.

Iridium pincer catalysts bound to monoanionic non-NHC derived PCP pincer bis(phosphine)$^{101-105}$ and bis(phosphinite)$^{106-109}$ ligands have the highest activities in the dehydrogenation of alkanes. Therefore it was of interest to investigate how the NHC analogues 1.40-1.42 would perform in both the transfer dehydrogenation and acceptorless dehydrogenation of cyclooctane (eq 1.3). Complex 1.40 showed limited activity under transfer hydrogenation conditions with norbornene (NBE) while attempts with the other complexes (1.41-1.42) and tert-butylethylene failed. Higher turnovers were reported in the acceptorless dehydrogenation utilizing the bulkier complexes 1.40 and 1.42 where the steric crowding may help stabilize Ir(I) intermediates.$^{100}$
The only other type of NHC pincer complexes of iridium appearing in the literature consist of the CNC motif with methyl substituents in the 3,5-positions of the central pyridine ring to avoid unwanted metal coordination modes.\textsuperscript{110} Substitution of the chloride ligand with neutral donors in the presence of a non-coordinating anion allowed for the isolation of 1.44-1.47 (Scheme 1.14). The CO stretching frequency ($\nu = 1980 \text{ cm}^{-1}$) in 1.46 indicates that the cationic Ir(I) centre is a relatively weak $\pi$ donor when compared to a related PNP system.\textsuperscript{111} The hydride 1.48 resulting from the elimination of acetone\textsuperscript{112} represents the first Ir(I) hydride complex supported by a pincer ligand containing an NHC, the reactivity of which has yet to be reported.

**Scheme 1.14.** Synthesis of neutral and cationic iridium CNC complexes.

\begin{align*}
1.44 & \quad L = \text{pyridine}, \quad A^- = \text{BAR}^4F^- \\
1.45 & \quad L = \text{MeCN}, \quad A^- = \text{PF}_6^- \\
1.46 & \quad L = \text{CO}, \quad A^- = \text{PF}_6^- \\
1.47 & \quad L = \text{CO}, \quad A^- = \text{PF}_6^- \\
1.48 & \quad \text{Ar} = 2,6\text{-diisopropylphenyl}
\end{align*}
1.5.3 NHC-Containing Pincer Complexes of Nickel

By far the most widely investigated NHC derived pincer complexes of the group 10 transition metals are those incorporating palladium and their capabilities in cross-coupling reactions. Although nickel alternatives are attractive as a more cost effective catalyst only a few examples exist, all of which are based on the CNC motif (Figure 1.8). The bis(imidazolin-2-ylidene) complexes represented as 1.50 without the CH$_2$ spacer (n = 0) have been tested as Heck coupling catalyst with promising results, while complexes featuring both ligand scaffolds have proved to be active in Suzuki-Miyaura couplings. The benzimidazolin-2-ylidene based system (1.51) behaves slightly differently; as a stronger $\sigma$-donor and weaker $\pi$-acceptor it increases the electron density on the metal centre resulting in the highest activity for Suzuki-Miyaura coupling of the three nickel complexes shown in Figure 1.8.

Figure 1.8. Scope of NHC-containing pincer complexes of nickel.

In an attempt to generate a Ni-Me complex stabilized by the CNC array an example of the non-innocent behaviour of these “spectator” ligands was exposed. Reacting NiMe$_2$(TMEDA) (TMEDA = N,N$'$,N$'$,N$''$-tetramethylethylenediamine) with 1.52
resulted in the unexpected opening of the NHC ring accompanied by migration of a methyl group onto the carbene carbon (1.53), the structure of which was confirmed by X-ray crystallography (eq. 1.4).\textsuperscript{116} The mechanism leading to 1.53 is not fully understood but is thought to begin with migration of one of the methyl groups from the nickel to the carbene carbon as studied previously with PdMe\textsubscript{2}(TMEDA) and a CNC ligand.\textsuperscript{117} Understanding this type of unanticipated reactivity is important to help understand how this relatively new class of ligands may behave in organometallic chemistry.

\begin{equation}
\begin{array}{c}
\text{Ar} \quad \text{NHC} \quad \text{NHC} \\
\text{Ar} \quad \text{NHC} \quad \text{NHC} \\
\end{array}
\end{equation}

\text{NiMe}_2\text{(TMEDA)}

\begin{equation}
\begin{array}{c}
\text{Ar} \quad \text{NHC} \quad \text{NHC} \\
\text{Ar} \quad \text{NHC} \quad \text{NHC} \\
\end{array}
\end{equation}

Ar = 2,6-diisopropylphenyl

1.5.4 \textit{NHC-Containing Pincer Complexes of Palladium}

As mentioned in the previous section the majority of the attention for group 10 transition metals has focused on CNC Pd(II) complexes whose remarkable activity in Heck coupling reactions is a direct result of the stability provided by the tridentate ancillary ligand.\textsuperscript{77,78,118,119} Important to furthering the applications of these types of complexes is fully understanding potential catalyst deactivation pathways. One such pathway observed in non-tridentate nickel and palladium systems is the formation of new carbene-carbon bonds via reductive elimination giving alkyl and aryl substituted imidazolium salts.\textsuperscript{120-122} More robust pincer ligands are also susceptible to this kind of reactivity as seen with the decomposition products of complexes 1.54 and 1.56 (Scheme
1.15). As transformations of this kind require that the carbene and alkyl groups are cis-disposed, this process is expected to follow dissociation of one arm of the tridendate ligand. This rationale is supported by the fast decomposition of 1.56 to the imidazolium salt 1.57, as the weaker amino donor should dissociate faster than the pyridyl group in 1.54.\textsuperscript{123}

**Scheme 1.15.** Reductive elimination of imidazolium salts from NCN palladium methyl complexes.

In the case of CNC motifs that lack any carbon spacers between the donor moieties a migratory insertion of a methyl group to the carbene carbon occurs without ligand dissociation. Reaction of the bis(imidazolium-2-ylidene) (1.58) with PdMe\(_2\)(TMEDA) gave 1.59 as the lone isolated product, the structure of which was determined by NMR spectroscopy and single crystal X-ray analysis (eq 1.5).\textsuperscript{117} Density functional calculations suggest that formation of a five coordinate intermediate followed by migratory insertion is a realistic mechanism for the formation of 1.59. The rigid planar
geometry in tandem with the formation of particularly stable five-membered chelate rings is likely responsible for the lack of ligand dissociation as seen for complexes 1.54 and 1.56.

Ar = 2,6-diallylphenyl

1.6 Scope of this Thesis

The introduction has highlighted the development of N-heterocyclic carbenes as important ligands in organometallic chemistry. The incorporation of carbene donors stabilized through a nitrogen donor atom in tridentate pincer ligand systems has provided a useful class of new complexes displaying unique catalytic possibilities. However there is still much to learn about the reactivity of these transition metal complexes as evident in the non-innocent behaviour exhibited by a number of these systems. The focus of this thesis will be on the synthesis and investigation of a new NHC-derived tridentate ligand suitable for coordination to late transition metals.

Chapter 2 describes the synthesis of a pincer ligand containing a saturated imidazolinium salt connected to two phosphine donors by aryl linkers, denoted PCP. Oxidative addition of this new ligand with group 10 transition metals generated a distinct group of metal hydrides. All three compounds are fully characterized and a thorough discussion of structural data is found within this chapter.
The following chapter outlines the non-innocent behaviour exhibited by this ligand set discovered during a survey of the reactivity of the nickel complex with small molecules. An unanticipated carbon-carbon coupling reaction occurs between the carbene carbon and one unit of ethylene gas. An in-depth analysis on the mechanism leading to this product is presented using isotopic labelling studies in conjunction with density functional calculations. These studies lend themselves to understanding the reactivity of the nickel complex with an alkyne.

The fourth chapter outlines the coordination of the neutral PCP ligand with rhodium with the intention of developing useful reactivity through C-H bond activation. Exploring the coordination chemistry of the resulting rhodium complex leads to the formation of a rare amido species. The catalytic potential of the rhodium hydride is demonstrated through hydrosilylation and dehydrogenation reactions.

Chapter 5 focuses on the synthesis of an iridium pincer complex intended for use in C-H activation processes. A variety of iridium complexes supported by the PCP ligand are synthesized and its applications in catalysis are explored. The iridium system also displays some interesting and unusual isomerization and rearrangement chemistry, which is investigated in detail.

The final chapter provides a synopsis of the work within this thesis including a discussion of the insights into the chemistry of NHC ligands complexes gained during this thesis work. Finally, a brief overview of the attempts to modify the PCP array based on its realized shortcomings is presented along with ideas for the future direction of this research.
Chapter Two

Synthesis and Coordination Chemistry of a Tridentate $o$-Phenylene-Bridged N-Heterocyclic Carbene Diphosphine Ligand

2.1 Introduction

The design of innovative ligand frameworks to support metal complexes capable of small molecule activation is at the forefront of research in the Fryzuk lab. Given the advantages of pincer systems containing NHCs presented in the previous chapter we sought to explore how this relatively new class of compounds may extend this area of chemistry. In previous work within the group involving an NCN ligand set we observed deleterious C-H activation of the $\alpha$-methylene unit of the ethylene linker,$^{83}$ likely a result of the flexibility imparted by the ethylene backbone (Scheme 2.1). In the past, we have developed tridentate diamidophosphine ligands with $o$-phenylene linkers, designated as [NPN]*, in an effort to introduce more rigidity into this latter ligand set as compared to the parent [NPN] system.$^{124}$ Therefore, in designing a new ligand motif it was decided to use a similar strategy and use phenylene linkers on each nitrogen atom in the NHC ring to avoid backbone C-H activation processes.

The effect of attaching a hemilabile amine arm on the NHC ring in a bidentate NC system has also been examined in our research group.$^{125}$ A ruthenium complex incorporating the NC ancillary ligand was tested as a catalyst for olefin metathesis and it

was determined the dangling amine arm can disrupt catalytic activity by coordinating to the metal centre (Scheme 2.1).\textsuperscript{126} To avoid this type of reversible coordination the design of the new tridentate ligand was expanded to include a soft phosphine donor that should strongly bind with low oxidation state late transition metals. The focus of this chapter is on the synthesis of a rigid PCP-array of donors using o-phenylene linkers, which is the first of its kind. Following a detailed discussion of the synthetic process the coordination of the new pincer scaffold with all three members of the group 10 triad is highlighted.

**Scheme 2.1.** Identified reactivity problems with previous multidentate NHC containing ligands designed in the Fryzuk lab.

\[
\begin{array}{c}
\text{R = Benzyl} \\
\text{Ar = Mesityl}
\end{array}
\]
2.2 *Synthesis of the PCP Ligand*

Our initial focus was on the *unsaturated* NHC-based PCP system shown in Scheme 2.2, which we reasoned could be assembled in a manner similar to that reported for IMes;\(^{127}\) condensation of an appropriate aryl amine with glyoxal would produce the corresponding diimine, which could then be converted to the parent [PCP]* via condensation with formaldehyde and HCl, followed by deprotonation of the intermediate imidazolium salt. The preparation of the *o*-diisopropylphosphinoaniline I (R = Pr\(^i\)) follows a literature report\(^{128}\) and involves double lithiation of \(^1\)BOC-aniline with \(^1\)BuLi and quenching with ClIPr\(^i\)\(^2\), followed by deprotection.

**Scheme 2.2.** Initial unsaturated NHC target via condensation starting from *o*-diisopropylphosphinoaniline I.

Unfortunately, all attempts to condense I (R = \(^i\)Pr) with glyoxal or even 2,3-butanedione were unsuccessful, leading only to complex mixtures of products. We eventually abandoned this strategy and developed a synthesis of the *saturated* NHC ligand as summarized in Scheme 2.3. Fortunately, this also uses I as a key intermediate.
Scheme 2.3. Saturated NHC target via alkylation starting from the \(\sigma\)-diisopropylphosphinoaniline I.

The assembly of the saturated NHC requires alkylation chemospecifically at the aryl amine site; to ensure that the nucleophilic \(\text{PPr}_2^i\) group does not interfere, it was protected as the phosphine sulfide. Reaction of this amine-phosphine-sulfide with 1,2-dibromoethane generates the corresponding \(\text{N,N’-bis(\(\sigma\)-diisopropylphosphinesulfide)}\)ethylenediamine in moderate yield; further reaction with triethylorthofomrate in the presence of \(\text{NH}_4\text{PF}_6\) produces the bis(phosphinesulfide)-imidazolinium salt, which could be reduced with excess Ra-Ni in MeOH to generate bis(phosphine) imidazolinium salt 2.1. This is outlined in Scheme 2.4.
**Scheme 2.4.** The synthesis of the imidazolinium diphosphine [(PCP)H][PF₆] (2.1) starting from phenylisocyanate via o-diisopropylphosphinoaniline (I).

Interestingly, our initial approach to the synthesis of imidazolinium 2.1 involved protection of the aryl phosphinoamine I as the phosphine oxide, and then assembly of the saturated NHC ring to generate phosphine oxide 2.3; however, under no conditions were we able to reduce bis(phosphineoxide) 2.3 to 2.1. A preliminary X-ray crystal structure of 2.3 revealed short contacts between the C-H of the NHC and the two oxygen atoms of phosphine oxide moieties that lie above and below the imidazolinium ring; the presence of these intramolecular H-bonds likely enhances the stability of the oxide.
The imidazolinium salt [(PCP)H][PF$_6$] (2.1) is soluble in THF and CH$_2$Cl$_2$, but insoluble in apolar solvents, like benzene or hexanes. While 2.1 is stable under nitrogen atmosphere, it slowly decomposes in air. Compound 2.1 was characterized by NMR spectroscopy, elemental analysis and single crystal X-ray crystallography. The $^{31}$P{$_1$H} NMR spectrum of 2.1 in d$_8$-THF shows a singlet at -6.4 ppm for the two tertiary phosphines and a septet at -143.8 ppm for the PF$_6^-$ counter ion. A resonance at 8.69 ppm in the $^1$H NMR spectrum can be assigned to the iminium hydrogen, which correlates to a resonance at 158 ppm in the $^{13}$C{$_1$H} NMR spectrum assigned to the iminium carbene carbon.

Compound 2.1 crystallizes in the monoclinic space group C2/c. The molecular structure of 2.1 consists of an organic cation (Figure 2.1) and the inorganic PF$_6$ anion. The structural characteristics of this central five-membered ring are virtually identical to 1,3-dimesitylimidazolinium chloride, the precursor to the synthesis of a stable diaminocarbene.$^{129}$ The short endocyclic C-N bonds (1.312(4) and 1.314(4) Å) are consistent with electron delocalization over the N-C-N fragment, which is observed in all iminium analogues. The NCN angle has a value of 114.0(3)$^\circ$. The remaining bond distances N1-C2, N2-C3 and C2-C3 bonds clearly identify these as single bonds.
Figure 2.1. Solid-state molecular structure (ORTEP) of [(PCP)H][PF$_6$] (2.1) showing the numbering scheme. The PF$_6$ counter anion and all hydrogen atoms (except H1) are omitted for clarity.

The imidazolinium ring is slightly puckered. The two methylene carbon centers, C2 and C3, deviate 1.6° above and 2.4° below the plane of the other three ring atoms, respectively. The o-phenylene linkers are not oriented parallel with the NHC ring; instead, the two dihedral angles defined by the atoms C1-N-C$_{ipso}$-C$_{ortho}$ have values of 47.8° and 41.0°, respectively. Thus, the two diisopropylphosphino moieties are located above and below the imidazolinium ring plane. As mentioned above, a preliminary solid state structure for the bis(phosphineoxide) 2.3 is similar to that for 2.1, which accounts for the close contacts of the oxygen atoms to the iminium C-H bond.
Table 2.1. Selected bond lengths (Å) and angles (°) in [(PCP)H][PF₆] (2.1).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length</th>
<th>Bond</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-N1</td>
<td>1.310(3)</td>
<td>C2-C3</td>
<td>1.530(4)</td>
</tr>
<tr>
<td>C1-N2</td>
<td>1.313(3)</td>
<td>N1-C4</td>
<td>1.436(3)</td>
</tr>
<tr>
<td>N1-C2</td>
<td>1.483(3)</td>
<td>N2-C16</td>
<td>1.437(3)</td>
</tr>
<tr>
<td>N2-C3</td>
<td>1.481(3)</td>
<td>P1-C9</td>
<td>1.847(3)</td>
</tr>
<tr>
<td>N1-C1-N2</td>
<td>114.1(3)</td>
<td>C1-N1-C2</td>
<td>109.8(2)</td>
</tr>
<tr>
<td>N1-C2-C3</td>
<td>102.9(2)</td>
<td>N2-C1-N1-C3</td>
<td>-2.5(3)</td>
</tr>
<tr>
<td>C1-N1-C4</td>
<td>126.5(2)</td>
<td>C1-N1-C4-C9</td>
<td>47.8(4)</td>
</tr>
<tr>
<td>C1-N1-C16</td>
<td>127.5(2)</td>
<td>C1-N2-C16-C21</td>
<td>41.0(4)</td>
</tr>
</tbody>
</table>

Deprotonation of the imidazolinium salt 2.1 with KN(SiMe₃)₂ in THF at room temperature yields the free carbene PCP (2.2) as a thermally stable but air-sensitive solid (Scheme 2.5). The ¹H NMR spectrum of 2.2 in C₆D₆ shows no peaks above δ 8, which is consistent with the loss of the iminium hydrogen; in addition, there are four multiplets between δ 7.58 and 7.17 that can be assigned to the four different aromatic protons of the o-phenylene spacer, one singlet at δ 3.94, due to the CH₂CH₂ backbone of the NHC, one septet at δ 2.22, due to the methine protons of the isopropyl groups, and a pair of doublet of doublets at δ 1.26 and δ 1.14 assigned to the CH₃ groups of the isopropyl moieties. A weak singlet, assigned to the carbene carbon, was apparent in the ¹³C{¹H} NMR spectrum at δ 244.7 and the ³¹P{¹H} NMR spectrum exhibits one singlet at δ –3.7.
**Scheme 2.5.** Reaction of [(PCP)H][PF$_6$] (2.1) with KN(SiMe$_3$)$_2$ and KO$_2$Bu.

When imidazolinium 2.1 is reacted with KO$_2$Bu in THF at room temperature the corresponding neutral “protected” carbene [PCP](H)(O$_2$Bu) 2.4 is formed (Scheme 2.5). In contrast to other examples, wherein related adducts eliminate alcohol, chloroform or amines to unmask the carbene,$^{130}$ in this particular reaction, the elimination of $^t$BuOH under vacuum or elevated temperatures was not observed.
2.3 Coordination of the PCP Ligand with Group 10 Metals

One of the most common methods to generate a metal NHC complex is the use of the free carbene itself, which normally requires prior abstraction of the acidic iminium proton of the imidazolium or imidazolinium precursor with an external base (e.g. KH or KN(SiMe$_3$)$_2$);$^{131,132}$ alternatively, these same NHC precursor salts can be added to metal complexes that already contain a basic ligand able to act as an internal base, such as in [(COD)M]$_2$(t-OEt)$_2$ (M = Rh, Ir) or in Pd(OAc)$_2$.$^{133}$ Another common way to introduce an NHC is via transmetalation using silver NHC complexes.$^{82,134-136}$ In each of these processes, coordination of the NHC requires loss of HX, either prior to addition to the metal complex or during the addition. In contrast, oxidative addition of the iminium C-H bond of the NHC precursor salt is a convenient route for the introduction of the NHC, as no base is required.$^{137-142}$

When equimolar quantities of the imidazolinium salt [(PCP)H][PF$_6$] (2.1) were stirred with Ni(COD)$_2$, Pd(PPh$_3$)$_4$ or Pt(PPh$_3$)$_4$ in THF at room temperature, a slight colour change in the solution was observed. Concentration of the solution and cooling to $-30^\circ$C led to the isolation of the (PCP)M-hydrido complexes 2.5 (M = Ni), 2.6 (M = Pd) and 2.7 (M = Pt) as the PF$_6$ salts in crystalline form in 72-77% yields (Scheme 2.6).
Scheme 2.6. C-H oxidative addition of [(PCP)H][PF₆] (2.1) to Ni(0), Pd(0), and Pt(0) precursors.

The formation of the metal hydrides 2.5-2.7 was confirmed by NMR spectroscopy, single-crystal X-ray diffraction and elemental analysis. In the ¹H NMR spectrum in d₈-THF, the metal-hydride resonances of 2.5 and 2.6 appear at -10.73 ppm (Ni) as a triplet ($J_{HP} = 53.5$ Hz) and at -6.15 ppm (Pd) as a singlet, respectively. The Pt-H resonance of 2.7 appears as a triplet ($J_{HP} = 14.5$ Hz) centered at -4.43 ppm with 195-Pt satellites ($J_{PtH} = 403.2$ Hz) (Figure 2.2). The reason that the hydride resonance in the palladium derivative 2.6 is observed as singlet is unclear, although structural data may help understand the lack of coupling (vide infra). A related neutral Pd pincer complex Pd[(2,6-C₆H₃(CH₂PBu₂)₂]H shows the expected triplet at -3.86 ppm ($J_{HP} = 13.5$ Hz).¹⁴³ The ³¹P{¹H} NMR spectra of these hydride complexes all show singlets that are shifted downfield of the free ligand to $\delta$ 47.6 (2.5), 46.1 (2.6) and 39.5 (2.7) upon coordination; the singlet for the platinum complex 2.7 also displays the expected Pt-195 satellites ($J_{PtP} = 1241.5$ Hz). In the ¹³C{¹H} NMR spectra, resonances assignable to the carbenic carbons of the coordinated NHC are observed as triplets at 189.28 ppm (2.5): $^2J_{CP} = 32$
Hz), 197.28 ppm (2.6: $^2J_{CP} = 13.5$ Hz) and 196.68 ppm (2.7: $^2J_{CP} = 25$ Hz), slightly downfield of related Pd pincer PCP complexes that have unsaturated NHC donors.$^{82,134}$

Figure 2.2. $^1$H NMR spectrum displaying the distinct hydride resonances for each of the cationic metal complexes 2.5-2.7.

2.3.1  **Structural Analysis of the Metal Hydrides [(PCP)MH][PF$_6$]**

Compounds 2.5-2.7 are noteworthy in that they are a set of completely identical group 10 metal hydride complexes that have been characterized by both solution spectroscopic and solid-state X-ray crystallographic methods.$^{144}$ A recent report described the insertion of the electron-rich, coordinately unsaturated $L_2M(0)$ complexes (M = Ni, Pd, L = 1,3-aryl-NHC) in the C-H bond of a imidazolium salt.$^{140}$ The first Pt-hydrides derived from oxidative addition of imidazolium salts to Pt(0)-phosphine
compounds were described separately. All three group 10 complexes 2.5-2.7 are surprisingly stable both in solution and in the solid state and can be stored under an inert atmosphere for an extended period of time.

**Figure 2.3.** Solid-state molecular structure (ORTEP) of the cation of the nickel hydride 2.5. The PF₆ counter ion and all hydrogen atoms except H(1) are omitted for clarity. The hydride ligand was located in the crystal structure and refined isotropically. Selected bond lengths and angles can be found in Table 2.2.

Complex 2.5 (Figure 2.3) crystallizes in the monoclinic space group P2₁/n, while for 2.6 (Figure 2.4) the triclinic space group P̅1 was found and the platinum hydride 2.7 (Figure 2.5) crystallizes in the monoclinic C2/c space group. In all three molecular structures the metal center adopts a slightly distorted square planar geometry, but the distortion in the nickel derivative 2.5 is largest, as shown by the deviation from linearity of the trans donors; for example the angle P1-Ni1-P2 in 2.5 is 169.03(2)°, noticeably smaller than the corresponding angles in 2.6 and 2.7. The NHC ring is twisted in each structure making an angle of 31.9/35.1° (2.5), 35.5°/41.5° (2.6) and 35.27° (2.7) with the metal plane. These values are similar to those found in Pd(II) pincer complexes of
[CCC], [CNC], and [PCP] and Pt(II) pyrazolyl complexes all of which have angles that range from 25.25°-49.10°. Hence, the twisting of the NHC in each of 2.5-2.7 is not caused by any geometrical constraints of this particular ligand, any observed twists match others observed with quite different ligands.

Figure 2.4. Solid-state molecular structure (ORTEP) of the cation of the palladium hydride 2.6. The PF₆ counter ion and all hydrogen atoms except H(1) are omitted for clarity. The hydride ligand was located in the crystal structure and refined isotropically. Selected bond lengths and angles can be found in Table 2.2.

Theoretical calculations for Pd(II)-PCP complexes with aryl linkers have revealed, that the rotational energy barrier about the Pd-NHC bond is rather small (ca. 4 kcal/mol). Similar low values can be anticipated for 2.5-2.7, as a fast interconversion (atropisomerization) between two enantiomeric conformers is observed in solution. This is evident from the ¹H NMR spectrum of 2.5 for example, which shows that the backbone ethylene unit of the NHC appears as a sharp singlet indicating that all four protons are
equivalent; if the chiral twisted conformation observed in the solid state were locked in solution (or undergoing slow interconversion on the NMR time scale), then each methylene unit would consist of two diastereotopic protons, which would generate a more complicated AA’BB’ pattern. Similar conformational changes were observed in lutidine- and meta-xylene-based pincer compounds of the type [Pd(CDC)Br]n+ (D = N, n = 1; D = C, n = 0) and [Pd(PCP)Cl]Cl, containing the PCP ligand with alkyl linkages. (vide supra).

\[\text{Figure 2.5. Solid-state molecular structure (ORTEP) of the cation of the platinum hydride 2.7. The PF}_6\text{ counter ion and all hydrogen atoms except H(1) are omitted for clarity. The hydride ligand was located in the crystal structure and refined isotropically. Selected bond lengths and angles can be found in Table 2.2.}\]

The bond distances in the coordination sphere of the complexes 2.5-2.7 exhibit no unusual features. The M1-C1 bond lengths have values of 1.8629(19) Å (2.5), 2.028(4) Å (2.6) and 2.005(4) Å (2.7) respectively. The Ni-CNHC bond length is slightly shorter than
those reported for other tridentate Ni(II) complexes\textsuperscript{113,114} which range between 1.891 Å and 1.932 Å, but not quite as short as the Ni(0)-carbene bonds in homoleptic Ni(IMes)\textsubscript{2} (1.827 and 1.830 Å).\textsuperscript{148} The Pd1-C1 bond length in 2.6 of 2.028(4) Å is in the range observed for pincer carbenes (ca 1.98-2.05 Å).\textsuperscript{72} A comparison of 2.6 with Pd-PCP complexes with alkyl linkers shows that latter have slightly shorter Pd-C\textsubscript{NHC} bonds (e.g. 1.961(4) Å in [Pd(PCP)(NCMe\textsubscript{3})][BF\textsubscript{4}]\textsubscript{2} and 1.983(7) Å in [Pd(PCP)Cl][Cl], while these same complexes\textsuperscript{134} have Pd-P distances that are about 0.3-0.8 Å longer than in 2.6. One explanation for these variations might be assigned to the different nature of the linker (sp\textsuperscript{3} vs. sp\textsuperscript{2}) in these systems or, more likely, due to the difference in the phosphorous donor substituents, PPh\textsubscript{2} vs. PPr\textsubscript{i2}, and/or the different coligands (hydride vs. chloride). Unfortunately for comparison purposes, no similar platinum tridentate pincer complexes have been reported.

**Table 2.2.** Selected bond lengths (Å) and angles (°) for the group 10 metal hydride complexes, [(PCP)MH][PF\textsubscript{6}].

<table>
<thead>
<tr>
<th></th>
<th>M = Ni</th>
<th>M = Pd</th>
<th>M = Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-C1</td>
<td>1.8629(19)</td>
<td>2.037(8)</td>
<td>2.008(4)</td>
</tr>
<tr>
<td>M-P1</td>
<td>2.1080(8)</td>
<td>2.266(2)</td>
<td>2.2484(12)</td>
</tr>
<tr>
<td>M-P2</td>
<td>2.1129(9)</td>
<td>2.257(2)</td>
<td>2.2474(13)</td>
</tr>
<tr>
<td>M-H1</td>
<td>1.38(4)</td>
<td>1.77(7)</td>
<td>1.53(5)</td>
</tr>
<tr>
<td>C1-N1</td>
<td>1.345(3)</td>
<td>1.315(10)</td>
<td>1.339(6)</td>
</tr>
<tr>
<td>C1-N2</td>
<td>1.341(3)</td>
<td>1.341(10)</td>
<td>1.341(5)</td>
</tr>
<tr>
<td>C1-M-H1</td>
<td>173.2(15)</td>
<td>177(2)</td>
<td>179(2)</td>
</tr>
<tr>
<td>P1-M-P2</td>
<td>169.03(2)</td>
<td>174.90(9)</td>
<td>178.00(4)</td>
</tr>
<tr>
<td>P1-M-C1</td>
<td>94.70(6)</td>
<td>89.1(2)</td>
<td>89.86(12)</td>
</tr>
<tr>
<td>P2-M-C1</td>
<td>95.90(6)</td>
<td>89.8(2)</td>
<td>89.32(12)</td>
</tr>
</tbody>
</table>
The Ni–H bond length of 1.38(4) Å in 2.5 is analogous to [Ni(NHC)₃(H)]BF₄ (1.38(5) Å), while Pd–H (1.81(5) Å) in 2.6 is significantly longer than the Pd–hydride distance observed in [Pd(NHC)₃(H)]BF₄ (1.57(3) Å). Interestingly, this latter compound consists of an unusual $\text{H}^\delta+\text{H}^\delta-$ interaction of the metal-hydride with one hydrogen atom of the ortho methyl groups at the mesityl-substituted NHC ligands. A weaker, but nevertheless significant $\text{H}^\delta+\text{H}^\delta-$ interaction was found in the molecular structures of 2.5 and 2.6 between the hydride and one of the hydrogen atoms of the isopropyl groups with a value of 2.170 Å ($\text{M} = \text{Ni}$) and 2.184 Å ($\text{M} = \text{Pd}$), respectively. The long Pd–H bond in the solid state correlates to the lack of coupling to $^{31}\text{P}$ already mentioned.

2.4 Conclusions

The target molecule of a neutral tridentate ligand consisting of a central NHC flanked by two phosphine donors through o-phenylene linkers has been successfully synthesized. Deprotonation of the cationic imidazolinium salt 2.1 allows for access to the free carbene 2.2 thereby broadening the scope of coordination pathways available for this particular ligand array, as will be discussed in chapters 4 and 5. The straightforward oxidative addition of 2.1 to various group 10 metal precursors to produce a series of identical metal-hydrides demonstrates the intended design aspect of a NHC containing pincer ligand suitable for coordination to late transition metals. The solid-state molecular structures of the metal hydrides 2.5-2.7 show considerable twisting of the ligand framework above and below the plane defined by the metal and the PCP donors. In solution, this twisting is not fixed, as the two possible chiral conformations are
exchanging fast on the NMR time scale, as evidenced by the lack of diastereotopic splitting in methylene units along the backbone.

Preliminary reactivity studies with the palladium derivative indicate that 2.6 is inert towards small molecules such as CO, alkenes and alkynes. Attempts to synthesize the analogous complex with a halide ligand cis to the carbene to investigate the capabilities of a PCP supported palladium complex for C-C bond coupling reactions were unsuccessful. However, the nickel complex (2.5) displays some very interesting reactivity in the presence of an alkene; this C-C bond forming reaction will be the topic of the next chapter.

2.5 Experimental

General Considerations. All reactions were performed by standard Schlenk techniques in an oxygen free nitrogen atmosphere unless otherwise noted. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on either a Bruker AV-400 instrument operating at 400.2 MHz or a Bruker AV-300 instrument operating at 300.13 MHz. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. Organic solvents were purchased anhydrous from Aldrich, sparged with nitrogen, and passed through columns containing activated alumina and molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed and dried over activated 3 Å molecular sieves prior to use. Phenyl isocyanate, tert-butanol, tert-butyllithium, chlorodiisopropylphosphine, 1,2-dibromoethane, triethyl orthoformate, and Raney-nickel (4200) were purchased from Aldrich and used without further purification. Ni(COD)$_2$, Pd(PPh$_3$)$_4$ and Pt(PPh$_3$)$_4$ were purchased from STREM and used as received.
**t-BOC-aniline.** To phenyl isocyanate (40 g, 0.34 mol) was added neat *tert*-butanol (27.7 g, 0.368 mol) at room temperature. The reaction mixture was then warmed gently to 60°C, stirred at this temperature for 1 h and additionally 1h at 80°C. During this time a white solid formed. The solid was dissolved in Et₂O (about 8 g per 125 mL) and recrystallized by slow cooling to -30°C. After filtration, the volume of the filtrate was reduced by half and a second crop collected after cooling at -30°C. The combined crystallized fractions were dried under vacuum. Yield: 53 g (82%).

**1H NMR (400.2 MHz, CDCl₃, 298 K):** δ = 7.36 (d, J_HH = 8 Hz, CH, 2H), 7.15 (t, J_HH = 7.8 Hz, CH, 2H), 6.89 (t, J_HH = 7.2 Hz, CH, 1H), 6.15 (s br, NH, 1H), 1.51 (s, CH₃, 9H).

**13C{1H} NMR (100.6 MHz, CDCl₃, 298 K):** δ = 138.2 (s), 128.9 (s), 122.9 (s), 118.5 (s), 28.3 (s).

**o-C₆H₄(NH-t-BOC)(PPrᵢ₂):** To a solution of *t*-BOC-aniline (65 g, 0.33 mol) in Et₂O (1 L) in a 3 L 2-necked round-bottom flask was added *tert*-BuLi (430 mL of a 1.7 M pentane solution, 0.735 mol) drop wise at -20°C. After the addition, the reaction mixture was stirred at -10°C for an additional 3h. During this time a white precipitate formed. The reaction mixture was then cooled to -80°C and a solution of ClPPrᵢ₂ (51 g, 0.33 mol) in 150 mL of Et₂O was added slowly; upon completion the reaction mixture was warmed to ambient temperature. After stirring for 14 h a saturated solution of NaCl in 400 mL of water was added, the organic phase separated and dried over MgSO₄, and the Et₂O distilled to give the product as a yellow-orange residue. The product contains small amounts (8-13 %) of unidentified side products as detected by ³¹P NMR spectroscopy (C₆D₆): δ = -8.6, -4.4 and 92.1. For the following step, further purification was not necessary. **¹H NMR (400.2 MHz, C₆D₆, 298 K):** δ = 8.80 (m, CH, 1H), 7.26 (t, J_HH = 7 Hz, CH, 1H), 7.20 (m, CH, 1H) 6.94 (t, J_HH = 7 Hz, CH, 1H), 1.94 (sep, J_HH = 7 Hz, CH,
1H), 1.48 (s, CH₃, 9H), 1.05 (dd, JHH = 7 Hz, JHP = 16 Hz, CH₃, 6H), 0.84 (dd, JHH = 6.85 Hz, JHP = 12.2 Hz, CH₃, 6H). ¹³C{}¹H{} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.4 (d, JCP = 1.5 Hz), 145.8 (d, JCP = 17.7 Hz), 133.2 (d, JCP = 3.1 Hz), 131 (s), 123.0 (s), 119.9 (d, JCP = 1.5 Hz), 80.5 (s) 29.1 (s), 24.1 (d, JCP = 9.9 Hz), 19.4 (d, JCP = 7.7 Hz). ³¹P{}¹H{} NMR (161.9 MHz, C₆D₆, 298 K): δ = -15.3 (s).

**o-C₆H₄(NH₂)(PPr²) (I).** To a solution of o-C₆H₄(NH-t-BOC)(PPr²) (98 g, 0.31 mol) in 500 mL CH₂Cl₂ was added HCl (94 mL of 10M solution, 0.94 mol) dropwise. Immediately, the evolution of carbon dioxide was observed and the temperature is raised to about 40ºC. In order to complete the deprotection of the BOC group the reaction mixture was stirred for 20h at room temperature. The orange reaction mixture was slowly treated with a 10 M solution of NaOH until the pH-value is about 10 and a milky aqueous phase and an orange organic layer were formed. Thereafter the organic phase was separated, dried over magnesium sulfate and the solvent was removed in vacuum. The product is extracted from the residue with 500 mL of Et₂O and the solvent is removed in vacuum. Afterward the product can be extracted with 300 mL of pentane. After removal of the solvent in vacuo, the crude product is obtained as pale yellow-orange oil. Yield: 60.3 g (92.7%). Mass spectroscopy analysis of the crude product revealed the presence of two side compounds: BOC-aniline (GC-MS: m/z = 193 [M⁺]) and P(iPr)₂OH (GC-MS: m/z = 134), each in varying amounts of 13-25%. The latter by-product gives rise to one singlet at δ 52.9 in the ³¹P{}¹H{} NMR spectrum. These impurities were not separated but carried on to the next step. ¹H NMR (400.2 MHz, C₆D₆, 298 K): δ = 7.11 (d, JHH = 7.3 Hz, CH, 1H) 7.06 (t, JHH = 7 Hz, CH, 1H), 6.67 (t, JHH = 7.3 Hz, CH, 1H), 6.52 (m, CH, 1H), 4.12 (s br, NH₂, 2H), 1.93 (sep, JHH = 7 Hz, CH, 2H), 1.10 (dd, JHH = 7 Hz, JHP =
15.5 Hz, CH₃, 6H), 0.90 (dd, J_HH = 7 Hz, J_HP = 12 Hz, CH₃, 6H). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ¹³C{¹H} NMR (100.6 MHz, C₆D₆, 298 K): δ = 153.1 (d, J_CP = 21.3 Hz), 133.0 (d, J_CP = 2.9 Hz), 130.1 (s), 117.5 (s), 116.8 (d, J_CP = 17.8 Hz), 115.24 (d, J_CP = 2.9 Hz), 23.4 (d, J_CP = 10.3 Hz), 19.0 (d, J_CP = 8.6 Hz). ³¹P{¹H} NMR (161.9 MHz, C₆D₆, 298 K): δ = -14.6 (s). MS (EI): m/z (%) = 209 (34) [M⁺], 167 (38) [M -C₃H₆], 124 (100) [M -C₆H₁₃].

**o-CH₄(NH₂)(PSPrᵢ₂).** Elemental sulfur (3.06 g, 0.098 mol) was slowly added to a solution of crude o-C₆H₄(NH₂)(PPrᵢ₂) (I) (20 g, 0.096 mol), in 150 mL of toluene at room temperature. After the addition, the solution was heated to reflux for approximately 1 h, and then the solvent was removed under vacuum. The remaining orange residue was dissolved in Et₂O and filtered through Celite, and the solvent was evaporated. The residue is washed with a mixture of pentane and Et₂O (2:1) and dried *in vacuo*. The crude product was crystallized by cooling a diethyl ether solution to −40 °C; a second crop of crystals can be obtained by adding pentane to the filtrate. Yield: 20.8 g (90.3%) in two batches. ¹H NMR (400.2 MHz, CDCl₃, 298 K): δ = 7.20 (t, J_HH = 7.5 Hz, CH, 1H), 7.08 (t, J_HH = 9 Hz, CH, 1H), 6.64 (m, CH, 2H), 5.93 (s br, NH₂, 2H), 2.52 (sep, J_HH = 7 Hz, CH, 2H), 1.27 (dd, J_HH = 7 Hz, J_HP = 17.7 Hz, CH₃, 6H), 1.14 (dd, J_HH = 7 Hz, J_HP = 17.3 Hz, CH₃, 6H). ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 298 K): δ = 153.6 (d, J_CP = 4.1 Hz), 132.3 (d, J_CP = 2.4 Hz), 130.8 (d, J_CP = 7.5 Hz), 118.1 (d, J_CP = 7.5 Hz), 116.1 (d, J_CP = 10.4 Hz), 105.1 (d, J_CP = 70.1 Hz), 28.6 (d, J_CP = 50.5 Hz), 16.5 (d, J_CP = 2.4 Hz), 15.9 (s). ³¹P{¹H} NMR (161.9 MHz, CDCl₃, 298 K): δ = 62.8 (s). Anal. Calcd. for C₁₂H₂₀NPS: C 59.72; H 8.35; N 5.80. Found: C 60.03; H 8.63; N 6.10.

**o-C₆H₄(PSPrᵢ₂)(NHCH₂CH₂NH)(PSPrᵢ₂)o-C₆H₄.** Following a similar literature procedure,¹⁴⁹ o-CH₄(NH₂)(PSPrᵢ₂) (11 g, 0.046 mol) was heated to 110 °C to generate a
melt, and to it was added neat 1,2-dibromoethane (2.14 g, 0.0114 mol) dropwise with stirring while the temperature was maintained at 110 °C. The mixture was further stirred for 2 h at 130 °C and then cooled to 80 °C, and aqueous KOH (6.2 M, 5 mL) was added while the stirring was maintained. Upon cooling to room temperature, the mixture was extracted with CH₂Cl₂, dried over MgSO₄, and filtered, and the solvent was removed under vacuum. The residue was extracted with 100 mL of Et₂O, and the solid residue dried under vacuum. The pale yellow Et₂O extract was concentrated under reduced pressure and cooled to −40 °C, giving 4.34 g of starting o-CH₄(NH₂)(PSPr₂) as pale yellow crystals, which can subsequently be recycled. The colorless product can be recrystallized by cooling a concentrated THF solution to −30 °C. Yield: 2.21 g (38.2%).

¹H NMR (400.2 MHz, CDCl₃, 298 K): δ = 8.26 (s, br, NH, 1H), 7.30 (t, J_HH = 7.75 Hz, CH, 1H), 7.09 (m, CH, 1H), 6.76 (m, CH, 1H), 6.64 (m, CH, 1H), 3.43 (s, CH₂, 4H), 2.51 (sep, J_HH = 7 Hz, CH, 4H), 1.25 (dd, J_HH = 7 Hz, J_HP = 17.7 Hz, CH₃, 12H), 1.14 (dd, J_HH = 7 Hz, J_HP = 17.3 Hz, CH₃, 12H). ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 298 K): δ = 155.1 (d, J_CP = 3.8 Hz), 133.9 (d, J_CP = 2.3 Hz), 132.3 (d, J_CP = 6.9 Hz), 115.9 (d, J_CP = 10.7 Hz), 113.1 (d, J_CP = 6.9 Hz), 105.5 (d, J_CP = 70.5 Hz), 43.7 (s), 29.6 (d, J_CP = 50.6 Hz), 17.5 (d, J_CP = 2.3 Hz), 16.8 (s). ³¹P{¹H} NMR (161.9 MHz, CDCl₃, 298 K): δ = 62.0 (s). Anal. Calcd. for C₂₆H₄₂N₂P₂S₂: C 61.39; H 8.32; N 5.50. Found: C 61.62; H 8.30; N 5.88.

[o-C₆H₄(PSPr₂)(NC₃H₅N)(PSPr₂)]o-C₆H₄PF₆. Following a literature procedure, an intimate mixture of o-C₆H₄(PSPr₂)(NHCH₂CH₂NH)(PSPr₂)o-C₆H₄ (2.12 g, 4.17 mmol), NH₄PF₆ (0.680 g, 4.17 mmol), and triethyl orthoformate (8 mL) was heated to 120 °C for 3 h with stirring. The ethanol formed during the reaction and excess triethyl orthoformate
were removed under vacuum. The crude product was washed with toluene, extracted with CH₂Cl₂, and filtered. After removal of the solvent, the product was washed with Et₂O. The colorless product can be recrystallized in a mixture of CH₂Cl₂ and Et₂O. Yield: 2.41 g (87.0%). ¹H NMR (400.2 MHz, CDCl₃, 298 K): δ = 7.72 (m, CH, 9H), 4.60 (s, CH₂, 4H), 2.63 (sep, J_HH = 6.8 Hz, CH, 4H), 1.27 (dd, J_HH = 6.7 Hz, J_HP = 18.4 Hz, CH₃, 12H), 1.07 (dd, J_HH = 6.9 Hz, J_HP = 18 Hz, CH₃, 12H). ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 298 K): δ = 158.5 (s), 140.2 (s), 134.2 (s), 132.9 (s), 131.2 (d, J_CP = 9.5 Hz), 130.4 (d, J_CP = 4.8 Hz), 125.8 (d, J_CP = 60.9 Hz), 55.3 (s), 30.9 (d, J_CP = 50.6 Hz), 16.9 (d, J_CP = 3.4 Hz), 16.0 (s). ³¹P{¹H} NMR (161.9 MHz, CDCl₃, 298 K): δ = 66.6 (s), -143.8 (sep). Anal. Calcd for C₂₇H₄₁F₆N₂P₃S₂: C 48.79; H 6.22; N 4.21. Found: C 48.53; H 6.33; N 4.27.

[(PCP)H][PF₆] (2.1). Desulfurization was carried out following a literature procedure.¹⁵¹ A mixture of [o-C₆H₄(PSPr₂)₂(NC₃H₅N)(PSPr₂)₂o-C₆H₄]PF₆ (2.32 g, 3.46 mmol) and Raney-nickel (20 g, 340.77 mmol) in methanol (70 mL) was stirred at room temperature for 24 h, during which time periodic monitoring by ³¹P NMR indicated that desulfurization was complete. The excess Raney-nickel and nickel sulfide were removed by filtration through Celite, and the solvent was removed under vacuum. The remaining residue was then dissolved in CH₂Cl₂ and filtered through Celite. Following removal of solvent the product was washed with Et₂O and dried under vacuum. The product was crystallized from a mixture of CH₂Cl₂, Et₂O, and hexanes. Yield: 1.12 g (53.8%). ¹H NMR (400.2 MHz, d₈-THF, 298 K): δ = 8.69 (s, CH, 1H), 7.88 (m, CH, 2H), 7.74 (d, J_HH = 7.6 Hz, CH, 2H), 7.57 (t, J_HH = 7.6 Hz, CH, 2H), 7.52 (t, J_HH = 7.4 Hz, CH, 2H) 4.69 (s, CH₂, 4H), 2.27 (sep, J_HH = 7.0 Hz, CH, 4H), 1.22 (dd, J_HH = 7.0 Hz, J_HP = 15.3 Hz, CH₃, 12H), 0.95 (dd, J_HH = 7.0 Hz, J_HP = 12.2 Hz, CH₃, 12H). ¹³C{¹H} NMR (100.6...
MHz, d$_8$-THF, 298 K): $\delta = 158.0$ (C$_{NH}$), 144.1 (d, $J_{CP} = 23.4$ Hz), 135.3 (s), 134.6 (d, $J_{CP} = 30.1$ Hz), 132.6 (s), 130.7 (s), 128.8 (s), 55.6 (d, $J_{CP} = 11.1$), 21.2 (d, $J_{CP} = 20.5$ Hz), 20.4 (d, $J_{CP} = 10.7$ Hz) $^{31}$P$_{\{^1H\}}$ NMR (161.9 MHz, d$_8$-THF, 298 K): $\delta = -6.4$ (s), -143.8 (sep). Anal. Calcd. for C$_{27}$H$_{41}$F$_6$N$_2$P$_3$: C 54.00; H 6.88; N 4.66. Found: C 54.16; H 7.01; N 4.87.

**[PCP]** (2.2). To a mixture of solid [(PCP)H][PF$_6$], 2.1 (100 mg, 0.167 mmol), and KN(SiMe$_3$)$_2$ (46.6 mg, 0.234 mmol) was added toluene (5 mL). After stirring for 1 h the solution was filtered through Celite and the solvent was removed. $^1$H NMR (C$_6$D$_6$, 300.13 MHz, 298 K): $\delta$ 7.56 (m, 2H, CH), 7.49 (m, 2H, CH), 7.32 (t, $J_{HH} = 7.5$ Hz, 2H, CH), 7.17 (t, $J_{HH} = 7.5$ Hz, 2H, CH), 3.94 (s, 4H, CH$_2$), 2.22 (sep, $J_{HH} = 7.0$ Hz, 2H, CH$_2$), 1.26 (dd, $J_{HH} = 7.0$ Hz, $J_{HP} = 13.1$ Hz, 12H, CH$_3$), 1.14 (dd, $J_{HH} = 7.0$ Hz, $J_{HP} = 12.9$ Hz, 12H, CH$_3$). $^{13}$C$_{\{^1H\}}$NMR (d$_8$-THF, 100.6 MHz, 298 K): $\delta$ 244.7 (C$_{NH}$), 150.2 (d, $J_{CP} = 20.7$ Hz), 133.1 (d, $J_{CP} = 3.3$ Hz), 129.1 (s), 125.3 (d, $J_{CP} = 3.5$ Hz), 125.0 (s), 52.8 (s), 24.4 (d, $J_{CP} = 14.8$ Hz), 20.0 (d, $J_{CP} = 13.8$ Hz). $^{31}$P$_{\{^1H\}}$ NMR (d$_8$-THF, 121.5 MHz, 298 K): $\delta$ -3.7 (s).

**[PCP](H)(O$_t$Bu)** (2.4) A J. Young NMR tube was charged with 100 mg (0.167 mmol) [(PCP)H][PF$_6$] and 18.7 mg (0.167 mmol) KO$_t$Bu in 1mL of THF-d$_8$. $^1$H, $^{13}$C$_{\{^1H\}}$ and $^{31}$P$_{\{^1H\}}$ NMR were recorded after 2 h at room temperature. $^1$H NMR (d$_8$-THF, 400.2 MHz, 298 K): $\delta$ 7.68 (m, 2H, CH), 7.37 (d, $J_{HH} = 7.6$ Hz, 2H, CH), 7.29 (t, $J_{HH} = 7.4$ Hz, 2H, CH), 7.07 (t, $J_{HH} = 7.3$ Hz, 2H, CH), 6.62 (s, 1H, CH), 4.12 (t, $J_{HH} = 6.6$ Hz, 2H, CH$_2$), 3.09 (t, $J_{HH} = 6.6$ Hz, 2H, CH$_2$), 2.21 (sep, $J_{HH} = 7.0$ Hz, 2H, CH$_2$), 2.07 (sep, $J_{HH} = 7.0$ Hz, 2H, CH$_2$), 1.26 (dd, $J_{HH} = 6.8$ Hz, $J_{HP} = 13.7$ Hz, 6H, CH$_3$), 1.13 (s, 9H, O$_t$Bu), 1.10 (dd, $J_{HH} = 7.3$ Hz, $J_{HP} = 12.3$ Hz, 6H, CH$_3$), 1.04 (dd, $J_{HH} = 7.1$ Hz, $J_{HP} = 13.6$ Hz,
6H, CH₃), 0.98 (dd, J_HH = 7.2 Hz, J_HP = 10.7 Hz, 6H, CH₃). \(^{13}\)C\(^{1}\)H\)NMR (d₈-THF, 100.6 MHz, 298 K): δ 150.9 (d, J_CP = 21.3 Hz, CH), 130.0 (s), 126.8 (s), 122.8 (d, CH, J_CP = 6Hz), 121.3 (s), 94.6 (s), 69.6 (s), 49.1 (s), 29.7 (s), 23.5 (d, J_CP = 18.0 Hz), 20.1 (d, J_CP = 13.8 Hz), 18.4 (d, J_CP = 16.9 Hz), 17.8 (d, J_CP = 14.2 Hz), 17.5 (d, J_CP = 15.2 Hz), 17.2 (d, J_CP = 13.5 Hz). \(^{31}\)P\(^{1}\)H\)NMR (d₈-THF, 161.9 MHz, 298 K): δ -1.9 (s), 143.8 (sep).

[(PCP)NiH][PF₆] (2.5). A mixture of [(PCP)H][PF₆], 2.1 (545 mg, 0.908 mmol), and Ni(COD)$_2$ (250 mg, 0.908 mmol) in THF (10 mL) was left to stir for 36 h at room temperature. During this time the pale yellow reaction mixture changed to yellow-brown and a precipitate is formed. The solution was then concentrated and cooled at −30 °C to generate a yellow solid. Yield: 438 mg (73.2%). X-ray quality crystals were grown by slowly cooling a concentrated THF solution to −30 °C. \(^{1}\)H NMR (d₈-THF, 300.13 MHz, 298 K): δ 7.65 (m, 4H, CH), δ 7.53 (m, 2H, CH), 7.32 (t, J_HH = 7.3 Hz, 2H, CH), 4.41 (s, 4H, CH$_2$), 2.62 (s, br, 4H, CH), 1.15 (dd, J_HH = 7.4 Hz, J_HP = 16.1 Hz, 12H, CH$_3$), 1.07 (dd, J_HH = 7.2 Hz, J_HP = 15.3 Hz, 12H, CH$_3$), -10.72 (t, J_HP = 53.5 Hz, NiH). \(^{13}\)C\(^{1}\)H\)NMR (CD$_2$Cl$_2$, 100.6 MHz, 298K): δ 189.28 (t, J_CP = 32 Hz), 144.51 (t, J_CP = 4.6 Hz), 133.56 (s), 131.93 (s), 127.16 (s), 121.21 (t, J_CP = 2.3 Hz), 117.48 (t, J_CP = 16.0 Hz), 52.54 (s), 19.51 (s), 18.48 (s). \(^{31}\)P\(^{1}\)H\)NMR (d₈-THF, 121.5 MHz, 298 K): δ 47.6 (s), -143.8 (sep). Anal. Calcd. C$_{27}$H$_{41}$N$_2$F$_6$P$_3$Ni: C 49.19; H 6.27; N 4.25. Found: C 49.28; H 6.30; N 4.14.

[(PCP)PdH][PF₆] (2.6). The procedure for 2.6 is similar to the synthesis of 2.5, although the consumption of the starting materials 311 mg (0.518mmol) [(PCP)H][PF₆] (2.1) and 600 mg (0.908 mmol) Pd(PPh$_3$)$_4$ in 10 mL THF is completed within 30 min, as
monitored by $^{31}$P NMR spectroscopy. Complex 2.6 was obtained as a slight-yellow crystalline product, after cooling the concentrated THF solution to -30°C and washing several times with Et$_2$O. Yield: 284 mg (77.6%). $^1$H NMR (d$_8$-THF, 300.13 MHz, 298 K): $\delta$ 7.64 (m, 6H, CH), 7.35 (t, $J_{HH} = 7.2$ Hz, 2H, CH), 4.50 (s, 4H, CH$_2$), 2.63 (s br, 4H, CH), 1.17 (dd, $J_{HH} = 8$ Hz, $J_{HP} = 16.1$ Hz, 12H, CH$_3$), 1.07 (dd, $J_{HH} = 8$ Hz, $J_{HP} = 16.1$ Hz, 12H, CH$_3$), -6.1 (s, 1H, PdH). $^{13}$C{$^{1}$H} NMR (CD$_2$Cl$_2$, 100.6 MHz, 298 K): $\delta$ 197.28 (t, $^2J_{CP} = 13.5$ Hz), 146.88 (t, $^2J_{CP} = 4.8$ Hz), 133.48 (s), 133.03 (s) 128.42 (s), 121.71 (s), 116.28 (t, $J_{CP} = 15.6$ Hz), 51.48 (s), 23.99 (t, $J_{CP} = 13.8$ Hz), 18.70 (s), 18.34 (s). $^{31}$P{$^{1}$H} NMR (d$_8$-THF, 121.5 MHz, 298 K): $\delta$ 46.1 (s), 143.8 (sep). Anal. Calc'd. for C$_{27}$H$_{41}$N$_2$F$_6$P$_3$Pd: C 45.90; H 5.84; N 3.96. Found: C 46.36; H 5.36; N 3.72.

[(PCP)PtH][PF$_6$] (2.7). The procedure for 2.7 is the same as for 2.5 starting with 100 mg (0.166 mmol) [(PCP)H][PF$_6$] 2.1 and 207 mg (0.166 mmol) Pt(PPh$_3$)$_4$, resulting in a yield of 96 mg (72.4%). $^1$H NMR (d$_8$-THF, 300.13 MHz, 298 K): $\delta$ 7.58 (m, 6H, CH), 7.37 (m, 2H, CH), 4.45 (s, 4H, CH$_2$), 2.65 (s br, 4H, CH), 1.17-1.04 (m, 24 H, CH$_3$), -4.43 (t with Pt satellites, $J_{HP} = 14.5$ Hz, $J_{PPh} = 403.2$ Hz, 1H, PPh). $^{13}$C NMR (d$_8$-THF, 100.6 MHz, 298 K): $\delta$ 196.68 (t, $^2J_{CP} = 25.3$ Hz), 148.42 (t, $^2J_{CP} = 14.8$ Hz), 133.90 (s), 133.76 (s), 126.07 (s), 122.49 (s), 115.88 (t, $J_{CP} = 20.1$ Hz) 51.97 (s), 24.58 (t, $J_{CP} = 18.2$ Hz), 18.63 (s), 18.52 (s). $^{31}$P{$^{1}$H} NMR (d$_8$-THF, 121.5 MHz, 298 K): $\delta$ 39.5 (s with Pt satellites $J_{PPP} = 1241.5$ Hz), -143.8 (sep). Anal. Calc'd. for C$_{27}$H$_{41}$N$_2$F$_6$P$_3$Pt: C 40.76; H 5.15; N 3.52. Found: C 41.11; H 5.00; N 3.43.
Chapter Three

Apparent *Trans* Coupling of the NHC unit of the PCP Ligand with Unsaturated Hydrocarbons Mediated by Nickel

3.1 Introduction

The substitution of phosphine ligands in existing organometallic complexes with an NHC donor has led to the development of various robust metal catalysts that often exhibit increased catalytic activity.\(^{152-154}\) However, as spectator ligands, NHCs have shown some potential drawbacks, as the carbene moiety in some instances is quite reactive which may lead to catalyst deactivation processes.\(^ {120,155}\) As discussed in chapter one, such pathways include migratory insertion,\(^ {156-158}\) reductive elimination,\(^ {159}\) heterocycle cleavage,\(^ {116,160}\) and abnormal binding\(^ {63,161,162}\) via C-H bond activation of the NHC ring. Understanding the types of non-innocent behaviour exhibited by NHC-metal complexes will help to design more robust catalysts, which should increase the performance of this class of compounds.

In the course of surveying the reactivity of the cationic nickel-hydride 2.5 in the presence of unsaturated hydrocarbons, we uncovered an unprecedented C-C bond-forming process to generate a Ni(0) derivative that apparently involves the NHC moiety and the *trans*-disposed hydride ligand. This led us to undertake detailed mechanistic and
computational studies that show this process is unlikely to involve square-planar Ni(II) intermediates.\textsuperscript{163} Although pincer complexes with the NHC positioned as the central donor should be less susceptible to these deactivation processes,\textsuperscript{134,164} following publication of our results, a similar reaction was reported involving a Zr(IV) centre supported by a tridentate bis(aryloxide) NHC ligand.\textsuperscript{165} Complex 3.1 is stable in non-coordinating solvents however, calculations show that upon addition of THF, the coordination of the Lewis base forces the benzyl unit into a pseudo-cis conformation leading to the C-C coupling product 3.2 (eq 3.1).

The focus of this chapter will be on understanding the mechanism by which the nickel hydride 2.5 converts to the Ni(0) migratory insertion product following addition of ethylene. A second reaction involving tert-butylacetylene leading to coupling with the carbene, followed by insertion into the nickel-carbene bond in the presence of excess alkyne will also be discussed. Both results provide insight into possible metal mediated complex degradation pathways between NHCs and unsaturated carbon bonds.
3.2 Reactivity of \([(PCP)NiH][PF_6]\) with Ethylene

In the process of examining the reactivity of the nickel hydride derivative, we added excess ethylene to a solution of 2.5 in tetrahydrofuran and observed a rapid color change from yellow to orange-red. Our expectation was the formation of a square-planar nickel(II) ethyl complex, \([(PCP)NiEt][PF_6]\) (3.3), via migratory insertion of ethylene into the Ni–H bond.\(^{166}\) Instead, the resultant product was the formally nickel(0) \(\eta^2\)-iminium diphosphine complex shown as 3.4 in Scheme 3.1, which was formed in 70\% isolated yield. That this was not the simple nickel(II) ethyl species 3.3 was evident from the \(^1\)H NMR spectrum, which showed rather broad signals, in particular, a set of two broad peaks due to the inequivalent methylene protons in the saturated carbene backbone, as well resonances due to the inequivalent isopropyl substituents.

Scheme 3.1. Reaction of ethylene with the nickel hydride complex 2.5 to produce 3.4. The role of the nickel ethyl complex 3.3 will be discussed in the mechanistic study found in this chapter.
Single crystals obtained from THF were analyzed by X-ray diffraction; the solid-state molecular structure is shown in Figure 3.1 along with selected bond lengths and bond angles. What is immediately apparent is that C−C bond formation has occurred, resulting in attachment of the ethyl moiety to C1 (formerly the carbene carbon), and that this ethylimidazolidinium unit is now π-bound to the formally Ni(0) center. In the solid state, this η²-C≡N interaction renders the two phosphine donors as well as the top and bottom of the π-bound heterocycle inequivalent. Interestingly, in solution, the ³¹P{¹H} NMR spectrum of 3.4 shows a singlet for the ligated phosphines even down to −80 °C, which suggests that fast exchange of the η²-C≡N unit between N1 and N2 occurs on the NMR time scale. While this process equilibrates the two phosphine arms, it does not exchange the two isopropyl groups on each phosphorus, as they remain inequivalent even at higher temperatures because of the different faces of the coordinated heterocycle above and below the P1–Ni–P2 plane.
Figure 3.1. Solid-state molecular structure (ORTEP) of the cation [(PCEtP)Ni][PF$_6$] (3.4). The PF$_6$ counter ion and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (˚): Ni1-P1, 2.2295(8); Ni1-P2, 2.1424(8); Ni1-N1, 1.967(2); Ni1-C1, 1.899(3); N1-C1, 1.436(3); P1-Ni1-P2, 137.33(3); N1-Ni1-C1, 43.54(10); N1-C1-N2; 107.3(2); P1-Ni1-N1, 89.68(7); C1-Ni1-P2, 92.35(8); C1-C28-C29, 115.3(2).

This product is somewhat reminiscent of the Pd(II)–(CNC) complex 1.57 described in chapter one, for which migratory insertion of one of the flanking NHCs of the tridentate ligand into a Pd–Me bond has been documented.$^{156}$ However, what distinguishes the conversion of nickel(II) hydride 2.5 into the nickel(0) derivative 3.4 is that the central NHC donor was originally trans to the hydride and protected by the flanking o-phenyldiisopropylphosphine arms.
3.3 Investigation into the Mechanism of Formation of [(PCEtP)Ni][PF$_6$]

On the basis of a literature precedent, we assumed that a likely intermediate would be the square-planar nickel ethyl complex 3.3, which would be formed via migratory insertion of added ethylene into the Ni–H bond and could undergo a C–C coupling process to generate the observed nickel(0) product 3.4. Another possible mechanism, but one with no precedent to our knowledge, would be direct insertion of ethylene into the Ni–carbene bond followed by C–H reductive elimination, which would also generate 3.4. Both of these proposals are outlined in Scheme 3.2. The obvious problem with both proposed mechanisms is that reductive elimination processes normally require that the two ligands undergoing the rearrangement be cis-disposed, but in each process shown in Scheme 3.2, the square-planar nickel(II) center requires that the two ligands be trans-disposed. Even in the presence of excess ethylene, any putative five-coordinate intermediate could not rearrange to allow trans-to-cis isomerization of the migrating/eliminating ligands. It was therefore decided to carry out experiments that would shed light on this process and perhaps distinguish the particular pathway (via 3.3 or B in Scheme 3.2) used in this transformation.
Scheme 3.2. Two possible mechanisms to generate 3.4: associative addition of ethylene to give the 5-coordinate species A, which can insert into the Ni-H to form the Ni-ethyl complex 3.3 or into the Ni-NHC bond to generate B.

3.3.1 Isotopic Labeling Studies

Labeling studies were performed in an effort to provide information on the mechanism and, in particular, to try to distinguish the site of insertion. The nickel deuteride $d_1\text{-}2.5$ was prepared simply by stirring the imidazolinium salt in deuterated methanol (CD$_3$OD) overnight. Addition of $d_1\text{-}2.1$ to Ni(COD)$_2$ resulted in the clean formation of $d_1\text{-}2.5$ with 90% deuterium incorporation. Subsequent reaction of the
deuteride with *excess* ethylene resulted in incorporation of deuterium mainly at the β position of the ethyl group in complex 3.4 (eq. 3.2), as indicated by decreases in the integrals of the $^1$H NMR signals due to those hydrogens (80% $d_1$ at this position); however, there was also evidence of deuterium incorporation in the methylene unit at the α position, as evidenced by a decrease in the integrals for these protons (between 15 and 25% $d_1$ at this position, depending on the experiment). As shown in Figure 3.2 the $^2$H NMR spectrum of the product resulting from reaction between 1.2 equivalents of ethylene with $d_1$-2.5 shows two broad peaks, one at ~1.5 ppm and one at ~0.9 ppm, indicative of deuterium incorporation at the α and β position respectively. The $^{13}$C{$_1$H} spectrum was also obtained to confirm the presence of the isotopic label in both positions; however, only the β carbon showed evidence of coupling with deuterium (Figure 3.2).
Figure 3.2. $^2$H NMR (top) and $^{13}$C{$^1$H} NMR (bottom) spectra indicating the presence of deuterium at both carbon positions of the ethyl moiety.

A complementary experiment was devised to confirm the presence of the isotopic label at the α-position using starting materials that have a higher purity of the labelling atom. Addition of ethylene-$d_4$ (98%-$d_4$) to nickel hydride 2.5 resulted in the formation of β-$d_4$-3.4 and α-$d_4$-3.4, as evidenced by $^1$H NMR spectroscopy: clearly evident were a singlet at δ 0.9 and a broad multiplet at δ 1.5 for β-$d_4$-3.4 and α-$d_4$-3.4, respectively, in a 4:1 ratio (eq. 3.3).

Interestingly, the amounts of α-$d_4$-3.4 and β-$d_4$-3.4 depended on the quantity of C$_2$D$_4$ present; when slightly more than 1 equiv of C$_2$D$_4$ was used, the quantities of these
labeled materials matched that shown in eq. 3.3, whereas when excess C$_2$D$_4$ (>10 equiv) was used, considerably smaller proton integrals were observed; in particular, loss of the signal due to $\alpha$-d$_4$-3,4 was readily apparent (Figure 3.3). This can be attributed to a reversible $\beta$-elimination process with dissociation of ethylene-d$_3$ and incorporation of more deuterium via reaction with the excess C$_2$D$_4$. This process is outlined in Scheme 3.3.

![Figure 3.3](image)

**Figure 3.3.** $^1$H NMR spectrum showing the diagnostic peaks used to determine the amount of isotope incorporated at each position: the original experiment giving 3,4 (purple), 2,5 and 1.2 equiv C$_2$D$_4$ (red), 2,5 and excess C$_2$D$_4$ (black).

Key to eliminating the possibility of direct insertion of ethylene into the Ni–carbene bond (see intermediate B in Scheme 3.2) are the production of $\alpha$-d$_4$-3,4 and the observation of d$_5$-3,4, both of which can only occur via a series of reversible $\beta$-
elimination and reinsertion steps into the Ni–H bond as shown in Scheme 3.3. The possibility that the released ethylene can reinsert into the Ni-H bond in different orientations accounts for the isotope scrambling observed. There is no precedent for reversible deinsertion of a coordinated NHC with an alkene.

Scheme 3.3. Reaction of C₂D₄ with nickel hydride 2.5 to generate labeled nickel(0) derivatives: loss of D₂C=CDH occurs to a small extent and results in the formation of the nickel deuteride, which goes on to generate d₅-3.4.
3.3.2 Computational Studies

The deuterium-labeling studies provide strong evidence that migratory insertion occurs at the hydride site, but there is still the issue of the apparent trans coupling of the ethyl and NHC moieties at the nickel(II) center (Scheme 3.2). Monitoring the reaction mixture by NMR spectroscopy showed no evidence for the formation of nickel ethyl complex 3.3 (or any other intermediate), yet it seems to be implicated on the basis of the deuterium-scrambling studies discussed above. In order to provide some guidance concerning possible reaction pathways, density functional theory (DFT) calculations were performed on the starting hydride 2.5, the observed ethylimidazolinium complex 3.4, and presumed intermediates using the ADF2007.01 program suite (BP86 functional, TZP basis set, frozen 1s cores on C and N, frozen 2p cores on P and Ni). Shown in Figure 3.4 are the computed relative energies of the starting hydride 2.5, the nickel ethyl complex 3.3, and the nickel(0) product 3.4.
Figure 3.4. DFT calculated structures and relative energies for hydride $2.5_c$, presumed intermediate ethyl $3.3_c$, and the final ethylimidazolinium product $3.4'_c$; the complexes are numbered with ‘subscript c’ to indicate that they are computed structures. Hydrogen atoms are omitted apart from those on Ni and the ethyl group.

The optimized structure $2.5_c$ agrees quite well with the solid-state structure of this hydride (Figure 2.3); the optimized structure of the final product has a slightly different conformation for the ethyl group as compared with the crystal structure of $3.4$, so it has been given the designation $3.4'_c$. The relative energies show that the ethyl complex $3.3_c$ is virtually isoenergetic with the starting hydride $2.5_c$. Most importantly, DFT correctly predicts that the nickel(0) product $3.4'_c$ is energetically favourable relative to the starting hydride plus ethylene. Armed with these results, we examined possible intermediates
between 2.5\textsubscript{c} and 3.4\textsubscript{c}. The most relevant species that was uncovered is shown in Figure 3.5 as 3.5\textsubscript{c}, which is an agostic nickel ethyl complex different from the anticipated square-planar ethyl species 3.3. In fact, 3.5\textsubscript{c} would result from the associative addition of ethylene to nickel hydride 2.5, as the agostic H on the apical ethyl moiety of 3.5\textsubscript{c} is essentially \textit{trans} to the NHC donor of PCP, and 3.5\textsubscript{c} is very closely related to the putative intermediate A in Scheme 3.2.

To rationalize the observed deuterium scrambling, the agostic C–H interaction would have to dissociate and the methyl group rotate around the ethyl C–C bond to form the calculated apical ethyl transition state 3.6\textsubscript{c}, which could then revert to 3.5\textsubscript{c} with H and D exchanged. Also shown in Figure 3.5 is a possible transition state for migratory insertion of the ethyl group from the nickel to the NHC carbon atom; the calculated structure 3.7\textsubscript{c} is only 11.1 kcal/mol higher in energy than the starting hydride and is easily accessible given the parameters of the observed reaction.
Figure 3.5. DFT calculated structures and relative energies for the agostic ethyl 3.5c, the apical ethyl 3.6c, and a potential transition state structure 3.7c; the complexes are numbered with ‘subscript c’ to indicate that they are computed structures. Hydrogen atoms are omitted except on the ethyl group.

Particularly gratifying is the fact that the originally anticipated but not observed nickel ethyl complex 3.3 (or 3.3c), while accessible, is not required in order to generate the final nickel(0) ethylimidazolinium complex 3.4. This obviates the need to invoke a trans coupling of the ethyl group from the nickel to the NHC carbon. It is interesting to note that a space-filling model view of 3.3c shows considerable steric crowding of the ethyl group with the isopropyl groups on the phosphorus atoms (Figure 3.6).
The effect of steric interactions was examined computationally by recalculating the structures of the “isopropyl-free” complexes corresponding to those shown in Figure 3.4; in this case, the relative energies of the species in which the flanking phosphine units are PH₂ instead of PiPr₂ are 0 kcal/mol for the hydride + ethene, −19.4 kcal/mol for the nickel ethyl complex, and −17.8 kcal/mol for the nickel(0) ethylimidazolinium product. This shows that with no steric bulk, the square-planar nickel ethyl complex rather than the Ni(0) complex would be the thermodynamic product. Clearly, increasing the steric bulk at phosphorus has a profound effect on this process. This rationalizes why the reaction fails with slightly bulkier alkenes such as propene.

3.4 Reactivity of [(PCP)NiH][PF₆] with tert-Butylacetylene

Although [(PCP)NiH][PF₆] (2.5) is inert towards sterically more demanding alkenes, its reactivity with alkynes was also investigated. Treatment of a suspension of 2.5 in THF with 5 equivalents of ’BuC≡CH resulted in a pale orange solution after 1 hour
stirring at ambient temperature. The reaction mixture was concentrated and cooled to -35 °C providing yellow crystals suitable for X-ray diffraction analysis. The crystallographic data revealed the formation of a cationic nickel species where the terminal carbon of one equivalent of alkyne had been formally inserted in the Ni-carbene bond converting the NHC into a imidazolinium salt, while a second equiv of ‘BuC≡CH is coordinated as a tert-butyl acetylide unit, completing the slightly distorted square planar geometry around the Ni(II) centre. The solid-state molecular structure of the product [(PCP{CHCH\textsubscript{2}Bu})NiC\textsubscript{t}Bu][PF\textsubscript{6}] (3.8) and selected bond lengths and angles are given in Figure 3.7. The structure could not be fully refined (R1 = 9.9%); however, the data is useful to show atom connectivity.

The Ni-P and Ni-C bond lengths of the cation 3.8 display no unusual features. The C28-C29 bond length of 1.220(8) Å is consistent with a carbon-carbon triple bond, whereas the C34-C35 and C1-C34 bond lengths of 1.503(8) Å and 1.425(8) Å respectively indicate a C-C single bond. Hence, the former carbon triple bond of the alkyne has become a C-C single bond, presumably through insertion of the unsaturated unit into a nickel-hydride bond as in the formation of 3.4.
Figure 3.7. Solid-state molecular structure (ORTEP) of the double insertion product \([(PCP\{CHCH_2^{1}Bu\})NiCC^{3}Bu][PF_6] (3.8)\). The PF$_6$ counterion and all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1-C34, 1.425(8); C34-C35, 1.503(8); C34-Ni1, 2.053(5); Ni1-C28, 1.857(5); C28-C29, 1.220(8); Ni1-P1, 2.203(6); Ni1-P2, 2.211(5); C1-C34-C35, 127.6(5); C1-C34-Ni1, 83.8(3); C28-Ni-C34, 176.0(2); P1-Ni1-P2, 173.35(3).

The solution spectroscopic data is consistent with the solid-state molecular structure of 3.8. The low symmetry of 3.8 results in separate signals in the $^1$H NMR spectrum belonging to each of the diastereotopic methylene protons of the NHC backbone at δ 4.82, 4.75, 4.31 and 4.11. The signals at δ 3.31, 3.22 and 2.85 can be assigned to the methine moieties of the isopropyl substituents. The $^{1}$Bu groups of the alkyldene unit appear as a singlet at 0.25 ppm, while a singlet belonging to the $^{1}$Bu groups of the inserted alkane are found slightly downfield at 1.18 ppm. The proton attached to the carbon atom connecting the Ni(II) centre and the former carbene carbon (C34 in Figure 3.7), is found at the same chemical shift as the two methine protons at
2.85 ppm. The signal for the CH₂ protons of the inserted alkyl group can not be assigned due to overlap with the CH₃ groups of the isopropyl substituents, showing as a series of multiplets in the range 1.57-0.86 ppm. The ³¹P{¹H} spectrum shows two doublets at 20.67 and 33.70 ppm (J_pp = 281.7 Hz) as well as a septet at -143.80 ppm due to the PF₆⁻ counterion.

To gain information about the formation of 3.8 the reaction between 2.5 and tert-butylacetylene was repeated with 1 equivalent of alkyne. This gave rise to a dark red solution after 45 minutes that differs significantly from the pale orange appearance of 3.8. The ³¹P{¹H} NMR spectrum of the reaction mixture indicated a reaction intermediate giving rise to a singlet at 38.33 ppm. Evaporation of all volatiles and washing with ether provided the product as a dark red powder in 76% yield. This complex was characterized by ¹H and ¹³C{¹H} NMR spectroscopy as well as elemental analysis, and based on similarities with 3.4 has been assigned as [(PC{CH=CH'tBu}P)Ni][PF₆][PF₆] (3.9) (eq 3.4).
The $^1$H NMR spectrum of 3.9 in d$_8$-THF shares many features with the carbene-carbon coupling product 3.4. Two complex multiplets for the CH$_2$ groups of the unsaturated backbone appear at $\delta$ 3.92 and 3.85, and two signals for the CH protons of the isopropyl groups are located at $\delta$ 2.70 and 2.39. In addition, the $^1$H NMR spectrum of 3.9 shows one singlet for the tBu group (0.64 ppm) and two doublets at 5.73 and 4.74 ppm ($^3J_{HH} = 15.8$ Hz), indicating coupling between vinylic protons positioned trans to one another.$^{169}$ The lack of further coupling between these olefinic protons and the phosphine donors indicates coordination of the CH=CH'tBu unit to the carbene carbon and not the nickel centre. The singlet observed in the $^{31}$P{$^1$H} NMR spectrum suggests a fast exchange of the $\eta^2$-C=N unit equilibrating the phosphines reminiscent of 3.4. The $^{13}$C{$^1$H} NMR spectrum shows a quaternary carbon located at 88.17 ppm that can be assigned to the former carbene carbon; a similar resonance is found for 3.4. The structure of 3.9 is supported by the 2D $^1$H/$^{13}$C HSQC NMR spectrum, which is shown in Figure 3.8. Assignment of the olefinic carbon atoms was assisted through the reaction of $d_1$-2.5 with one equivalent of tert-butylacetylene, resulting in a disappearance of the doublet at 4.74 ppm, identifying this as the vinylic proton of the HC-C(CH$_3$)$_3$ moiety.
Figure 3.8. $^1\text{H}/^{13}\text{C}$ HSQC spectrum of 3.9, correlating $^1\text{H}$ and $^{13}\text{C}$ nuclei connected by one bond.

3.4.1 Mechanistic Rationale for the Reaction of [(PCP)NiH][PF$_6$] with tert-Butylacetylene

The mechanistic insight gained studying the reaction of [(PCP)NiH][PF$_6$] (2.5) with ethylene allows us to propose a reasonable rationale for the formation of 3.8 and 3.9. The expected mechanism is shown in Scheme 3.4. The initial step is insertion of one equivalent of alkyne into the nickel-hydride bond, affording the syn-insertion product.\textsuperscript{170} Again, steric repulsion created by the phosphine substituents does not allow production of a square planar Ni(II) complex, instead a transition state similar to the calculated structure 3.7$_c$ forms in which the resulting alkene is oriented in a pseudo-cis position to the carbene carbon. From this position a C-C bond coupling reaction gives the energetically favoured product 3.9. The syn stereochemistry of the alkene is maintained.
as evidenced by the characteristic trans-coupling between the vinylic hydrogens. Oxidative addition of a second equivalent of alkyne at the reactive Ni(0) centre of 3.9 provides access to a four-membered transition state involving the imidazolinium salt and the Ni-H bond well suited for insertion of the alkene. The final step, insertion of the alkene, leads to the isolated double insertion product 3.8.

**Scheme 3.4.** Mechanistic rationale for the formation of [(PC{CH=CH\textsuperscript{t}Bu}P)Ni][PF\textsubscript{6}] (3.9) and [(PCP\{CH\text{CH\textsubscript{2}}\text{Bu}\})NiCC\text{Bu}][PF\textsubscript{6}] (3.8).

3.5 **Conclusions**

The reaction of an alkene with a metal hydride to generate a metal alkyl derivative via migratory insertion is a fundamental process in organometallic chemistry\textsuperscript{167} and a key step in numerous catalytic processes.\textsuperscript{172} In the work reported in this chapter, the reaction of ethylene with a square-planar nickel(II) hydride complex involves a different process in which the trans-disposed NHC donor of the tridentate ligand is transformed via a C-C
bond-forming process that generates an nickel(0) ethylimidazolidinium species. The results of deuterium-labeling studies are consistent with a process that involves a series of β-elimination, alkene rotation, and readdition steps that scrambles the labels. The actual C-C bond-forming step is best viewed as arising from an apical agostic ethyl complex that is positioned cis to the NHC carbon of the PCP ancillary ligand. This avoids invoking a trans coupling process, which remains as an unreasonable assumption. DFT calculations show that the effect of steric interactions is the overriding feature of this process: the apical ethyl moiety is a result of the large isopropyl substituents on phosphorus, which destabilize the formation of the square-planar nickel ethyl complex and cause the C-C bond-forming process to be the energetically favored pathway.

The detailed mechanistic study on the reaction of [(PCP)NiH][PF₆] (2.5) with ethylene provided valuable information in understanding the reactivity of 2.5 with tert-butylacetylene. In this case addition of a second equivalent of the unsaturated hydrocarbon leads to a double insertion product with an alkyl moiety inserted into the carbene-nickel bond and one coordinated tert-butylacetylide unit. Both of these reactions provide insight into possible metal mediated complex degradation pathways between NHCs and unsaturated carbon bonds. The trans-phosphine donors of the PCP ligand allow the non-innocent ligand to remain coordinated to nickel following the C-C coupling process. This finding is in contrast with NHC-containing pincer complex bearing weaker amine donors, which result in dissociation of imidazolium salts from the metal centre.
3.6 Experimental

General Considerations. All reactions were performed by standard Schlenk techniques in an oxygen free nitrogen atmosphere. $^1$H, $^{13}$C and $^{31}$P-NMR spectra were recorded on either a Bruker AV-400 instrument operating at 400.2 MHz or a Bruker AV-300 instrument operating at 300.13 MHz. Chemical shifts are given relative to TMS and were referenced to the residual proton solvent resonances as internal standards. Organic solvents were purchased anhydrous from Aldrich, sparged with nitrogen, and passed through columns containing activated alumina and molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed and dried over activated 3 Å molecular sieves prior to use. Deuterated ethylene ($C_2D_4$, 98%-d4) was purchased from Cambridge Isotope Laboratory. tert-butylacetylene was purchased from Aldrich, distilled over molecular sieves and degassed prior to use.

$[(PCP)NiD][PF_6]$ (d1-2.5). Same procedure as described for 2.5 with the exception of replacing 2.1 with the deuterated ligand $[(PCP)Ni][PF_6]$. $^2$H NMR (THF, 61.43 MHz, 298 K): $\delta$ -10.69 (t, $^2J_{PD} = 8$ Hz, NiD).

$[(PCEtP)Ni][PF_6]$ (3.4). A yellow suspension of $[(PCP)NiH][PF_6]$ (2.5) (150 mg, 0.228 mmol) in THF (4 mL) was subjected to three freeze-pump-thaw cycles and then exposed to an atmosphere of ethylene. The colour of the solution immediately changed to orange-red. The mixture was stirred for 30 min and then concentrated and slowly cooled to -30 °C, giving orange-red crystals. Yield: 109.5 mg (70.0%). $^1$H NMR (d8-THF, 400.2 MHz, 298 K): $\delta$ 7.86 (d br, 2H, CH), 7.77 (d br, 2H, CH), 7.62 (t, $J_{HH} = 7.4$ Hz, 2H, CH), 7.56 (t, $J_{HH} = 7.3$ Hz, 2H, CH), 3.96 (t br, 2H, CH2), 3.75 (t br, 2H, CH2), 2.77 (m br, 2H, CH), 2.35 (m br, 2H, CH), 1.51 (quar, $J_{HH} = 7.0$ Hz, 2H, CH2), 1.36 (dd, $J_{HH} = 6.4$ Hz, $J_{HP} = 16.4$ Hz, 6H, CH3), 1.29 (dd, $J_{HH} = 6.8$ Hz, $J_{HP} = 17.3$ Hz, 6H, CH3), 1.18 (dd, $J_{HH} = 6.4$ Hz, 6H, CH3).
= 7.0 Hz, \( J_{HP} = 12.8 \) Hz, 6H, CH\(_3\)), 1.11 (dd, \( J_{HH} = 6.7 \) Hz, \( J_{HP} = 15.7 \) Hz, 6H, CH\(_3\)), 0.96 (t, \( J_{HH} = 7.1 \) Hz, 3H, CH\(_3\)). \(^{13}\)C\{\(^1\)H\} NMR (d\(_8\)-THF, 100.6 MHz, 298K): \( \delta \) 150.66 (t, \( J_{CP} = 9.5 \) Hz), 134.68 (s), 132.98 (s), 129.44 (s), 128.99 (s), 128.76 (m), 95.47 (s), 57.94 (s), 27.58 (t, \( J_{CP} = 7.9 \) Hz), 25.34 (s), 24.32 (t, \( J_{CP} = 10.4 \) Hz), 21.57 (t), 20.29 (s), 19.52 (t, \( J_{CP} = 4.7 \) Hz), 19.42 (s), 10.24 (s). \(^{31}\)P\{\(^1\)H\} NMR (d\(_8\)-THF, 161.9 MHz, 298 K): \( \delta \) 36.8 (s), -143.8 (sep). Anal. Calc. for C\(_{29}\)H\(_{45}\)N\(_2\)F\(_6\)P\(_3\)Ni: C 50.68; H 6.60; N 4.08. Found: C 50.22; H 6.38; N 4.05.

**General Procedure for Ethylene Reactions.** A J. Young NMR tube with a total volume of 2.75 mL was charged with 2.5 or \( d_1\)-2.5 (30 mg, 0.05 mmol) and d\(_8\)-THF (~1.25 mL). The suspension was then subjected to three freeze-pump-thaw cycles, and to the headspace was added a specified quantity of unlabeled or labeled ethylene gas, after which the tube was immediately sealed. The hydride dissolved upon shaking, and the mixture was monitored by NMR spectroscopy. The diagnostic peaks of the ethyl unit at \( \delta \) 1.51 (CH\(_2\)) and 0.96 (CH\(_3\)) in the \(^1\)H NMR spectrum were used throughout to determine the amount of isotope incorporated. \(^2\)H NMR (CH\(_2\)Cl\(_2\), 61.43 MHz, 298 K): \( \delta \) 1.53 (br s), 0.95 (br s).

\([\text{PCP}\{\text{CHCH}_2\text{tBu}\}]\text{NiCC}_\text{tBu}[\text{PF}_6]\) (3.8). To a yellow suspension of \([\text{PCP}\text{NiH}][\text{PF}_6]\) (2.5) (100 mg, 0.152 mmol) in THF (5 mL) was added tert-butylacetylene (6.2 mg, 0.760 mmol) and the mixture was left to stir for 1 h. During this time the reaction became a homogenous pale orange solution. After 1 h, all volatiles were removed under reduced pressure and the remaining residue was washed with ether, and the product was pumped to dryness. This gave the product as an orange powder. Yield: 89.7 mg (72%). X-ray quality crystals were formed by slowly cooling a concentrated THF solution to -35 °C. \(^1\)H
NMR (d$_8$-THF, 400.2 MHz, 298 K): δ 7.82 (m, 2H, CH), 7.75 (t, $J_{HH} = 7.5$ Hz, 1H, CH), 7.37 (t, $J_{HH} = 7.2$ Hz, 1H, CH), 4.82 (m, 1H, CH), 4.75 (m, 1H, CH), 4.31 (q, $J_{HH} = 9.4$ Hz, 1H, CH), 4.11 (t, $J_{HH} = 8.0$ Hz, 1H, CH), 3.31 (m, 1H, CH), 3.22 (m, 1H, CH), 2.90 (m, 1H, CH), 2.85 (m, 2H, CH), 1.61 (m, 6H, CH), 1.51 (dd, $J_{HH} = 7.1$ Hz, $J_{HP} = 18.2$ Hz, 3H, CH), 1.42 (dd, $J_{HH} = 6.7$ Hz, $J_{HP} = 16.8$ Hz, 3H, CH), 1.27 (m, 3H, CH), 1.23 (m, 2H, CH), 1.18 (s, 9H, CH), 0.98 (dd, $J_{HH} = 7.0$ Hz, $J_{HP} = 11.2$ Hz, 3H, CH), 0.89 (dd, $J_{HH} = 7.2$ Hz, $J_{HP} = 11.7$ Hz, 3H, CH), 0.25 (s, 9H, CH).

$^{13}$C{${^1}$H} NMR (d$_8$-THF, 100.6 MHz, 298K): δ 155.60 (s), 146.15 (d, $J_{CP} = 9.2$ Hz), 144.40 (d, $J_{CP} = 8.5$ Hz), 133.69 (s), 133.57 (s), 133.24 (s), 132.87 (s), 132.29 (s), 127.15 (dd, $J_{CP} = 19.6$ Hz, $J_{CP} = 3.4$ Hz), 125.98 (dd, $J_{CP} = 26.0$ Hz, $J_{CP} = 4.6$ Hz), 123.32 (dd, $J_{CP} = 22.9$ Hz, $J_{CP} = 2.6$ Hz), 120.27 (d, $J_{CP} = 27.8$ Hz), 80.01 (t, $J_{CP} = 51.5$ Hz), 51.74 (s), 49.18 (s), 41.85 (s), 33.42 (s), 31.42 (s), 28.65 (s), 26.93 (d, $J_{CP} = 32.5$ Hz), 24.39 (d, $J_{CP} = 32.3$ Hz), 23.75 (d, $J_{CP} = 21.1$ Hz), 23.42 (d, $J_{CP} = 23.0$ Hz), 23.12 (t, $J_{CP} = 6.8$ Hz), 21.23 (d, $J_{CP} = 4.6$ Hz), 20.63 (d, $J_{CP} = 4.0$ Hz), 20.19 (d, $J_{CP} = 4.6$ Hz), 19.72 (d, $J_{CP} = 2.8$ Hz), 19.48 (d, $J_{CP} = 2.9$ Hz), 15.87 (d, $J_{CP} = 7.0$ Hz), 15.62 (d, $J_{CP} = 6.8$ Hz).

$^{31}$P{${^1}$H} NMR (d$_8$-THF, 161.9 MHz, 298 K): δ 33.70, 20.67 (d, $J_{PP} = 281.7$ Hz), -143.8 (sep). Anal. Calc. for C$_{39}$H$_{61}$N$_2$F$_6$P$_3$Ni: C 56.88; H 7.47; N 3.40. Found: C 57.79; H 7.88; N 3.31.

$[(PC{CH=CH'Bu}P)Ni][PF_6]$ (3.9). To a yellow suspension of $[(PCP)NiH][PF_6]$ (2.5) (100 mg, 0.152 mmol) in THF (5 mL) was added tert-butylacetylene (13.6 mg, 0.166 mmol) and the mixture was left to stir for 1 h. During this time the reaction became a homogenous dark red solution. After 1 h, all volatiles were removed under reduced pressure and the remaining residue was washed with ether, and the product was pumped...
to dryness. This gave the product as a red powder. Yield: 85.4 mg (76%). $^1$H NMR (d$_8$-THF, 400.2 MHz, 298 K): $\delta$ 7.85 (m, 2H, CH), 7.63 (m, 4H, CH), 7.53 (m, 2H, CH), 5.73 (d, $^3J_{HH} = 15.8$ Hz, 1H, $-HC=\text{CH}(^{t}\text{Bu})$), 4.74 (d, $^3J_{HH} = 15.8$ Hz, 1H, $-HC=\text{CH}(^{t}\text{Bu})$), 3.92 (m, 2H, CH$_2$), 3.85 (m, 2H, CH$_2$), 2.70 (m, 2H, CH), 2.39 (m, 2H, CH), 1.30 (m, 12H, CH$_3$), 1.22 (m, 6H, CH$_3$), 1.05 (m, 6H, CH$_3$), 0.64 (s, 9H, CH$_3$). $^{13}$C {$^1$H} NMR (d$_8$-THF, 100.6 MHz, 298K): $\delta$ 151.69 (t, $J_{CP} = 8.2$ Hz), 145.52 (s), 134.46 (s), 133.12 (s), 129.47 (s), 128.93 (s), 128.30 (t, $J_{CP} = 16.29$ Hz), 116.36 (s), 88.37 (s), 58.24 (s), 34.49 (s), 28.39 (s), 27.32 (t, $J_{CP} = 9.1$ Hz), 24.78 (t, $J_{CP} = 8.7$ Hz), 21.70 (s), 21.02 (s), 19.84 (s), 19.77 (s). $^{31}$P {$^1$H} NMR (d$_8$-THF, 161.9 MHz, 298 K): $\delta$ 38.33 (s), -143.8 (sep). Anal. Calc. for C$_{33}$H$_{51}$N$_2$F$_6$P$_3$Ni: C 53.46; H 6.93; N 3.28. Found: C 52.91; H 6.99; N 3.72.
Chapter Four

Exploring the Coordination Chemistry of the PCP Ligand with Rhodium

4.1 Introduction

Several tridentate, non-NHC derived pincer complexes of rhodium utilizing either a central aryl donor or aryl linkers have been reported (Figure 4.1). These systems have a range of applications including: C-H bond activation,\textsuperscript{101,173,174} carbon dioxide reduction,\textsuperscript{175} and catalytic alkyne dimerization.\textsuperscript{176} A rhodium complex incorporating the lutidine-based PNP ligand set shown in Figure 4.1 has also been show to stabilize a rare, mononuclear Rh(II) oxidation state.\textsuperscript{177} Formally neutral tridentate ancillary ligands offer complementary chemistry to their monoanionic counterparts, particularly in the case of low-valent late transition metals.\textsuperscript{178} This makes our neutral PCP ligand an interesting candidate to explore its coordination chemistry with rhodium, focusing on small molecule and C-H bond activation processes.
The development of efficient catalysts for the activation and functionalization of C-H bonds is crucial for more efficient utilization of our hydrocarbon resources.\textsuperscript{179,180} A number of catalytic systems capable of selectively activating C-H bonds under mild conditions have been reported;\textsuperscript{181} one such complex incorporates the non-NHC derived PNP pincer ligand coordinated to rhodium.\textsuperscript{173} Synthesis of the (PNP)RhCH\textsubscript{3} complex 4.1 provided access to the hydroxide derivative (PNP)RhOH (4.2) in the presence of H\textsubscript{2}O (Scheme 4.1). Heating a sample of 4.2 at 60 °C generates the deuterated phenyl complex (PNP)RhC\textsubscript{6}D\textsubscript{5} (4.3) via activation of an arene C-D bond and the loss of HOD. This reaction is in contrast to the majority of late transition metal C-H activation catalysts, which are often inhibited by water or alcohols that may be present as a reactant or product.\textsuperscript{182}
The focus of this chapter will be on the coordination of our NHC-containing PCP pincer ligand with rhodium in hopes of developing useful reactivity through the activation of C-H bonds. Of particular interest is how the reactivity of complexes supported by a saturated NHC donor may differ from the non-NHC ligand motifs. These studies led to a series of new \((\text{PCP})\text{RhL}\) complexes, where \(L\) is a variety of small molecules. Finally some catalytic conversions employing the aforementioned rhodium compounds will be reported.

4.2 Coordination to Rhodium

Highly selective catalysts capable of converting alkanes to alkenes requiring little energy input are attractive as a way to transform relatively inert saturated hydrocarbons to olefins for further functionalization.\(^{179}\) A neutral rhodium(III) dihydride complex supported by the monoanionic \(\text{PCarylP}\) ligand shown in Figure 4.1 has been successful in alkane dehydrogenation catalysis.\(^{101}\) Although its iridium congener displays higher activity, as will be discussed in Chapter 5, the synthesis of a cationic rhodium dihydride \([\text{(PCP)RhH}_2][\text{PF}_6]\) was envisioned as a way to investigate how changing to a cationic species might affect C-H bond activation. The synthetic pathway shown in eq. 4.1 was
selected to build on the success with the group 10 metals already discussed in Chapter 2, through oxidative addition of 2.1 with [Rh(COD)Cl]$_2$ (COD = 1,5-cyclooctadiene).

![Diagram of 2.1 and reaction](image)

Formation of a product other than that in eq. 4.1 was apparent after acquiring a $^1$H NMR spectrum of the reaction mixture, which contained no upfield signals indicative of a rhodium hydride. Fortunately, slowly cooling a concentrated THF solution of the product provided crystals suitable for X-ray diffraction analysis, albeit in low yield. Crystallographic data showed that the product was instead the chloride-bridged dication $[(PCP)_2$Rh$_2$Cl$_2$(μ-Cl)$_2$][PF$_6$]$_2$ (4.4) as shown in eq. 4.2. The solid state molecular structure of 4.4 is shown in Figure 4.2; the geometry is quite similar to an iodide-bridged dimer containing a meridional CCC type tridentate ligand with NHC’s occupying the two positions trans to one another.$^{85}$ The Rh-C$_{NHC}$ bond lengths Rh1-C1 and Rh1A-C1A of
4.4 are 1.981(13) Å and 1.969(15) Å, respectively. Although these values are slightly shorter than the iodide complex reported previously, they are well within the expected range of Rh(III)-C\textsubscript{NHC} bond lengths.\textsuperscript{72} It is noteworthy that the dication 4.4 does not contain the iminium hydrogen from 2.1; further experiments to determine the fate of this atom were not explored. Although the structure of 4.4 confirms coordination of the PCP ligand with rhodium, the resulting dinuclear species was not the intended mononuclear cation [(PCP)RhHCl][PF\textsubscript{6}]. For this reason further analysis of 4.4 was abandoned and a new synthetic strategy was designed.
Figure 4.2. Solid-state molecular structure (ORTEP) of the rhodium chloride dication \(4.4\). The PF\(_6\) counterions and all hydrogen atoms have been omitted for clarity. No bond distances or angles are reported as the structure is meant to show atom connectivity.

In an attempt to obtain a mononuclear rhodium(1) chloride through dissociation of the labile COD ligands the neutral version of the PCP ligand \(2.2\) was stirred in a THF solution of \([\text{Rh}(\text{COD})\text{Cl}]_2\), resulting in clean formation of \((\text{PCP})\text{RhCl} (4.5)\). After approximately 30 minutes at room temperature the dark brown solution had turned bright red. Removal of the THF and filtration of an ether suspension of \(4.5\) allowed isolation of the product in 78% yield (eq. 4.3).
Slowly evaporating a concentrated THF solution of \( \text{4.5} \) provided crystals suitable for X-ray diffraction analysis. Figure 4.3 shows the solid-state molecular structure of \( \text{4.5} \). Complex \( \text{4.5} \) crystallizes in the triclinic space group \( P\overline{1} \) with a slightly distorted square planar geometry similar to the cationic palladium and platinum hydrides \( \text{2.6} \) and \( \text{2.7} \) described in Chapter 2. The NHC ring is once again twisted above and below the metal plane with torsion angles of \( 46.23^\circ \) and \( 37.38^\circ \) respectively. The Rh-C1 bond length of \( 1.929(5) \) Å is relatively short when compared to other Rh(I)-C\(_{\text{NHC}}\) bond lengths which have a mean average distance of \( 2.026 \) Å.\(^{183}\) The metal-ligand bond strength of strong \( \sigma\)-donating ligands in square planar \( d^8\) -complexes is greater when highly electronegative ligands are oriented in the \textit{trans} position.\(^{184}\) Therefore, the shorter Rh-carbene bond in \( \text{4.5} \) can be explained by the influence of the electronegative chloride ligand \textit{trans} to the carbene.
Figure 4.3. Solid-state molecular structure (ORTEP) of (PCP)RhCl (4.5). All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1-Rh1, 1.929(5); P1-Rh1, 2.3042(14); P2-Rh1, 2.2910(13); Rh1-Cl1, 2.4029(16); C1-N1, 1.370(6); C1-N2, 1.379(7); C1-Rh1-C1I, 179.61(16); P1-Rh1-P2, 173.05(5); P1-Rh1-C1, 86.13(16); P1-Rh1-C1I, 93.87(5).

4.3 Synthesis of Rh(I) and Rh(III) Hydrides

The (PCP)RhCl (4.5) complex is a valuable mononuclear starting material that has allowed access to a series of new metal complexes through ligand substitution reactions. Exchanging the chloride for a hydride ligand would give a coordinatively unsaturated square-planar Rh(I) complex with two open coordination sites available to participate in oxidative addition reactions (e.g. addition of a C-H bond). To generate the rhodium hydride, potassium triethylborohydride was added to a THF solution of an equal molar amount of 4.5 (eq. 4.4). This led to a colour change from bright red to deep green over a time period of thirty minutes. Filtration of the product followed by evaporation of
the solvent allowed the isolation of (PCP)RhH (4.6) in 77% yield. Unfortunately X-ray quality crystals of the hydride could not be obtained; however, its formation was evident by a distinctive doublet of triplets at -4.1 ppm ($J_{\text{RhH}} = 15$ Hz, $^2J_{\text{HP}} = 22$ Hz) in the $^1$H NMR spectrum (Figure 4.4). Rhodium hydride compounds with coordinated NHC ligands have exhibited similar splitting patterns as reported previously.\(^{185}\)

**Figure 4.4.** $^1$H NMR spectrum of the hydride region showing the peak belonging to the monohydride 4.6 (A) and the peaks belonging to the trihydride 4.7 (B).

Also of interest was a rhodium trihydride that may be capable of hydrogenating unsaturated hydrocarbons. This species was obtained through oxidative addition of one
equivalent of H₂ gas to 4.6. Initially a hydride signal could not be located in the ¹H NMR spectrum. However, upon cooling a sealable J-Young NMR tube of 4.6 under a hydrogen atmosphere down to 230 K, a sharpening of the ¹H NMR spectrum was observed. An apparent quartet at -8.6 ppm and a broad multiplet at -10.3 ppm that integrate in a 2:1 ratio of hydrogen atoms indicates the presence of the trihydride species (B in Figure 4.4). The lone doublet found in the ³¹P{¹H} spectrum at 62 ppm (J_{RhP} = 107 Hz) and the two equivalent hydride signals indicate a meridional, octahedral geometry for (PCP)RhH₃ 4.7. This complex was not isolable as upon removal of the hydrogen atmosphere 4.7 reverted back to the monohydride 4.6 (eq. 4.5). This was seen as evidence that our PCP rhodium system prefers to be in the Rh(I) oxidation state. The attempted C-H activation using these two complexes will be discussed in a later section of this chapter.

4.4 Synthesis of (PCP)RhL (L = CH₃, NH₃, NH₂, OH, CCPh)

As mentioned in the introduction of this chapter, the activation of hydrocarbons leading to further functionalization is an important organometallic challenge. A step towards this goal is placing reactive small molecules at a metal centre capable of undergoing further reactivity. The work outlined in Chapter 3 clearly indicates there is a size restriction to the ligands that can be accommodated trans to the NHC in our (PCP)M systems. So far, we have been able to prepare rhodium PCP systems with a chloride and
hydride ligand \textit{trans} disposed to the NHC as shown in 4.5 and 4.6, and we can also access a Rh(III) trihydride, 4.7. Therefore, it was of interest to explore what other types of small molecules can be placed into the coordination site \textit{trans} to the central NHC, and how the steric bulk around this binding site may help in stabilizing otherwise reactive species.

Considering experiments had shown that, due to steric constraints, an ethylene group cannot insert into the metal hydride bond of \([(PCP)NiH][PF_6]\) (2.5) to form a square planar Ni-Et species, it was of interest to see if a similar size restriction exists within the rhodium system. The methyl complex was successfully prepared by reaction of 4.5 with a slight excess of methyl lithium at 0 °C to form (PCP)RhCH\textsubscript{3} (4.8) in 55% isolated yield (eq. 4.6). In the \textsuperscript{1}H NMR spectrum, the protons on the CH\textsubscript{3} ligand appear at 0.55 ppm as a doublet of triplets ($^2J_{\text{RhH}} = 1.5$ Hz, $^3J_{\text{HP}} = 6.5$ Hz) and the carbon atom was located in the \textsuperscript{13}C\textsubscript{\textsuperscript{1}H} NMR spectrum as a doublet of triplets at -10.3 ppm ($J_{\text{RHC}} = 19$ Hz, $^2J_{\text{PC}} = 13$ Hz). These values are similar to a comparable tridentate (PNP)RhCH\textsubscript{3} complex that has been structurally characterized by X-ray crystallography.\textsuperscript{173} However, multiple attempts to synthesize a related ethyl complex with EtMgBr were unsuccessful as no signal indicative of an ethyl moiety could be identified in the \textsuperscript{1}H NMR spectrum, although 4.5 seems to have been consumed. This is in accordance with the steric crowding around the metal centre that was discussed in detail in Chapter 3.
One compound still of interest was a cationic metal dihydride for comparison to the proven neutral PCP C-H activation catalysts.\textsuperscript{101-104,106,186} For this the inorganic acid ammonium hexafluorophosphate (pKa = 9.2)\textsuperscript{187} was selected in an attempt to protonate the metal centre of 4.6 leaving a [(PCP)RhH\textsubscript{2}][PF\textsubscript{6}] species. Protonation of metal hydrides with inorganic acids can be a simple route to metal dihydrides although the outcome depends on many factors such as choosing the right acid and the basicity of ligands.\textsuperscript{188} In this case protonation provided the new cationic ammonia compound 4.9 following the loss of dihydrogen (eq. 4.7).

\[
\text{NH}_4\text{PF}_6 + \text{THF} \rightarrow \text{[(PCP)RhNH}_3\text{][PF}_6]} \quad (4.7)
\]

As the reaction proceeds overnight a bright orange precipitate is formed. Filtration of this suspension allows for isolation of [(PCP)RhNH\textsubscript{3}][PF\textsubscript{6}] (4.9) in 79 % yield. Slow evaporation of a concentrated THF solution of 4.9 provided crystals suitable for X-ray diffraction analysis (Figure 4.5). The cationic Rh(I) complex crystallizes in the monoclinic space group P2(1)/c and adopts a distorted square planar geometry similar to the cationic group 10 metal hydrides 2.5-2.7.
Figure 4.5. Solid-state molecular structure (ORTEP) of the cation [(PCP)RhNH$_3$][PF$_6$] (4.9). The PF$_6$ counterion and all hydrogen atoms except those on the NH$_3$ unit have been omitted for clarity. Selected bond lengths (Å) and angles (°): C1-Rh1, 1.938(2); P1-Rh1, 2.2937(8); P2-Rh1, 2.2971(8); Rh1-N3, 2.143(2); C1-N1, 1.372(3); C1-N2, 1.362(3); C1-Rh1-N3, 178.58(11); P1-Rh1-P2, 170.17(2); P1-Rh1-C1, 85.01(7); P1-Rh1-N3, 94.08(8).

Although transition metal ammine compounds have been known even before the days of Alfred Werner the closely related terminal amido (NH$_2$) complexes are quite rare.$^{189}$ Only a handful of these examples utilize a tridentate pincer ligand, all of which are monoanionic$^{190-192}$ (4.10-4.13 Figure 4.6), including the first example of the oxidative addition of ammonia at a metal centre (4.13).$^{193}$ However, no examples of the Rh(I) oxidation state have been reported. This was an interesting synthetic challenge and provided an opportunity to utilize the steric bulk created by the isopropyl groups of the phosphine donor to potentially help stabilize an otherwise very reactive moiety trans to the NHC donor of the PCP ligand. The method selected to synthesize the rhodium amido product was deprotonation of the ammine with potassium hexamethyldisilazane. (eq. 4.8).
Figure 4.6. Transition metal complexes supported by a pincer ligand capable of stabilizing a terminal amido ligand.

Stirring a suspension of 4.9 in toluene with a slight excess of KHMDS resulted in an immediate colour change from bright orange to purple and produced a rare example of a Rh(I) complex stabilizing a terminal amido ligand. This is seen through the loss of a signal at 2.4 ppm in the $^1$H NMR spectrum belonging to the ammine group and the appearance of a new signal assigned to the amido protons at 1.1 ppm, as well as a disappearance of the characteristic PF$_6$ signal in the $^{31}$P{$^{1}$H} NMR spectrum. The upfield shift of the amido protons is indicative of an increase in electron density. In addition, X-ray quality crystals were formed via slow evaporation of a concentrated THF solution. The data obtained confirmed the atom connectivity of the new rhodium complex (PCP)RhNH$_2$ (4.14); however, the structure could not be fully refined due to the presence of a second new species in the unit cell (PCP)RhOH (4.15). This was presumably
an unwanted side product that formed through the reaction of 4.9 with adventitious water. The presence of the hydroxide complex 4.15 is observed during the synthesis of 4.14 if proper care is not taken to remove water. (PCP)RhOH appears as a second doublet found in the $^3$P$\{^1$H$\}$ NMR spectrum of 4.14 integrating to approximately 8% when compared to (PCP)RhNH$_2$.

In order to confirm the presence of the hydroxide complex 4.15 a slight excess of H$_2$O was added to a toluene solution of (PCP)RhH (eq. 4.9). This clearly showed production of the Rh(I) hydroxide compound by the loss of the diagnostic hydride signal of 4.6 giving way to a broad singlet at -0.43 ppm in the $^1$H NMR spectrum as well as the expected doublet at 23 ppm ($J_{RhP} = 151$ Hz) in the $^3$P$\{^1$H$\}$ NMR spectrum that was observed as a side product in the deprotonation of 4.14. These values compare nicely with a similar (PNP)RhOH complex previously reported.$^{173}$ The reactivity of 4.14 and 4.15 will be discussed in a later section of this chapter.

The non-innocent behaviour of the cationic nickel hydride 2.5 in the presence of an alkyne was documented in the previous chapter; therefore, it was of interest how the reactivity of the neutral rhodium hydride 4.6 might compare. Allowing a THF solution of
4.6 to stir with one equivalent of phenylacetylene led to a colour change from green to dark red almost immediately, after allowing the reaction solution to stir for one hour evaporation of all volatiles gave 4.16 in 86% yield (eq. 4.10). The $^1$H NMR spectrum of the product showed a complete disappearance of the hydride signal and a new set of signals in the aromatic region, while the $^{31}$P{$^1$H} NMR spectrum clearly revealed the formation of a single new product ($\delta$ 30.40, $J_{RhP}$ = 138.4 Hz). Interestingly the same product (4.16) results from the reaction of other (PCP)RhL (L = CH$_3$, OH, NH$_2$) starting materials with phenylacetylene.

Allowing a THF solution of 4.16 to react with excess phenylacetylene over 7 days (eq. 4.11) resulted in precipitation of crystals suitable for X-ray analysis of a new Rh(III) complex in which 4.16 has initiated C-H activation of a second equivalent of PhCCH resulting in coordination of two acetylide units and one hydride (Figure 4.7). The slightly distorted octahedral structure of (PCP)RhH(CCPh)$_2$ (4.17) crystallizes in the monoclinic space group C2/c. There are no unusual features when compared to the previously crystallized PCP complexes; for example the Rh1-C1 distance of 2.034(3) Å is within the
range of Rh(III)-C\textsubscript{NHC} bond lengths reported previously.\textsuperscript{72} Complex 4.17 represents the only monomeric Rh(III) compound of our PCP ligand set to be analyzed by X-ray crystallography to date. Following this achievement the parallel reaction was run with tert-butylacetylene as the reagent providing the analogous Rh(I) tert-butylacetylide. However, any attempts to facilitate further C-H activation and generate a Rh(III) bis(acetylide) monohydride similar to 4.17 were unsuccessful. The length of time required to fully convert 4.16 to 4.17 (7 days) suggests that access to the rhodium centre is sterically restricted so the bulky tert-butyl group would be inhibited by increased steric repulsion. For instance a far less sterically encumbered rhodium centre provides much quicker access to both the acetylide complex and the bis(acetylide) monohydride.\textsuperscript{194} Alternatively, the solid-state molecular structure of 4.17 indicates limited steric interaction between the isopropyl substituents and the alkyne; therefore, the differences in reactivity may be attributed to the decreased acidity of the terminal hydrogen on tert-butylacetylene (pKa values of 23.2 vs. 25.5).\textsuperscript{195}
Figure 4.7. Solid-state molecular structure (ORTEP) of \((\text{PCP})\text{RhH}(\text{CCPh})_2\) (4.17). All hydrogen atoms except H100 have been omitted for clarity. The hydride ligand was located in the crystal structure and refined isotropically. Selected bond lengths (Å) and angles (°): C1-Rh1, 2.034(3); P1-Rh1, 2.2742(7); Rh1-H100, 1.62(4); C1-N1, 1.353(2); Rh1-C28, 2.034(2); C1-Rh1-H100, 180.000(17); P1-Rh1-P2, 175.74(3); C36-Rh1-C28, 176.59(12); C1-Rh1-P1, 87.868(16); C1-Rh1-C28, 91.70(6); P1-Rh1-H100, 92.132(16).

4.5 **Intramolecular \(\text{C-P}\) Bond Activation of \((\text{PCP})\text{RhL}\) \((L = \text{H, CH}_3)\)**

Many transition metal mediated catalytic processes require elevated reaction temperatures, for this reason the thermal reactivity of \((\text{PCP})\text{RhH}\) (4.6) was investigated. Monitoring a solution of 4.6 in \(d_6\)-benzene at 60 °C by NMR shows a disappearance of the hydride signal after 24 hours. The \(^{31}\text{P}\{^1\text{H}\}\) spectrum of the product contains two doublets of doublets at 53.7 ppm \((J_{\text{RhP}} = 97 \text{ Hz}, J_{\text{PP}} = 31 \text{ Hz})\) and 38.3 ppm \((J_{\text{RhP}} = 86 \text{ Hz}, J_{\text{PP}} = 31 \text{ Hz})\), which indicates two inequivalent phosphorous nuclei \(\text{cis}\) coupled to each other and also coupling to rhodium. This information rules out \(\text{C-H}\) activation of the
benzene solvent, similar to the PNP system shown in Scheme 4.1 as a possible explanation for the observed reactivity. Fortunately, slow evaporation of a concentrated THF solution of the product provided crystals suitable for X-ray diffraction. The solid-state molecular structure confirms the loss of symmetry anticipated by the NMR analysis and the formation of a new rhodium complex resulting from intramolecular C-P bond activation of the PCP ligand (Figure 4.8).

**Figure 4.8.** Solid-state molecular structure (ORTEP) of (PCC)Rh[HP(Pr)_2] (4.18). All hydrogen atoms except H100 have been omitted for clarity. Selected bond lengths and bond angles are listed in Table 4.1.

A possible mechanism of formation of this product is outlined in Scheme 4.2. The elevated temperature must provide enough activation energy to cleave the P-C bond, leading to oxidative addition. Attraction between the resulting phosphide and the metal hydride combined with the affinity of our rhodium system to be in the first oxidation state triggers reductive elimination giving 4.18. Transition metal mediated C-P bond activation
has previously been observed experimentally\textsuperscript{106-199} but this represents the first example, to the best of our knowledge, of this type of ligand rearrangement in a tridentate array.

**Scheme 4.2.** Mechanistic proposal for the thermal rearrangement of (PCP)RhH to (PCC)Rh[HP(\textsuperscript{i}Pr)\textsubscript{2}].

The initial concern following this discovery was that this particular pincer ligand would be too thermally unstable to allow for practical catalytic opportunities. For this reason several other species from the library of rhodium complexes were exposed to the same conditions including (PCP)RhL (L = Cl, CH\textsubscript{3}, NH\textsubscript{2}). The only one that displayed similar reactivity was the methyl derivative. It too underwent C-P bond activation to generate (PCC)Rh[CH\textsubscript{3}P(\textsuperscript{i}Pr)\textsubscript{2}] (4.19); the solid-state molecular structure is shown in Figure 4.9. The only difference between the two structures, 4.18 and 4.19, is the extent to which the phosphine deviates from the square plane in the methyl case. This is likely to help reduce the steric repulsion with the bulkier methyl substituent. In order to further probe the mechanism reaction kinetics were studied by following the rate at which the
Figure 4.9. Solid-state molecular structure (ORTEP) of (PCC)Rh[CH\textsubscript{3}P(\textsuperscript{3}Pr)\textsubscript{2}] (4.19). All hydrogen atoms except those on C28 have been omitted for clarity. Selected bond lengths and bond angles are listed in Table 4.1.

product develops in the $^{31}$P\{\textsuperscript{1}H\} NMR spectrum. The rhodium hydride rearranges to 4.18 at an average rate constant of $k = 4.7 \times 10^{-5}$ s$^{-1}$ with a half life of 3.9 h that is independent of concentration, indicating first order reaction kinetics (Figure 4.10). Unfortunately the conversion of 4.8 to 4.19 does not proceed cleanly enough to obtain reliable kinetic data. However, the ligand rearrangement reaction in the case of the methyl complex 4.8 proceeds in about half the time (12 h) required to convert the hydride 4.6 to 4.18 (22 h). This suggests the ability to alleviate steric repulsion between the isopropyl groups and the ligand trans to the NHC helps drive this reaction.
Table 4.1. Selected bond lengths (Å) and angles (°) for the C-P bond activation products 4.18 and 4.19.

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<td>89.87(9)</td>
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4.6 Reactivity of (PCP)RhL

4.6.1 Attempted C-H Bond Activation

Although the initial goal of synthesizing a cationic rhodium dihydride complex to examine C-H bond activation was not met, the rhodium hydride 4.6 does have two coordination sites available to promote oxidative addition reactions. The dehydrogenation enthalpy of cyclooctane (COA) is one of the lowest among alkanes at 23.3 kcal/mol\textsuperscript{106} making COA an excellent test substrate. When excess COA was added to a solution of 4.6 and heated at temperatures up to 110 °C no dehydrogenation products are observed in the \textsuperscript{1}H NMR spectra, instead the formation of the C-P bond activation product 4.17 was detected. Although this would seem to support the theory that it may not be possible to explore the reactivity of (PCP)RhH at elevated temperatures, successful catalytic conversions above ambient temperature with 4.6 will be discussed later. Interestingly (PCP)RhH is also unreactive under an atmosphere of ethylene gas, further evidence that the complex degradation pathway uncovered with the cationic nickel hydride 2.5 is the atypical case. To investigate hydrogenation of unsaturated hydrocarbons the rhodium trihydride 4.7 was generated under an atmosphere of H\textsubscript{2} in the presence of cyclohexene. Again no reaction was observed in the \textsuperscript{1}H NMR spectra under any conditions, likely a cause of the required H\textsubscript{2} atmosphere forcing formation of the trihydride. In an effort to install functionalization to simple hydrocarbons the hydroxide complex 4.15 was exposed to both methane and ethylene gas; however, in each case the rhodium complex remains intact.
4.6.2 Reactivity of (PCP)RhNH$_2$ with Small Molecules

Monomeric terminal amido species similar to 4.14 are generally quite unstable which is thought to be a result of the incompatibility of the ‘soft’ metal acid and the ‘hard’ nitrogen donor.$^{189,200}$ This is especially true for low oxidation state late transition metals where an empty d$\pi$ orbital is not be available for delocalization of the lone pair on the nitrogen atom.$^{201}$ This decrease in electron delocalization can afford enhanced reactivity of the amido ligand and given that these types of complexes are relatively rare reactivity information is scarce. Therefore, it was important to examine the capacity of 4.14 to undergo further reactivity with a variety of small molecules that may be able to gain access to the sterically protected amido moiety. Scheme 4.3 summarizes the attempted small molecule activation with the rhodium amido complex 4.14.

**Scheme 4.3.** The scope of reactions that were attempted with (PCP)RhNH$_2$.

Several of the reagents shown above did not lead to any new or identifiable products, these include: ethylene, dioxygen, benzonitrile and benzaldehyde. Attempts to deprotonate the amido group with methyl lithium in hopes of generating an anionic
rhodium imido complex provided instead the previously synthesized methyl compound 4.8 (eq 4.12). The formation of 4.8 can be rationalized based on computational data that finds the Rh-C bond is approximately 225 kJ/mol stronger than the Rh-N bond.  

\[
\text{Reaction with hydrogen gas converted 4.14 back to the rhodium hydride species 4.6 as seen through the emergence of the diagnostic hydride peak as well as ammonia (-0.15 ppm, t, } J_{\text{NH}} = 44 \text{ Hz) in the } ^1\text{H NMR spectrum. This outcome was confirmed by reacting 4.14 with deuterium gas to give (PCP)RhD. Of note the monohydride species was only observable upon releasing the excess H}_2 \text{ in the system as this was generating the trihydride 4.7. Attempts to run the reverse reaction and produce the rhodium amido complex via reaction of 4.6 under an atmosphere of ammonia were unsuccessful. A similar outcome was found by reaction of the monoanionic PCP ruthenium system 4.10 with hydrogen gas, giving a new ruthenium hydride and ammonia. The proposed mechanism for this transformation involves activation of the H-H bond followed by 1,2-addition of the dihydrogen unit and finally loss of NH}_3 \text{. A similar mechanistic route is proposed to explain the reaction between 4.14 and hydrogen gas (Scheme 4.4). }
\]

Considering complex 4.6 converts to the trihydride 4.7 under H₂ the possibility of oxidative addition to give (PCP)RhH₂(NH₂) preceding the loss of ammonia must be
considered, although examples of reductive elimination of N-H bonds by d^6 metals are rare.\textsuperscript{98,204}

**Scheme 4.4.** Proposed mechanism for the formation of (PCP)RhH via reaction of the terminal amido complex (PCP)RhNH\textsubscript{2} and H\textsubscript{2}.

Addition of one equivalent of acetonitrile to complex 4.14 yielded the alkyl cyanide complex (PCP)RhCH\textsubscript{2}CN (4.20) shown in Scheme 4.5. The formation of Rh-CH\textsubscript{2}CN bonds have been reported before and shown to be quite stable.\textsuperscript{205} The methylene group is identifiable in the \textsuperscript{1}H NMR spectrum as a doublet of triplets at 1.04 ppm (\textsuperscript{2}J\textsubscript{RhH} = 2.5 Hz, \textsuperscript{3}J\textsubscript{HP} = 7 Hz) that is not present in the analogous reaction of 4.14 with CD\textsubscript{3}CN. The amido group of a Ru(H)(NH\textsubscript{2})(dmpe)\textsubscript{2} complex (dmpe = 1,2-bis(dimethylphosphino)ethane) has been shown to behave as a nucleophile in deprotonating organic C-H bonds followed by the loss of NH\textsubscript{3}.\textsuperscript{206} The authors have been able to isolate a variety of intermediate cationic ruthenium ammonia complexes after the
deprotonation step. Based on these findings the reaction between (PCP)RhNH₂ and CH₃CN is believed to proceed via a similar cationic intermediate, although it could not be observed experimentally (Scheme 4.5). A similar pathway can be envisioned for the reaction of 4.14 with phenylacetylene mentioned in section 4.4.

**Scheme 4.5.** Possible mechanism of formation of the rhodium alkyl cyanide complex following deprotonation by the lone pair of the terminal amido on 4.14.

![Diagram](image)

The final reagent, BH₃(THF) was of particular interest due to the presence of an electron deficient boron atom that requires stabilization by one molecule of THF. When a slight excess of BH₃(THF) was syringed into a purple solution of 4.14, a colour change to dark green reminiscent of (PCP)RhH (4.6) was observed within 10 minutes of the addition. The NMR spectrum of the final product confirmed that the parent amido 4.14 had indeed been completely converted to 4.6. This was clearly evident in the $^{31}$P{¹H} NMR spectrum for which both compounds are known and easily differentiated as $\Delta \delta = 22$ ppm. In addition the distinct hydride symbol of 4.6 was observed once again in the $^1$H NMR spectrum. Two possible pathways to explain this result are shown in Scheme 4.6, the possibility of oxidative addition of a B-H bond was considered rather unlikely since very little experimental evidence is available in the case of Lewis base stabilized boranes.²⁰⁷,²⁰⁸
Scheme 4.6. Two possible pathways leading to (PCP)RhH from 4.14 and BH₃(THF).

Pathway A is comparable to that seen between 4.14 with dihydrogen owing to the ability of B-H bonds to participate in similar side-on ($\eta^2$) binding through back donation from the metal into the empty p-orbital on boron.⁰⁹ Although the above reaction with borane proceeds too quickly to observe intermediates several well-characterized examples of 2-electron 3-centre transition-metal B-H bonding have been reported.²¹⁰-²¹⁴

As for pathway B, the nucleophilic amido ligand could replace the THF molecule in stabilizing the empty p-orbital of the boron followed by a $\beta$-hydride elimination to give 4.6. Unfortunately there was no deuterium labelling experiment that could be envisioned to help distinguish these two proposals. The similarities between this reaction and the dehydrogenation of ammonia borane led us to explore the capabilities of the rhodium system as a possible hydrogen releasing catalyst.
4.7  Dehydrogenation of Ammonia Borane

In recent years a significant amount of research has been aimed towards the ability to store hydrogen in a high-density form from which it can be released upon demand for use as a clean fuel source.\textsuperscript{215} For this purpose ammonia borane (H\textsubscript{3}N\cdotBH\textsubscript{3}), which contains both protic N-H and hydridic B-H bonds, has received considerable attention as a possible fuel source because of its high potential capacity of 19.6 wt. % H\textsubscript{2}.\textsuperscript{216} Taking into account that reaction of (PCP)RhNH\textsubscript{2} (4.14) with BH\textsubscript{3}(THF) proceeds to give the rhodium hydride 4.6 and the reported success of group 9 metals in the dehydrogenation of amine boranes,\textsuperscript{217,218} it was decided to investigate how effective (PCP)RhH might be for releasing H\textsubscript{2}. Initial test reactions between 4.6 and H\textsubscript{3}N\cdotBH\textsubscript{3} (AB) resulted in immediate vigorous gas evolution. Following addition of a 10 equivalent excess of AB and allowing sufficient time for gas evolution to cease the \textsuperscript{11}B NMR spectrum reveals complete consumption of the AB and the appearance of signals consistent with dehydrogenation products reported previously,\textsuperscript{217,219,220} as well as a new product exhibiting an unfamiliar \textsuperscript{11}B NMR shift (Figure 4.11).
Although the compound giving rise to the peak at -40 ppm in the $^{11}$B NMR spectrum shown above has not been isolated, information about the nature of this species has been gained experimentally. Reaction of 4.6 with BH$_3$(THF) or the chloride 4.5 with NaBH$_4$ results in the formation of the same product according to $^1$H and $^{31}$P{$^1$H} NMR spectroscopy (Scheme 4.7), each with a $^{11}$B NMR signal at approximately -40 ppm. The $^1$H NMR spectrum contains two resonances in the hydride region, one broad at -5.5 ppm (H$_a$) and one sharp multiplet at -7.3 ppm (H$_b$) integrating to one proton each. A very broad resonance can also be located from 0 to -1 ppm assignable to the two terminal hydrogens on the quadrupolar boron nucleus (Figure 4.12). The unusual $\sigma$(B-H) bonding mode in complex 4.21 is inferred based on comparison with the bis(phosphinite) system ($t$BuPOCOP)IrH$_2$ shown in Scheme 4.7, which forms a similar complex under the same conditions and has been structurally characterized.\textsuperscript{213}
Scheme 4.7. Synthesis of our postulated PCP rhodium σ borane complex 4.21 and the previously reported POCOP iridium system 4.24.

The side-on bound iridium borane complex 4.24 was detected during ammonia borane dehydrogenation experiments after long reaction times, although its exact structure was unknown at the time.\textsuperscript{218} The solid-state molecular structure was determined using neutron diffraction and the distance of 1.74(5) Å between the boron atom and the cis-hydride suggests the BH\textsubscript{3} moiety is stabilized by a noncovalent interaction with the adjacent H atom.\textsuperscript{213} Tests have shown this complex to be a dormant catalytic state and therefore, complex 4.21 is expected to be a cause of catalyst deactivation in our systems.
The mechanism by which transition metals dehydrogenate ammonia borane is the subject of much research,\textsuperscript{207,209,221,222} and still not well understood. The number of dehydrogenation products resulting from reaction of \textbf{4.6} with AB is a testament to the how complicated this process can be. Of particular interest was information about the quantity of gas a catalytic amount of \textbf{4.6} was able to liberate from AB. For this a THF solution of AB was syringed into a closed system containing 2 mol\% of (PCP)RhH and equipped with a glass gas syringe. Over a span of 3.5 hours an increase in volume of 15 mL was trapped by the syringe. This equates to 0.7 equivalents of the available H\textsubscript{2} which is just slightly below the capabilities of the best transition metal complexes reported, although at a slower rate.\textsuperscript{218,223,224} The one outstanding example is a Ni-NHC catalyst capable of releasing up to 2.8 equivalents of H\textsubscript{2}.\textsuperscript{225} These preliminary results are quite promising and could likely be improved upon as the production of H\textsubscript{2} in the closed system would move the equilibrium between \textbf{4.6} and \textbf{4.7} (eq. 4.5) in favour of the rhodium trihydride and impede catalytic activity.
4.8 Hydrosilylation of Alkynes

The successful activation of terminal alkynes by (PCP)RhH in combination with the reported\(^9\) catalytic hydrosilylation of alkynes using the related NHC-containing PCP rhodium complexes 1.27-1.29 described in Chapter 1 led us to explore this area of reactivity. As the generally accepted mechanism of hydrosilylation begins with oxidative addition of the silane to the metal, it is perceived that the (PCP)RhH system should be perfectly suited for entry into the catalytic cycle. The subsequent steps include insertion of the alkyne into a M-H (Chalk-Harrod mechanism\(^226\)) or M-Si (modified Chalk-Harrod mechanism\(^227\)) bond, followed by reductive elimination. The gas evolution observed upon addition of the silane to 4.6 suggests a mechanism of the latter type (Scheme 4.8).

**Scheme 4.8.** Anticipated mechanistic pathway for the hydrosilylation of alkynes by (PCP)RhH showing the Rh-Si insertion. Only the E-isomer is shown for simplicity.

Preliminary tests with dimethylphenylsilane and phenyl acetylene as substrates indicated the presence of a catalytic cycle; however, the selectivity and overall reaction times were somewhat disappointing (Table 4.2). Taking into account the steric demands already well understood for the PCP ligand set, the less bulky phenyl silane was
substituted into the reaction, which resulted in lower temperatures and shorter reaction times to achieve good conversions as outlined in Table 4.2.

**Table 4.2.** Product ratios following hydrosilylation of terminal alkynes catalyzed by (PCP)RhH. All samples were run in either C₆D₆ or d₈-Tol. Product ratios are based on integration of the corresponding NMR spectra.

\[
\begin{align*}
R-\equiv H &+ \text{PhR'}_2\text{SiH} \xrightarrow{\text{cat.}} R\text{SiR'}_2\text{Ph} + R\equiv\text{SiR'}_2\text{Ph} + \text{PhR'}_2\text{Si} \\
\text{trans} &+ \text{cis} & \text{R} & \alpha
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>R =</th>
<th>R' =</th>
<th>mol% cat.</th>
<th>Conditions: Temp. (°C) Time</th>
<th>trans</th>
<th>cis</th>
<th>α</th>
<th>Conversion (%)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>Me</td>
<td>2</td>
<td>100, 22 hr</td>
<td>50</td>
<td>37</td>
<td>9.8</td>
<td>100⁰</td>
</tr>
<tr>
<td>2</td>
<td>Ph</td>
<td>H</td>
<td>2</td>
<td>60, 40 min</td>
<td>93</td>
<td>0</td>
<td>7</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>Ph</td>
<td>H</td>
<td>0.5</td>
<td>60, 1.5 hr</td>
<td>79</td>
<td>0</td>
<td>21</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>tBu</td>
<td>H</td>
<td>2</td>
<td>60, 2 hr</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>tBu</td>
<td>H</td>
<td>2</td>
<td>60, 18 hr</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>16</td>
</tr>
</tbody>
</table>

²Conversion based on limiting reagent whether it be silane or alkyne.

Table 4.2 Continued.

Clearly the bulkiness of both the silane and the alkyne play a role in the overall catalytic activity. Most noticeable is the complete absence of the cis isomer as a product in entries 2-5. Secondly the more sterically demanding alkyne tert-butylacetylene results in a drastic decrease in vinylsilane production as evident by the very low conversion percentage. These results coincide with the previously discussed results where only one tert-butyl acetylide unit could be coordinated to the rhodium centre unlike the Rh(III) complex (4.17) formed with excess phenylacetylene. Although these results do not provide improvement in terms of stereoselectivity or yield over the best reported catalyst,²²⁸ the omission of a cis product does imply the rearrangement step required to produce this isomer does not take place in our system.²²⁹
Interestingly in the case of the 1-hexyne products the α isomer has not been reported previously and thus this, to the best of our knowledge, is the first report of its synthesis. Although spectroscopic data are unavailable in the literature for this compound its presence is supported by NMR data provided for the parallel 1-octyne reactions as well as the small (~3 Hz) coupling constant of the vinylic protons and GC-MS data. The regio and stereoselectivity of hydrosilylation with PhSiH₃ has been shown to be dependent on conditions such as solvent, temperature, and substrate ratio. When entry 2 was run with d₈-THF in place of C₆D₆ no differences were noticed between reaction times or selectivity. As well, performing these reactions at room temperature only had the effect of slowing the time required for complete conversion. Finally various substrate ratios were employed and seemed to have little impact on the amount of each vinylsilane produced.

4.9 Conclusions

The synthesis of the mononuclear rhodium chloride supported by the PCP ancillary ligand was accomplished through coordination of the neutral tridentate donor. The bulky isopropyl substituents allow for the stabilization of reactive small molecules in the coordination site trans to the NHC, including a rare Rh(I) amido complex. Although the rhodium hydrides and were unsuccessful in the hydrogenation/dehydrogenation of hydrocarbons, (PCP)RhH proved to be capable of activating the C-H bond of terminal alkynes. The rhodium monohydride demonstrated catalytic activity in the dehydrogenation of ammonia borane, a process with applications in hydrogen storage. The catalytic scope of was then extended for use in hydrosilylation reactions, an important source of valuable vinylsilanes for organic
synthesis. The ability of 4.6 to remain active at elevated temperatures suggests the intramolecular C-P bond activation reported is not problematic in the case of active catalytic conversions.

4.10 Experimental Section

General Considerations. All reactions were performed by standard Schlenk techniques in an oxygen-free nitrogen atmosphere unless otherwise noted. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on either a Bruker AV-400 instrument operating at 400.2 MHz or a Bruker AV-300 instrument operating at 300.13 MHz. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. Organic solvents were purchased anhydrous from Aldrich, sparged with nitrogen, and passed through columns containing activated alumina and molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, and dried over activated 3 Å molecular sieves prior to use. Gases were removed by three freeze-pump-thaw cycles. Elemental analysis and mass spectrometry (GC/MS) were performed at the Department of Chemistry at the University of British Columbia. The synthesis of the PCP ligand\textsuperscript{232} and $[\text{Rh(COD)Cl}]_2$\textsuperscript{233} have been previously reported. Ammonia borane and BH$_3$(THF) were purchased from Aldrich and used as received. Dimethylphenylsilane, Phenylsilane, Phenylacetylene, tert-Butylacetylene, and 1-Hexyne were purchased commercially and distilled over activated 3 Å molecular sieves then degassed.

$\left[\text{(PCP)}_2\text{Rh}_2\text{Cl}_2(\mu-\text{Cl})_2\right]\left[\text{PF}_6\right]$ (4.4). A Schlenk flask was charged with $\left[\text{(PCP)H}\right][\text{PF}_6]$, 2.1 (75 mg, 0.13 mmol), and $[\text{Rh(COD)Cl}]_2$ (30.8 mg, 0.062 mmol) in THF (5 mL). The resulting yellow solution was left to stir for 1 h and then the volume was reduced until the first sign of precipitation. At this point the mixture was warmed to dissolve any
precipitate and the solution was slowly cooled to -35 °C providing yellow crystals of 4.4 that were collected upon filtration. Yield: 28 mg (45%). \(^1\)H NMR (d\(_8\)-THF, 300.13 MHz, 298 K): \(\delta\) 8.25 (m, 2H, CH), 7.76 (t, \(J_{HH} = 7.1\) Hz, 2H, CH), 7.61 (m, 4H, CH), 4.18 (br, 4H, CH\(_2\)), 2.64 (br, 4H, CH), 1.30 (m, 24H, CH\(_3\)). \(^3\)P\(_{\{^1\}H}\) NMR (d\(_8\)-THF, 121.5 MHz, 298 K): \(\delta\) 25.44 (d, \(J_{RhP} = 143.9\) Hz), -143.00 (sep).

**(PCP)RhCl (4.5).** A mixture of 2.2 (660 mg, 1.45 mmol) and [Rh(COD)Cl]\(_2\) (325 mg, 0.659 mmol) in THF (10 mL) was allowed to stir for 30 min. At this point the reaction mixture had changed from a dark brown to a deep red solution. The solvent was then evaporated and a suspension was obtained by adding 10 mL of ether. Filtration of the precipitate and further washing with ether provided the product as a red powder. Yield: 560 mg (78%). X-ray quality crystals were formed by slow evaporation of a concentrated THF solution. \(^1\)H NMR (C\(_6\)D\(_6\), 300.13 MHz, 298 K): \(\delta\) 7.35 (m, 2H, CH), 7.16 (m, 2H, CH), 6.90 (t, \(J_{HH} = 7.3\) Hz, 2H, CH), 6.58 (d, \(J_{HH} = 7.3\) Hz, 2H, CH), 3.07 (s, 4H, CH\(_2\)), 2.36 (m, br, 4H, CH), 1.34 (m, 24H, CH\(_3\)). \(^{13}\)C\(_{\{^1\}H}\) NMR (C\(_6\)D\(_6\), 100.6 MHz, 298 K): \(\delta\) 201.51 (m, Rh-C), 148.12 (t, \(J_{CP} = 6.1\) Hz), 130.95 (s), 129.34 (s), 122.38 (s), 121.48 (t, \(J_{CP} = 11.3\) Hz), 117.63 (s), 49.95 (s), 25.33 (t, \(J_{CP} = 10.8\) Hz), 19.17 (s), 18.29 (s). \(^3\)P\(_{\{^1\}H}\) NMR (C\(_6\)D\(_6\), 121.5 MHz, 298 K): \(\delta\) 22.42 (d, \(J_{RhP} = 142.57\)). Anal. Calcd. C\(_{27}\)H\(_{46}\)N\(_2\)P\(_2\)ClRh: C 54.72; H 6.75; N 4.72. Found: C 54.98; H 6.77; N 4.74.

**(PCP)RhH (4.6).** To a stirred solution of 4.5 (335 mg, 0.566 mmol) in 5 mL toluene was added KBEt\(_3\)H (85 mg, 0.616 mmol). A colour change from red to dark green is observed upon stirring for 10 min. The reaction was allowed to proceed for 30 min total. Filtration through Celite followed by evaporation of all volatiles provided a dark green powder. Yield: 242 mg (77%) \(^1\)H NMR (C\(_6\)D\(_6\), 300.13 MHz, 298 K): \(\delta\) 7.39 (m, 2H, CH), 7.19
(m, 2H, CH), 6.94 (t, \( J_{HH} = 7.3 \) Hz, 2H, CH), 6.67 (d, \( J_{HH} = 7.7 \) Hz, 2H, CH), 3.17 (s, 4H, CH\(_2\)), 2.22 (m, 4H, CH), 1.21 (m, 24H, CH\(_3\)), -4.13 (dt, \( J_{RHH} = 15 \) Hz, \( ^2J_{HP} = 22 \) Hz, RhH). \(^{13}\)C\(^{1}\)H NMR (C\(_6\)D\(_6\), 100.6 MHz, 298 K): \( \delta \) 209.68 (m, Rh-C), 149.53 (t, \( ^2J_{CP} = 6.5 \) Hz), 131.49 (s), 129.16 (s), 121.81 (s), 121.11 (t, \( J_{CP} = 9.3 \) Hz), 117.76 (s), 48.76 (s), 24.61 (t, \( J_{CP} = 11.1 \) Hz) 18.76 (s), 18.33 (s). \(^{31}\)P\(^{1}\)H NMR (C\(_6\)D\(_6\), 121.5 MHz, 298 K): \( \delta \) 49.23 (d, \( J_{RhP} = 151.59 \)). Anal. Calcd. C\(_{27}\)H\(_{41}\)N\(_2\)P\(_2\)Rh: C 58.10; H 7.35; N 5.02. Found: C 57.58; H 7.39; N 4.61.

(\textit{PCP})\textit{RhH}_3 (4.7). A J-Young NMR tube is charged with 4.6 (10 mg, 0.0179 mmol) and d\(^8\)-Toluene (0.75 mL). The solution is then degassed via one freeze-pump-thaw cycle and exposed to an atmosphere of hydrogen gas (1 atm) and sealed. \(^1\)H NMR (d\(^8\)-Tol., 400.2 MHz, 230 K): \( \delta \) 7.23 (m, br, 2H, CH), 7.14 (m, br, 2H, CH), 7.01 (m, br, 2H, CH), 6.62 (m, br, 2H, CH), 3.11 (s, br, 4H, CH\(_2\)), 2.07 (m, br, 4H, CH), 1.15 (m, br, 24H, CH\(_3\)), -8.58 (q, 2H, RhH), -10.27 (m, br, 1H, RhH). \(^{31}\)P\(^{1}\)H NMR (d\(^8\)-Tol., 161.7 MHz, 260 K): \( \delta \) 61.69 (d, \( J_{RhP} = 106.6 \) Hz).

(\textit{PCP})\textit{RhCH}_3 (4.8). To a stirring solution of 4.5 (80 mg, 0.135 mmol) in 5 mL of toluene at 0 °C was added 0.085 mL of MeLi in (1.6 M, 0.136 mmol) drop wise via syringe. This resulted in an immediate colour change from red to dark grey. Allowing the mixture to stir for 30 min followed by filtration and evaporation of solvents provided the product as a dark grey powder. Yield: 42.5 mg (55%). \(^1\)H NMR (C\(_6\)D\(_6\), 300.13 MHz, 298 K): \( \delta \) 7.47 (m, 2H, CH), 7.18 (m, 2H, CH), 6.94 (t, \( J_{HH} = 7.3 \) Hz, 2H, CH), 6.62 (d, \( J_{HH} = 8.2 \) Hz, 2H, CH), 3.12 (s, 4H, CH\(_2\)), 2.44 (m, br, 4H, CH), 1.26 (m, 24H, CH\(_3\)), 0.55 (dt, \( ^2J_{RHH} = 1.5 \) Hz, \( ^3J_{HP} = 6.5 \) Hz, 3H, RhCH\(_3\)). \(^{13}\)C\(^{1}\)H NMR (C\(_6\)D\(_6\), 100.6 MHz, 298 K): \( \delta \) 204.3 (m, Rh-C\(_{NHC}\)), 148.68 (t, \( ^2J_{CP} = 6.8 \) Hz), 130.74 (s), 129.09 (s), 122.11 (t, \( J_{CP} = 9.9 \) Hz)
121.84 (s), 117.77 (s), 49.22 (s), 25.41 (t, $J_{CP} = 9.9$ Hz), 19.38 (s), 18.88 (s), -10.0 (m, Rh-CH$_3$). $^{31}$P($^1$H) NMR (C$_6$D$_6$, 121.5 MHz, 298 K): $\delta$ 32.17 (d, $J_{RhP} = 154.1$ Hz). Anal. Calcd. C$_{28}$H$_{43}$N$_2$P$_2$Rh: C 58.74; H 7.57; N 4.89. Found: C 58.68; H 7.03; N 4.79.

[(PCP)RhNH$_3$][PF$_6$] (4.9). A mixture of 4.6 (315 mg, 564 mmol) and NH$_4$PF$_6$ (95 mg, 582 mmol) in 8 mL THF was left to stir at room temperature for 18 h. During this time the green solution had become bright orange and a precipitate had formed. Filtration of the suspension provided 4.9 as a bright orange powder. Yield: 320 mg (79%). X-ray quality crystals were grown by slow evaporation of a concentrated THF solution. $^1$H NMR (d$_8$-THF, 400.2 MHz, 298 K): $\delta$ 7.52 (m, 2H, CH), 7.48 (t, $J_{HH} = 7.4$ Hz, 2H, CH), 7.26 (d, $J_{HH} = 8.5$ Hz, 2H, CH), 7.22 (t, $J_{HH} = 7.5$ Hz, 2H, CH), 4.13 (s, 4H, CH$_2$), 2.47 (br, 3H, NH$_3$), 2.38 (m, br, 4H, CH), 1.22 (dd, $J_{HH} = 7.2$ Hz, $J_{HP} = 14.4$ Hz, 12H, CH$_3$), 1.16 (dd, $J_{HH} = 7.2$ Hz, $J_{HP} = 14.4$ Hz, 12H, CH$_3$). $^{13}$C($^1$H) NMR (d$_8$-THF, 100.6 MHz, 298 K): $\delta$ 145.9 (s), 128.69 (s), 127.86 (s), 121.77 (s), 118.35 (s), 117.53 (s), 48.85 (s), 23.67 (s), 16.57 (s), 16.11 (s). The Rh-C could not be located due to poor solubility. $^{31}$P($^1$H) NMR (d$_8$-THF, 161.9 MHz, 298 K): $\delta$ 33.53 (d, $J_{RhP} = 139.2$ Hz), -142.26 (sep). Anal. Calcd. C$_{27}$H$_{43}$N$_3$P$_3$F$_6$Rh: C 45.09; H 5.98; N 5.84. Found: C 44.89; H 5.99; N 5.82.

(PCP)RhNH$_2$ (4.14). To a stirring suspension of 4.9 (320 mg, 0.445 mmol) in toluene (8 mL) containing activated molecular sieves was added a slight excess of KN(Si(CH$_3$)$_3$)$_2$ (98 mg 0.492 mmol). An immediate colour change from bright orange to purple was observed and the reaction contents were allowed to stir for 60 min. At this time the solution was filtered through celite and all volatiles were removed under vacuum providing the desired product as a purple powder. Yield: 180 mg (71%). $^1$H NMR (C$_6$D$_6$, 400.19 MHz, 298 K): $\delta$ 7.37 (m, 2H, CH), 7.22 (t, $J_{HH} = 7.7$ Hz, 2H, CH), 6.97 (t, $J_{HH} =
7.4 Hz, 2H, CH), 6.77 (d, \( J_{HH} = 8.1 \) Hz, 2H, CH), 3.15 (s, 4H, CH\(_2\)), 2.31 (m, br, 4H, CH), 1.28 (m, 24H, CH\(_3\)) 1.04 (br, 2H, NH\(_2\)). \(^{13}\)C\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 100.6 MHz, 298 K): \( \delta \) 204.1 (m, Rh-C), 148.59 (t, \( J_{CP} = 6.3 \) Hz), 130.58 (s), 129.29 (s), 121.73 (s), 119.66 (t, \( J_{CP} = 10.9 \) Hz), 117.34 (s), 49.47 (s), 24.61 (t, \( J_{CP} = 10.2 \) Hz), 18.99 (s), 18.24 (s).

\(^{31}\)P\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 161.9 MHz, 298 K): \( \delta \) 25.72 (d, \( J_{RhP} = 151.1 \) Hz). Anal. Calcd. C\(_{27}\)H\(_{42}\)N\(_3\)P\(_2\)Rh: C 56.55; H 7.38; N 7.33. Found: C 56.70; H 7.24; N 6.98.

**(PCP)RhOH (4.15).** To a stirred solution containing 4.6 (75 mg, 0.134 mmol) in toluene (10 mL) was added degassed water (0.0024 mL, 0.134 mmol) and the solution was allowed to stir for 1 hour. At which point the green solution had turned burgundy in colour and all volatiles were removed under vacuum. This provided the product as a burgundy powder. Yield 57 mg (82%) \(^1\)H NMR (C\(_6\)D\(_6\), 400.2 MHz, 298 K): \( \delta \) 7.31 (m, 2H, CH), 7.21 (t, \( J_{HH} = 7.7 \) Hz, 2H, CH), 6.95 (t, \( J_{HH} = 7.3 \) Hz, 2H, CH), 6.63 (d, \( J_{HH} = 8.0 \) Hz, 2H, CH), 3.09 (s, 4H, CH\(_2\)), 2.27 (m, br, 4H, CH), 1.31 (m, 24H, CH\(_3\)) -0.43 (br, 1H, RhOH). \(^{13}\)C\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 100.6 MHz, 298 K): \( \delta \) 204.0 (m, Rh-C), 148.59 (t, \( J_{CP} = 6.2 \) Hz), 130.65 (s), 129.36 (s), 121.79 (s), 119.69 (t, \( J_{CP} = 11.0 \) Hz), 117.17 (s), 49.21 (s), 24.61 (t, \( J_{CP} = 10.3 \) Hz), 18.99 (s), 18.25 (s). \(^{31}\)P\{\(^1\)H\} NMR (C\(_6\)D\(_6\), 161.9 MHz, 298 K): \( \delta \) 22.73 (d, \( J_{RhP} = 150.7 \) Hz). Anal. Calcd. C\(_{27}\)H\(_{42}\)N\(_3\)P\(_2\)ORh: C 56.48; H 7.14; N 4.88. Found: C 55.11; H 6.60; N 4.60.

**(PCP)RhCCPh (4.16).** A mixture of 4.6 (65 mg, 0.116 mmol) and phenylacetylene (0.013 mL, 0.119 mmol) in benzene (5 mL) was allowed to stir for 1 h. At which point a colour change from green to deep red was observed and evaporation of all volatiles provided the product as a deep red powder. Yield 65 mg (85%). \(^1\)H NMR (C\(_6\)D\(_6\), 300.13 MHz, 298 K): \( \delta \) 7.76 (d, \( J_{HH} = 8.1 \) Hz, 2H, CH), 7.28 (m, 4H, CH), 7.16 (t, \( J_{HH} = 7.7 \) Hz,
2H, CH), 7.02 (t, $J_{HH} = 7.4$ Hz, 1H, CH), 6.69 (t, $J_{HH} = 7.4$ Hz, 2H, CH), 6.59 (d, $J_{HH} = 8.2$ Hz, 2H, CH), 3.10 (s, 4H, CH$_2$), 2.28 (m, br, 4H, CH), 1.36 (m, 24H, CH$_3$). $^{13}$C{${}^1$H} NMR (C$_6$D$_6$, 100.6 MHz, 298 K): $\delta$ 209.1 (m, Rh-C$_{NHC}$), 148.11 (t, $^2J_{CP} = 6.0$ Hz), 131.06 (s), 130.28 (s), 129.17 (s), 123.42 (s), 122.85 (s), 122.06 (t, $J_{CP} = 10.1$ Hz), 118.11 (s), 49.72 (s), 25.47 (t, $J_{CP} = 10.9$ Hz), 18.78 (s), 18.6 (s). $^{31}$P{${}^1$H} NMR (C$_6$D$_6$, 121.5 MHz, 298 K): $\delta$ 30.40 (d, $J_{RhP} = 138.4$ Hz). Anal. Calcd. C$_{35}$H$_{45}$N$_2$P$_2$Rh: C 63.86; H 6.84; N 4.26. Found: C 64.64; H 6.85; N 3.73.

trans-(PCP)RhH(CCPh)$_2$ (4.17). A solution of 4.16 (50 mg, 0.0760 mmol) and excess phenylacetylene (0.083 mL, 0.760 mmol) was left mixing for 7 days at room temperature. At which point X-ray quality crystals had crashed out of the solution. Decanting of the mother liquor provided yellow crystals of 4.17. Yield 30 mg (52%). $^1$H NMR (d$_8$-THF, 400.2 MHz, 298 K): $\delta$ 7.55 (br, 2H, CH), 7.41 (t, $J_{HH} = 7.2$ Hz, 2H, CH), 7.34 (m, 2H, CH), 7.23 (t, $J_{HH} = 7.3$ Hz, 2H, CH), 6.79 (t, $J_{HH} = 7.3$ Hz, 4H, CH), 6.71 (m, 2H, CH), 6.44 (d, $J_{HH} = 7.5$ Hz, 4H, CH), 4.48 (m, 2H, CH$_2$), 4.01 (m, 2H, CH$_2$), 2.80 (m, 4H, CH), 1.42 (dd, $J_{HH} = 7.2$ Hz, $J_{HP} = 15.6$ Hz, 6H, CH$_3$), 1.35 (dd, $J_{HH} = 7.7$ Hz, $J_{HP} = 16.8$ Hz, 6H, CH$_3$), 1.04 (dd, $J_{HH} = 5.5$ Hz, $J_{HP} = 11.5$ Hz, 6H, CH$_3$), 0.95 (dd, $J_{HH} = 7.4$ Hz, $J_{HP} = 14.9$ Hz, 6H, CH$_3$), -8.86 (q, $J_{RhH} \approx J_{HP} = 12.9$ Hz, 1H, RhH). $^{13}$C{${}^1$H} NMR (d$_8$-THF, 100.6 MHz, 298 K): $\delta$ 146.22 (t, $^2J_{CP} = 4.6$ Hz), 141.23 (s), 137.72 (s), 129.59 (s), 128.33 (s), 128.08 (s), 125.87 (d, 8.4 Hz), 120.89 (s), 120.22 (s), 119.48 (t, $J_{CP} = 16.7$ Hz), 118.03 (t, $J_{CP} = 7.5$ Hz), 48.62 (s), 19.95 (t, $J_{CP} = 14.1$ Hz), 17.36 (s), 16.53 (s), 14.27 (t, $J_{CP} = 4.5$ Hz), 13.42 (s). The Rh-C$_{NHC}$ could not be identified due to poor solubility of the product. $^{31}$P{${}^1$H} NMR (d$_8$-THF, 121.5 MHz, 298 K): $\delta$ 47.17 (d, $J_{RhP} = 92.9$ Hz). Anal. Calcd. C$_{43}$H$_{51}$N$_2$P$_2$Rh: C 67.89; H 6.76; N 3.68. Found: C 68.84; H 6.58; N 3.45.
(PCC)Rh[HP(tPr)2] (4.18). A J-Young NMR tube is charged with 4.6 (15 mg, 0.0269 mmol) in d^8-Toluene. The NMR tube is then immersed in an oil bath at 60 °C for 22 h at which point a precipitate is formed. The solution is decanted and the remaining product is dried under vacuum providing 4.18 as a purple powder. Yield: 13 mg (87%). X-ray quality crystals were grown through slow evaporation of a concentrated THF solution. \(^1\)H NMR (d^8-THF, 400.2 MHz, 298 K): \(\delta\) 7.78 (t, \(J_{HH} = 6.4\) Hz, 1H, CH), 7.48 (br, 1H, CH), 7.39 (t, \(J_{HH} = 7.3\) Hz, 2H, CH), 6.73 (m, 2H, CH), 6.42 (m, 1H, CH), 4.51 (m, 1H, PH), 4.13 (t, \(J_{HH} = 9.2\) Hz, 2H, CH\(_2\)), 3.78 (t, \(J_{HH} = 9.3\) Hz, 2H, CH\(_2\)), 2.56 (d of q, \(J_{HH} = 6.6\) Hz, \(J_{HP} = 13.3\) Hz, 2H, CH), 2.39 (d of q, \(J_{HH} = 6.7\) Hz, \(J_{HP} = 12.8\) Hz, 2H, CH), 1.40 (dd, \(J_{HH} = 7.1\) Hz, \(J_{HP} = 9.6\) Hz, 6H, CH\(_3\)), 1.25 (dd, \(J_{HH} = 7.3\) Hz, \(J_{HP} = 18.1\) Hz, 6H, CH\(_3\)), 1.15 (dd, \(J_{HH} = 7.0\) Hz, \(J_{HP} = 15.1\) Hz, 6H, CH\(_3\)), 1.10 (dd, \(J_{HH} = 6.9\) Hz, \(J_{HP} = 12.6\) Hz, 6H, CH\(_3\)). \(^{13}\)C\({^1}\)H NMR (d^8-THF, 100.6 MHz, 298 K): \(\delta\) 151.50 (s), 148.88 (d, 12.6 Hz), 140.37 (s), 133.29 (s), 122.59 (s), 122.30 (s), 120.94 (s), 117.64 (s), 117.41 (s), 117.21 (d, \(J_{CP} = 5.3\) Hz), 107.59 (s), 49.82 (s), 43.73 (s), 28.84 (d, \(J_{CP} = 17.1\) Hz), 26.19 (d, \(J_{CP} = 18.4\) Hz), 24.47 (s) 24.17 (d, \(J_{CP} = 12.6\) Hz), 20.68 (d, \(J_{CP} = 7.4\) Hz), 19.00 (s). The Rh-C\(_{NHC}\) and Rh-C\(_{ortho}\) could not be identified. \(^{31}\)P\({^1}\)H NMR (d^8-THF, 121.5 MHz, 298 K): \(\delta\) 52.33 (dd, \(J_{PP} = 30.3\) Hz, \(J_{RhP} = 127.9\) Hz), 36.91 (dd, \(J_{PP} = 30.4\) Hz, \(J_{RhP} = 116.6\) Hz). Anal. Calcd. C\(_{27}\)H\(_{41}\)N\(_2\)P\(_2\)Rh: C 58.10; H 7.35; N 5.02. Found: C 57.01; H 6.86; N 4.81.

(PCC)Rh[CH\(_3\)P(tPr)2] (4.19). Follows the same procedure as that for 4.18 starting with 4.8 (15 mg, 0.0262 mmol). The result is a black powder after 12 h of heating. Yield 7 mg (50%). \(^1\)H NMR (d^8-THF, 300.13 MHz, 298 K): \(\delta\) 7.78 (t, \(J_{HH} = 6.7\) Hz, 1H, CH), 7.57 (m, 1H, CH), 7.37 (t, \(J_{HH} = 7.7\) Hz, 2H, CH), 7.07 (m, 1H, CH), 7.00 (t, \(J_{HH} = 7.3\) Hz,
1H, CH), 6.75 (t, $J_{HH} = 6.7$ Hz, 2H, CH), 6.43 (d, $J_{HH} = 7.0$ Hz, 1H, CH), 4.14 (t, $J_{HH} = 9.1$ Hz, 2H, CH2), 3.75 (t, $J_{HH} = 8.9$ Hz, 2H, CH2), 2.51 (sep, $J_{HH} = 7.0$ Hz, 4H, CH), 1.26 (d, $J_{HP} = 4.6$ Hz, 3H, CH3), 1.14 (m, 24H, CH3). $^{13}$C{^1H} NMR (d8-THF, 100.6 MHz, 298 K): $\delta$ 150.00 (s), 148.48 (m), 139.06 (s), 137.59 (s), 132.65 (s), 130.09 (s), 128.81 (s), 128.06 (s), 125.18 (s), 121.15 (s), 119.42 (s), 115.76 (d, $J_{CP} = 4.6$ Hz), 106.48 (s), 48.94 (s), 42.89 (s), 28.10 (d, $J_{CP} = 15.0$ Hz), 27.09 (d, $J_{CP} = 17.1$ Hz), 22.15 (d, $J_{CP} = 12.3$ Hz), 19.76 (d, $J_{CP} = 9.3$ Hz), 18.44 (s), 17.72 (s), 6.61 (m, P-CH3). The Rh-CNHC could not be located. $^{31}$P{^1H} NMR (d8-THF, 121.5 MHz, 298 K): $\delta$ 40.12 (dd, $^{2}J_{PP} = 26.8$ Hz, $J_{RHP} = 119.6$ Hz), 27.24 (dd, $^{2}J_{PP} = 26.7$ Hz, $J_{RHP} = 130.2$ Hz). Anal. Calcd. C$_{28}$H$_{43}$N$_{2}$P$_{2}$Rh: C 58.77; H 7.52; N 4.90. Found: C 59.44; H 7.71; N 4.47.

(4.21). A scalable vessel equipped with a Kontes valve was charged with 4.5 (50.0 mg, 0.085 mmol), and NaBH$_4$ (3.8 mg, 0.100 mmol). The solids were dissolved in THF (8 mL) and the reaction mixture was left to stir at 60 °C for 4 h. After stirring the solution was filtered through Celite and all volatiles were removed under vacuum. This provided the product 4.21 as a dark yellow powder. Yield: 42.3 mg (87%). $^{1}$H NMR (d8-THF, 400.2 MHz, 298 K): $\delta$ 7.34 (m, 2H, CH), 7.30 (t, $J_{HH} = 7.6$ Hz, 2H, CH), 7.16 (d, $J_{HH} = 7.9$ Hz, 2H, CH), 7.10 (t, $J_{HH} = 7.4$ Hz, 2H, CH), 3.99 (m, 2H, CH$_2$), 3.52 (m, 2H, CH$_2$), 2.50 (m, 2H, CH), 2.01 (m, 2H, CH), 1.25 (m, 18H, CH$_3$), 0.93 (dd, $J_{HH} = 6.5$ Hz, $J_{HP} = 12.5$ Hz, 6H, CH$_3$), 0.50 (br, 2H, BH$_2$), 5.44 (br, 1H, BH), 7.14 (m, 1H, RhH). $^{13}$C{^1H} NMR (d8-THF, 100.6 MHz, 298 K): $\delta$ 150.04 (t, $^{2}J_{CP} = 6.2$ Hz), 132.00 (s), 130.44 (s), 123.63 (s), 123.32 (s), 123.00 (t, $J_{CP} = 15.0$ Hz), 50.84 (s), 31.79 (m), 24.49 (t, $J_{CP} = 11.9$ Hz), 22.18 (t, $J_{CP} = 6.1$ Hz), 20.02 (s), 16.83 (s). The Rh-CNHC could not be located. $^{31}$P{^1H} NMR (d8-THF, 121.5 MHz, 298 K): $\delta$ 45.45 (d, $J_{RHP} = 145.5$ Hz).
NMR (d₈-THF, 128.4 MHz, 298 K): δ -40.69 (br). Anal. Calcd. C₂₇H₄₄N₂P₂BRh: C 56.66; H 7.75; N 4.89. Found: C 55.53; H 7.48; N 3.69.

**Kinetic study on the conversion of (4.6) to (4.18).** A J-Young NMR tube was charged with 4.6 (8 mg, 0.0143 mmol) in exactly 0.75 mL of THF. The tube is then sealed and placed in an oil bath at 60 °C. The reaction progress is monitored by NMR and the concentration of the C-P activation product is determined by integration of the ³¹P{¹H} NMR spectrum by comparison with the peak belonging to 4.6.

**Quantification of H₂ evolution during AB dehydrogenation.** A two necked Schlenk is charged with 4.6 (10 mg, 0.0179 mmol) and sealed with two unused rubber septa. A glass gas syringe equipped with a long needle is then inserted into one of the septa and removed from the glovebox. The point of entry is sealed using a 5 min epoxy and sufficient time is allowed for pressure equilibration. At which point a syringe containing 27 mg of ammonia borane (0.871 mmol) in THF (5 mL) is inserted into the other neck and sealed with epoxy. The solution is then introduced to the system and stirred at which point gas evolution begins. A total volume of 15 mL gas was collected over a period of 3.5 h.

**General Procedure for the Catalytic Hydrosilylation of Terminal Alkynes.** In a typical procedure the appropriate catalyst loading of 4.6 is mixed with a solution of the appropriate silane (1-1.2 equiv.) and alkyne (1-1.2 equiv.) in 0.75 mL C₆D₆ and sealed in a J. Young NMR tube. The mixture was then placed in an oil bath and maintained at 60 °C for required amount of time for complete conversion of the limiting reagent. The reaction progress was monitored by ¹H NMR observing the distinct proton signal of the silane or the acetylynic hydrogen of the alkyne. GC/MS data was acquired following
removal of all volatiles and then re-dissolving the products in hexane and filtering off any insoluble material. Assignment of the trans-, cis- and α- isomers was based on literature comparison.\textsuperscript{228,229}
Chapter Five

Exploring the Coordination Chemistry of the PCP

Ligand with Iridium

5.1 Introduction

The catalytic conversion of alkanes to the corresponding alkenes is an important application of transition metal systems due to the versatility of alkenes as organic starting materials. The first metal complexes shown to activate the stoichiometric dehydrogenation of alkanes consisted of an iridium centre stabilized with tertiary phosphine ligands. This chemistry was later extended through the use of a hydrogen acceptor to the catalytic dehydrogenation of alkanes with the same iridium bis(phosphine) complexes. One drawback of these earlier systems was ligand decomposition as a result of the high temperatures required for activation of C-H bonds. To address this problem iridium complexes incorporating a more thermally robust pincer ligand (5.1) were investigated and displayed high activity with and without a sacrificial hydrogen acceptor. Further studies broadened the scope of alkane substrates reactive towards the tridentate systems by alteration of the phosphine substituents (5.2). An example of the high thermal-stability of these iridium complexes has been observed upon moving to a more rigid anthraphos ligand set where reaction temperatures up to 250 °C have been achieved without catalyst decomposition (5.3 in Figure 5.1).
More recently, tuning the phosphine donors to an iridium-bis(phosphinite) system 5.4 has led to higher turnover frequencies and less inhibition by the hydrogen acceptor.106,186

![Chemical Structures]

**Figure 5.1.** Iridium complexes incorporating pincer ligands capable of alkane dehydrogenation.

The mechanism of the acceptorless dehydrogenation of alkanes has been examined experimentally and computationally, the results support a dissociative mechanism via an Ir(III)/Ir(I) pathway as outlined in Scheme 5.1. The initial loss of H₂ is considered the rate-determining step and requires constant removal of the released hydrogen gas from the system.105 The transfer dehydrogenation mechanism utilizes an olefinic hydrogen acceptor (in this case tert-butylethylene or TBE) to abstract the hydrides from the iridium centre and generate the active 14-electron species (Scheme 5.1). The higher efficiency of the bis(phosphinite) system 5.4 can be attributed to a more electron deficient metal centre with a lower affinity for the added hydrogen acceptor: TBE is only π-bound to the metal centre versus oxidative addition in the earlier systems. As a result, TBE is only a weak inhibitor of the catalytically active species and high acceptor concentrations can be used.106
Scheme 5.1. Comparison between the mechanisms of acceptorless (left) and transfer (right) dehydrogenation of cyclooctane (COA) to cyclooctene (COE). The pincer ligands have been omitted for clarity.

Following the success of PCP iridium pincer complexes in the dehydrogenation of alkanes, it was of interest to examine how moving to complexes incorporating our NHC-derived PCP ligand may behave under similar conditions. The classification of NHCs as strong $\sigma$-donors and relatively poor $\pi$-acceptors should lead to an electron-rich metal centre, which is important in activating C-H bonds. Of particular interest would be to gain access to a cationic iridium system to examine how the electrophilicity of a positively charged complex may influence catalytic activity. As discussed in the introduction chapter, very few examples of NHC-containing pincer complexes of iridium have been reported and the work herein aims to broaden the scope of understanding of these types of complexes.

5.2 Coordination to Iridium

Although oxidative addition of the cationic $[\text{PCPH}][\text{PF}_6]$ ligand (2.1) did not yield a new metal hydride complex in the case of rhodium (eq. 4.2) this synthetic strategy has proven successful with other Ir NHC systems. These include the first example of a NHC
iridium hydride\textsuperscript{241} as well as an iridium hydride featuring an NHC in an abnormal binding mode,\textsuperscript{242} a pyridine based NHC system\textsuperscript{243} and even some iridium pincer complexes.\textsuperscript{100,244} The target compound for exploring C-H activation was a cationic iridium dihydride [(PCP)IrH\textsubscript{2}][PF\textsubscript{6}], which should be accessible from the hydrido-chloro complex shown in equation 5.1.

\begin{equation}
\text{In search of this cationic complex a THF solution of 2.1 was stirred with the iridium dimer [Ir(COD)Cl\textsubscript{2}} (eq. 5.2). The lack of a typical hydride resonance in the \textsuperscript{1}H NMR spectrum of the isolated product indicated that the reaction had not proceeded as shown above. Slow cooling a concentrated THF solution of the product to -35 °C provided crystals suitable for X-ray diffraction analysis in low yield. The crystallographic data revealed a cationic dinuclear iridium complex where each iridium atom is bound to one phosphine donor of the PCP ligand in addition to a terminal chloride and chelating COD molecule, while the iminium hydrogen remains intact (Figure 5.2).} \end{equation}
A similar coordination mode following reaction of \([\text{Ir(CODCl)}_2]\) with alkyldiisopropylphosphines has previously been reported\(^{245,246}\). As the dinuclear species \(5.5\) was not viewed as a step towards our target complex, further analysis was not pursued and instead the synthetic pathway that led to a mononuclear rhodium chloride complex was extended with the iridium starting material. Mixing a THF solution of the neutral PCP ligand \((2.2)\) and \([\text{Ir(COD)Cl)}_2]\) at ambient temperature resulted in a immediate colour change from dark brown to red. Acquisition of the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum after 30 minutes revealed complete consumption of the neutral PCP starting material and the emergence of a lone product observed as a singlet at 16.13 ppm. The expectation was that the product would be the Ir(I) chloride species \((\text{PCP})\text{IrCl}\), analogous

\[\text{IrCl(COD)}_2\{\text{PCHP}\}[\text{PF}_6] \quad (5.5)\]

### Figure 5.2

Solid-state molecular structure (ORTEP) of the cationic dinuclear iridium species \([\text{IrCl(COD)}_2\{\text{PCHP}\}[\text{PF}_6]\) \((5.5)\). The PF6 counterion and all hydrogen atoms except H1 have been omitted for clarity. No bond distances or angles are reported as the structure is meant to show atom connectivity.
to (PCP)RhCl 4.5. However, slow cooling a concentrated THF solution provided crystals suitable for X-ray diffraction analysis that revealed the Ir(III) complex 5.6 shown in Figure 5.3.

![Figure 5.3. Solid-state molecular structure (ORTEP) of (PCP)IrHCl2 (5.6). All hydrogen atoms except H1 have been omitted for clarity. The hydride ligand was located in the crystal structure and refined isotropically. Selected bond lengths (Å) and angles (°): C1-Ir1, 1.953(4); P1-Ir1, 2.3325(10); Ir1-P2, 2.3265(10); Ir1-Cl2, 2.5209(11); Ir1-Cl1, 2.4577(10); Ir1-H1, 1.78(4); C1-N1, 1.379(5); C1-N2, 1.374(5); P1-Ir1-Cl1, 96.88(4); P1-Ir1-Cl2, 90.20(4); P1-Ir-H1, 87.9(11); C1-Ir1-Cl1, 172.83(11); P1-Ir1-P2, 173.53(4); Cl2-Ir1-H1, 174.6(11), C1-Ir1-P2, 87.20(11).](image)

Compound 5.2 crystallizes in the monoclinic space group P2(1)/c displaying a slightly distorted octahedral geometry. The Ir1-C1 distance of 1.953(4) is similar to distances reported for another set of iridium NHC pincer complexes consisting of both a halide and a hydride ligand.\(^{244}\) Interestingly, the \(^1\)H NMR spectrum of the isolated product includes a hydride signal around -19.97 ppm (t, \(^2J_{HP} = 13.3\) Hz), however, integration of the spectrum reveals the Ir-H signal accounts for only about 5% of the product compared to the protons of the ligand backbone. Based on the stoichiometry of
the reaction the six-coordinate species 5.6 was not expected to be the major product and its origin is unclear. The $^1$H NMR spectrum revealed formation of the Ir(I) chloride species 5.7 constitutes approximately 95% of the product from the reaction shown in equation 5.3, which is simply less prone to crystallization. It is noteworthy that solid-state molecular structure data collected on a second recrystallization of the products in the reaction mixture containing 5.6 and 5.7 once again verified only the structure of the Ir(III) species 5.6.

Further evidence for the formation of (PCP)IrCl as the major product came upon exchange of the nitrogen atmosphere from the product mixture of equation 5.3 with hydrogen gas. The resulting $^1$H NMR spectrum indicated the presence of two inequivalent hydride resonances one at -9.70 ppm and another at -22.14 ppm (dt, $^2J_{HH} = 6.4$ Hz, $^2J_{HP} = 16.4$ Hz), and was accompanied by an overall reduction in symmetry. This arises from the oxidative addition of H$_2$ to form (PCP)IrClH$_2$ (5.8) with the hydride ligands situated cis to one another (Figure 5.4).

Attempts to synthesize the monohydride (PCP)IrH by reaction of 5.7 with KBE$_3$H were unsuccessful and led to the production of an appreciable amount of the iridium trihydride (vide infra). This is likely a consequence of the fact that NHC Ir(I) hydrides are rarely observed$^{110}$ and presumably quite reactive. Efforts to promote the synthesis of a single product (5.7) by performing the ligand coordination reaction in the presence of excess NEt$_3$ to remove any unwanted HCl were ineffective; likewise attempts
to selectively form 5.6 by addition of Et$_3$N·HCl to 5.7 were unsuccessful. The source of the hydride found on complex 5.6 remains unclear but it is believed to result from an impurity in the [Ir(COD)Cl]$_2$ starting material as incomplete deprotonation of the PCP ligand would give the isolated cation 5.5. The possibility of solvent acting as the hydride source has been ruled out, as the results are the same regardless of whether the reaction proceeds in deuterated or standard solvents.

![Chemical structures](image)

**Figure 5.4.** Selected region of the $^1$H NMR spectrum displaying hydride signals following reaction between 5.7 and H$_2$ gas giving 5.8. The small triplet at -20.2 ppm is assigned to the hydride of 5.6.

### 5.3 *Synthesis of PCPIrH$_3$*

As mentioned in the previous section attempts to convert the iridium monochloride 5.7 to (PCP)IrH with KBEt$_3$H provided instead an appreciable amount of what was identified as (PCP)IrH$_3$ 5.9. This reaction alone cannot convert all of 5.7 to the
trihydride complex as unreacted starting material was still observed in the $^{31}$P-$^1$H NMR spectrum. Therefore, a benzene solution of 5.7 was stirred with a slight excess of KBEt$_3$H under an H$_2$ atmosphere, which also converts any of the Ir(III) side product to the desired complex (eq 5.4). This resulted in a colour change from red to yellow over a period of one hour. At which point filtration followed by slow evaporation of a concentrated solution provided crystals suitable for X-ray diffraction analysis of (PCP)IrH$_3$ (5.9) (Figure 5.5).

This reaction resulted in what, to the best of our knowledge, is the first fully characterized example of an iridium trihydride supported by a NHC-containing tridentate ligand. The ability to isolate complex 5.9 shows a significant difference in stability of the M(III) oxidation state between 5.9 and the rhodium congener 4.7 (which could only exist under a hydrogen environment). Complex 5.9 crystallizes in the orthorhombic space group Pbcn with octahedral geometry. The PCP backbone is twisted along the Ir-C1 axis at a torsion angle of 30.77° above and below the plane. The Ir-C1 bond length of 2.005(3) Å is just slightly longer then the Ir-C$_{NHC}$ lengths reported for other tridentate NHC complexes bearing one hydride ligand.\textsuperscript{110,244} The hydride resonances appear in the $^1$H NMR spectrum at -13.19 ppm (dt, $^2$J$_{HH}$ = 5.6 Hz, $^2$J$_{HP}$ = 17.3 Hz, 2H) and -13.80 ppm (tt, $^2$J$_{HH}$ = 5.6 Hz, $^2$J$_{HP}$ = 17.6 Hz, 1H).
Figure 5.5. Solid-state molecular structure (ORTEP) of (PCP)IrH$_3$ (5.9). All hydrogen atoms except H1, H2 and H3 have been omitted for clarity. The hydride atoms were located in the crystal structure and refined isotropically. Selected bond lengths (Å) and angles (°): C1-Ir1, 2.005(3); P1-Ir1, 2.2612(5); Ir1-H1, 1.64(3); Ir1-H2, 1.59(3); C1-N1, 1.380(3); C1-Ir1-H2, 180.000(5); C1-Ir1-H1, 93.8(8); C1-Ir1-P1, 89.920(14); P1-Ir1-H2, 90.080(14); P1-Ir1-H1, 89.6(9).

5.4 Alkane Dehydrogenation Studies

Although the accepted mechanism of alkane transfer dehydrogenation by iridium pincer complexes involves a 14-electron complex as the active catalytic species,$^{106}$ the steric constraints around the metal centre created by the phosphine substituents of our PCP ligand could allow a 16-electron complex to be useful for this process. If oxidative addition of a C-H bond of a selected alkane such as cyclooctane does occur, the subsequent β-hydride elimination step of the coordinated alkane would be aided by steric repulsion with the isopropyl groups. Based on bond strength and polarity the H-H bond is considered the closest relative to the C-H bond$^{247}$ and given that the iridium chloride 5.7
was shown to undergo oxidative addition of dihydrogen to generate (PCP)IrClH₂, complex 5.7 was tested as a possible candidate for the activation of C-H bonds. Unfortunately no reaction was observed between 5.7 and the test substrate COA at 100 °C over 24 h. Another method to form a potentially active complex is similar to the pathway outlined in Scheme 5.1 for transfer dehydrogenation; in our case addition of a hydrogen acceptor to 5.9 could generate (PCP)IrH in-situ (Scheme 5.2). Norbornene (NBE) was chosen as the hydrogen acceptor as TBE was found to be ineffective with other NHC-containing pincer iridium systems. After reaction of a toluene solution consisting of (PCP)IrH₃, NBE and COA in a sealed reaction vessel for 24 h at 160 °C no cyclooctene or C-H activation products were detected by ¹H NMR spectroscopy.

Scheme 5.2. Potential transfer dehydrogenation pathway towards production of an active (PCP)IrH species.

The likelihood of the hydrogen acceptor to abstract two hydride ligands from 5.9 is limited by the lack of an open site for coordination of the π-electrons of the incoming
olefin at the iridium centre. However, reaction of 5.9 with a excess of phenylacetylene at a temperature of 100 °C for 2 days gives the PCP iridium acetylide dihydride complex (PCP)IrH$_2$(CCPh) 5.10 (eq. 5.5). The cis-disposed hydrides of 5.10 are observed in the $^1$H NMR spectrum as a pair of inequivalent doublets of triplets at -12.01 ppm and -13.92 ppm ($^2$J$_{HH}$ = 5.9 Hz, $^2$J$_{HP}$ = 16.1 Hz). Interestingly, following the formation of the C-H activation product 5.10 by $^1$H NMR spectroscopy reveals the presence of an equivalent of styrene, indicating the first step of the reaction is hydrogenation of the alkyne followed by oxidative addition of a second equivalent of phenylacetylene to (PCP)IrH. Based on this result the transfer dehydrogenation experiment was repeated using phenylacetylene as the hydrogen acceptor. The thought was that because of the long reaction time required to synthesize 5.10, the high enthalpy of dehydrogenation of COA (23.3 kcal/mol)$^{106}$ would allow the Ir(I) intermediate to invoke C-H activation of the alkane preferentially. Unfortunately, no COE or alkane activation complexes were detected in the $^1$H NMR spectrum. This result suggests the 16-electron iridium monohydride does not possess the necessary coordinative unsaturation to activate the C-H bond of alkanes.

Complex 5.8 was utilized in an attempt to generate a more electronically favourable cationic iridium dihydride through reaction with various halide abstraction reagents (eq. 5.6). The intended cation would be well suited for examination as a dehydrogenation catalyst with an open coordination site and provide valuable information.
about tailoring the electrophilicity at the metal centre. Experiments show that the desired product remains elusive as in each case the result was either no reaction or a mixture of unidentifiable products.

Electronic factors may not be the only property hindering the performance of 5.9 in alkane transfer dehydrogenation experiments. A look at a space-filling model of the crystal structure of 5.9 shows the very sterically congested iridium centre (Figure 5.6). The iridium atom may in fact be too protected by the isopropyl phosphine substituents to allow initial insertion of the hydrogen acceptor into an Ir-H bond, which is necessary for

**Figure 5.6.** Space-filling model of (PCP)IrH₃ showing the steric crowding restricting access to the metal centre. Model was generated from the crystal structure of 5.9.
entry into the transfer dehydrogenation catalytic cycle. For this reason the Ir(III) hydride was exposed to an atmosphere of carbon dioxide in hopes that our complex might mimic another (PNP)IrH₃ system in the hydrogenation of the smaller CO₂ molecule. With the PNP system the catalytic cycle begins with the reversible insertion of CO₂ in an Ir-H bond to give the iridium formate complex shown in Scheme 5.4. Unfortunately with 5.9 no CO₂ insertion was observed in the ¹H NMR spectrum after 24 hours. This was surprising as the (PNP)IrH₃ pincer complex displayed immediate reaction with CO₂ suggesting that insertion of a central NHC donor into the ligand framework has a significant effect on complex reactivity.

**Scheme 5.3.** The initial reversible insertion step of CO₂ into a Ir-H to give a iridium formate dihydride with a PNP framework.

5.5 *Synthesis and Reactivity of (PCP)IrCH₃*

One possible route to the PCP iridium monohydride considered was via synthesis of the methyl derivative 5.11 (eq. 5.7). Heating of a pincer Ir(III) methyl dihydride complex has been shown to eliminate methane, which should lead to the desired (PCP)IrH species. Drop-wise addition of one equivalent of MeLi to a toluene solution of 5.7 at -35 °C and allowing the reaction to slowly warm to room temperature resulted in a colour change from red to black. The ¹H NMR spectrum of the product contains a
triplet assigned to the coordinated methyl group located at 1.80 ppm ($J_{HP} = 6.0$ Hz); a similar resonance has been reported for iridium pincer complex (PONOP)IrCH$_3$. The methyl complex 5.11 is very stable under an inert atmosphere, which is remarkable considering the difficulty in obtaining the monohydride.

Immediate reaction between a solution of 5.11 in C$_6$D$_6$ and one equivalent of hydrogen gas in a J. Young NMR tube was observed through a colour change from a black to yellow solution. The $^1$H NMR spectrum of the yellow product displays separate peaks for both the methylene groups of the NHC and the methine groups of the isopropyl substituents. In addition only a single complex multiplet integrating for two hydrides is present in the upfield region centred at -10.63 ppm (Figure 5.7); this signal collapses to a singlet in the $^1$H{$^{31}$P} NMR spectrum. These features are inconsistent with the expected cis-coordination of dihydrogen to 5.11. However, over a period of 48 hours at ambient temperature a $^1$H NMR spectrum of the reaction mixture shows the original hydride signal has been replaced by two doublets of triplets, each integrating for one proton, located at -11.89 and -13.72 ppm as shown in Figure 5.7. This splitting pattern suggest formation of the anticipated dihydride complex (PCP)IrH$_2$CH$_3$ (5.13).
Figure 5.7. $^1$H NMR spectra showing hydride signals resulting from reaction of 5.7 with one equivalent of hydrogen after 15 min (top) and 48 hours (bottom).

Repeating the reaction with a concentrated sample of 5.11 (20 mg, in 0.75 mL C$_6$D$_6$) led to precipitation of crystals suitable for X-ray diffraction analysis of the initial product after approximately 30 minutes. The solid state molecular structure shown in Figure 5.8 reveals a facial pincer coordination geometry designated as $fac$-(PCP)IrH$_2$CH$_3$ (5.12) that precedes formation of the expected meridional ancillary unit (5.13). The $fac$ isomer crystallizes in the monoclinic space group P2(1)/n and the Ir1-C1 distance of 1.979(2) Å is consistent with the Ir-C$_{NHC}$ bond lengths found for the other PCP iridium complexes structurally characterized (5.6 and 5.9). The coordination geometry of 5.12 allows for assignment of the corresponding hydride signal as an AA’XX’ spin system with cis hydride ligands (A, A’) coplanar with cis pincer PPr$_2$ groups (X, X’). The
structure of 5.13 represents the first time the facial coordination mode of our PCP ligand was observed.

Figure 5.8. Solid-state molecular structure (ORTEP) of fac-(PCP)RhH$_2$CH$_3$ (5.12). All hydrogen atoms except H100 and H101 have been omitted for clarity. The hydride atoms were located in the crystal structure and refined isotropically. Selected bond lengths (Å) and angles (°): C1-Ir1, 1.979(2); Ir1-C28, 2.174(2); P1-Ir1, 2.3169(9); Ir1-P2, 2.2873(9); Ir1-H100, 1.574(5); Ir1-H101, 1.525(4); C1-Ir1-C28, 167.36(9); C1-Ir1-P2, 94.32(6); P1-Ir1-P2, 114.81(2); P1-Ir1-H100, 80.24(7); P1-Ir1-H101, 162.95(3).

A non-NHC derived iridium pincer complex (PCaryl)IrCO undergoes a similar isomerization when exposed to 3 atm of hydrogen upon warming from -60 °C. The authors in this case have determined by variable temperature NMR that the oxidative addition of H$_2$ is reversible, and warming the solution favours production of the thermodynamically preferred meridional isomer.$^{251}$ That the fac to mer isomerization in our system occurs with the addition of only one equivalent of H$_2$ and at room temperature led us to examine a possible mechanism for this process. Following the reaction of 5.11 with deuterium gas by NMR spectroscopy shows clean conversion of fac-(PCP)IrD$_2$CH$_3$.
to mer-(PCP)IrD₂CH₃ over 48 hours and without incorporation of any hydrogen atoms in the hydride sites. This eliminates the possibility of a cooperative mechanism between the hydride and PCP or methyl ligands. Allowing a THF solution of the isolated fac isomer 5.12 to stir over the 48 hr period in a nitrogen atmosphere resulted in complete conversion to the mer isomer 5.13, which suggested the isomerization process does not require the reversible addition of H₂ to 5.11. This information led us to propose the intramolecular isomerization pathway outlined in Scheme 5.4.

Scheme 5.4. Intramolecular pathway allowing the isomerization of 5.12 to 5.13 via rotation of a η₂-dihydrogen ligand.

In the first stage of the reaction oxidative addition of hydrogen occurs across the P-Ir-P axis giving the kinetically favoured product fac-(PCP)IrH₂CH₃. The stereochemical preference for H₂ addition to d⁸ iridium complexes has been studied
previously and shown to act under either steric or electronic control.\textsuperscript{252} The steric environment is essentially unchanged on moving from the iridium chloride 5.7, for which the fac isomer was not observed, to the methyl complex 5.11. Therefore, the addition of H\textsubscript{2} across the P-Ir-P axis is electronic in nature as bending back a pair of trans ligands can lead to improved orbital overlap between the metal and approaching dihydrogen molecule (Figure 5.9).\textsuperscript{252} The π-acceptor capability of a CO ligand in the bending plane can also assist in the stereochemical preference of H\textsubscript{2} binding by reducing electron density in the filled d\textsubscript{z\textsuperscript{2}} orbital that creates a repulsive interaction with the H-H σ-bond. A similar but opposite effect could explain why the fac isomer is not observed with the iridium chloride 5.7 when exposed to hydrogen gas. If the PCP phosphines bend back a slight rehybridization of the empty metal acceptor orbital will occur and, if of the right symmetry, can accept electron density through π-back-donation from the chloride ligand increasing the barrier to bond formation.

![Figure 5.9](image)

**Figure 5.9.** Orbital interactions leading to M-H bond formation via σ-donation into a vacant p\textsubscript{z} orbital (I), back-bonding from a filled metal orbital into the H\textsubscript{2} σ\textsuperscript{*} anti-bonding orbital (II), and a repulsive interaction between the filled H\textsubscript{2} σ-bond and the filled d\textsubscript{z\textsuperscript{2}} orbital (III).

In the next step, the preference of the rigid PCP ligand to coordinate in a meridional arrangement drives the reductive elimination of the cis hydride ligands to form the short-lived five coordinate σ-bound dihydrogen species shown in Scheme 5.4.
The ability of $\eta^2$-dihydrogen ligands to freely rotate is well documented;\textsuperscript{253-255} a rotation of 90° followed by oxidative addition of the dihydrogen molecule provides the thermodynamically stable mer-(PCP)IrH$_2$CH$_3$ (5.13). Further evidence for the involvement of a dihydrogen ligand in the isomerization reaction was gained when a solution of (PCP)IrD$_2$CH$_3$ was left to mix in a sealed NMR tube under a hydrogen atmosphere (~6 equiv). The $^1$H NMR spectrum of the final product shows approximately 30% hydride incorporation at each position in the meridional complex indicating that dissociation of the weakly bound dihydrogen ligand can occur but is not required during isomerization. Heating the reaction mixture up to 80 °C for 12 h did not lead to any methane elimination and only served to speed up the isomerization process.

### 5.6 Reaction of PCP Iridium Complexes with Ammonia

Activation of ammonia by a transition metal complex is an attractive route towards hydroamination of carbon-carbon multiple bonds to generate carbon-nitrogen bonds.\textsuperscript{256} Of particular interest is the formal oxidative addition of ammonia to a metal centre to form an amido hydride species. The development of homogenously catalyzed processes based on the activation of ammonia leading to cleavage of a N-H bond has only recently become feasible following the first examples of oxidative addition of ammonia by iridium pincer complexes.\textsuperscript{192,193} Given the successful stabilization of a rhodium amido unit by our PCP ligand set (4.14) it was decided to examine the reactivity of ammonia with the available iridium complexes discussed in this chapter. The two candidates with open coordination sites available for oxidative addition were the Ir(I) chloride 5.7 and methyl complex 5.11. However, in each case, the metal complex was unreactive to added
ammonia. All attempts to synthesize an iridium amido species through addition of LiNH$_2$ to the chloride 5.7 were equally discouraging showing only starting materials in the relevant NMR spectra. Inspired by the successful reaction between the rhodium hydride 4.6 and NH$_4$PF$_6$ leading to the new cationic rhodium ammonia complex 4.9 a THF solution of (PCP)IrH$_3$ (5.9) was stirred with one equivalent of NH$_4$PF$_6$. After stirring for 12 hours NMR spectroscopic analysis of the product was consistent with the new iridium ammonia dihydride [(PCP)IrH$_2$NH$_3$][PF$_6$] (5.14) (eq. 5.8).

![Chemical diagram](image)

Although the chemical shift difference between 5.14 and 5.9 in the $^{31}$P{$^1$H} NMR spectra is small (~ 2 ppm) a slightly broader signal is found for complex 5.14. The broader signal in the $^{31}$P{$^1$H} NMR spectrum results if the twisting of the ligand backbone evident in the solid-state molecular structure of 5.9 (Figure 5.5) places the linker arms in slightly different environments as one is pointing towards the NH$_3$ ligand and the other towards the hydride. A slow oscillation between these two conformers on the NMR time will render the phosphines inequivalent. Secondly, integration of the $^{31}$P{$^1$H} NMR spectrum of 5.14 gives a 2:1 ligand to counterion ratio indicative of a new cationic species. Peak broadening in the $^1$H NMR spectrum resulted in two broad sets of signals assignable to the methylene protons of the NHC backbone at $\delta$ 4.32 and 4.19 as well as two broad signals at $\delta$ 2.42 and 2.22 assignable to the methine moieties of the
isopropyl substituents. The two inequivalent hydride resonances appearing as doublets of triplets found at -10.84 ppm ($J_{HH} = 6.0$ Hz, $J_{HP} = 15.9$ Hz) and -22.12 ppm ($J_{HH} = 5.7$ Hz, $J_{HP} = 16.2$ Hz) are consistent with hydride ligands situated cis to each other. Most important is the appearance of a new singlet located at 1.92 ppm integrating for three protons (Figure 5.10), which we ascribe to the coordinated ammine (Ir-NH$_3$).

![Figure 5.10](image)

**Figure 5.10.** $^1$H NMR spectrum of [(PCP)IrH$_2$NH$_3$][PF$_6$] (5.14) in d$_8$-THF showing the singlet assigned to the coordinated ammonia at 1.92 ppm. The hydride peaks are not shown.

Studies on a cationic gold complex supported by a cyclic (alkyl)(amino)carbene (CAAC) ligand successful in the hydroamination of alkynes have determined that the resting state of the catalyst is a cationic gold ammonia complex.$^{256}$ As the PCP iridium trihydride was shown to be reactive towards phenylacetylene (eq. 5.5) it was of interest if the cation 5.14 would be reactive towards this alkyne. The $^1$H NMR spectrum after 1.5 h at 80 °C of a mixture of 5.14 and excess phenylacetylene contains some of the hydrogenation product styrene and a loss of the signals belonging to the PCP ligand,
suggesting complex decomposition. As a result, complex 5.14 was not suitable for promoting hydroamination; therefore, in an attempt to alter its reactivity complex 5.14 was subjected to the same conditions that provided the amido species (PCP)RhNH₂ (4.14).

Upon addition of one equivalent of KHMDS an immediate darkening of the solution was observed and a ³¹P{¹H} NMR spectrum of the reaction mixture reveals the emergence of two new doublets at δ 52.76 and 22.72 with a large P-P coupling constant ($J_{PP} = 348.0 \text{ Hz}$) indicating the presence of inequivalent trans phosphine donors. However, a signal belonging to 5.14 remained in the ³¹P{¹H} NMR spectra constituting about half of the reaction mixture and a second equivalent of KHMDS was required to convert all starting material to the new species. The requirement of a second equivalent of base along with the inequivalent phosphine environments was evidence that something more complicated than the intended deprotonation to give an Ir-NH₂ complex had taken place. The ¹H NMR spectrum in Figure 5.11 shows clean conversion to a new product with reduced symmetry leading to seven individual peaks for the aromatic protons of the phenylene linker. Furthermore, separate peaks are found for each of the diastereotopic protons of the NHC backbone (3.5-3.1 ppm) and the methine groups of the isopropyl groups (2.9-2.0 ppm), while the hydride signals remain inequivalent, each has split into doublets of doublets of doublets. The signals assigned to the hydride ligands collapse into doublets with coupling constants typical of cis hydride coordination ($J_{HH} = 5.1 \text{ Hz}$) in the ¹H{³¹P} NMR spectrum. A total of five protons are found in the chemical shift region between 3.5 and 3.1 ppm, four of which were easily assigned as the methylene protons of the NHC with the assistance of 2D ¹H/¹³C HSQC NMR spectroscopy, however, no cross
peak was found relating the final proton to a carbon atom. This proton was identified as an N-H group with 2D $^1$H/$^{15}$N HSQC NMR spectroscopy correlating $^1$H and $^{15}$N nuclei separated by one bond length.

![Figure 5.11](image)

**Figure 5.11.** $^1$H NMR spectrum in $d_8$-THF of the product resulting from the reaction of 5.14 with 2 equiv of KHMDS. The hydride signals are shown above.

Slow evaporation of a THF solution of the reaction mixture resulted in crystals suitable for X-ray diffraction analysis; the solid-state molecular structure is shown in Figure 5.12. The crystallographic data revealed a product resulting from cleavage of the C-N bond between the NHC ring and an aryl ring on the PCP ligand to form a new iridium (III) dihydride complex containing two bidentate ligand frameworks, one of which coordinates through the nitrogen atom originating from the ammine moiety. The iridium complex, denoted (PNH)IrH$_2$(CP) (5.15), crystallizes in the monoclinic space group P2(1)/n with an Irl-C1 distance of 2.035(5) Å that is similar in length to the Ir-
C_{NHC} distances found for the other crystallographically characterized complexes within this chapter. The proton located on the nitrogen of the NHC is expected to be very acidic due to the electron delocalization necessary to stabilize the carbene atom. As a result, in solution this proton will be involved in hydrogen bonding with the lone pair on the oxygen atom of the THF solvent; this interaction explains the secondary signal next to the solvent signal in the $^1H$ NMR spectrum of 5.15 (Figure 5.11). The N-H proton discovered in the 2D experiment mention above is assigned to the coordinated amido (H103 in Figure 5.12) while assignment of the remaining N-H proton of the NHC ring is considerably more difficult. Although no cross peak associated with this N-H bond was located it is believed that the signals belonging to the methyl groups of the isopropyl substituents between 1.3 and 0.6 ppm in the $^1H$ NMR spectrum may mask what is expected to be a broad resonance for H102. Furthermore, the signal to noise ratio in the $^1H/^15N$ HSQC spectrum in this region is significantly worse then in the remainder of the spectrum thereby interfering with a reliable N-H correlation assignment.
Figure 5.12. Solid-state molecular structure (ORTEP) of (PNH)IrH₂(ÇP) (5.15). All hydrogen atoms except H100, H101, H102 and H103 have been omitted for clarity. The hydride atoms were located in the crystal structure and refined isotropically. Selected bond lengths (Å) and angles (°): Ir1-C1, 2.035(5); C1-N1, 1.330(7); C1-N2, 1.358(7); N1-H102, 0.73(6); N3-Ir1, 2.139(5); N3-H103, 0.67(5); P1-Ir1, 2.2827(13), P2-Ir1, 2.2584(12); Ir1-H100, 1.62(6); Ir1-H101, 1.55(5); C1-Ir1-N3, 89.5(2); C1-Ir1-P2, 85.72(15); N3-Ir1-P2, 103.56; C1-Ir1-P1, 96.71(14); N3-Ir1-P1, 80.72(14); P2-Ir1-P1, 175.13(4); C1-Ir1-H100, 174.8(19); N3-Ir1-H101, 172.7(19).

The proposed mechanistic pathway leading to the ligand rearrangement product 5.15 is outlined in Scheme 5.5 and begins with a single deprotonation of the coordinated ammonia ligand to form the anticipated octahedral Ir-NH₂ species. Formation of the reactive amido ligand leads to nucleophilic attack of the phenyl ring, which is assisted by the transfer of one of the amido protons to the NHC nitrogen. The requirement of more than one equivalent of base accounts for the base-catalyzed proton transfer step that leads to the anionic imido species found in Scheme 5.5. Intramolecular proton transfer between nitrogen sites in aprotic solvents has been reported previously using triethylamine as the
This unique reaction path exposes another pincer ligand rearrangement possibility in the presence of reactive ligands such as the Ir-NH$_2$ fragment. The difference in reactivity between 5.14 and the square planar rhodium amido complex 4.14 can be attributed to protection of the amido unit by the bulky phosphine donors when it is located in the P-Rh-P plane. In comparison complex 5.14 exhibits a slightly distorted octahedral geometry that, upon deprotonation, leaves the amido ligand above the P-Ir-P plane where it can undergo further deprotonation to generate a reactive imido fragment that promotes cleavage of the aryl C-N bond of the ligand backbone.

**Scheme 5.5.** Proposed ligand rearrangement pathway following reaction of 5.14 with two equivalents of base to give (PNH)IrH$_2$(CP) (5.15).
5.7 Conclusions

As was the case with rhodium, the synthesis of a mononuclear iridium complex required coordination with the neutral version of our PCP ligand 2.2. The electronic and steric environment of the octahedral (PCP)IrH$_3$ (5.9) complex rendered it unsuccessful in alkane transfer hydrogenation experiments. Isolation of a PCP iridium monohydride remains elusive, although its presence is implied during the hydrogenation of a terminal alkyne by 5.9 followed by C-H activation to an Ir(I)-H intermediate. Addition of hydrogen to the iridium methyl derivative 5.11 led to an isomerization between the facial coordination mode to the more thermodynamically stable planar binding. The isomerization process is believed to involve rotation of a η$_2$-dihydrogen ligand in which dihydrogen dissociation can occur but is not required. The isolable Ir(I) species 5.7 and 5.11 proved to be unreactive in the presence of ammonia, however, an iridium ammonia complex was obtained via reaction of 5.9 with NH$_4$PF$_6$. Reaction of this species in the presence of excess base led to unexpected ligand rearrangement process activated by a nucleophilic imido unit.
5.8 Experimental section

General Considerations. All reactions were performed by standard Schlenk techniques in an oxygen-free nitrogen atmosphere unless otherwise noted. $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on either a Bruker AV-400 instrument operating at 400.2 MHz or a Bruker AV-300 instrument operating at 300.13 MHz. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. Organic solvents were purchased anhydrous from Aldrich, sparged with nitrogen, and passed through columns containing activated alumina and molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, and dried over activated 3 Å molecular sieves prior to use. Gases were removed by three freeze-pump-thaw cycles. Elemental analysis and mass spectrometry (GC/MS) were performed at the Department of Chemistry at the University of British Columbia. The synthesis of the PCP ligand$^{232}$ and [Ir(COD)Cl]$^2$ have been previously reported. Phenylacetylene was purchased commercially and distilled over activated 3 Å molecular sieves then degassed.

[IrCl(COD)]$_2$[PCHP][PF$_6$] (5.5). A mixture of [(PCP)H][PF$_6$], 2.1 (125 mg, 0.208 mmol), and [Ir(COD)Cl]$_2$ (140 mg, 0.208 mmol) in THF (5 mL) was left to stir for 12 h at room temperature. After the reaction had gone to completion according to a $^{31}$P{$^1$H} NMR spectrum of the reaction mixture, the solution was concentrated and cooled at -35 °C to generate dark orange crystals of 5.5. Yield 165 mg (62 %). $^1$H NMR (d$_8$-THF, 300.13 MHz, 298 K): δ 8.94 (s, 1H, CH), 8.12 (m, 2H, CH), 7.81 (t, $J_{HH} = 7.4$ Hz, 2H, CH), 7.67 (m, 4H, CH), 4.95 (s, br, 4H, =CH), 4.18 (s, 4H, CH$_2$), 3.46 (s, br, 4H, =CH), 2.40 (m, 4H, CH), 2.17 (m, br, 8H, -CH$_2$), 1.51 (m, 8H, -CH$_2$), 1.29 (m, 24H, CH$_3$).

$^{31}$P{$^1$H} NMR (d$_8$-THF, 121.5 MHz, 298 K): δ 18.27 (s), -143.00 (sep).
(PCP)IrCl (5.7). To a stirring solution of PCP (2.2) (756 mg, 1.67 mmol) in THF (8 mL) was added [Ir(COD)Cl]_2 (510 mg, 0.759 mmol) at which point a colour change from brown to dark red was observed. After allowing the mixture to stir for 1 h the solvent was then evaporated and a suspension was obtained by adding 10 mL of ether. Filtration of the precipitate and further washing of any excess 2.2 with ether provided the product as a dark red powder. Yield 705 mg (68%). 1H NMR (C_6D_6, 300.13 MHz, 298 K): \( \delta \) 7.41 (m, 2H, CH), 7.17 (m, 2H, CH), 6.92 (t, \( J_{HH} = 7.4 \) Hz, 2H, CH), 6.16 (d, \( J_{HH} = 8.1 \) Hz, 2H, CH), 2.97 (s, 4H, CH_2), 2.76 (m, 4H, CH), 1.34 (m, 24H, CH_3). 13C{\(^1\)H} NMR (C_6D_6, 100.6 MHz, 298 K): \( \delta \) 175.04 (t, \( 2J_{CP} = 11.4 \) Hz, Ir-C), 149.33 (t, \( 2J_{CP} = 5.5 \) Hz), 130.65 (s), 130.06 (s), 121.37 (s), 119.13 (t, \( J_{CP} = 16.6 \) Hz), 116.95 (t, \( 2J_{CP} = 2.5 \) Hz), 49.66 (s), 25.09 (t, \( J_{CP} = 14.6 \) Hz), 18.78 (s), 18.28 (s). 31P{\(^1\)H} NMR (C_6D_6, 121.5 MHz, 298 K): \( \delta \) 16.13 (s). Anal. Calcd. C_{27}H_{40}N_2P_2ClIr: C 47.51; H 5.87; N 4.10. Found: C 47.31; H 5.88; N 3.88.

(PCM)IrH_2Cl (5.8). A solution of 5.7 (100 mg, 0.147 mmol) in 4 mL toluene contained inside a bomb equipped with a Kontes valve is freeze-pumped-thawed. After which the headspace is filled with 1 atm of H_2 gas and the solution is left to stir for 24 h. Removal of the solvent under vacuum allows for the isolation of 5.8 as a off-white powder. Yield 86 mg (86%). 1H NMR (C_6D_6, 400.19 MHz, 298 K): \( \delta \) 7.20 (m, 2H, CH), 7.13 (m, 2H, CH), 6.96 (t, \( J_{HH} = 6.8 \) Hz, 2H, CH), 6.67 (d, \( J_{HH} = 7.4 \) Hz, 2H, CH), 3.28 (s, 2H, CH_2), 3.17 (s, 2H, CH_2), 2.68 (m, br, 2H, CH), 1.24 (m, 12H, CH_3), 1.03 (m, 12H, CH_3), -9.68 (dt, \( J_{HH} = 6.0 \) Hz, \( J_{HP} = 16.2 \) Hz, 1H, IrH), -22.11 (dt, \( J_{HH} = 6.0 \) Hz, \( J_{HP} = 15.3 \) Hz, 1H, IrH). 13C{\(^1\)H} NMR (C_6D_6, 100.6 MHz, 298 K): \( \delta \) 195.7 (m, Ir-C), 149.29 (t, \( 2J_{CP} = 4.7 \) Hz), 131.43 (s), 130.06 (s), 122.54 (s), 120.56 (t, \( J_{CP} = 17.5 \) Hz) 119.17 (s), 49.49 (s),
22.74 (t, $J_{CP} = 15.4$ Hz), 18.19 (s), 18.06 (s), 17.72 (s), 17.21 (s). $^{31}$P$\{^1$H$\}$ NMR (C$_6$D$_6$, 161.9 MHz, 298 K): $\delta$ 20.13 (s). Anal. Calcd. C$_{27}$H$_{42}$N$_2$P$_2$ClIr: C 47.39; H 6.19; N 4.09. Found: C 47.22; H 5.78; N 4.27.

(PCP)IrH$_3$ (5.9). A Schlenk flask was charged with 5.7 (200 mg, 0.293 mmol) and KBEt$_3$H (80 mg, 0.588 mmol) and then placed under vacuum. After starting a flow of H$_2$ into the reaction vessel 10 mL of benzene that had H$_2$ bubbled through it for 10 min was added via syringe. The reaction was left to stir for 2 h at which point the yellow solution was filtered and the volume of solvent was reduced to 3 mL. Allowing the concentrated solution to sit overnight provided X-ray quality crystals of 5.9. Yield 115 mg (61%). $^1$H NMR (d$_8$-THF, 400.2 MHz, 298 K): $\delta$ 7.47 (m, 2H, CH), 7.34 (t, $J_{HH} = 7.7$ Hz, 2H, CH), 7.23 (d, $J_{HH} = 8.2$ Hz, 2H, CH), 7.14 (t, $J_{HH} = 7.3$ Hz, 2H, CH), 4.04 (s, 4H, CH$_2$), 2.03 (m, 4H, CH), 0.98 (m, 24H, CH$_3$), -13.19 (dt, $J_{HH} = 5.6$ Hz, $J_{HP} = 17.3$ Hz, 2H, IrH), -13.80 (tt, $J_{HH} = 5.6$ Hz, $J_{HP} = 17.6$ Hz, 1H, IrH). $^{13}$C$\{^1$H$\}$ NMR (d$_6$-THF, 100.6 MHz, 298 K): $\delta$ 194.7 (m, Ir-C), 148.26 (t, $^2J_{CP} = 5.7$ Hz), 127.60 (s), 127.55 (s), 119.52 (t, $J_{CP} = 17.2$ Hz), 119.37 (s), 116.48 (t, $^2J_{CP} = 2.7$ Hz), 47.18 (s), 24.56 (t, $J_{CP} = 17.0$ Hz), 16.01 (s), 15.80 (s). $^{31}$P$\{^1$H$\}$ NMR (d$_8$-THF, 161.9 MHz, 298 K): $\delta$ 25.86 (s). Anal. Calcd. C$_{27}$H$_{43}$N$_2$P$_2$Ir: C 49.91; H 6.67; N 4.31. Found: C 49.88; H 6.57; N 4.33.

(PCP)IrH$_2$(CCPh) (5.10). A sealable vessel equipped with a Kontes valve was charged with 5.9 (115 mg, 0.177 mmol) and to it was added phenylacetylene (39.7 mg, 0.389 mmol) in toluene (5 mL). This solution was placed in an oil bath operating at 100 °C and left to stir for 48 h. The resulting pale yellow solution was then evaporated to dryness. Ether was then added to the residue and a suspension was formed which was then filtered providing the product as a yellow powder. Yield 112 mg (84%). $^1$H NMR (d$_8$-toluene,
400.2 MHz, 298 K): δ 7.33 (m, 1H, CH), 7.23 (m, 2H, CH), 7.09 (m, 2H, CH), 6.99 (m, 2H, CH), 6.89 (t, \( J_{HH} = 7.5 \) Hz, 3H, CH), 6.81 (t, \( J_{HH} = 7.3 \) Hz, 1H, CH), 6.63 (d, \( J_{HH} = 8.1 \) Hz, 2H, CH), 3.21 (m, 4H, CH\(_2\)), 2.56 (m, 2H, CH), 1.96 (m, 2H, CH), 1.20 (m, 12H, CH\(_3\)), 1.01 (m, 12H, CH\(_3\)), -12.16 (dt, \( J_{HH} = 5.5 \) Hz, 1H, IrH), -14.04 (dt, \( J_{HH} = 5.8 \) Hz, \( J_{HP} = 17.6 \) Hz, 1H, IrH). 13C\(_1\){\(^1\)H} NMR (d\(_8\)-toluene, 100.6 MHz, 298 K): δ 193.66 (m, Ir-\( C\)NHC), 149.58 (s), 131.36 (s), 130.92 (s), 129.90 (s), 127.39 (s), 122.41 (s), 122.27 (s), 121.68 (t, \( J_{CP} = 17.9 \) Hz), 118.90 (s), 49.26 (s), 24.72 (t, \( J_{CP} = 16.4 \) Hz), 23.95 (t, \( J_{CP} = 16.0 \) Hz), 18.33 (s), 18.11 (s), 17.85 (s), 17.58 (s). 31P\(_1\){\(^1\)H} NMR (d\(_8\)-THF, 161.9 MHz, 298 K): δ 17.02 (s). Anal. Calcd. C\(_{35}\)H\(_{47}\)N\(_2\)P\(_2\)Ir: C 56.06; H 6.32; N 3.74. Found: C 56.07; H 6.42; N 3.68.

(PCP)IrCH\(_3\) (5.11). A stirring mixture of 5.7 (100 mg, 0.147 mmol) in toluene (5 mL) was cooled to -35 °C at which point an ether solution of 0.09 mL MeLi (1.6 M, 0.147 mmol) was added drop wise. The reaction was then allowed to slowly warm to room temperature over 2 h followed by removal of all volatiles under vacuum. The remaining black product is dissolved in benzene, filtered through Celite, and the benzene is evaporated providing 5.11 as a black powder. Yield 68 mg (70.0%). \(^1\)H NMR (C\(_6\)D\(_6\), 300.13 MHz, 298 K): δ 7.53 (m, br, 2H, CH), 7.17 (m, 2H, CH), 6.98 (t, \( J_{HH} = 7.4 \) Hz, 2H, CH), 6.68 (d, \( J_{HH} = 8.3 \) Hz, 2H, CH), 2.98 (s, 4H, CH\(_2\)), 2.84 (m, 4H, CH), 1.80 (t, \( J_{HP} = 6.0 \) Hz, 3H, IrCH\(_3\)), 1.27 (dd, \( J_{HH} = 7.4 \) Hz, \( J_{HP} = 14.8 \) Hz, 12H, CH\(_3\)), 1.21 (dd, \( J_{HH} = 6.7 \) Hz, \( J_{HP} = 13.4 \) Hz, 12H, CH\(_3\)). 13C\(_1\){\(^1\)H} NMR (C\(_6\)D\(_6\), 100.6 MHz, 298 K): δ 149.96 (t, \( J_{CP} = 6.7 \) Hz), 131.32 (s), 129.80 (s), 120.33 (s), 117.02 (s), 115.80 (t, \( J_{CP} = 16.5 \) Hz), 48.72 (s), 24.16 (t, \( J_{CP} = 13.6 \) Hz), 19.30 (s), 18.78 (s), 1.44 (s, Ir-CH\(_3\)). The Ir-\( C\)NHC could not be located. 31P\(_1\){\(^1\)H} NMR (C\(_6\)D\(_6\), 121.5 MHz, 298 K): δ 16.71 (s). Anal. Calcd.
C_{28}H_{43}N_{2}P_{2}Ir: C 50.81; H 6.55; N 4.23. Found: C 52.33; H 6.85; N 4.19.

fac-(PCP)IrH_{2}CH_{3} (5.12). In a sealable bomb a concentrated solution of 5.11 (80 mg, 0.121 mmol) in benzene (5 mL) was subjected to three freeze-pump-thaw cycles and exposed to 1 atm of hydrogen upon warming to room temperature. Almost instantly a colour change from black to light yellow is observed and after mixing the solution for 15 minutes X-ray quality crystal of 5.12 began to precipitate from the solution. The crystals could then be collected on a sintered frit, allowing for isolation of light yellow crystals of 5.12. Yield: 61 mg (74%). \(^1\)H NMR (C_{6}D_{6}, 400.2 MHz, 298 K): \(\delta \) 7.45 (t, \(J_{HH} = 6.3 \text{ Hz}, 2\text{H, CH}), 7.12 \text{ (t, } J_{HH} = 7.7 \text{ Hz}, 2\text{H, CH}), 6.97 \text{ (t, } J_{HH} = 7.3 \text{ Hz}, 2\text{H, CH}), 6.79 \text{ (m, 2H, CH}), 3.45 \text{ (t, } J_{HH} = 7.5 \text{ Hz}, 2\text{H, CH}_2), 3.12 \text{ (m, 2H, CH}), 2.71 \text{ (t, } J_{HH} = 7.9 \text{ Hz}, 2\text{H, CH}_2), 2.28 \text{ (m, 2H, CH}), 1.50 \text{ (dd, } J_{HH} = 7.1 \text{ Hz}, J_{HP} = 12.0 \text{ Hz}, 6\text{H, CH}_3), 1.41 \text{ (dd, } J_{HH} = 6.8 \text{ Hz}, J_{HP} = 15.3 \text{ Hz}, 6\text{H, CH}_3), 0.89 \text{ (m, 12H, CH}_3), 0.80 \text{ (t, } J_{HP} = 7.0 \text{ Hz}, 3\text{H, IrCH}_3), -10.63 \text{ (m, 2H, IrH)}. \(^{31}\)P\{\(^1\)H\} NMR (C_{6}D_{6}, 121.5 MHz, 298 K): \(\delta \) -7.42. A \(^{13}\)C\{\(^1\)H\} NMR spectrum was not obtained due to isomerization occurring over the long experiment times required. Anal. Calcd. C_{28}H_{45}N_{2}P_{2}Ir: C 50.66; H 6.83; N 4.22. Found: C 50.51; H 6.77; N 4.23.

mer-(PCP)IrH_{2}CH_{3} (5.13). Dissolving 5.12 (61 mg, 0.092 mmol) in a solution of THF and allowing it to stir for 48 h will convert all of the facial isomer to 5.13. Removal of the solvent and washing with ether provides 5.13 as an orange powder. Yield 55 mg (90%). \(^1\)H NMR (C_{6}D_{6}, 400.2 MHz, 298 K): \(\delta \) 7.26 (m, 2H, CH), 7.12 (t, \(J_{HH} = 7.8 \text{ Hz}, 2\text{H, CH}), 6.99 \text{ (t, } J_{HH} = 7.4 \text{ Hz}, 2\text{H, CH}), 6.70 \text{ (d, } J_{HH} = 8.2 \text{ Hz}, 2\text{H, CH}), 3.19 \text{ (m, 4H, CH}_2), 2.37 \text{ (m, 2H, CH)}, 2.02 \text{ (m, 2H, CH)}, 1.11 \text{ (m, 24H, CH}_3), -0.12 \text{ (t, } J_{HP} = 4.8 \text{ Hz}, 3\text{H, IrCH}_3), -11.89 \text{ (dt, } J_{HH} = 4.5 \text{ Hz}, J_{HP} = 17.2 \text{ Hz}, 1\text{H, IrH}), -13.72 \text{ (dt, } J_{HH} = 5.8 \text{ Hz}, J_{HP} = 18.7 \text{ Hz,
\[ \text{1H, IrH).} \ 13^C{\{^1\text{H}\}} \text{ NMR (d}_8\text{-THF, 100.6 MHz, 298 K): } \delta 150.04 (s), 130.60 (s), 130.04 (s), 122.01 (s), 120.99 (s), 118.95 (s), 50.01 (s), 22.59 (t, } J_{CP} = 14.8 \text{ Hz}, 18.71 (s), 18.01 (s), 17.85 (s), 16.47 (s), -43.29 (m, Ir-CH}_3\). \ 31^P{\{^1\text{H}\}} \text{ NMR (C}_6\text{D}_6, 121.5 \text{ MHz, 298 K): } \delta 17.45 (s). \text{ Anal. Calcd. C}_{28}\text{H}_{45}\text{N}_2\text{P}_2\text{Ir: C 50.66; H 6.83; N 4.22. Found: C 50.51; H 6.77; N 4.23.}

\[(\text{PCP})\text{IrH}_2\text{NH}_3]\text{[PF}_6\] (5.14). To a clear solution of the iridium trihydride 5.9 (150 mg, 0.231 mmol) in THF (5 mL) was added NH_4PF_6 (38.0 mg, 0.233 mmol) and the mixture was left to stir for 12 h. Over this period no colour change is observed however, a broadening of the peak in the \(31^P{\{^1\text{H}\}} \text{ NMR spectrum indicates the reaction has completed after this time. After 12 h the solution was evaporated to dryness and the remaining residue is washed with ether and dried in vacuo, giving 5.14 as a light brown powder. Yield 122 mg (79%).} \ 1^H \text{ NMR (d}_8\text{-THF, 300.13 MHz, 298 K): } \delta 7.50 (m, 6H, \text{CH}), 7.26 (t, } J_{HH} = 6.8 \text{ Hz, 2H, CH}), 4.32 (s, br, 2H, CH_2), 4.19 (s, br, 2H, CH_2), 2.42 (s, br, 2H, CH), 2.22 (s, br, 2H, CH), 1.92 (s, 3H, NH_3), 1.05 (m, 24H, CH_3), -10.84 (dt, } J_{HH} = 6.0 \text{ Hz, } J_{HP} = 15.9 \text{ Hz, 1H, IrH}), -22.12 (dt, } J_{HH} = 5.7 \text{ Hz, } J_{HP} = 16.2 \text{ Hz, 1H, IrH}). \ 13^C{\{^1\text{H}\}} \text{ NMR (d}_8\text{-THF, 100.6 MHz, 298 K): } \delta 190.99 (t, } J_{CP} = 9.9 \text{ Hz, Ir-C}), 149.01 (t, } J_{CP} = 4.4 \text{ Hz}), 132.35 (s), 132.16 (s), 124.15 (s), 121.71 (s), 118.31 (s, br), 50.94 (s), 22.90 (s, br), 17.59 (s, br), 16.72 (s, br). \ 31^P{\{^1\text{H}\}} \text{ NMR (d}_8\text{-THF, 121.5 MHz, 298 K): } \delta 19.93 (s, br), -143.8 (sep). \text{ Anal. Calcd. C}_{27}\text{H}_{45}\text{N}_3\text{P}_3\text{F}_6\text{Ir: C 40.00; H 5.59; N 5.18. Found: C 40.04; H 5.87; N 5.60.}

\((\text{PNH})\text{IrH}_2\text{(CP)} \ (5.15). \text{ To a vial charged with 5.14 (100 mg, 0.150 mmol) was added 5 mL THF. To the resulting clear solution was added 2 equivalents of KN(Si(CH}_3)_2 \ (62 mg, 0.312 mmol) with stirring and the solution immediately turned dark brown. A}
\(^{31}\)P\(^{1}\)H\) NMR spectrum of the resulting reaction mixture indicates completion of the reaction after 15 minutes. Slow evaporation of the THF solution led to precipitation of the product. Washing of this precipitate with toluene followed by a pentane wash and drying the product under vacuum gave 5.15 as a dark yellow powder. Yield 73 mg (69%).

\(^1\)H NMR (d\(_8\)-THF, 400.2 MHz, 298 K): \(\delta\) 7.26 (t, \(J_{HH} = 7.6\) Hz, 1H, CH), 7.10 (q, \(J_{HH} = 9.2\) Hz, 2H, CH), 6.69 (m, 1H, CH), 6.61 (t, \(J_{HH} = 7.2\) Hz, 1H, CH), 6.49 (t, \(J_{HH} = 7.3\) Hz, 1H, CH), 6.27 (m, 1H, CH), 5.79 (t, \(J_{HH} = 7.1\) Hz, 1H, CH), 3.49 (m, 1H, NH), 3.48 (m, 2H, CH\(_2\)), 3.31 (m, 1H, CH\(_2\)), 3.20 (m, 1H, CH\(_2\)), 2.85 (m, 1H, CH), 2.44 (m, 1H, CH), 2.12 (m, 1H, CH), 2.05 (m, 1H, CH), 1.37 (dd, \(J_{HH} = 7.3\) Hz, \(J_{HP} = 10.7\) Hz, 3H, CH\(_3\)), 1.17 (m, 6H, CH\(_3\)), 0.99 (m, 9H, CH\(_3\)), 0.88 (dd, \(J_{HH} = 7.2\) Hz, \(J_{HP} = 14.9\) Hz, 3H, CH\(_3\)), 0.74 (dd, \(J_{HH} = 6.8\) Hz, \(J_{HP} = 14.4\) Hz, 3H, CH\(_3\)), -14.38 (ddd, \(J_{HH} = 5.4\) Hz, \(J_{HP} = 11.1\) Hz, 25.9 Hz, 1H, IrH), -20.69 (ddd, \(J_{HH} = 5.3\) Hz, \(J_{HP} = 12.8\) Hz, 1H, IrH). \(^{13}\)C\(^{1}\)H\) NMR (d\(_8\)-THF, 100.6 MHz, 298 K): \(\delta\) 177.12 (m, Ir-C\(_{NHC}\)), 172.09 (dd, \(^2J_{CP} = 3.8\) Hz, 22.9 Hz), 152.52 (d, \(J_{CP} = 10.3\) Hz), 134.07 (s), 130.35 (s), 129.98 (s), 117.54 (s), 116.18 (s), 115.23 (s), 106.72 (s), 55.63 (s), 48.57 (s), 28.15 (dd, \(J_{CP} = 21.7\) Hz, \(^2J_{CP} = 5.4\) Hz), 25.83 (m), 24.60 (m), 21.61 (m), 20.31 (s), 19.14 (s), 18.46 (s), 17.18 (d, \(^2J_{CP} = 9.1\) Hz), 16.29 (s). \(^{31}\)P\(^{1}\)H\) NMR (d\(_8\)-THF, 121.5 MHz, 298 K): \(\delta\) 52.76 and 22.72 (d, \(J_{PP} = 348.0\) Hz).

Anal. Calcd. C\(_{27}\)H\(_{44}\)N\(_3\)P\(_2\)Ir: C 48.78; H 6.67; N 6.32. Found: C 50.95; H 6.86; N 5.79.
Chapter Six

Conclusions and Future Outlook

6.1 Thesis Synopsis

The goal at the outset of this thesis work was to synthesize a rigid tridentate ligand consisting of a central NHC donor connected to two phosphines using \( o \)-phenylene linkers. Incorporation of NHCs into chelating arrays has been shown to generate particularly robust catalyst systems capable of withstanding harsh reaction conditions.\(^{72,78}\)

Research in the Fryzuk lab focuses on new ligand designs for use in transition metal mediated small molecule activation. Of particular interest with this proposed ligand set was examination of the effect that a strong \( \sigma \)-donating NHC might have on the activation of C-H bonds following successful coordination to members of the group 9 triad (Rh, Ir).

Chapter Two described the successful synthesis of a new NHC-containing PCP ligand framework where the central carbon donor is a saturated NHC, first as the imidazolinium salt (2.1) and then following deprotonation, the neutral version (2.2). Oxidative addition of 2.1 to all three of the group 10 metals resulted in the corresponding (PCP)M-hydrido complexes as the PF\(_6\) salts. This group of complexes was fully characterized by both solution spectroscopy and solid-state X-ray crystallography. The X-ray data revealed a square planar geometry for each new (PCP)M-H complex with considerable twisting of the ligand backbone above and below the plane defined by the...
PCP donors with the metal atom. A reactivity study of the nickel complex formed with the PCP ligand was discussed in the next chapter.

In the process of studying the reactivity of the PCP nickel hydride an example of non-innocent ancillary ligand behaviour was discovered when complex 2.5 was exposed to ethylene gas. As outlined in Chapter 3 the anticipated product was ethylene insertion into the Ni-H bond, instead the ethyl moiety had formed a new carbon-carbon bond with the carbene to give complex 3.4. This process was not foreseen, as it would be expected to involve a trans C-C coupling reaction between a Ni-ethyl intermediate and the carbene carbon. Deuterium labelling studies revealed a series of β-hydride elimination and alkene readdition steps that led to isotope scrambling in the ethyl unit, ruling out insertion of ethylene into the Ni-carbene bond as a possible reaction pathway. Computational studies indicated an apical agostic ethyl complex invoked by the bulky isopropyl substituents on the phosphine donors that places the ethyl group cis disposed to the carbene. This energetically achievable arrangement is responsible for the observed C-C coupling reaction and eliminates the necessity of a trans reductive elimination.

Chapter Four was the first to discuss the synthesis of a group 9 metal supported by the PCP array with the aim of creating a suitable catalyst for the activation and functionalization of C-H bonds. The focus of this chapter was on the chemistry of rhodium and in contrast to the group 10 metals the successful coordination of the PCP ligand required the neutral ligand (2.2). This allowed access to a series of new rhodium complexes utilizing both the Rh(I) and Rh(III) oxidation state. The steric bulk imparted by the phosphine substituents help to stabilize the coordination of reactive small molecules in the site trans to the carbene. This includes a rare example of a Rh(I) amido
complex (PCP)RhNH₂ (4.14), which through its reactivity towards BH₃(THF) led us to the discovery of (PCP)RhH as an active catalyst for the dehydrogenation of ammonia borane, a compound with interesting applications in hydrogen storage. The rhodium monohydride also showed promise as a hydrosilylation catalyst for less sterically congested alkynes using H₃SiPh. Finally, a thermally activated ligand rearrangement reaction involving cleavage of a C-P bond of the ligand backbone was reported; this process was shown not to interfere with the catalytic hydrosilylation of alkynes at temperatures up to 100 °C.

The coordination chemistry of the PCP ligand was extended to iridium in Chapter Five, and although the desired cationic iridium dihydride could not be synthesized a stable Ir(III) trihydride complex was isolated and fully characterized. Isolation of the new PCP iridium complexes is an important step considering the relatively few NHC-containing pincers ligands that have been successfully coordinated to iridium to date. The aim of this area of research was to develop a catalyst system for the conversion of saturated hydrocarbons to the corresponding alkenes. Unfortunately, the steric and electronic properties of the isolated PCP iridium complexes tested were shown to hinder alkane C-H bond activation processes. Addition of hydrogen to the iridium methyl species 5.11 uncovered an isomerization between the facial to the meridional coordination geometry of the PCP ligand. This process was proposed to occur via an intramolecular mechanism involving rotation of a η²-dihydrogen ligand. Reaction of the iridium ammine cation 5.14 with excess base led to an unexpected ligand rearrangement process initiated by a reactive imido fragment.
In conclusion, the target molecule was successfully synthesized and its versatility in forming new metal complexes was demonstrated through oxidative addition with group 10 metals, and by utilizing the neutral ligand with rhodium and iridium. The reaction between ethylene and the Ni-H species to form a new C-C bond can be viewed as a possible catalyst degradation pathway in the case of NHC complexes. Although the steric bulk of the isopropyl substituents was responsible for this unwanted reactivity it is this same property that was responsible for the successful coordination of a variety of reactive small molecules with rhodium. The rhodium hydride species proved to be a versatile catalyst, while the goal of designing an iridium catalyst suitable for C-H activation led to a series of complexes that help in understanding this relatively new class of compounds.

6.2 Thesis Extension: Attempts at Altering the PCP Steric Environment

A recurring issue while studying the coordination chemistry of the PCP ligand was the impact of the steric environment associated with the isopropyl substituents on the phosphine donors. To better understand the role these alkyl groups are playing a significant effort was made to reduce the steric repulsion around the metal centre. The first adjustment considered was to pull back on the size of the alkyl group on the phosphine substituent. To accomplish this the ethyl analog o-C₆H₄(NH₂)(PSEt₂) was synthesized following the same procedure as that reported for the isopropyl derivative. The successful synthesis of the less bulky aryl amine was confirmed through comparison of the NMR spectrum of the ethyl version with the established o-C₆H₄(NH₂)(PSPr₂) molecule. Unfortunately all attempts to form the ethylene backbone through alkylation of
the aryl amine with 1,2-dibromoethane were unsuccessful (eq. 6.1). Why the change from isopropyl to ethyl substituents results in complete failure of this simple nucleophilic substitution is not straightforward as a similar procedure has been shown to work with a variety of aryl amines.\(^\text{259}\)

\[
\begin{align*}
\text{NH}_2 & \quad \text{BrCH}_2\text{CH}_2\text{Br} \\
\begin{array}{c}
\text{HN} \\
\text{P} \\
\text{S} \\
\text{B} \\
\text{C} \\
\text{H}_2 \\
\text{C} \\
\text{H}_2 \\
\text{B} \\
\text{r}
\end{array} & \quad \begin{array}{c}
\text{N} \\
\text{H} \\
\text{P} \\
\text{S} \\
\text{H} \\
\text{N} \\
\text{P} \\
\text{S}
\end{array}
\end{align*}
\]

(eq. 6.1)

Due to the difficulty found in forming the diamine bridge a different synthetic strategy was chosen with the aim of reducing the steric bulk around the metal. A look at the solid-state molecular structure of the PCP ligand (1,3-bis(2-diphenylphosphanylethyl)-3H-imidazol-1-ium chloride) that, when coordinated to rhodium as shown in Scheme 1.8, has previously been applied in hydrosilylation experiments shows the ability of the flexible ethyl linkers to assist in relieving steric constraints.\(^\text{81}\) The expected synthetic route based on the literature report is shown in Scheme 6.1 and would lead to the unsaturated heterocycle as a chloride salt.

**Scheme 6.1.** Predicted route leading to a new PCP ligand utilizing alkyl linkers.
A few problems arose upon switching from HPPh$_2$ to HPPr$_i^2$ that seem to be a consequence of increasing the pK$_a$ from 22.9 to 35.0 respectively.$^{260}$ The first issue was that the KPPPr$_i^2$ reacted with DMSO, which is the only suitable solvent that sufficiently dissolves the chloride starting material. The basicity of the potassium salt also led to deprotonation of the imidazolium carbene so it was decided to selectively deprotonate the carbene and then attempt the chloride phosphine exchange in a THF solution at elevated temperature, but this resulted in a mixture of products in the $^{31}$P{$^1$H} NMR spectrum. The failures in trying to generate the isopropyl version of ethyl linked PCP ligand using the strategy in Scheme 6.1 is not entirely surprising as to date only diphenylphosphine substituents have been successfully installed.

An alternate route was envisioned starting from the amino phosphine Pr$_i^2$P(CH$_2$)$_2$NH$_2$ which was synthesized according to a literature procedure.$^{261}$ Following reaction with elemental sulfur, the protected amino phosphine was stirred with 1,2-dibromoethane according to the procedure outlined in Chapter Two (eq. 6.2). Although the $^{31}$P{$^1$H} NMR spectrum was indicative of a 50/50 mixture of amino phosphine and new product formation, the $^1$H NMR spectrum did not contain a resonance that could be assigned to a ethylenediamine bridge. This strategy of forming the diamine bridge was seemingly not as widely applicable as thought and for this reason a final attempt was made at synthesizing a more flexible version of the PCP ligand that would not require this step.

\[
\begin{align*}
\text{Pr}_i^2\text{P} & \xrightarrow{\text{S}_8} \text{Pr}_i^2\text{PS} \xrightarrow{\text{BrCH}_2\text{CH}_2\text{Br}} \text{Pr}_i^2\text{P} \xrightarrow{?} \text{Pr}_i^2\text{S}_2\text{H} \xrightarrow{\text{Pr}_i^2\text{P} \text{S}_2\text{H}} \text{Pr}_i^2\text{P} \\
\end{align*}
\]

(6.2)
In order to circumvent the 1,2-dibromoethane step a compound was sought where
the diamine backbone was already installed, this led us to the preparation of \(N,N'\)-bis(2-
chloroethyl)ethylenediamine Dihydrochloride (BCE·2HCl) according to a literature
procedure.\(^{262}\) In the next step, phosphine substitution requires first protecting the nitrogen
atoms with two equivalents of trimethylsilane (TMS). Unfortunately, all attempts to
protect the nitrogen atoms were unsuccessful as the \(^1\)H NMR spectrum of the product
indicated a molecule with only one TMS group incorporated (eq. 6.3); the rationale for
the absence of a second TMS protecting group is unclear. Protection of the nitrogen is
essential as the basic KPP\(\text{Pr}^2\) will induce formation of an aziridine ring as was observed
when BCE·2HCl was reacted with KOH.

![Chemical structure](image)

\[\text{eq. 6.3}\]

\[\text{6.3 Future Outlook}\]

A recent report on the synthesis of expanded ring NHCs\(^{263}\) (ring size greater than
five) may help in forming the central ring, which was a significant hurdle in attempting to
modify the PCP ligand in order to reduce steric bulk. The procedure involves initial
reaction between triethylorthoformate and an aryl amine followed by addition of a second
equivalent of the amine leading to a formamidine linkage (Scheme 6.2). The ring is then
closed in this example with 1,3-dibromopropane providing the product as the halide salt.
This modified synthetic route has enabled the development of six and seven membered
rings containing a large variety of substituents and therefore may be applicable to the o-
C₆H₄(NH₂)(PSEt₂) and Pr₁₂P(CH₂)₂NH₂ amines allowing access to a five membered ring with 1,2-dibromoethane.

**Scheme 6.2.** Synthesis of expanded ring heterocyclic salts.

Some interesting work involving the established PCP framework remains, in particular regarding the reaction of (PCP)RhNH₂ with borane. Scheme 4.6 detailed two possible pathways that may lead to the outcome of this reaction being the rhodium hydride 4.6. Unfortunately the ability to obtain further information about this process in the laboratory seems to be limited and for this reason it would be valuable to perform a computational study. The computational calculations obtained in the C-C coupling observed between [(PCP)NiH][PF₆] and ethylene proved to be a powerful tool in determining a energetically favourable pathway that could not have been examined experimentally. In the case of the rhodium amido complex understanding which pathway is more likely could help provide insight into the mechanism of ammonia borane dehydrogenation and thus aid in developing a more efficient dehydrogenation catalyst.
Another area of interest for expanding the chemistry of the PCP ligand would be through its coordination to iron, which is attractive for use as a more cost effective transition metal catalyst. Some very preliminary work was performed through reaction of the neutral PCP ligand with Fe(II) starting materials and NMR spectroscopy indicated the presence of a paramagnetic species, unfortunately no structural data has been obtained to this point. A terminal dinitrogen complex of iron supported by a tridentate bis-NHC ligand has recently been reported. As dinitrogen activation is an area of chemistry that is always relevant in the Fryzuk group it would be interesting to see how the PCP ligand, that was successful in stabilizing a terminal amido group, may behave following reduction in the presence of N$_2$. 

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(86) Hahn, F. E.; Jahnke, M. C.; Pape, T. Organometallics 2006, 25, 5927.
(87) Hahn, F. E.; Jahnke, M. C.; Pape, T. Organometallics 2006, 25, 5927.
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(90) Hahn, F. E.; Jahnke, M. C.; Pape, T. Organometallics 2006, 25, 5927.
(91) Hahn, F. E.; Jahnke, M. C.; Pape, T. Organometallics 2006, 25, 5927.
(92) Hahn, F. E.; Jahnke, M. C.; Pape, T. Organometallics 2006, 25, 5927.
(93) Hahn, F. E.; Jahnke, M. C.; Pape, T. Organometallics 2006, 25, 5927.
(94) Hahn, F. E.; Jahnke, M. C.; Pape, T. Organometallics 2006, 25, 5927.
(95) Hahn, F. E.; Jahnke, M. C.; Pape, T. Organometallics 2006, 25, 5927.
(96) Hahn, F. E.; Jahnke, M. C.; Pape, T. Organometallics 2006, 25, 5927.
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Appendices

Supplementary Information

A.1 X-ray Crystallographic Data

General Considerations. All crystals were mounted on a glass fiber and measured on a Bruker X8 diffractometer with graphite monochromated Mo-Kα radiation. The data was collected at a temperature of -100.0 ± 0.1°C with the Bruker APEX II CCD area-detector set at distance of 36.00 mm. Data was collected and integrated using the Bruker SAINT software package and corrected for absorption effects using the multi-scan technique (SADABS). The data was corrected for Lorentz and polarization effects and the structure was solved by direct methods. Neutral atom scattering factors for all non-hydrogen atoms were taken from Cromer and Waber. Anomalous dispersion effects were included in Fcalc. The values for Δf' ' and Δf'' were those of Creagh and McAuley. The values for mass attenuation coefficients are those of Creagh and Hubbell. Crystal system 2.5 exhibited merohedral twinning and a twin law of 00-1, 0-10, -100 was employed in the refinement of the structure. Crystal systems 2.6 and 4.5 crystallized with disordered solvent in the lattice. The disordered solvent molecules could not be modeled reasonably; therefore the PLATON/SQUEEZE program was used to correct the data for any unresolved residual electron density in the lattice. Also one scan-set for 2.6 was omitted as the data was found to be inconsistent with other scan-sets. All
non-hydrogen atoms were refined anisotropically, while all hydrogen atoms except amino hydrogens and hydrides were placed in calculated positions but were not refined. Hydride atoms and amino protons were located in a difference map and refined isotropically. All refinements were performed using the SHELXTL\textsuperscript{273} crystallographic software package of Bruker-AXS.
Table A.1. Crystallographic structural refinement information for [(PCP)H][PF$_6$] (2.1), [(PCP)NiH][PF$_6$] (2.5), and [(PCP)PdH][PF$_6$] (2.6).

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Table A.2. Crystallographic structural refinement information for [(PCP)PtH][PF₆] (2.7), [(PCEtP)Ni][PF₆] (3.4), and [(PCP{CHCH₂tBu})NiCCtBu][PF₆] (3.8).

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Table A.3. Crystallographic structural refinement information for [(PCP)$_2$Rh$_2$Cl$_2$(µ-Cl)$_2$][PF$_6$]$_2$ (4.4), (PCP)RhCl (4.5), and [(PCP)RhNH$_3$][PF$_6$] (4.9).

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Table A.4. Crystallographic structural refinement information for \textit{trans-}(PCP)RhH(CC\textsubscript{Ph})\textsubscript{2} (4.17), (PCC)Rh[HP(\textsuperscript{i}Pr)\textsubscript{2}] (4.18), and (PCC)Rh[CH\textsubscript{3}P(\textsuperscript{i}Pr)\textsubscript{2}] (4.19).

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<th>Compound</th>
<th>4.17</th>
<th>4.18</th>
<th>4.19</th>
</tr>
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<tbody>
<tr>
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<td>mf817</td>
<td>mf767</td>
<td>mf790</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{43} H\textsubscript{51} N\textsubscript{2} P\textsubscript{2} Rh</td>
<td>C\textsubscript{27} H\textsubscript{41} N\textsubscript{2} P\textsubscript{2} Rh</td>
<td>C\textsubscript{28} H\textsubscript{43} N\textsubscript{2} P\textsubscript{2} Rh</td>
</tr>
<tr>
<td>Formula weight (g/mol)</td>
<td>760.71</td>
<td>558.47</td>
<td>572.47</td>
</tr>
<tr>
<td>$\lambda$/\textsubcircumflex{}</td>
<td>0.71069</td>
<td>0.71073</td>
<td>0.71069</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C 2/c</td>
<td>P 2\textsubscript{1}/n</td>
<td>C 2/c</td>
</tr>
<tr>
<td>a/\textsubcircumflex{}</td>
<td>14.561(5)</td>
<td>15.0053(7)</td>
<td>29.629(5)</td>
</tr>
<tr>
<td>b/\textsubcircumflex{}</td>
<td>13.629(5)</td>
<td>8.3101(4)</td>
<td>8.564(5)</td>
</tr>
<tr>
<td>c/\textsubcircumflex{}</td>
<td>20.206(5)</td>
<td>20.9494(9)</td>
<td>27.107(5)</td>
</tr>
<tr>
<td>$\alpha$/\textdegree{}</td>
<td>90.000(5)</td>
<td>90</td>
<td>90.000(5)</td>
</tr>
<tr>
<td>$\beta$/\textdegree{}</td>
<td>109.730(5)</td>
<td>93.044(2)</td>
<td>115.799(5)</td>
</tr>
<tr>
<td>$\gamma$/\textdegree{}</td>
<td>90.000(5)</td>
<td>90</td>
<td>90.000(5)</td>
</tr>
<tr>
<td>$V$/\textsubcircumflex{}\textsuperscript{3}</td>
<td>3775</td>
<td>2608.6(2)</td>
<td>6193(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Dc/ g cm\textsuperscript{-1}</td>
<td>1.339</td>
<td>1.422</td>
<td>1.371</td>
</tr>
<tr>
<td>$\mu$/mm\textsuperscript{-1}</td>
<td>0.57</td>
<td>0.795</td>
<td>0.681</td>
</tr>
<tr>
<td>$F$(000)</td>
<td>1592</td>
<td>1168</td>
<td>2666</td>
</tr>
<tr>
<td>Crystal size/mm\textsuperscript{3}</td>
<td>0.35 x 0.25 x 0.15</td>
<td>0.25 x 0.15 x 0.08</td>
<td>0.30 x 0.20 x 0.10</td>
</tr>
<tr>
<td>$\theta_{\text{min}}$ - $\theta_{\text{max}}$/\textdegree{}</td>
<td>2.11 to 25.12</td>
<td>2.64 to 30.13</td>
<td>1.70 to 29.57</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>13168</td>
<td>28142</td>
<td>43466</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3366 [0.0384]</td>
<td>7639 [0.0429]</td>
<td>8575 [0.0785]</td>
</tr>
<tr>
<td>[R(int)]</td>
<td>99.70%</td>
<td>99.20%</td>
<td>98.70%</td>
</tr>
<tr>
<td>Completeness to $\theta_{\text{max}}$</td>
<td>Max. and min. transmission</td>
<td>0.9889 and 0.7865</td>
<td>0.9383 and 0.7129</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3366/0/220</td>
<td>7639/0/293</td>
<td>8575/0/348</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.034</td>
<td>1.078</td>
<td>1.017</td>
</tr>
<tr>
<td>$R [I &gt; 2\sigma(I)]$</td>
<td>$R_1 = 0.0250$, wR2 = 0.0571</td>
<td>$R_1 = 0.0370$, wR2 = 0.0885</td>
<td>$R_1 = 0.0453$, wR2 = 0.0954</td>
</tr>
<tr>
<td>$R$ (all data)</td>
<td>$R_1 = 0.0310$, wR2 = 0.0599</td>
<td>$R_1 = 0.0442$, wR2 = 0.0931</td>
<td>$R_1 = 0.0822$, wR2 = 0.1068</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e/\textsubcircumflex{}\textsuperscript{3})</td>
<td>0.392 and -0.371</td>
<td>1.249 and -0.834</td>
<td>2.586 and -1.197</td>
</tr>
</tbody>
</table>
Table A.5. Crystallographic structural refinement information for [IrCl(COD)]$_2${PCHP}[PF$_6$] (5.5), (PCP)IrHCl$_2$ 5.6, and (PCP)IrH$_3$ 5.9.

<table>
<thead>
<tr>
<th>Compound</th>
<th>5.5</th>
<th>5.6</th>
<th>5.9</th>
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<td>Dataset ID</td>
<td>mf700</td>
<td>mf729</td>
<td>mf748</td>
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<tr>
<td>Empirical formula</td>
<td>C$<em>{51}$ H$</em>{79}$ Cl$_2$ F$_6$ Ir$_2$ N$_2$</td>
<td>C$<em>{27}$ H$</em>{41}$ Cl$_2$ Ir N$_2$ P$_2$</td>
<td>C$<em>{27}$ H$</em>{43}$ N$_2$ P$_2$ Ir</td>
</tr>
<tr>
<td>Formula weight (g/mol)</td>
<td>1381.76</td>
<td>718.66</td>
<td>649.43</td>
</tr>
<tr>
<td>$\lambda$/Å</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P 2$_1$/c</td>
<td>Pbcn</td>
</tr>
<tr>
<td>a/Å</td>
<td>11.2353(12)</td>
<td>11.1009(14)</td>
<td>21.5417(9)</td>
</tr>
<tr>
<td>b/Å</td>
<td>16.9037(15)</td>
<td>15.045(2)</td>
<td>9.6641(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>17.2194(16)</td>
<td>18.087(3)</td>
<td>17.6329(8)</td>
</tr>
<tr>
<td>$\alpha$/°</td>
<td>75.826(4)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$/°</td>
<td>87.053(4)</td>
<td>107.117(6)</td>
<td>90</td>
</tr>
<tr>
<td>$\gamma$/°</td>
<td>83.350(4)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V/Å$^3$</td>
<td>3148.5(5)</td>
<td>2887.0(8)</td>
<td>3670.8(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>$Dc$/ g cm$^{-1}$</td>
<td>1.492</td>
<td>1.653</td>
<td>1.458</td>
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<tr>
<td>$\mu$/mm$^{-1}$</td>
<td>4.436</td>
<td>4.94</td>
<td>3.753</td>
</tr>
<tr>
<td>$F$(000)</td>
<td>1404</td>
<td>1432</td>
<td>1640</td>
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<tr>
<td>Crystal size/mm$^3$</td>
<td>0.22 x 0.18 x 0.15</td>
<td>0.25 x 0.15 x 0.10</td>
<td>0.35 x 0.15 x 0.09</td>
</tr>
<tr>
<td>$\theta_{\text{min}}$ to $\theta_{\text{max}}$/°</td>
<td>1.83 to 22.77</td>
<td>1.79 to 25.39</td>
<td>1.89 to 27.90</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>27332</td>
<td>20146</td>
<td>52337</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8449/5/616</td>
<td>5206/0/319</td>
<td>4321/0/218</td>
</tr>
<tr>
<td>Complete to $\theta_{\text{max}}$</td>
<td>99.30%</td>
<td>97.90%</td>
<td>98.20%</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9356 and 0.6776</td>
<td>0.6101 and 0.4074</td>
<td>0.7134 and 0.4581</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>8449/0/218</td>
<td>5206/0/198</td>
<td>4321/0/218</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>0.966</td>
<td>1.02</td>
<td>1.081</td>
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<tr>
<td>R [I &gt; 2$\sigma$(I)]</td>
<td>R$_1$ = 0.0619, wR$_2$ = 0.1475</td>
<td>R$_1$ = 0.0264, wR$_2$ = 0.0467</td>
<td>R$_1$ = 0.0172, wR$_2$ = 0.0333</td>
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<tr>
<td>R (all data)</td>
<td>R$_1$ = 0.1171, wR$_2$ = 0.1654</td>
<td>R$_1$ = 0.0412, wR$_2$ = 0.0498</td>
<td>R$_1$ = 0.0305, wR$_2$ = 0.0391</td>
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<tr>
<td>Largest diff. peak and hole (e/Å$^3$)</td>
<td>2.000 and -1.634</td>
<td>0.728 and -0.641</td>
<td>0.907 and -0.608</td>
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</table>
Table A.6. Crystallographic structural refinement information for *fac-(PCP)IrH₂CH₃* (5.12), and *(PNH)IrH₂(CP)* (5.15).

<table>
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<tr>
<th>Compound</th>
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<tr>
<td>Empirical formula</td>
<td>C₂₈H₄₅N₂P₂Ir</td>
<td>C₂₇H₄₄N₃P₂Ir</td>
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<tr>
<td>Formula weight (g/mol)</td>
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<td>664.79</td>
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<td>λ/Å</td>
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<td>0.71069</td>
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<td>Crystal system</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2₁/n</td>
<td>P 2₁/n</td>
</tr>
<tr>
<td>a/Å</td>
<td>14.488(5)</td>
<td>8.970(5)</td>
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<td>b/Å</td>
<td>15.425(5)</td>
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<td>c/Å</td>
<td>14.728(5)</td>
<td>21.508(5)</td>
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<td>α/°</td>
<td>90.000(5)</td>
<td>90.000(5)</td>
</tr>
<tr>
<td>β/°</td>
<td>104.510(5)</td>
<td>96.110(5)</td>
</tr>
<tr>
<td>γ/°</td>
<td>90.000(5)</td>
<td>90.000(5)</td>
</tr>
<tr>
<td>V/Å³</td>
<td>3186.4(19)</td>
<td>2749.5(19)</td>
</tr>
<tr>
<td>Z</td>
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<td>4</td>
</tr>
<tr>
<td>Dc/ g cm⁻¹</td>
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<td>1.606</td>
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<td>µ/mm⁻¹</td>
<td>4.316</td>
<td>4.992</td>
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<tr>
<td>F(000)</td>
<td>1504</td>
<td>1336</td>
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<tr>
<td>Crystal size/mm³</td>
<td>0.35 x 0.22 x 0.12</td>
<td>0.25 x 0.20 x 0.10</td>
</tr>
<tr>
<td>θmin – θmax /°</td>
<td>1.76 to 25.13</td>
<td>1.71 to 24.91</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>23208</td>
<td>33451</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5710 [0.0262]</td>
<td>4678 [0.0376]</td>
</tr>
<tr>
<td>Completeness to θmax</td>
<td>100.00%</td>
<td>97.50%</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.5958 and 0.4909</td>
<td>0.6070 and 0.2167</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5710/0/360</td>
<td>4678/0/314</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.031</td>
<td>1.063</td>
</tr>
<tr>
<td>R [I &gt; 2σ(I)]</td>
<td>R1 = 0.0159, wR2 = 0.0383</td>
<td>R1 = 0.0282, wR2 = 0.0697</td>
</tr>
<tr>
<td>R (all data)</td>
<td>R1 = 0.0183, wR2 = 0.0392</td>
<td>R1 = 0.0307, wR2 = 0.0718</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e/Å³)</td>
<td>0.625 and -0.360</td>
<td>3.137 and -1.761</td>
</tr>
</tbody>
</table>
A.2 Computational Methods

Density functional calculations were carried out using the Amsterdam Density Functional program suite ADF 2007.01. The generalized gradient approximation was employed, using the local density approximation of Vosko, Wilk, and Nusair together with the nonlocal exchange correction by Becke and nonlocal correlation corrections by Perdew. TZP basis sets were used with triple-ζ accuracy sets of Slater type orbitals and two polarisation functions added. The cores of the atoms were frozen up to 1s for C, N and O and 2p for P and Ni. Stationary points were confirmed by frequency calculations. The minima showed all +ve frequencies except 2.5c which had two very small imaginary frequencies of –i6 and –i26 cm⁻¹ associated with the ‘Pr groups. The transition states each showed a single imaginary frequency whose motion was associated with, in the case of 3.6c, rotation of the methyl group of the ethyl ligand and, in the case of 3.7c, motion of the ethyl group towards the carbene carbon atom.

Table A.7. Thermodynamic data from frequency calculations, T = 298.15K. Energies referenced to 2.5c + ethene.

<table>
<thead>
<tr>
<th></th>
<th>v(cm⁻¹)</th>
<th>E(SCF)/eV</th>
<th>Δ(E)</th>
<th>ZPE/eV</th>
<th>Δ(ZPE)</th>
<th>S(cal/mol_K)</th>
<th>Δ(S)</th>
<th>U(Kcal/ mol)</th>
<th>Δ(U)</th>
<th>ΔG(Kcal/ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5c</td>
<td>!-i6 and</td>
<td>-i26</td>
<td>-413.66</td>
<td>0</td>
<td>16.512</td>
<td>0</td>
<td>207.2</td>
<td>0</td>
<td>402.8</td>
<td>0</td>
</tr>
<tr>
<td>ethene</td>
<td>all +ve</td>
<td>-31.512</td>
<td>0</td>
<td>1.343</td>
<td>0</td>
<td>52.4</td>
<td>0</td>
<td>32.9</td>
<td>0</td>
<td>0</td>
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<tr>
<td>3.3c</td>
<td>all +ve</td>
<td>-445.13</td>
<td>0.042</td>
<td>18.093</td>
<td>0.238</td>
<td>226.5</td>
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<td>442</td>
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<td>3.5c</td>
<td>all +ve</td>
<td>-444.926</td>
<td>0.246</td>
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<td>-31.4</td>
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<td>3.6c</td>
<td>!-i104</td>
<td>-444.725</td>
<td>0.447</td>
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<td>4.6</td>
<td>27.0595041</td>
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<tr>
<td>3.4c</td>
<td>all +ve</td>
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<td>0.196</td>
<td>228</td>
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<td>441.1</td>
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<td>4.5903341</td>
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<td>3.7c</td>
<td>!-i235</td>
<td>-444.63</td>
<td>0.542</td>
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<td>0.13</td>
<td>227.9</td>
<td>-31.7</td>
<td>439.5</td>
<td>3.8</td>
<td>28.1555491</td>
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