INVESTIGATIONS OF C-H AND N-H ACTIVATION WITH ELECTRON DEFICIENT IRIDIUM PINCER COMPLEXES

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ABSTRACT

ALISON CARTWRIGHT SYKES: Investigations of C-H and N-H Activation with Electron Deficient Iridium Pincer Complexes
(Under the direction of Professor Maurice Brookhart)

Transition metal reactions that involve C-H and N-H bond activation provide a potential method for functionalizing hydrocarbons and amines. For the past three decades there have been numerous advances in this field; however, developing new approaches to activation of these bonds continues to be a significant endeavor. Recently pincer ligands have been successfully used to stabilize metal complexes at elevated temperatures. When chelated to iridium, these pincer complexes have been shown to be very active as transfer dehydrogenation catalysts. This has been exemplified by Kaska, Goldman, and Jensen using Ir complexes containing the 2,6-(CH₂PrBu₂)₂C₆H₃ (PCP) ligand and by Brookhart using the Ir complexes of the more electron-deficient bis(phosphinite) pincer ligand (POCOP). This dissertation explores alternative reactivity of these bis(phosphinite)iridium complexes.

Chapter 2 focuses on the reactions of [(POCOP)Ir] with N-H bonds, in particular those of both anilines and benzamides. The electronic character of the anilines plays an important role in the reactivity; more electron-withdrawing anilines favor oxidative addition while the more electron-donating anilines favor σ-bond formation. An explanation for this behavior is
provided along with a kinetic analysis of the oxidative addition and reductive elimination of anilines. A comparison of the reactivity of anilines to that of benzamides is also discussed.

In Chapter 3, cationic [(POCOP)Ir(H)(L)][BArF] complexes are examined that contain tetrakis(trifluoromethyl)borate (BArF) as a non-coordinating counterion. Since these complexes are cationic, the metal center is even more electron deficient than those mentioned above. The structure of [(POCOP)Ir(H)(H₂)][BArF] was determined based on an H-D coupling constant of 33 Hz. In addition to the structural analysis, the rate of exchange between the hydride and the dihydrogen has also been determined.

Cationic olefin complexes, [(POCOP)Ir(H)(L)][BArF] (L = C₂H₄, C₃H₆, norbornene, methyl acrylate) have also been synthesized. Their dynamic behavior has been assessed using both line-broadening and spin-saturation transfer NMR techniques. The rates of olefin rotation and insertion into the Ir-H bond were analyzed and energy barriers to these processes were calculated. A brief examination of the reactivity of the cationic norbornene complex with nucleophiles has also been explored; however the results showed no C-Nuc bond formation.
To My Family:

Craig and Rusty

Mom, Dad, and Mark
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<tr>
<td>‡</td>
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<tr>
<td>°C</td>
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<td>δ</td>
<td>chemical shift</td>
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<tr>
<td>ΔG</td>
<td>change in Gibbs’ free energy</td>
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<td>ν</td>
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<td>Ar</td>
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<td>atm</td>
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<td>BArF</td>
<td>[(\text{B}(3,5\text{-bis}(\text{CF}_3)\text{C}_6\text{H}_3)_4)]^-</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>Definition</td>
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<td>--------</td>
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CHAPTER ONE

Funtionalization of Carbon-Hydrogen Bonds through the Activation of C-H and N-H Bonds by Transition Metal Complexes: Introduction and Background

Since the first example of C-H oxidative addition of benzene to a soluble transition metal complex was observed by Chatt and Davidson in 1965, the understanding and potential of C-H activation reactions has been extensively studied. Activation of saturated alkanes was believed to be more difficult than that of arenes despite the lower bond strength (~95 kcal/mol), but this was finally achieved nearly simultaneously by Bergman and Graham using Ir(I) complexes. Throughout the 1980’s and into the 1990’s, a significant amount of research was focused on better understanding C-H bond activation through investigations of intermediates, thermodynamics and kinetics, and selectivity of various stoichiometric reactions.

There had been reactions in which the oxidative addition of a saturated alkane had been postulated, but it was not until Bergman’s findings in 1982 that a stable intermediate M(H)(alkyl) species was observed. Irradiation of Cp*Ir(PMe3)H2 in an alkane solvent was shown to induce loss of H2 followed by formation of the Cp*Ir(PMe3)(H)(alkyl) complex which was observed by 1H NMR spectroscopy (Scheme 1.1). In this early stage it was
shown that activation of a primary C-H bond is favored over a secondary C-H bond. Graham observed the same results with after irradiation of Cp*Ir(CO)$_2$ in neopentane and cyclohexane solvent.$^3$ Shortly thereafter, Jones reported similar behavior of an analogous rhodium system.$^6$ The LnRh(H)(alkyl) species, however, are significantly less stable and undergo reductive elimination of the alkane at -15°C.

Scheme 1.1. First observation of an alkyl hydride complex by Bergman in 1982$^2$

$$\text{Me}_5\text{IrH}\text{PMe}_3 \xrightarrow{\text{hv}, \text{RH}} \left[ \text{Me}_5\text{Ir}\text{PMe}_3 \right] \xrightarrow{\text{RH}} \text{Me}_5\text{IrH}\text{PMe}_3$$

One striking outcome of this research was a deeper understanding of the selectivity of alkane activation. The [Cp*Ir(PMe$_3$)] species prefers activation of the stronger rather than the weaker C-H bond of alcanes (i.e. 1° > 2° >> 3°). This preference was ascribed to steric effects. This finding was especially interesting because the regioselectivity shown by this reaction was the reverse of that seen in radical-induced alkane functionalization (3° > 2° > 1°).

Following detailed studies of stoichiometric C-H oxidative addition reactions, the next goal was to develop transition metal-catalyzed processes to functionalize C-H bonds of alcanes. Such catalytic reactions have been particularly challenging. While numerous routes to functionalized products have been discovered, problems including over oxidation forming either a mixture of products or the undesired product, poor region- or chemoselectivity, competing side reactions, and slow rates are encountered in developing such processes.
One still elusive goal is the practical oxidation of methane to methanol catalyzed by a transition metal.\textsuperscript{23-26} This reaction is of significance as it would provide a safe, convenient, and economical method for converting methane to a liquid fuel. Observed in 1972 by Shilov, oxidation of methane to methanol under reasonably mild conditions was achieved using a platinum(II) catalyst. This reaction had one major fault that prevented its use commercially: although it was catalytic in platinum(II), a stoichiometric amount of platinum(IV) was needed to reoxidize the platinum(II) (Scheme 1.2).

\textbf{Scheme 1.2.} Shilov’s oxidation of methane to methanol by Pt(II)/Pt(IV)\textsuperscript{23-26}

More recently, Periana and coworkers, then at Catalytica, improved upon Shilov’s system. They developed a platinum catalyzed system that catalytically functionalizes methane to methyl bisulfate, a methanol derivative, and at moderate temperatures with yields of 72\% (Scheme 1.3).\textsuperscript{27} This reaction is performed in concentrated sulfuric acid in which SO\textsubscript{3} serves as the oxidant.
Scheme 1.3. Catalytic conversion of methane to methyl bisulfate by a platinum catalyst developed by Periana and coworkers

\[
\begin{align*}
\text{CH}_4 + 2\text{H}_2\text{SO}_4 \xrightarrow{(\text{bpym})\text{PtCl}_2} & \text{CH}_3\text{OSO}_3\text{H} + 2\text{H}_2\text{O} + \text{SO}_2 \\
\text{bpym} = \text{biprimidine}
\end{align*}
\]

Often thermodynamics and kinetics work against the functionalization of alkanes, so strategies to overcome these barriers must be developed. Two methods of circumventing this problem are the use of a secondary reaction to offset the energy requirements or driving the reaction photochemically.

Insertion of carbon monoxide into a C-H bond, or carbonylation, for example, is an endothermic process. There exist only a few examples of this reaction that involve alkanes. One such reaction was discovered by Tanaka using the rhodium complex, \( \text{Rh}(\text{PMe}_3)_2(\text{CO})(\text{Cl}) \) (Scheme 1.4). In this case, light is used to drive the reaction. Remarkably, this reaction showed significant regioselectivity, and the linear product was favored by about 45:1 as shown in Scheme 1.3\textsuperscript{28}

Scheme 1.4. Carbonylation of pentane by \( \text{Rh}(\text{PMe}_3)_2(\text{CO})(\text{Cl}) \) reported by Tanaka\textsuperscript{28}

Another important reaction based on C-H oxidative addition is alkane dehydrogenation. This reaction provides a method of converting alkanes to alkenes, one of the most important feedstocks used in industry. As in the carbonylation reactions mentioned above,
Dehydrogenation is a thermodynamically uphill process (ca. +33 kcal/mol). Since the entropy of this process is positive, in some systems under elevated temperatures the equilibrium might lie on the side of the dehydrogenated products. However, for these reactions to proceed under moderate reaction conditions, the use of a sacrificial hydrogen acceptor is often used to offset the energy requirement. The sacrificial hydrogen acceptor, often tert-butylethylene (TBE), is hydrogenated to tert-butylethane, a thermodynamically downhill reaction. Through the removal of hydrogen from the catalyst precursor, TBE allows the formation of the active species. Scheme 1.5 shows the dehydrogenation of cyclopentane by a cationic iridium catalyst with the addition of the hydrogen acceptor, TBE, reported by Crabtree and coworkers. Cyclopentane can be dehydrogenated twice followed by oxidative addition to the iridium to form the cyclopentadienyl complex.

Scheme 1.5. Dehydrogenation of cyclopentane to cyclopentadiene with the use of a hydrogen acceptor

\[
\text{[IrH}_2\text{(solv)}_2\text{(PPh}_3\text{)}_2\text{][BF}_4\text{]} + \text{cyclopentane} + 3 \text{H}_{\text{2}} \xrightarrow{1 \text{,2-dichloroethane}, 80^\circ\text{C}} \text{Ir}(\eta^4\text{-pentadiene})\text{PPh}_3 + 3 \text{H}_2
\]

Around the same time as Crabtree’s report, Felkin showed that heptahydridobis(triarylphosphine)rhenium catalyzed the dehydrogenation of not only cycloalkanes but also of linear alkanes. In this reaction, the dehydrogenated product, \(\eta^4\)-trans-1,3-pentadiene remains coordinated to rhenium. However, addition of trimethylphosphite allows for the selective formation of 1-pentene. This was a promising result in that it showed selective conversion of linear alkanes to the \(\alpha\)-olefin product. (Scheme 1.6)

(Scheme 1.6)
Scheme 1.6. Selective dehydrogenation of \( n \)-pentane by \((\text{Ar}_3\text{P})_2\text{ReH}_7\) to form 1-pentene$^{30}$

In the past decade, iridium pincer complexes such as those shown in Figure 1.1 have been used as catalysts for dehydrogenation of alkanes. The pioneering studies on complex 1 began in the late 1990’s by Kaska, Jensen and Goldman.$^{31-34}$ The pincer ligand stabilized the iridium dihydride complexes so that little or no decomposition occurred during dehydrogenation even at extremely high temperatures (150-200°C). As in the dehydrogenation reactions described above, TBE was added to the reaction mixture as a hydrogen acceptor. However, when the reactions are run at 200°C, the use of TBE was not necessary (“acceptorless” conditions) because at this temperature hydrogen reductively eliminates from 1 and is driven off through vigorously refluxing the solvent. This complex showed versatility as it not only dehydrogenates cycloalkanes, but also reacts with tetrahydrofuran$^{31}$, ethylbenzene$^{31}$, and ethylcyclohexane, and more recently tertiary amines to form enamines.$^{35}$ Catalyst 2 selectively dehydrogenates \( n \)-alkanes to \( \alpha \)-olefins at 150°C with moderate conversions.$^{36}$

Figure 1.1. Pincer complexes shown to be active transfer dehydrogenation catalysts
In 2004, our group developed the bis(phosphinite) pincer complexes 3-8 (Figure 1.2), with the idea that removing more electron density from the iridium center might achieve higher rates and turnover numbers for transfer dehydrogenation than the parent system and still retain stability at high temperatures.\textsuperscript{37-39} In fact this was the case. The bis(phosphinite) complex, 8, with the most electron-withdrawing substituent on the ligand backbone was the most active derivative for this reaction with a turnover number of 2210 at 200°C when cyclooctane (3030:1, COA:Ir) was used as a substrate. Active catalysts are generated by the addition of 1.1 equivalents of NaOT\textsubscript{Bu} to the hydridochloride to form the active 14-electron intermediate. Under the same reaction conditions, the parent system, (PCP)Ir(H)(Cl), the catalyst precursor to 1, showed an activity of only 230 TO’s.\textsuperscript{38}

![Figure 1.2. Bis(phosphinite)Ir(H)(Cl) complexes 3-8 developed in the Brookhart lab\textsuperscript{38}](image)

Late transition metals have shown potential in hydroamination, a reaction of intense current interest.\textsuperscript{40-46} Hydroamination provides a synthetically convenient method for the formation of C-N bonds. Molecules that contain nitrogen atoms, such as amines, are of interest industrially, especially for pharmaceutical products. However, currently amines are
typically formed by multistep syntheses. Application of hydroamination to synthesize these types of products could lead to fewer or even one step processes.

There are two mechanisms that are widely accepted for hydroamination by late-transition metals (Scheme 1.7). In the first mechanism,\textsuperscript{40,47} often seen in palladium and platinum systems, the alkene coordinates to the metal center, activating it toward nucleophilic attack. The amine nucleophile can then attack the olefin with loss of a proton. Two possible products can then be formed. Through protonolysis of the M-C bond, the hydroamination product can result. Alternatively, β-hydride elimination can occur and the oxidative amination product is formed.\textsuperscript{40}

**Scheme 1.7.** Mechanism for late-transition metal hydroamination

![Mechanism for late-transition metal hydroamination](image)

For rhodium and iridium, hydroamination typically occurs via activation of the amine by oxidative addition, followed by olefin insertion into either the M-H bond or M-N bond. Reductive elimination of the product yields the desired amine.\textsuperscript{40,48} (Scheme 1.7) Reactions
involving the oxidative addition of nitrogen-hydrogen bonds to a transition metal center are surprisingly much less studied than C-H bond activation despite the similarities in homolytic bond strength. In fact, there exist only a few examples of catalytic reactions involving the oxidative addition of an N-H bond to a metal center. Casalnuovo and Milstein have shown that hydroamination of norbornene by a coordinatively unsaturated iridium complex occurs by the initial activation of amine. In this case the active Ir(I) catalyst, “Ir(PEt$_3$)$_2$Cl,” is formed by dissociation of two ethylene molecules from Ir(PEt$_3$)$_2$(C$_2$H$_4$)$_2$Cl. Aniline then undergoes oxidative addition to the iridium center followed by coordination of norbornene. Iridium has a two-fold role in this reaction; it not only activates the norbornene to nucleophilic attack but also activates the lone pair on the aniline. This lone pair attacks the olefin forming a metallacyclic intermediate. The catalyst is regenerated and the product is formed by C-H reductive elimination and dissociation of the product amine. (Scheme 1.8)

**Scheme 1.8.** Hydroamination of norbornene by Casalnuovo and Milstein with an iridium catalyst
The Ir(I) pincer complex 1, described above as a good transfer dehydrogenation catalyst, also shows reactivity with N-H bonds,\textsuperscript{50} although to date no hydroamination reactions have been reported. As illustrated in Scheme 1.9, the aniline N-H bond can be activated through oxidative addition to the iridium center of 9 to form 10. The dihydride complex 1 is converted to the 14-electron active species 9 by reaction with the hydrogen acceptor tbutylethylene (TBE).

Scheme 1.9. The oxidative addition of aniline to (PCP)IrH\textsubscript{2}, 1\textsuperscript{50}

![Scheme 1.9](image)

Even more significant is that reaction of (PCP)Ir(H)(Cl)(NH\textsubscript{3}) and KN(SiMe\textsubscript{3})\textsubscript{2} generated the amido hydride complex 12 at -78°C (Scheme 1.10). (PCP)Ir(H)(Cl)(NH\textsubscript{3}) 11 was formed from the reaction of (PCP)Ir(H)(Cl) ammonia.\textsuperscript{50} This is one of only a few examples in the literature were the amido hydride of ammonia has been observed.\textsuperscript{51,52} If 12 is warmed to room temperature the σ-bound ammonia complex 13 is formed. Complex 13 can also be formed directly from the addition of ammonia and TBE at room temperature to 1.\textsuperscript{50}
Typically, by adding more electron density to a metal center oxidative addition to the metal becomes more favorable. Based on this trend, Goldman and Hartwig et. al. developed a new iridium(I) pincer complex that has a more electron-donating aliphatic ligand backbone, 14. This ligand significantly altered the reactivity of the Ir pincer complex to favor oxidative addition. Indeed, when complex 14 was treated with ammonia at room temperature the amido hydride complex 15 was formed (Scheme 1.11).53

Scheme 1.10. Reaction of PCP iridium complexes with ammonia50

Scheme 1.11. Oxidative addition of ammonia at room temperature by a pincer complex with an electron-donating ligand.
Research Goals and Achievements

As mentioned above the functionalization of C-H bonds is a desirable process. Recent studies of Ir(I) pincer complexes have shown that they are reactive with C-H and N-H bonds of numerous substrates. The most useful reaction based on C-H activation by these complexes has been dehydrogenation of alkanes to alkenes. However, there is still a significant amount of research needed to fully explore the potential of these iridium pincer complexes. The goal of the research presented in the following chapters is to obtain a better understanding of the reactivity of Ir(I) pincer complexes containing the more electron-withdrawing bis(phosphinite) pincer ligand.

Chapter one describes the reactivity of the [(POCOP)Ir] moiety with various anilines, NH₂Ar. The active [(POCOP)Ir] fragment is generated in situ in these reactions by treating (POCOP)Ir(H)(Cl) with NaOtBu in an aromatic solvent (benzene or toluene). The aromatic solvent is necessary to stabilize the reactive intermediate. When anilines are present an equilibrium is established between (POCOP)Ir(H)(Ar), (POCOP)Ir(NH₂Ar) and (POCOP)Ir(H)(NHAr). Electronic effects were probed by examining the change in the equilibrium ratios of these three species as a function of the substituents on the aniline.

Details of the oxidative addition and reductive elimination of the anilines were further studied to gain mechanistic information on these reactions. A comparison of the rates reductive elimination of the more electron-withdrawing anilines from the d⁶ five-coordinate (POCOP)Ir(H)(NHAr) and the d⁶ six-coordinate (POCOP)Ir(H)(CO)(NHAr) is also presented. The mechanisms of these two processes are compared to known mechanisms for reductive elimination from d⁶ systems. A brief comparison of the oxidative addition of the anilines to similar reactions of benzamide is presented as well.
Chapter Two describes the synthesis of more electron-deficient cationic iridium(III) pincer complexes, \([(\text{POCOP})\text{Ir(H)(L)}][\text{BArF}]\) (BArF = tetrakis(3,5-bis(trifluoromethylphenyl))-borane). These complexes (L = olefin) were prepared with the goal of using them for catalytic hydroamination as shown below for the simple case \(L = \text{C}_2\text{H}_4\) (Scheme 1.12).

**Scheme 1.12.** Potential catalytic cycle for hydroamination with \([(\text{POCOP})\text{Ir(H)(L)}][\text{BArF}]\) \(L = \text{C}_2\text{H}_4\)

![Potential catalytic cycle for hydroamination](attachment:image)

Although implementations of this catalytic cycle were not successful, a number of new complexes of the type \([(\text{POCOP})\text{Ir(H)(L)}][\text{BArF}]\) were prepared and found to have interesting structural and dynamic features.

An in-depth analysis of \([(\text{POCOP})\text{Ir(H)(H}_2)][\text{BArF}]\) is described. NMR data provides evidence supporting a dihydrogen/hydride complex rather than a trihydride complex. Exchange rates among the hydrogens are measured and presented as well.

The dynamics of the complexes where \(L\) equals ethylene, propylene, norbornene, and methyl acrylate are studied as well, in particular the rotation of the olefin, as well as the rate
of insertion of the olefin into the M-H bond. Attempts at C-H functionalization of the olefins were attempted with the addition of aniline and thiol to the cationic olefin complexes.
References


CHAPTER TWO

Reactions of Anilines and Benzamides with a Fourteen-Electron Iridium(I) Bis(Phosphinite) Complex: N-H Oxidative Addition versus Lewis Base Coordination

(This chapter has been adapted with permission from: Sykes, A. C., White, P., Brookhart, M. Organometallics 2006, 25, 1664-1675. Copyright 2006 American Chemical Society.)

Introduction

Carbon-hydrogen bond activation by late transition metal complexes has received intense scrutiny over the past two decades since the classic work of Bergman\(^1\), Jones\(^2\), and Graham\(^3\). Fundamental studies including kinetics, thermodynamics, and selectivities of the oxidative addition reactions of C-H bonds to a variety of transition metal centers together with theoretical investigations have appeared\(^4,5\). More recently, these reactions have been incorporated into catalytic cycles, and there are now numerous useful catalytic organic transformations based on C-H bond activation reactions\(^6-12\).

Although N-H and C-H bonds exhibit similar homolytic bond strengths, many fewer investigations of late metal activation of N-H bonds have been carried out\(^13-16\). Such studies
could impact the rapidly growing number of metal-catalyzed transformations of amine and related compounds including hydroaminations of alkenes, styrenes, dienes, and alkynes.\textsuperscript{17-20} Some of these transformations appear to involve oxidative addition of N-H bonds,\textsuperscript{21,22} while the mechanisms of many other transformations are unknown, but some could involve an N-H oxidative addition step.

An early instructive example of oxidative addition of N-H bonds to late transition metal centers was reported by Merola who showed that the N-H bonds of pyrroles and indoles oxidatively add to the Ir(I) moiety, (COD)(PMe$_3$)$_3$Ir$^+$, to yield the eighteen-electron, octahedral Ir(III) species as illustrated in Scheme 2.1.\textsuperscript{23}

**Scheme 2.1.** Example of oxidative addition of N-H bonds to a Ir(I) moiety by Merola

\[
(COD)Ir(PMe_3)_3^+ + \text{HN}R_1R_2R_3 \rightarrow\]

The Goldman, Jensen, and Kaska groups have shown that the 14-electron complex (PCP)Ir (PCP = 2,6-(CH$_2$P(t-Bu)$_2$)$_2$C$_6$H$_3$), 1, generated from treatment of the dihydride (PCP)Ir(H)$_2$ with acceptors such as tert-butylethylene, readily oxidatively adds C-H bonds of alkanes and arenes.\textsuperscript{24,25} Such species are highly active for catalytic transfer dehydrogenation of alkanes and can also be used for synthesis of enamines through transfer dehydrogenation of tertiary amines.\textsuperscript{26} Goldman and Hartwig have recently observed that the (PCP)Ir complex 1 oxidatively adds the N-H bond of aniline to produce the Ir(III) anilino hydride 2 as shown in Scheme 2.2.\textsuperscript{27} In benzene, adduct 2 equilibrates with the phenyl hydride complex 3. The equilibrium favors the anilino hydride complex with a K$_{eq} = 105$ at 22°C (Scheme 2.3).
Scheme 2.2. Oxidative addition of aniline to [(PCP)Ir] to form (PCP)Ir(H)(NHC₆H₅) by Goldman and Hartwig

\[
\begin{align*}
(\text{tBu})₂P & \quad \text{Ir} \quad P(\text{tBu})₂ \\
\text{H} & \quad \text{H} \\
\xrightarrow{\text{H₂NPh}} \\
(\text{tBu})₂P & \quad \text{Ir} \quad P(\text{tBu})₂ \\
\text{H} & \quad \text{HN} \quad \text{Ph}
\end{align*}
\]

Scheme 2.3. Equilibrium between (PCP)Ir(H)(Ph) + NH₂C₆H₅ and (PCP)Ir(H)(NHC₆H₅) + C₆H₆ at room temperature

\[
\begin{align*}
(\text{tBu})₂P & \quad \text{Ir} \quad P(\text{tBu})₂ \\
\text{H} & \quad \text{Ph} \\
\xrightarrow{K_{eq} = 105} \\
(\text{tBu})₂P & \quad \text{Ir} \quad P(\text{tBu})₂ \\
\text{H} & \quad \text{NHPh} \quad \text{C₆H₆}
\end{align*}
\]

Attempted oxidative addition of the better σ-donor ammonia results in the Ir(I) ammonia complex 4. The amido hydride 5 could be independently generated by dehydrochlorination of 6 at -78°C. Warming to 25°C resulted in conversion to ammonia complex 4, indicating that thermodynamically the ammonia complex is favored over the amido hydride (Scheme 2.4). When a more electron-donating saturated backbone is incorporated in the pincer ligand, oxidative addition of ammonia occurs rather than simple coordination. Treatment of 7 with ammonia forms the Ir(III) amido hydride in high yields at 25°C (Scheme 2.5).
Scheme 2.4. Generation of (PCP)Ir(H)(NH₂) at low temperature followed by formation of (PCP)Ir(NH₃) by warming to room temperature

Scheme 2.5. Activation of ammonia at room temperature by an iridium(I) complex with an electron-donating pincer backbone

Our laboratory²⁹-³¹ has investigated the chemistry of more electron-deficient Ir pincer complexes based on the bis(phosphinite) ligand, POCOP = 2,6-(OPtBu₂)₂C₆H₃. The highly active 14-electron complex 10 can be conveniently generated in situ by treatment of the hydrido chloride 9 with sodium tert-butoxide (Scheme 2.6). Generation of 10 in a cyclooctane/tert-butylethylene mixture produces a highly active catalyst system for transfer dehydrogenation and production of cyclooctene and cyclooctadiene (Scheme 2.7). Detailed mechanistic studies of this system have complemented the studies of Goldman on 1 and
provided interesting contrasts suggesting the phosphinite POCOP system prefers the Ir(I) oxidation state relative to the PCP systems.\textsuperscript{29-31}

**Scheme 2.6.** In situ formation of the active 14-electron iridium species, [(POCOP)Ir]

\[
\begin{align*}
\text{Scheme 2.7.} & \quad \text{Transfer dehydrogenation of cyclooctane with (POCOP)Ir(H)(Cl) as the catalyst precursor} \\
\end{align*}
\]

This chapter describes the reaction of a series of substituted anilines and benzamides with the phosphinite pincer complex 10. In the case of the anilines, either the Ir(III) oxidative addition adduct, the Ir(I) σ-complex, or a mix of these products is formed depending on the nature of the \textit{para}-substituent. Rates of reductive elimination of the Ir(III) species have been measured, as well as the equilibria in benzene between the aniline adducts and the phenyl hydride. Information on the mechanism of reductive elimination was attained through the study of low temperature reactions of both the \textit{p}-chloroaniline and the \textit{p}-methoxyaniline complexes.
Results and Discussion

I) Reaction of (POCOP)Ir pincer complexes with various anilines (11a-g)

a) Equilibration of (POCOP)Ir(H)(C₆H₅) (12) with various (POCOP)Ir(NH₂Ar) (13) and (POCOP)Ir(H)(NHAr) (14)

The reactions of anilines shown in Figure 2.1 with the fourteen-electron (POCOP)Ir pincer complex 10 were carried out by treatment of the hydrochloride complex 9 with NaOtfBu and anilines 11a-g in benzene at room temperature for 1.5 hours. The phenyl hydride complex 12 is in rapid equilibrium with 10, and thus reacts with the aniline to form either the σ-complex 13 or the oxidative addition adduct 14. The three species, 12, 13, and 14 depicted in Scheme 2.8 are all in equilibrium at 25 °C. ³¹P NMR spectroscopy was used to determine the ratios of the three species. Complex 12 exhibits a ³¹P shift at 182 ppm while the Ir(I) sigma complexes show resonances in the 173.4-173.6 ppm range and ³¹P signals of the Ir(III) oxidative addition adducts occur in the 171.7-173.3 ppm range. The ¹H NMR data, as well as a crystal structure of 14f (see below), confirm the structural assignments of these species. The σ-complexes exhibit a broad 2H resonance around 5.2 ppm, distinct from the ArNH₂ resonance for free anilines, indicating these species are exchanging slowly on the NMR time scale. The ArNHIr ¹H signals for the oxidative addition adducts appear in the 3.0-5.6 ppm range and are paired with a Ir-H triplet (J_{ph} = 12.6-13.5 Hz) at high fields (-34.1 to -42.2 ppm range). The Ir hydride signal for 12 cannot be detected at room temperature due to rapid exchange with benzene via complex 10.
Figure 2.1. Anilines of varying electron withdrawing/donating ability (11a-g)

Scheme 2.8. Equilibria between (POCOP)Ir(H)(Ph) (12), (POCOP)Ir(NH₂Ar) (13), and (POCOP)Ir(H)(NHAr) (14)

The equilibrium constants, $K_1$, $K_2$ and $K_3$ measured by $^{31}$P NMR spectroscopy at 25°C are summarized in Table 2.1. For the electron-rich $p$-methoxyaniline 11a, only the Ir(I) $\sigma$-adduct 13a can be observed. As the substituents become more electron-withdrawing, the Ir(III) oxidative addition adduct becomes increasingly favored. For example, a 1:1 ratio of Ir(III):Ir(I) is now observed for $p$-chloroaniline 11d. For even less electron-rich anilines 11e-g, the Ir(I) species can no longer be spectroscopically detected and $K_2$ cannot be measured. The equilibrium constants $K_3$ between the aryl hydride and Ir(III) complexes can still be determined since benzene is in large excess relative to aniline and 12 can be detected. The reasons for the trends in these substituent effects will be discussed below.
Table 2.1. Equilibrium constants\textsuperscript{a} for $12 + \text{NH}_2\text{Ar} \rightleftharpoons 13 + \text{Benzene} \rightleftharpoons 14 + \text{Benzene}$ at 25°C.

<table>
<thead>
<tr>
<th>Aniline (11)</th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$K_3 = (K_1K_2)$</th>
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<tbody>
<tr>
<td>a</td>
<td>1130</td>
<td>$-^b$</td>
<td>$-^b$</td>
</tr>
<tr>
<td>b</td>
<td>456</td>
<td>0.04</td>
<td>18</td>
</tr>
<tr>
<td>c</td>
<td>188</td>
<td>0.1</td>
<td>19</td>
</tr>
<tr>
<td>d</td>
<td>55</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>e</td>
<td>$-^c$</td>
<td>$-^c$</td>
<td>260</td>
</tr>
<tr>
<td>f</td>
<td>$-^c$</td>
<td>$-^c$</td>
<td>2190</td>
</tr>
<tr>
<td>g</td>
<td>$-^c$</td>
<td>$-^c$</td>
<td>2770</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Equilibrium values are based on an average of 2-3 runs.
\textsuperscript{b} Concentration of $14a$ too low to detect
\textsuperscript{c} Concentrations of $13e-g$ too low to detect

To confirm the structures of the anilino hydrides, a single crystal X-ray diffraction analysis of a crystal of $14f$ grown from pentane at -35°C was carried out. An ORTEP diagram of the structure, including key bond distances and angles, is shown in Figure 2.2. The complex is square pyramidal with the hydride in an apical position. There is an empty coordination site \textit{trans} to the hydride. The dihedral angle Ir(1)--N(1)--C(2)--C(7) is 32.5° indicating the arene ring sits approximately perpendicular to the square plane and the filled $p$-orbital on nitrogen lies parallel to the square plane. The N-H bond lies \textit{anti} to the Ir-H bond (H-Ir(1)-N(1)-H dihedral angle = 177.3°), and thus there can be no N-H--H-Ir interaction as seen in related systems such the iridium complex shown in Figure 2.3.\textsuperscript{32,33}
Figure 2.2. ORTEP diagram of 14f. Only the hydrogens on iridium and nitrogen are shown for clarity. Key bond distances (Å) and bond angles (degrees): Ir(1)–N(1) 2.145 Å, N(1)–C(2) 1.348 Å, Ir(1)–C(22) 2.013 Å, Ir(1)–P(1) 2.294 Å, Ir(1)–P(2) 2.309 Å, C(22)–Ir(1)–N(1) 177.32°, P(1)–Ir(1)–N(1) 99.20°, P(2)–Ir(1)–N(1) 101.42°, Ir(1)–N(1)–C(2)–C(7) 32.5°, H-Ir(1)–N(1)–H 177.31°

Figure 2.3. An example of an unconventional hydrogen bond by Crabtree et. al.
It is worth noting that the crystal structure of 14f is representative of the (POCOP)Ir(III) complexes of the electron-withdrawing anilines 14e-g. The $^1$H resonance of the hydride in these complexes falls between -41 and -43 ppm, which is characteristic of hydride shifts in these (POCOP)Ir pincer complexes when there is an empty coordination site $trans$ to the hydride. However, for the (POCOP)Ir(III) complexes of the less electron-withdrawing anilines 14b-d the chemical shift for the hydride falls between -33.3 and -35.9 ppm. This surprisingly downfield chemical shift might be indicative of a change in orientation of the aniline substituent, where the hydride and the $N$-hydrogen are $cis$ to each other with a possible hydrogen bonding interaction.\(^{33}\) A corresponding shift in the ArNH signal occurs moving from ca. 3.0-4.4 ppm in the adducts involving electron-withdrawing anilines (14e-g) to 5.6 ppm for $p$-chloroaniline adduct 14d.

By comparing the equilibrium data for reaction with aniline with those of Goldman and Hartwig,\(^{27}\) it is clear that the more electron-withdrawing (POCOP) phosphinite Ir system more strongly prefers the Ir(I) oxidation state relative to the (PCP)Ir system. At room temperature, the reaction of 1 with H$_2$NC$_6$H$_5$ favors the oxidative addition product and forms only the Ir(III) anilino hydride complex. In benzene solution, an equilibrium is established between (PCP)Ir(H)(NHC$_6$H$_5$) and (PCP)Ir(H)(C$_6$H$_5$) with a $K_{eq}$ of 105 favoring the formation of the iridium anilino complex.\(^{27}\) In the POCOP system, reaction of 10 with NH$_2$C$_6$H$_5$ favors the Ir(I) $\sigma$-complex with an equilibrium ratio of Ir(I):Ir(III) complexes of ca. 10:1 (See Scheme 2.9). These results are also supported by IR data. Comparison of the IR stretching frequency of coordinated carbon monoxide in (POCOP)Ir(CO) (15) ($\nu_{co} = 1949$ cm$^{-1}$)\(^{31}\) and (PCP)Ir(CO) (16) ($\nu_{co} = 1927.7$ cm$^{-1}$)\(^{34}\) shows a higher frequency C≡O stretch for
15 than for 16, indicating that the more electron-withdrawing ligand leads to a more electron-deficient metal center.

Scheme 2.9. Comparison of the reactions of (PCP)Ir(H)(Ph) (3) and (POCOP)Ir(H)(Ph) (10) with NH$_2$C$_6$H$_5$.

The increasing donor ability of the lone pair of electrons on the aniline is reflected, as expected, by the increasing stability of the Ir(I) $\sigma$-aniline complexes relative to the Ir(III) phenyl hydride complex (compare $K_1$ values, Table 1). The stability of the Ir(III) anilino hydride complexes relative to the Ir(III) phenyl hydride increases as the arene ring of the aniline becomes more electron-withdrawing ($K_3$ values). This behavior can be rationalized in two ways. In the d$^6$-Ir(III) complexes, 14, all the $d\pi$ orbitals are filled and thus there are unfavorable $p_{\pi}$-$d_{\pi}$ interactions$^{35,36}$ in 14e-g. The crystal structure of 14f shows that the Ir-N-C plane lies perpendicular to the Ir(III) square plane. As illustrated in Figure 2.4, there is repulsive interaction between the filled Ir $d_{xy}$ orbital and the filled N $p_y$ orbital. As the
arene becomes more electron-withdrawing, the energy of the $p_y$ orbital is lowered and the destabilizing interaction is reduced. This can account for the substituent effect on relative stabilities. An alternative view is that the electron-withdrawing-substituents stabilize the negative charge on the anilino ligand, enhancing the electrostatic interaction between the metal and the anilino group, thus strengthening the Ir-N bond.$^{37,38}$

**Figure 2.4.** The destabilizing interaction between the filled N-$\pi$ orbital ($p_y$) and the filled Ir $d_{xy}$ orbital. (Apical hydride not shown)

b) **Rates of oxidative addition of anilines to (POCOP) iridium pincer complexes.**

Low temperature $^1$H and $^{31}$P studies showed that in the case of $p$-chloroaniline (which yields a 1:1 equilibrium mixture of 13d and 14d) the kinetic product of reaction with 10 is the $\sigma$-complex 13d. Generation of the tolyl hydride complexes 17 (a mixture of the *meta* and *para* isomers$^{31}$) in toluene was achieved in the usual way by reaction of the hydrochloride complex in toluene with NaO$t$Bu. Treatment of this solution with excess $p$-chloroaniline (10 equivs.) at -50°C initially yields only the $\sigma$-complex, 13d (Scheme 2.10). Slow formation of the oxidative addition product 14d is observed at this temperature. While it seems likely that the oxidative addition occurs directly from the $\sigma$-complex, we have no direct proof of this. After formation of the $\sigma$-complex 13d, the rate of oxidative addition of the $p$-chloroaniline to form 14d was measured at -12°C via $^1$H low temperature NMR spectroscopy. The first-order
rate constant was found to be $4.8 \times 10^{-4}$ s$^{-1}$ with $\Delta G^\ddagger = 19.7$ kcal/mol. (A sample of a first-order plot for the conversion of 13d to 14d can be found in Appendix I, Figure I.1)

**Scheme 2.10.** Formation of the (POCOP)Ir(NH$_2$(p-ClC$_6$H$_4$)) at low temperature followed by oxidative addition upon warming to form (POCOP)Ir(H)(NH(p-ClC$_6$H$_4$))

![Scheme 2.10](image)

Similar low temperature experiments were conducted with 3,5-bis(CF$_3$)aniline 11g. At the highest achievable concentrations of aniline, a trace of a species tentatively assigned to the $\sigma$-complex ($^{31}$P = 173.2, max concentration ca 3.0%) could be detected as a transient during reactions carried out at -37°C. (Scheme 2.11). These results are consistent with formation of the $\sigma$-complex as the kinetic product which never builds up to significant concentrations due to rapid oxidative addition to form 14g (Path A). Again, we can not rule out direct formation of 14g from reaction of 10 with 11g (Path B).
**Scheme 2.11.** Possible mechanism for oxidative addition of 11g.

\[
\begin{align*}
\text{(tBu)}_2P&\text{Ir}\text{-Ph}_2P\text{(tBu)}_2 & \xrightarrow{k_1} & \text{Me} & + & \text{H}_2\text{N}\text{-Ph}_3 \text{CF}_3 \rightarrow & \text{10} + \text{13g} \rightarrow \text{14g} \\
\hline
\text{Path A} & & & & \text{Path B} \\
\end{align*}
\]

**c) Rates of reductive elimination of electron-withdrawing anilines from five-coordinate (POCOP) iridium pincer complexes using ethylene as a trapping ligand.**

The rates of reductive elimination of 14e, 14f, and 14g were measured by heating the Ir(III) adducts in the presence of ethylene as a trapping ligand, L, to form the iridium(I) ethylene adduct 18, as shown below in Scheme 2.12. Complexes 14e-g were chosen for study since K_2 and K_3 are sufficiently large that the Ir(III) complexes can be prepared cleanly with no contamination by aryl hydride 12 or Ir(I) complexes. The trapping ligand must be chosen so that the 18-electron Ir(III) six-coordinate complex is not formed. A survey of several trapping ligands revealed that ethylene was ideal for this purpose (PMe_3 and carbon monoxide form the octahedral complexes 19^{39} and 20 prior to reductive elimination, see below).
The disappearance rates of adducts 14e-g were measured at 9 °C in the presence of excess ethylene and found to be independent of ethylene concentration (Scheme 2.13). Measured rate constants and free energies of activation are summarized in Table 2.2. A sample rate plot for the reductive elimination of pentafluoroaniline from 14f can be found in Appendix I, Figure I.2.

The reductive eliminations follow the same trend as the equilibrium reactions above; the more electron-withdrawing aniline reductively eliminates more slowly (Table 2.2). This is also evident by comparing the free energies of activation, $\Delta G^\ddagger$ values, for the reductive eliminations. As the electron-withdrawing ability of the aniline increases, the $\Delta G^\ddagger$ also increases from 20.8 kcal/mol for aniline 11e to 22.1 kcal for 11g.
Table 2.2. Rates of reductive elimination of anilines (11e-g) from (POCOP)Ir(H)(NHAr) at 9°C in toluene.

<table>
<thead>
<tr>
<th>Ir(III) Complex</th>
<th>Concentration of C₂H₄, M</th>
<th>k, s⁻¹ x 10⁴</th>
<th>average k, s⁻¹ x 10⁴</th>
<th>ΔG‡ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>14e (0.022 M)</td>
<td>0.087 4.0</td>
<td>4.2</td>
<td>20.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.28 4.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14f (0.022 M)</td>
<td>0.022 3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14g (0.036 M)</td>
<td>0.19 2.6</td>
<td>2.8</td>
<td>21.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.18 0.42</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.34 0.47</td>
<td>0.45</td>
<td>22.1</td>
<td></td>
</tr>
</tbody>
</table>

In order to determine if these barriers are the true barriers for reductive elimination of anilines from 14e-g, several mechanistic scenarios, consistent with the observation that the rates of formation of ethylene complex 18 are independent of ethylene concentration, were considered. These are summarized in cases A-C in Scheme 2.14. In case A, slow reductive elimination leads directly to 10 followed by fast trapping by ethylene leading to formation of ethylene complex, 18. In view of the above experiments with p-chloroaniline which suggest the σ-complex is the precursor to oxidative addition adducts, case A seems less likely than cases in which reductive elimination initially leads to the σ-complex. In case B, the σ-complex 13 is the precursor to 10 which is then rapidly trapped by ethylene. It is possible that the rate of formation of 13 is rate-determining (i.e., k₂ > k₁, k₁) or that 13 and 14 are in equilibrium followed by slow formation of 10 (k₂ < k₁). (In this latter case, the measured ΔG‡’s do not correspond to the true barriers for reductive elimination of 14e-g) In case C,
formation of 13 is rate-determining, followed by rapid associative displacement of the aniline by ethylene.

**Scheme 2.14.** Three possible mechanisms for the reductive elimination of NH₂Ar from 14

To probe whether displacement of anilines from 13 by ethylene is associative or dissociative we examined the reaction of 13a, a system for which the σ-complex 13a can be generated free of the Ir(III) oxidative addition adduct, 14a. Generation of 13a in toluene at room temperature followed by exposure to ethylene at -8°C results in quantitative formation of ethylene complex 18 (Scheme 2.15). A sample plot of this reaction can be found in Appendix I, Figure I.3.
Scheme 2.15. Displacement of NH$_2$C$_6$H$_4$pOMe from 13a with ethylene through a dissociative mechanism

Using 0.015-0.019 M 13a and excess ethylene concentrations of 0.25 M and 0.48 M, clean first-order kinetics are observed at -8°C with measured rate constants of 3.3 x 10$^{-4}$ s$^{-1}$ and 2.7 x 10$^{-4}$ s$^{-1}$, respectively. No dependence of the rate on ethylene is observed which implies that dissociation of p-methoxyaniline from 13a is rate-determining with a free energy of activation, $\Delta G^\ddagger$, of 19.8 kcal/mol. This result rules out case C above and indicates case B as the most likely choice.

In examining case B more closely, it is instructive to consider free energy diagrams for both the p-chloroaniline system 13d/14d and 14e-g (for simplicity consider 14f as representative of 14e-g). (Figure 2.5 and 2.6) In the case of 13d=14d, $K_{eq} = 1$; therefore, barriers for reductive elimination and oxidative addition are the same, 19.7 kcal/mol. Now consider 14f. Since 14f is somewhat more stable than 13f one would expect the $\Delta G^\ddagger_1$ to be slightly greater than 19.7 kcal/mol, say 19.7 + $\delta$, and $\Delta G^\ddagger_{-1}$ to be slightly less, 19.7 - $\delta'$, as shown in Figure 2.6. Since (CF$_3$)$_2$C$_6$H$_3$NH$_2$ is a poorer donor than p-methoxyaniline, the barrier for dissociation from (POCOP)Ir should be somewhat less than the 19.8 kcal/mol measured for 13a, designated in Figure 2.6 as 19.8 - $\delta''$. It is difficult to predict whether $\delta'$ or
δ" is larger and thus which transition state, TS₁ or TS₂, is higher in energy, but it is likely that the difference is quite small. The ΔG‡₁ for 14f cannot exceed 21.1 kcal/mol (see Table 2.1) but is certainly greater than 19.7 kcal/mol and thus is narrowly bracketed. In view of this analysis the ΔG‡ values in Table 1 likely reflect fairly accurately the barriers for reductive elimination of 14e-g.

**Figure 2.5.** Reaction coordinate diagram for the interconversion of 13d and 14d

![Reaction Coordinate Diagram](image)

**Figure 2.6.** Reaction coordinate diagram for the conversion of 14f to 18

![Reaction Coordinate Diagram](image)
It is informative to compare the barriers of reductive elimination observed here which are in the 21-22 kcal/mol range to the barrier of reductive elimination of (POCOP)Ir(H)(Ar') (Ar' = 3,5-Me2C6H3-) of 14.1 kcal/mol. This likely reflects a stronger Ir-N bond relative to the Ir-C bond.

d) Reaction of (POCOP)Ir(H)(NHAr) complexes (14e,f) with carbon monoxide

Generation of the tolyl hydrides 17 at -78°C as described above followed by treatment with C6F5NH2 (ca. 1.1 equiv.) and CO resulted in formation of (POCOP)Ir(CO)(H)(NHC6F5), 20f, as the major product via CO trapping of 14f. (Minor amounts of (POCOP)IrCO, 15, are formed presumably by CO displacement of aniline from (POCOP)Ir(NH2C6F5) since reductive elimination of aniline from either 14f or 20f is very slow at -78°C.) Removal of toluene and addition of a minimal amount of pentane at -78°C resulted in the precipitation of 20f in low yield. Key NMR parameters of 20f include a 31P signal at 157 ppm and a ¹H resonance for the iridium hydride at -8.6 ppm. The downfield hydride shift is indicative of ligand coordination trans to the apical hydride. A solution of 20f in toluene at 25°C undergoes slow reductive elimination; (POCOP)Ir(CO) and free pentafluoroaniline are visible by ¹H NMR spectroscopy after 18 hours.

X-ray quality crystals of 20f were obtained through slow crystallization from pentane at -35°C. The ORTEP diagram of 20f (Figure 2.7) indicates an Ir(III) octahedral complex with the CO bound in an apical site trans to the hydride and the aniline ligand trans to Cipso. Since the crystal structure of 14f showed an empty coordination site in the position trans to the hydride, CO coordination to this site is consistent with rapid addition of CO to generate 20f as the kinetic product. Interestingly, there is a change in the orientation of the aniline
ligand upon binding of CO. As mentioned earlier, in 14f the dihedral angle H-Ir(1)-N(1)-H was 177° with the hydride and N-H trans to each other. The dihedral angle H(1)-Ir(1)-N(11)-H(11) in 20f after CO coordination is now 42°, indicating that the aniline ligand has rotated ca. 125° and the hydride and N-H are now nearly cis to each other.

Reaction of (POCOP)Ir(H)(NHAr-pCF3) (14e) with CO was also investigated. Complex 14e was generated in situ at 25°C by treatment of tolyl hydrides 17 with CF3C6H4NH2 (ca. 1.5 equiv) at 25°C. Cooling the toluene solution to -78°C and purging with CO resulted in formation of four complexes. The major product was the expected CO addition product, (POCOP)Ir(H)(CO)(NHC6H5-pCF3), 20e. The 1H and 31P NMR data support a structure analogous to 20f. Two minor complexes corresponded to para and meta tolyl hydride carbonyl complexes (POCOP)Ir(tolyl)(H)(CO). These structures were fully characterized by 2D 1H NMR spectroscopy and independently generated by treatment of 17 with CO. Distinct 1H NMR signals for these complexes are the downfield shifts (8.05-8.16ppm) of the aryl protons ortho to Ir, and the two Ir hydride triplets at -8.69 and -8.70ppm. The fourth complex, also verified by independent synthesis, is (POCOP)Ir(H)(Cl)(CO) from CO trapping of unreacted starting material. By increasing the concentration of aniline used, formation of the tolyl complexes was inhibited. We were unable to crystallize 20e and column chromatography resulted in its decomposition.
Figure 2.7. ORTEP diagram of (POCOP)Ir(H)(CO)(NHC$_6$F$_5$) (20f). Only the hydrogens on iridium and nitrogen are shown for clarity. Key bond distances (Å) and bond angles (degrees): Ir(1)–N(11) 2.168 Å, N(11)–C(12) 1.361 Å, Ir(1)–C(9) 2.046 Å, Ir(1)–P(1) 2.337 Å, Ir(1)–P(2) 2.329 Å, H(1)–Ir(1)–N(11)–H(11) 42.22°, C(9)–Ir(1)–N(11) 173.3°, P(1)–Ir(1)–N(11) 98.82°, P(2)–Ir(1)–N(11) 100.97°, Ir(1)–N(11)–C(12)–C(13) 139.79°.

Complex 20e undergoes reductive elimination at a much slower rate than the five-coordinate analogue 14e. Heating an in situ generated toluene-$d_8$ solution of (POCOP)Ir(H)(CO)(NHAr-pCF$_3$), 20e, at 63°C results in the formation of (POCOP)Ir(CO) and free 4-trifluoromethylaniline. In contrast, reductive elimination of five-coordinate 14e occurs at 9°C. A detailed kinetic analysis of the reductive elimination was not carried out due to the difficulties in preparing 20e cleanly and complications due to the presence of excess product aniline. However, qualitatively the rate of reductive elimination is retarded.
when carried out under 1-3 atmospheres of carbon monoxide. This is consistent with loss of CO to form five-coordinate $14e$ prior to reductive elimination as might be expected based on previous work concerning reductive elimination of six-coordinate Pt(IV) complexes.$^{41}$

e) Reductive elimination of $\text{NH}_2\text{C}_6\text{H}_4-\text{pCF}_3$ from 6-coordinate (POCOP)Ir(H)(NHAr)(CO)

Although there are some examples of reductive elimination occurring directly from a $d^6$ six-coordinate species, the majority of reductive eliminations occur after ligand dissociation to generate a five-coordinated complex prior to reductive elimination. This phenomenon has been extensively documented and reviewed by Goldberg.$^{41}$ For example, it has been shown that the six-coordinate (dppe)PtMe$_4$ (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) complex reductively eliminates ethane after the dissociation of a chelating arm of the dppe ligand at high temperatures ($165^\circ$C-$205^\circ$C). When a more rigid chelating ligand dppbz ($\text{dppbz} = \text{o-PPh}_2(\text{C}_6\text{H}_4)\text{PPh}_2$) is used a depression of the rate is observed.$^{41,42}$ This supports the proposed mechanism since a more rigid ligand would be harder to dissociate. Whether dissociation prior to reductive elimination occurs depends on the coordination strength and/or chelating strength of the ligand, as well as, how facile the reductive elimination is (i.e. C-H reductive elimination typically has a lower energy barrier than C-C reductive elimination).$^{41}$ For example, the rates of reductive elimination of methane from $\text{fac-}(\text{dppe})\text{PtMe}_3\text{H}$ and $\text{fac-}(\text{dppbz})\text{PtMe}_3\text{H}$ at room temperature were of similar rates. Therefore, the rigidity of the chelating ligand is not a factor in the rate, indicating that the C-H reductively elimination via a direct elimination mechanism.$^{41}$ On the other hand, C-H reductive elimination by $\text{Tp}^\text{Me}_2\text{Pt}(\text{CH}_3)\text{H}$ ($\text{Tp}^\text{Me}_2 = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$) occurs through a five-coordinate Pt complex after dissociation of an arm of the $\text{Tp}^\text{Me}_2$ ligand.$^{43}$
For Ir(III), Rh(III), Os(II), and Ru(II) systems, mechanisms for both direct elimination and
dissociation prior to reductive elimination have both been described in the literature.\textsuperscript{41}
Therefore, it was of interest to investigate the mechanism of N-H reductive elimination from
the d\textsuperscript{6} six-coordinate iridium complex, (POCOP)Ir(H)(CO)(NHC\textsubscript{6}H\textsubscript{4}-pCF\textsubscript{3}) \textit{20e}. Schemes
2.16 and 2.17 illustrate the two possible mechanisms for reductive elimination of NHC\textsubscript{6}H\textsubscript{4}-
pCF\textsubscript{3} from \textit{20e}.

**Scheme 2.16.** Direct reductive elimination of NHC\textsubscript{6}H\textsubscript{4}-pCF\textsubscript{3} \textit{11e} from (POCOP)
Ir(H)(CO)(NHC\textsubscript{6}H\textsubscript{4}-pCF\textsubscript{3}) \textit{20e}

\[
\begin{align*}
\text{H} & \quad \text{LnIr} \quad \text{NHAr} \\
\text{CO} & \quad \textit{20e} \\
\hline
\text{H} & \quad \text{LnIr} \quad \text{CO} \\
\text{CO} & \quad \textit{15} \\
\end{align*}
\]

\[
\begin{array}{c}
\text{H} \\
\text{LnIr} \quad \text{NHAr} \\
\text{CO} \\
\textit{20e} \\
\hline
\text{H} \\
\text{LnIr} \quad \text{CO} \\
\textit{15} \\
\end{array}
\]

**Scheme 2.17.** Mechanism for the reductive elimination of \textit{11e} from \textit{20e} via dissociation of
CO prior to reductive elimination

\[
\begin{align*}
\text{Step} & \quad \text{H} \quad \text{LnIr} \quad \text{NHAr} \quad \text{CO} \\
1 & \quad \text{H} \quad \text{LnIr} \quad \text{NHAr} + \text{CO} \\
\text{H} & \quad \text{LnIr} \quad \text{NHAr} \\
\text{CO} & \quad \textit{20e} \\
\hline
\text{H} & \quad \text{LnIr} \quad \text{CO} \\
\text{CO} & \quad \textit{14e} \\
\end{align*}
\]

\[
\begin{array}{c}
\text{H} \\
\text{LnIr} \quad \text{NHAr} \\
\text{CO} \\
\textit{20e} \\
\hline
\text{H} \\
\text{LnIr} \quad \text{CO} \\
\textit{14e} \\
\end{array}
\]

\[
\begin{align*}
\text{Step} & \quad \text{H} \quad \text{LnIr} \quad \text{NHAr} \quad \text{CO} \\
2 & \quad \text{H} \quad \text{LnIr} \quad \text{NHAr} + \text{CO} \\
\text{H} & \quad \text{LnIr} \quad \text{NHAr} \\
\text{CO} & \quad \textit{14e} \\
\hline
\text{H} & \quad \text{LnIr} \quad \text{CO} \\
\text{CO} & \quad \textit{10} \\
\end{align*}
\]

\[
\begin{array}{c}
\text{H} \\
\text{LnIr} \quad \text{NHAr} \\
\text{CO} \\
\textit{14e} \\
\hline
\text{H} \\
\text{LnIr} \quad \text{CO} \\
\textit{10} \\
\end{array}
\]

\[
\begin{align*}
\text{Step} & \quad \text{H} \quad \text{LnIr} \quad \text{NHAr} \quad \text{CO} \\
3 & \quad \text{H} \quad \text{LnIr} \quad \text{NHAr} + \text{CO} \\
\text{H} & \quad \text{LnIr} \quad \text{NHAr} \\
\text{CO} & \quad \textit{14e} \\
\hline
\text{H} & \quad \text{LnIr} \quad \text{CO} \\
\text{CO} & \quad \textit{15} \\
\end{align*}
\]

\[
\begin{array}{c}
\text{H} \\
\text{LnIr} \quad \text{NHAr} \\
\text{CO} \\
\textit{14e} \\
\hline
\text{H} \\
\text{LnIr} \quad \text{CO} \\
\textit{15} \\
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{LnIr} \quad \text{NHAr} \\
\text{CO} \\
\textit{14e} \\
\hline
\text{H} \\
\text{LnIr} \quad \text{CO} \\
\textit{15} \\
\end{array}
\]
The course of reductive elimination of 11e was monitored using variable temperature NMR spectroscopy under varying carbon monoxide pressures and varying concentrations of aniline 11e. In order to accurately compare the reactions, J. Young tubes were used to maintain constant CO pressure throughout the reactions. Each NMR tube was charged with 0.03 mol/L of 20e in toluene-\(d^8\), after which 11e and/or CO was added to the reaction mixture. The reductive elimination was monitored by measuring the decrease in integration of either an aniline aryl resonance or the NH resonance of 20e in the \(^1\)H NMR spectrum at 345K.

While keeping the concentration of aniline constant, the half-life \((t_{1/2})\) for the reductive elimination increases as more carbon monoxide is introduced into the system (Table 2.3). This shows an inverse dependence of the reaction rate on CO concentration, indicating that CO must reversibly dissociate from the metal center. This effect is graphically represented in Figure 2.8. As mentioned above the dissociation of CO is not unexpected based on previous studies by Goldberg et. al.\(^{41}\) If this was a simple inverse first-order dependence on CO concentration, the half-life should increase by the same factor that the carbon monoxide pressure increased. By comparing entries 1-4 and 6-7 in Table 2.3, it is clear that this is not the case. The half life increases as the concentration of carbon monoxide increases, but by less than expected for an inverse first-order dependence.
Table 2.3. Qualitative comparison of the half-lives for the reductive elimination of NH$_2$Ar from a 6-coordinate iridium complex at 345K

<table>
<thead>
<tr>
<th>Entry</th>
<th>$P_{\text{CO}}$ (atm)</th>
<th>11e $^a$ (M)</th>
<th>1st $t_{1/2}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.060</td>
<td>2193</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.067</td>
<td>2669</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.064</td>
<td>3170</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>0.064</td>
<td>3533</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0.20</td>
<td>4943</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0.63</td>
<td>7547</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>0.63</td>
<td>14729</td>
</tr>
</tbody>
</table>

$^a$ Concentration of 11e at the start of the reaction.

b) $[\text{Ir}]_0 = 0.03 \text{ mol/L}$
Carbon Monoxide Dependence on Reductive Elimination of \(\text{NH}_2\text{C}_6\text{H}_4^p\text{CF}_3\), 11e, from (POCOP)Ir(CO)(H)(NHC_6H_4^pCF_3), 20e, at 345K

\[\text{Time (s)}\]

\[-\ln[20e] \text{ (normalized to intersect 0)}^*\]

0 ATM
1 ATM
2 ATM
3 ATM

* To account for slight difference in concentrations, the value at \(t_0\) was subtracted out to force the curve through the 0,0 point. This allows for an easier comparison.

**Figure 2.8.** Graphical depiction of the depression of rate as the concentration of carbon monoxide increases for the reductive elimination of \(\text{NH}_2\text{C}_6\text{H}_4^p\text{CF}_3\) from 20e

When the CO pressure remains constant while the concentration of 11e is varied, an increase in \(t_{1/2}\) is also observed, indicating that the aniline concentration is also part of the rate expression. These results are shown in Table 2.3 as a simple half-life value, as well as graphically in Figure 2.9. A comparison of entries 4-6 in Table 2.3 shows an increase in half-life as the concentration of 11e increases, but as in the case for carbon monoxide, this rate is not a simple inverse first-order dependence on 11e
Dependence of the Initial Concentration of 11e on the Reductive Elimination of 11e, from (POCOP)Ir(CO)(H)(NHC₆H₄-pCF₃), 20e, at 345K

![Graphical depiction of the depression of rate as the concentration of NH₂C₆H₄-pCF₃ increases for the reductive elimination of NH₂C₆H₄-pCF₃ from 20e](image)

* To account for slight difference in concentrations, the value at t₀ was subtracted out to force the curve through the 0,0 point. This allows for an easier comparison.

**Figure 2.9.** Graphical depiction of the depression of rate as the concentration of NH₂C₆H₄-pCF₃ increases for the reductive elimination of NH₂C₆H₄-pCF₃ from 20e

The dependence on carbon monoxide concentration rules out the direct reductive elimination mechanism, suggesting that reversible CO dissociation must occur prior to reductive elimination. However, it is not immediately evident, given a rate suppression by both CO and aniline 11e, how the results fit with the mechanism shown in Scheme 2.17 and what step is the rate-determining step. To gain a qualitative insight into the mechanism, energy diagrams describing the possible mechanistic scenarios are analyzed (Figures 2.10-2.12)

Figure 2.10 describes a situation where the first step is reversible and reductive elimination of 11e is rate-determining. If this were the case, the rate would be inversely proportional to
the CO concentration (Rate ≈ 1/[CO]) and there would be no dependence on the concentration of aniline. This scheme does not fit the experimental observations.

\[ \Delta G^{\ddagger} = 20.8 \text{kcal/mol} \]

**Figure 2.10.** Free energy diagram of the reductive elimination of 11e from 20e where the first step is reversible and reductive elimination of 11e is rate-determining

A second possibility is shown in Figure 2.11, where both steps 1 and 2 are reversible and the re-coordination of carbon monoxide (step 3) is the rate-determining step. In this case the rate is only inversely proportional to the concentration of aniline (Rate ≈ 1/[11e]). The concentration of carbon monoxide does not affect the rate since both its dissociation and association to irdium are included in the rate expression and therefore cancel each other out.
Since a inverse dependence on carbon monoxide is observed, however, step 3 as the rate-determining step can be ruled out as well.

![Free energy diagram of the reductive elimination of 11e from 20e if re-coordination of CO is the rate-determining step](image)

**Figure 2.11.** Free energy diagram of the reductive elimination of 11e from 20e if re-coordination of CO is the rate-determining step

A qualitative explanation which fits the observed rate data is a reaction in which the ΔG‡ for both the reductive elimination of aniline 11e and the re-coordination of CO are similar. (Figure 2.12) In this case, there is no clear rate-determining step and a rate suppression by both CO and 11e would be expected but in each case the rate dependence would be less than full inverse first-order.
Figure 2.12. Free energy diagram of the reductive elimination of 11e from 20e if the reductive elimination of aniline and re-coordination of CO had similar $\Delta G^{\dagger}$.
II) Reaction of the (POCOP)Ir pincer complex with benzamides C_6H_5(CO)NH_2 (21a) and C_6F_5(CO)NH_2 (21b)

Reaction of (POCOP)Ir, 10, (generated by reaction of (POCOP)Ir(H)(Cl), 9, with NaO\text{tBu}) with NH_2(CO)C_6H_5, 21a, and NH_2(CO)C_6F_5, 21b, yields Ir(III) oxidative addition adducts 22a,b (Scheme 2.18). These adducts are substantially more stable than the anilino hydrides and can be readily isolated as stable solids at room temperature.

Scheme 2.18. Formation of benzamide complexes 21a,b from (POCOP)Ir(H)(Cl) and NaO\text{tBu}

An X-Ray diffraction study was carried out on a crystal of 22b obtained from pentane at -35°C. The ORTEP diagram is shown in Figure 2.13 along with key bond distances and angles. Like the anilino complexes, the amide nitrogen lies in the square plane trans to C_{ipso} of the aryl ring of the POCOP ligand. The N-C-O amide plane is perpendicular to the iridium square plane with the carbonyl oxygen anti to the axial Ir-H. The Ir-O bond distance of 2.55 Å suggests weak coordination of the amide oxygen to the open axial site trans to hydride. It is of interest to compare the iridium-oxygen bond distance in 22b with Ir-O distances in other iridium amide complexes 23^{44}, 24^{45}, 25^{46} shown in Figure 2.14. In the eighteen-electron Ir(III) complexes 23 and 24 the Ir-O distances of 3.401Å and 3.412Å clearly show no Ir-O interaction. The Ir(III) complex 25 is formally a sixteen-electron
complex in the absence of a Ir-O interaction. The Ir-O distance of 2.290 Å is considerably shorter than the Ir-O distances in 23 and 24 and clearly suggests a significant bonding interaction. The fact that the amide in 25 is an alkyl amide with a much more basic oxygen then that in the benzamide of 22b with a strongly electron-withdrawing C₆F₅ group may in part account for the shorter Ir-O distance in 25.

The ¹H chemical shifts of the hydride ligands in 22a and 22b also support an axial Ir-O interaction. (POCOP)Ir hydride complexes with an empty coordination site trans to hydride exhibit hydride shifts in the -41 ppm range. In six-coordinate complexes the hydride shifts to much lower values. For example, in carbonyl adduct 20f, the ¹H shift is -8.56. The intermediate shifts of the hydrides in 22a and 22b of -30.25 and -35.72 support a significant Ir-O interaction. The higher field shift of -35.7 ppm in 22b suggests a decreased Ir-O interaction compared to 22a, consistent with a decreased oxygen basicity due to the strongly electron-withdrawing C₆F₅ group.
Figure 2.13. ORTEP diagram of (POCOP)Ir(H)(NH(CO)C₆F₅) (22b). Only the hydrogens on iridium are shown for clarity. Key bond distances (Å) and bond angles (degrees): Ir(1)–N(1) 2.171 Å, N(1)–C(2) 1.279 Å, Ir(1)–C(29) 2.034 Å, Ir(1)–P(1) 2.412 Å, Ir(1)–P(2) 2.359 Å, H(1)-Ir(1)–N(1)–H(2) -18.67°, C(29)–Ir(1)–N(1) 176.66°, P(1)–Ir(1)–N(1) 104.30°, P(2)–Ir(1)–N(1) 96.77°, Ir(1)–N(1)–C(2)–C(4) -175.64°
a) Rates of reductive elimination of H$_2$N(CO)C$_6$H$_5$ from (POCOP)Ir(H)(NH(CO)C$_6$H$_5$) complexes

Since benzamides form significantly more stable Ir(III) species than their analogous anilino complexes, the rates of reductive elimination were measured at 100°C. Ethylene proved to be a poor choice for a trapping ligand since ethylene concentrations were difficult to control at elevated temperatures. Therefore, triphenyl phosphine which competes reversibly with benzamide for coordination to iridium was used. The equilibrium between (POCOP)Ir(H)(NH(CO)Ph), 22a, + PPh$_3$ and (POCOP)Ir(PPh$_3$) + H$_2$N(CO)C$_6$H$_5$ as shown in Scheme 2.19 was measured at three different concentrations of PPh$_3$ (0.29, 0.59, and 1.18 M) at 100°C. From these data a $K_{eq}$ of 0.18 favoring 22a was calculated. For the more electron-withdrawing pentafluorobenzamide complex 22b, the equilibrium constant decreases to 0.07 consistent with the substituent effects observed in the aniline equilibrium studies. At room temperature a one to one ratio of benzamide 21a (0.0094 M) and triphenylphoshine (0.0094 M) was added to 10 (0.0046 M), generated in the usual manner. $^{31}$P NMR analysis showed the formation of 22a and 26 in a ratio of 2:1. Since interconversion of these species is slow
at 25°C, this ratio represents kinetic trapping and differs from the thermodynamic ratio of ca. 6:1.

**Scheme 2.19** Equilibrium between 22a,b + PPh₃ and 26 + NH₂(CO)Ar

\[
\begin{align*}
\text{22a,b} + \text{PPh}_3 & \rightleftharpoons \text{26} + \text{NH}_2(\text{CO})\text{Ar} \\
\text{Keq} = 0.18 \quad (22a) \\
& 0.07(22b)
\end{align*}
\]

Generating 22a and analyzing the reversible reaction (Scheme 2.19) in the presence of 10 equiv. of 21a and 10 equiv. of PPh₃, the half-life for reductive elimination of benzamide was found to be ca. 1.7 hours, corresponding to a ∆G‡ of ca. 29 kcal/mol. (A sample first-order rate plot of this reaction is shown in Appendix I, Figure I.4.) This increased barrier to reductive elimination of benzamide relative to that for anilines is due to stronger binding of the benzamido fragment to (POCOP)Ir. The Ir-O interaction as well as a decrease in the repulsive dπ-p interaction as a result of the electron-withdrawing ability of the acyl moiety can account for the increased binding energy.

**Summary**

Reaction of a series of anilines 11a-g with (POCOP)Ir(C₆H₅)(H), 12, leads to equilibrium mixtures of 12, the Ir(I) σ-complexes (POCOP)Ir(NH₂Ar), 13, and the Ir(III) oxidative addition adducts (POCOP)Ir(H)(NHAr), 14. Previous studies have shown that 12 undergoes rapid reductive elimination of benzene to form the 14-electron species (POCOP)Ir, 10, so
complexes 13 and 14 arise from reaction of anilines with 10. Equilibrium constants connecting these three species have been measured and several features are apparent. As expected, as the basicity of the aniline increases, the equilibrium ratio of 13 + benzene : 12 + aniline increases. Surprisingly, however, as the basicity of the aniline decreases, the ratio of the Ir(III) species 14, to Ir(I) species 13 increases, as does the ratio of 14 + benzene : 12 + aniline. The increased stability of the oxidative addition adducts bearing electron-withdrawing aryl groups (-pCF3C6H4 14e, -C6F5 14f, 3,5-(CF3)2C6F3- 14g) was attributed to decreased repulsion between the filled dπ and N-p orbitals.

Low temperature NMR experiments employing p-chloroaniline show that reaction with 12 forms the Ir(I) σ-complex (POCOP)Ir(NH2C6H4Cl), 13d, as the kinetic product which equilibrates with the oxidative addition adduct 14d at temperatures above -50°C. Complexes 14e-g undergo reductive elimination at 9°C in the presence of ethylene to yield quantitatively (POCOP)Ir(C2H4), 18, and the respective aniline. Rate measurements demonstrate that these reactions are cleanly first-order and independent of ethylene concentration. Mechanistic analysis suggests that the rate-determining step is formation of the σ-complex followed by loss of the aniline to form 10 which is rapidly trapped by ethylene. The reductive elimination barriers of 14e-g fall in the range of 21-22 kcal/mol and increase with electron-withdrawing ability of the aryl groups.

Complex 14f is square pyramidal with the hydride occupying the apical site. Trapping 14f with CO forms the 18-electron complex (POCOP)Ir(H)(CO)(NHC6F5), 20f. X-Ray analysis of a single crystal of 20f indicates CO has added at the vacant site trans to hydride. The six-coordinate CO adducts are much more stable with respect to reductive elimination. Complex 20e undergoes reductive elimination at 72°C at rates similar to 14e reductive elimination at
9°C. Qualitative rate measurements suggest CO must dissociate prior to reductive elimination.

Reaction of 12 with benzamides yields quantitatively the Ir(III) oxidative addition adducts, (POCOP)Ir(H)(NHC(O)Ar), 22. X-Ray analysis of 22b (Ar = C₆F₅) shows significant interaction of the carbonyl oxygen with Ir in the site trans to hydride. The barrier to reductive elimination of 22a, 29 kcal/mol, is substantially higher than for complexes 14e,f,g. The increased binding energy of the –NH(CO)Ar group to Ir is ascribed to Ir-O interaction as well as a decrease in the repulsive \(d_{π}-p\) interaction as a result of the strong electron-withdrawing ability of the acyl moiety.

**Experimental Section**

**General Considerations:** All manipulations were carried out using standard Schlenk, high-vacuum, and glove box techniques. Argon and nitrogen were purified by passage through columns of BASF R3-11 (chemalog) and 4Å molecular sieves. THF was distilled from sodium benzophenone ketyl under nitrogen. Pentane and toluene were passed through columns of activated alumina and deoxygenated by purging with N₂. Benzene was dried with 4Å molecular sieves and degassed by either freeze-pump-thaw methods or by purging with argon. Toluene was further treated by purging with argon to remove nitrogen. Toluene-\(d₈\) and benzene-\(d₆\) were dried over 4Å molecular sieves and stored under argon in the glove box. Hydrogen and carbon monoxide were used as received from National Specialty Gases of Durham, NC. NMR spectra were recorded on Bruker DRX 400, AMX 300 and 500 MHz instruments and are referenced to residual protio solvent peaks. \(^{31}\)P chemical shifts are
referenced to an external H$_3$PO$_4$ standard. Since there is a strong $^{31}$P-$^{31}$P coupling in the pincer complexes, many of the $^1$H and $^{13}$C signals exhibit virtual coupling and appear as triplets. These are specified as $v_t$ with the *apparent* coupling simply noted as $J$. IR spectra were recorded on an ASI ReactIR 1000 spectrometer. Elemental analyses were carried out by Atlantic Microlab, Inc. of Norcross, GA. All reagents were purchased from Sigma-Aldrich and used without further purification. The POCOP bis(phosphinite) ligand and (POCOP)Ir(H)(Cl), 9, were prepared by literature procedures$^{30}$. The [IrCODCl]$_2$ can be purchased from Strem or synthesized using literature procedures.$^{47}$

(POCOP)Ir(H)(Ph) (12): Complex 12 was generated *in situ* by treatment of (POCOP)Ir(H)(Cl), 9, with 1.1 equiv. of NaOtBu in benzene at 75°C for 30 minutes.$^{29}$

**General Procedure for the *in situ* generation of complexes 13 and 14:** (POCOP)Ir(H)(Cl) 2 was placed in a medium-walled screw-cap NMR tube with 1.1 equiv. of NaOtBu in 0.5 mL of benzene or toluene and heated to 75°C for 45 minutes to generate the aryl hydride complex. The aniline was added to this mixture and allowed to react for 45 minutes at room temperature.

(POCOP)Ir(NH$_2$(p-OCH$_3$C$_6$H$_4$)) (13a): The general procedure was employed using 9 (0.033 mmol, 21 mg), NaOtBu (0.037 mmol, 3.5 mg) and 11a (0.099 mmol, 13.5 mg).
$^1$H NMR (300 MHz, C$_6$D$_6$): δ 6.99 (d, $^3J_{H-H} = 8.7$ Hz, 2H, 2' and 6'-H), 6.95 (t, $^3J_{H-H} = 7.8$ Hz, 1H, 1-H), 6.83 (d, $^3J_{H-H} = 7.8$ Hz, 2H, 2' and 6-H), 6.59 (d, $^3J_{H-H} = 8.7$ Hz, 2H, 3' and 5'-H), 5.15 (s, 2H, -NH$_2$), 3.29 (s, 3H, OCH$_3$), 1.28 (vt, $J = 6.5$ Hz, 36H, 2 x P(tBu)$_2$).

$^{31}$P{$^1$H} NMR (121.5 MHz, C$_6$D$_6$): δ 173.6. $^{13}$C{$^1$H} NMR (75.5 MHz, C$_6$D$_6$): δ 167.9 (C$_q$, vt, $J = 8.6$ Hz, C3 and C5), 158.2 (C$_q$, s, C4'), 138.5 (C$_q$, s, C1'), 124.6 (CH, s, C3' and C5'), 121.3 (CH, s, C1), 114.1 (CH, s, C2' and C6'), 103.3 (CH, vt, $J = 5.7$ Hz, C2 and C6), 55.2 (CH$_3$, s, OCH$_3$), 41.1 (C$_q$, vt, $J = 11.0$ Hz, C(CH$_3$)$_3$), 28.6 (CH$_3$, vt, $^2J_{P-H} = 3.8$ Hz, C(CH$_3$)$_3$). C4 not observed due to low intensity.

**POCOP**Ir(NH$_2$Ar-Me) (13b): The general procedure, 13b was employed using 9 (0.035 mmol, 22 mg), NaO-tBu (0.038 mmol, 3.9 mg) and 11b (0.1 mmol, 11 mg).

$^1$H NMR (400 MHz, C$_6$D$_6$): 13b: δ 6.77 – 6.96 (7H, aromatic protons), 2.04 (s, 3H, CH$_3$), 1.27 (vt, $J = 6.4$ Hz, 36H, 2 x P(tBu)$_2$). 14b: Concentration of 14b is very low, resulting in the only distinguishing $^1$H resonance as the hydride, -33.25 (t, $J_{P-H} = 12.7$ Hz, 1H, Ir-H). $^{31}$P{$^1$H} NMR (121.5 MHz, C$_6$D$_6$): δ 173.6 (13b), 171.3 (14b). $^{13}$C{$^1$H} NMR (100.6 MHz, C$_6$D$_6$): 13b: δ 167.8 (C$_q$, vt, $J = 8.7$ Hz, C3 and C5), 144.7 (C$_q$, s, C1'), 135.3 (C$_q$, s, C4'), 129.4 (CH, s, C2' and C6'), 127 (C$_q$, C4), 123.1 (CH, s, C3' and C5'), 121.2 (CH, s, C1), 103.2 (CH, vt, $J = 5.9$ Hz, C2 and C6), 41.1 (C$_q$, vt, $J = 11.0$ Hz, C(CH$_3$)$_3$), 28.5 (CH$_3$, vt, $J = 3.4$ Hz, C(CH$_3$)$_3$), 20.6 (CH$_3$, s, CH$_3$).
(POCOP)Ir(NH₂C₆H₅) (13c)/(POCOP)Ir(H)(NHC₆H₅) (14c): The general procedure was employed using 9 (0.024 mmol, 15 mg), NaOttBu (0.026 mmol, 2.5 mg) and 11c (0.048 mmol, 4.4 μL). The equilibrating set of complexes 12, 13c and 14c as well as 10% unreacted 9 were all present in the sample thus the ¹³C NMR spectrum was not useful for structural assignments.

![Chemical structures](image)

¹H NMR (400 MHz, C₆D₆): 13c: δ 6.69 – 6.96 (aromatic protons), 5.19 (s, 2H, NH₂), 1.26 (vt, J = 6.4 Hz, 36H, P(tBu)₂), 14c: The concentration of 14c is very low, resulting in the only distinguishing ¹H resonance as the hydride, -34.05 (t, J = 12.6 Hz). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 173.8 (13c), 172.0 (14c).

(POCOP)Ir(NH₂(p-ClC₆H₄)) (13d)/(POCOP)Ir(H)(NH(p-ClC₆H₄)) (14d): The general procedure was employed using 9 (0.024 mmol, 15 mg), NaOttBu (0.026 mmol, 2.5 mg) and 11d (0.048 mmol, 6.1 μL). The equilibrating set 12, 13d and 14d, as well as 3% unreacted 9 were present in the NMR sample.

![Chemical structures](image)

¹H NMR (400 MHz, C₆D₆): δ 6.61-6.97 (m, 14H, aromatic protons for 13d and 14d), 5.60 (s, 1H, NH), 5.06 (s, 2H, NH₂), 1.08, 1.24 (m, 72H, P(tBu)₂), -35.94 (t, Jₚ-H = 13.2 Hz, 1H, IrH). ³¹P{¹H} NMR (162 MHz, C₆D₆): δ 173.9 (13d), 172.6 (14d).
(POCOP)Ir(H)(NH(p-CF₃C₆H₄)) (14e): The general procedure was employed using 9 (0.032 mmol, 20 mg), NaOtBu (0.032 mmol, 3.1 mg) and 11e (0.08 mmol, 10 μL).

\[
\begin{align*}
\text{1H NMR (500 MHz, C}_6\text{D}_6):} & \quad \delta 7.43 (d, ^3J_{H-H} = 8.5 \text{ Hz}, 2H, 3'-\text{and 5'}-H), 6.82 (t, ^3J_{H-H} = 7.8 \text{ Hz}, 1H, 1-H), 6.73 (d, ^3J_{H-H} = 8.0 \text{ Hz}, 2H, 2-\text{and 6-H}), 6.46 (d, ^3J_{H-H} = 8.5 \text{ Hz}, 2H, 2'-\text{and 6'}-H), 4.37 (s, 1H, NH), 1.108 (vt, J = 7.5 \text{ Hz}, 18H, P(tBu)_2), 1.046 (vt, J = 7.0 \text{ Hz}, 18H, P(tBu)_2), -40.265 (t, J_{P-H} = 13.3 \text{ Hz}, 1H, IrH).
\end{align*}
\]

\[
\begin{align*}
\text{31P{1H} NMR (162 MHz, C}_6\text{D}_6):} & \quad \delta 173.3. \\
\text{19F NMR (376.5 MHz, C}_6\text{D}_6):} & \quad \delta -59.1. \\
\text{13C{1H} NMR (125.8 MHz, C}_6\text{D}_6):} & \quad \delta 168.0 (C_q, vt, J_C = 5.5 \text{ Hz}, C3 \text{ and C5}), 164.0 (C_q, s, C1'), 127.0 (C_q, q, ^3J_{F-C} = 238.9 \text{ Hz}, CF_3), 126.4 (CH, q, ^3J_{F-C} = 3.6 \text{ Hz}, C3' \text{ and C5'}), 126.3 (CH, s, C1), 123.7 (C_q, br, C4), 117.1 (CH, s, C2' \text{ and C6'}), 112.7 (C_q, q, ^2J_{F-C} = 32.2 \text{ Hz}, C4'), 104.8 (CH, t, J_{P-H} = 5.2, C2 \text{ and C6}), 42.7 (C_q, vt, J = 10.8 \text{ Hz}, C(CH_3)_3), 38.9 (C_q, vt, J = 12.8 \text{ Hz}, C(CH_3)_3), 28.0 (CH_3, vt, J = 3.2 \text{ Hz}, C(CH_3)_3), 27.6 (CH_3, vt, J_{P-H} = 3.2 \text{ Hz}, C(CH_3)_3).
\end{align*}
\]

(POCOP)Ir(H)(NHC₆F₅) (14f): Simultaneously, 9 (0.034 mmol, 21 mg), NaOtBu (0.037 mmol, 3.6 mg), 11f (0.068 mmol, 12.4 mg), and benzene-d₆ (0.5 mL) were added to a medium-walled screw-cap NMR tube and heated to 75°C for 1 hour.

\[
\begin{align*}
\text{1H NMR (500 MHz, C}_6\text{D}_6):} & \quad \delta 7.43 (d, ^3J_{H-H} = 8.5 \text{ Hz}, 2H, 3'-\text{and 5'}-H), 6.82 (t, ^3J_{H-H} = 7.8 \text{ Hz}, 1H, 1-H), 6.73 (d, ^3J_{H-H} = 8.0 \text{ Hz}, 2H, 2-\text{and 6-H}), 6.46 (d, ^3J_{H-H} = 8.5 \text{ Hz}, 2H, 2'-\text{and 6'}-H), 4.37 (s, 1H, NH), 1.108 (vt, J = 7.5 \text{ Hz}, 18H, P(tBu)_2), 1.046 (vt, J = 7.0 \text{ Hz}, 18H, P(tBu)_2), -40.265 (t, J_{P-H} = 13.3 \text{ Hz}, 1H, IrH).
\end{align*}
\]
$^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 6.82-6.72 (m, 3H, 1-’, 2-’, 6-H), 3.01 (s, 1H, NH), 1.09-1.03 (m, 36H, P(tBu)$_2$) -42.15 (t, $J_{P-H} = 13.5$ Hz, 1H, IrH). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$): $\delta$ 172.8. $^{19}$F NMR (376.5 MHz, C$_6$D$_6$): $\delta$ -167.3 (m), -168.9 (m), -187.3 (m). $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$): $\delta$ 168.5 (C$_q$, vt, $J = 5.5$ Hz, C3 and C5), 140.4-135.8 (m, C$_q$, Ar-F$_5$: C2’, C6’, C3’, C5’, and C4’), 126.7 (CH, s, C1), 122.6 (C$_q$, t, C4), 104.9 (CH, t, $J_{P-H} = 5.3$ Hz, C2 and C6), 42.6 (C$_q$, vt, $J = 11.1$ Hz, C(CH$_3$)$_3$), 39.1 (C$_q$, vt, $J = 12.6$ Hz, C(CH$_3$)$_3$), 27.7 (CH$_3$, vt, $J = 3.2$ Hz, C(CH$_3$)$_3$), 27.2 (CH$_3$, vt, $J = 3.0$ Hz, C(CH$_3$)$_3$). C1’ not observed due to low intensity.

(POCOP)Ir(H)(NH(3,5-(CF$_3$)$_2$C$_6$H$_3$)) (14g): The general procedure was employed using
9 (0.035 mmol, 22 mg), NaOtBu (0.039 mmol, 3.7 mg) and 11g (0.07 mmol, 10.9 $\mu$L).

$^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 6.98 (s, 1H, 4'-H), 6.87 (s, 2H, 2'- and 6'-H), 6.81 (t, $J_{H-H} = 7.9$ Hz, 1H, 1-H), 6.73 (d, $J_{H-H} = 7.9$ Hz, 2H, 2- and 6-H), 3.74 (s, 1H, NH), 1.06 (vt, $J = 7.4$ Hz, 18H, P(tBu)$_2$), 0.99 (vt, $J = 6.8$ Hz, 18H, P(tBu)$_2$), -41.77 (t, $J_{P-H} = 13.5$ Hz, 1H, IrH). $^{31}$P{$^1$H} NMR (162 MHz, C$_6$D$_6$): $\delta$ 174.0 (d). $^{19}$F NMR (376.5 MHz, C$_6$D$_6$): $\delta$ -63.2 $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$): $\delta$ 168.5 (C$_q$, vt, $J = 5.6$ Hz, C3 and C5), 161.4 (C$_q$, s, C1’), 132.0 (C$_q$, q, $J_{F-C} = 31.4$ Hz, C3’ and C5’), 127.0 (CH, s, C1), 125.5 (C$_q$, q, $J_{F-C} = 273.3$ Hz, CF3), 124.5 (C$_q$, m, C4), 115.7 (CH, m, C2’ and C6’), 105.0 (CH, t, $J = 5.2$ Hz, C2 and C6), 102.4 (CH, septet, $J_{F-C} = 4.0$ Hz), 42.8 (C$_q$, vt, $J = 10.9$ Hz, C(CH$_3$)$_3$), 38.7 (C$_q$,...
vt, $J = 12.8$ Hz, C(CH$_3$)$_3$), 28.0 (CH$_3$, vt, $J = 3.2$ Hz, C(CH$_3$)$_3$), 27.3 (CH$_3$, vt, $J = 3.1$ Hz, C(CH$_3$)$_3$).

**General Procedure for Determining Equilibrium Constants $K_1$, $K_2$, $K_3$ (Scheme 1):**

Samples were prepared as described below in benzene. Molarities of species were determined by carefully measuring the final volume of solution. Both $^1$H and $^{31}$P spectra were used to determine ratios of species. $^{31}$P spectra were taken with a delay time of 15 seconds to ensure the integrals were accurate based on the 5 x T1 of 14f.

**Reaction of (POCOP)Ir(H)(C$_6$H$_5$) (12) and $p$-CH$_3$OC$_6$H$_4$NH$_2$ (11a):** To a vial in the glovebox under argon, 9 (0.088 mmol, 55.35 mg), NaOtBu (0.8 equiv., 0.07 mmol, 6.0 mg), 11a (0.041 mmol, 5.1 mg, 0.010 M), and benzene (4 mL) were added. The reaction mixture was allowed to stir for 1.5 hours. An aliquot was removed and analyzed by $^{31}$P NMR. The equilibrium constants were calculated based on the concentrations of all the species in solution, ($K_1 = 1014$, $K_2 = n/a$). A second aliquot was removed after another hour to ensure reaction was at equilibrium. The reaction was repeated with an increase in the concentration of 11a to 0.05 M ($K_1 = 1189$, $K_2 = n/a$). No 14a could be detected.

**Reaction of (POCOP)Ir(H)(C$_6$H$_5$) (12) and $p$-CH$_3$C$_6$H$_4$NH$_2$ (11b):** The general procedure for 11a was followed using 9 (0.069 mmol, 43.45 mg), NaOtBu (0.9 equiv., 0.062 mmol, 6.0 mg), 11b (0.20 mmol, 21.43 mg, 0.050 M), and benzene (4 mL). ($K_1 = 462$, $K_2 = n/a$).
0.04). The reaction was repeated with an increase in the concentration of \textbf{11b} to 0.10 M (K$_1$ = 448, K$_2$ = 0.04).

**Reaction of (POCOP)Ir(H)(C$_6$H$_5$) (12) and C$_6$H$_5$NH$_2$ (11c):** The general procedure for \textbf{11a} was followed using \textit{9} (0.075 mmol, 46.9 mg), NaO\textit{t}Bu (0.9 equiv., 0.067 mmol, 6.47 mg), \textit{11c} (0.2 mmol, 0.18 \textmu L, 0.050 M), and benzene (4.0 mL). (K$_1$ = 188, K$_2$ = 0.07). The reaction was repeated with an increase in the concentration of \textit{11c} to 0.10 M (K$_1$ = 189, K$_2$ = 0.08).

**Reaction of (POCOP)Ir(H)(C$_6$H$_5$) (12) and \textit{p}-ClC$_6$H$_4$NH$_2$ (11d):** The general procedure for \textbf{11a} was followed using \textit{9} (0.074 mmol, 46.15 mg), NaO\textit{t}Bu (0.9 equiv., 0.066 mmol, 6.4 mg), \textit{11d} (0.392 mmol, 50 mg, 0.10 M), and benzene (4 mL). (K$_1$ = 50, K$_2$ = 1). The reaction was repeated with an increase in the concentration of \textit{11d} to 0.15 mol/L (K$_1$ = 60, K$_2$ = 1).

**Reaction of (POCOP)Ir(H)(C$_6$H$_5$) (12) and \textit{p}-CF$_3$C$_6$H$_4$NH$_2$ (11e):** The general procedure for \textbf{11a} was followed using \textit{9} (0.138 mmol, 86.6 mg), NaO\textit{t}Bu (0.9 equiv., 0.124 mmol, 11.9 mg), \textit{11e} (0.08 mmol, 12.9 mg, 0.010 M), and benzene (8 mL). (K$_3$ = 272). The reaction was repeated with an increase in the concentration of \textit{11e} to 0.050 M (K$_3$ = 259). No \textit{13e} could be detected.

**Reaction of (POCOP)Ir(H)(C$_6$H$_5$) (12) and C$_6$F$_5$NH$_2$ (11f):** The general procedure for \textbf{11a} was followed using \textit{9} (0.038 mmol, 23.75 mg), NaO\textit{t}Bu (0.9 equiv., 0.0343 mmol, 3.3
mg), 11f (0.0721 mmol, 13.2 mg, 0.009 M), and benzene (8 mL) was added. (K₃ = 2010). The reaction was repeated with an increase in the concentration of 11f to 0.012 M (K₃ = 2300). No 13f could be detected.

Reaction with (POCOP)Ir(H)(C₆H₅) (12) and 3,5-(CF₃)₂C₆H₃NH₂ (11g): The general procedure for 11a was followed using 9 (0.158 mmol, 99.05 mg), NaOtBu (0.9 equiv., 0.142 mmol, 13.65 mg), 11g (0.08 mmol, 18 mg, 0.010 M), and benzene (8 mL). (K₃ = 2700). The reaction was repeated with an increase in the concentration of 11g to 0.050 M (K₃ = 2850). No 13g could be detected.

Low Temperature Oxidative Addition of p-Chloroaniline to 10: To a screw cap NMR tube, 10 was generated by reaction of 9 (0.023 mmol, 15 mg) with NaOtBu (0.023 mmol, 2.3 mg) in 0.4 mL of toluene-d₈ at 100°C for 1h. The reaction mixture was cooled to -78°C in a dry ice/acetone bath and a 0.1 mL of a 2.3M solution of p-chloroaniline (0.23 mmol) was added via syringe. The reaction warmed in the NMR probe until the solution consisted solely of 13c, after which the oxidative addition was monitored at -12°C. A data plot is included in supporting information.

Kinetic Analysis of the Reductive Elimination Reactions of 14e-g: In a screw cap NMR tube, 10 was generated by reaction of 9 (0.023 mmol, 15 mg) with NaOtBu (0.023 mmol, 2.3 mg) in 0.5 mL of toluene-d₈ at 100°C for 1h. Aniline 11e, f or g were added to the solution of 10 and allowed to react for 45 minutes. The NMR tube was cooled to -78°C in a
dry ice/acetone bath, followed by addition of ethylene to the reaction mixture via syringe. The NMR tube was warmed to 9°C in the probe and the reductive elimination was monitored by ¹H NMR spectroscopy. A plot of kinetic data for 14f is included in supporting information.

Kinetic Analysis of the Dissociation of H₂NC₆H₄-pOMe (11a) from 13a: (POCOP)Ir(H)(Cl) 9 (10 mg, 0.016 mmol), NaOtBu (1.7 mg, 0.018 mmol), and toluene-d₈ (0.4 mL) were heated for 1 hr. at 100°C in a J. Young NMR tube to generate the tolyl hydride complexes 17. p-Methoxyaniline 11a (3.5 mg, 0.024 mmol) and 1,3,5-trimethoxybenzene (0.1 mL, 0.11 M solution in toluene-d₈) was added to the NMR tube. After freeze-pump-thawing the NMR sample, ethylene (10-20 equiv., 3.6-7.2 mL at 23°C) was introduced via a gas tight syringe at liquid nitrogen temperature. The reaction was then monitored via low temperature NMR spectroscopy at -8°C. A plot of kinetic data is included in supporting information.

(POCOP)Ir(H)(NHC₆F₅)(CO) (20f): To a Schlenk flask, 9 (101 mg, 0.16 mmol), NaOtBu (17mg, 0.18mmol), 11f (33mg, 0.18 mmol), and toluene(5 mL) were added and stirred at room temperature for 1 hour. The reaction mixture was cooled to -78°C then CO was purged through the solution until the color lightened. The toluene was removed under vacuum and the product was extracted with pentane. The pentane was reduced under vacuum until the product began to precipitate. The pentane was then cooled to -78°C and the precipitate was filtered and washed with cold pentane. (60 mg, 46% yield).
\[ \text{Reductive Elimination of } p\text{-trifluoromethylaniline from } (\text{POCOP})\text{Ir(H)}(\text{CO})(\text{NHC}_6\text{H}_4-p\text{CF}_3) \text{ 20e:} \]

In a J. Young NMR tube, tolyl complexes 17 were generated by heating the reaction mixture of (POCOP)Ir(H)(Cl) 9 (15 mg, 0.024 mmol), NaOtBu (2.3 mg, 0.024 mmol), and 0.5 mL of toluene-\(d_8\) for 1 hour at 100°C. The reaction mixture was cooled to room temperature. The addition of \(p\text{-CF}_3\)-aniline 11e (6.0 \(\mu\)L, 0.048 mmol) formed complex 14e. After freeze-pump-thawing the reaction mixture, a gastight syringe was used to add sufficient CO at liquid N\(_2\) temperature to generate pressures of 1, 2,
and 3 atmospheres of CO in the head space at 25°C. The reaction was monitored at 63°C by $^1$H NMR spectroscopy.

**Procedure for Monitoring Reaction of Benzamide Complex 22a with PPh$_3$:** A stock solution of (POCOP)Ir(H)(NH(CO)Ar) was prepared in the glovebox under Ar by stirring (POCOP)Ir(H)(Cl) 9 (112.7 mg, 0.18 mmol), NaO$_{tBu}$ (20.7 mg, 0.22 mmol), benzamide 21a (26.2 mg, 0.22 mmol), and toluene-$d_8$ (3.0 mL) until the color of the solution turned pale orange, ca. 30 minutes. The excess benzamide and NaO$_{tBu}$ were filtered out through a 0.02 micron syringe filter. The concentration of the stock solution (0.063 M) was measured via $^1$H NMR using 2.0 μL of mesitylene as a standard. Aliquots (0.5mL) of the stock solution were added to three J. Young NMR tubes containing known amounts of PPh$_3$ (0.147 mmol, 0.294 mmol, 0.588 mmol). The NMR tubes were heated to 100°C for three days, after which the reaction was stopped by placing the NMR tubes in cold water. The $K_{eq}$ was calculated by measuring the ratios of 22a and 26 by $^{31}$P NMR. $K_{eq} = 0.18$.

**Procedure for Monitoring Reaction of Benzamide Complexes 22b with PPh$_3$:** A stock solutions was prepared using 9 (92.5 mg, 0.148 mmol), NaO$_{tBu}$ (71.0 mg, 0.74 mmol), 22b (161.6 mg, 0.74 mmol), and toluene-$d_8$ (6.0 mL). Aliquots of the stock solution (0.6 mL, 0.021 M) were placed in three J. Young tubes with known amounts of PPh$_3$ (0.126 mmol, 0.252 mmol, 0.378 mmol). The reaction was heated to 100°C overnight, after which the reaction was stopped by placing the NMR tubes in cold water. The the $K_{eq}$ was calculated by measuring the ratios of 22b and 26 by $^{31}$P NMR. $K_{eq} = 0.067$. 
(POCOP)Ir(PPh₃) (24): In a Schlenk flask 9 (104 mg, 0.166 mmol), NaOrBu (17.6 mg, 0.183 mmol), PPh₃ (46 mg, 0.174 mmol), and toluene (10 mL) were combined and stirred overnight. Toluene was removed under vacuum until the product precipitated. The product was filtered, washed with cold toluene, and dried under vacuum to yield an orange solid (74 mg, 52% yield).

¹H NMR (500 MHz, C₆D₆): δ 8.06 (t, 6H, PPh₃), 6.9-7.1 (m, 12H, aromatic protons), 1.072 (vt, J_P-H = 6.8 Hz, 36H, P(tBu)₂). ^3¹P{¹H} NMR (162 MHz, C₆D₆): δ 181.2 (d, J_P-P = 5.2 Hz), 15.8 (t, J_P-P = 5.5 Hz). ^1³C{¹H} NMR (100.6 MHz, C₆D₆): δ 166.4 (C_q, vt, J_P-C = 6.5 Hz, C3 and C5), 141.5, 135.7, 133.7, 129, 127.0, 125.7 (CH, s, C1), 102.7 (CH, t, vt, C2 and C6), 41.0 (C_q, vt, J_P-H = 11.6 Hz, C(CH₃)₃), 28.7 (CH₃, s). Elemental analysis calculated for C₄₀H₅₄O₂P₃Ir (851.99): C: 56.39, H: 6.39. Found: C: 56.19, H: 6.37. Crystallographic data is included in the supporting information.

Kinetic Analysis of the Reductive Elimination of Benzamide 22a: A stock solution (0.06 M) of (POCOP)Ir(H)(NH(CO)C₆H₅) 23a was prepared under Ar by stirring (POCOP)Ir(H)(Cl) 9 (75.1 mg, 0.12 mmol), NaOrBu (12.7 mg, 0.132 mmol), benzamide 22a (16.0 mg, 0.132 mmol), and toluene-d₈ (2 mL) until the color of the solution turned pale orange. The excess benzamide and NaOrBu were filtered out through a 0.02 micron syringe filter. To a screw cap NMR tube, 10 equiv. of 22a (15 mg, 0.124 mmol), 10 equiv. of PPh₃ (32.5 mg, 0.124 mmol), the stock solution of 23a (0.21 mL, 0.06 M), and toluene-d₈ (0.4 mL) were added. The reaction was heated to 100°C in the NMR probe and over time the disappearance of 23a signals were monitored via ^¹H NMR. A plot of kinetic data is included in supporting information.
(POCOP)Ir(H)(NH(CO)(Ph) (22a):  (POCOP)Ir(H)(Cl) (9) (100 mg, 0.16 mmol), NaOttBu (18.4 mg, 0.192 mmol), H2N(CO)C6H5 (21a) (23.2 mg, 0.192 mmol), and 5.0 mL of benzene were added to a Schlenk flask and allowed to stir for 1.5 hours until color changed to a light orange color. The solution was filtered through a 0.2 micron syringe filter, and the benzene was sublimed at 0°C to yield a yellow/orange colored solid (71.6 mg, 63% yield).

\[
\text{\begin{center}
\begin{tikzpicture}
\begin{scope}
\draw (0,0) -- (1,1) -- (2,0) -- (1,-1) -- cycle;
\filldraw[fill=white, draw=black] (1,1) circle (0.1cm);
\filldraw[fill=white, draw=black] (1,-1) circle (0.1cm);
\filldraw[fill=white, draw=black] (0,0) circle (0.1cm);
\filldraw[fill=white, draw=black] (2,0) circle (0.1cm);
\end{scope}
\end{tikzpicture}
\end{center}
\]

\text{(POCOP)Ir(H)(NH(CO)(Ph) (22a))}

\[\text{^1H NMR (500 MHz, C}_6\text{D}_6): \delta 7.64-7.62 (m, 2'H, 2'- and 6'-H), 7.12-7.07 (m, 3'H, 3', 4', and 5'-H), 6.87-6.79 (m, 3'H, 1', 2'-, and 3-H), 5.90 (bs, 1'H, NH), 1.40 (vt, J_{P-H} = 6.9 Hz, 18H, P(tBu)2), 1.28 (vt, J_{P-H} = 7.0 Hz, 18H, P(tBu)2), -30.25 (t, J_{P-H} = 13.2 Hz, 1H, IrH). \]  

\[\text{^31P\{}^1\text{H\} NMR (162 MHz, C}_6\text{D}_6): \delta 164.2. \]

\[\text{^{13}C\{}^1\text{H\} NMR (125.8 MHz, C}_6\text{D}_6): \delta 176.4 (C_q, t, J_{P-C} = 1.3 Hz, CO), 166.6 (C_q, vt, J_{P-C} = 6.0 Hz, C3 and C5), 138.4 (C_q, s, C1'), 130.1 (CH, s, C4'), 128.3 (CH, s, C3' and C5'), 126.3 (CH, s, C2' and C6'), 124.1 (CH, s, C1'), 118.5 (C4), 104.5 (CH, t, J_{P-C} = 5.4 Hz, C2 and C6), 42.5 (Cq, vt, J_{P-H} = 12.0 Hz, C(CH3)3), 39.9 (Cq, vt, J_{P-H} = 11.8 Hz, C(CH3)3), 28.8 (CH3, vt, J_{P-H} = 3.3 Hz, C(CH3)3), 27.6 (CH3, bvt, J_{P-H} = 2.2 Hz, C(CH3)3). \]


(POCOP)Ir(H)(NH(CO)(C6F5) (22b):  (POCOP)Ir(H)(Cl) (9) (100 mg, 0.16 mmol), NaOttBu (18.4 mg, 0.192 mmol), H2N(CO)C6F5 (21b) (40.5 mg, 0.192 mmol), and 5.0 mL of benzene were added to a Schlenk flask and allowed to stir for 1.5 hours until the color
changed to a light orange color. The solution was filtered through a 0.2 micron syringe filter, and the benzene was sublimed at 0°C to yield a yellow/orange colored solid (101.6 mg, 79% yield).

![Image of a diagram]

1H NMR (500 MHz, C6D6): \(\delta\) 6.87-6.78 (m, 3H, 1-, 2-, 6-H), 5.49 (bs, 1H, NH), 1.44 (vt, \(J_{P-H} = 7.0\) Hz, 18H, P(tBu)2), 1.22 (vt, \(J_{P-H} = 7.0\) Hz, 18H, P(tBu)2), -35.72 (t, \(J_{P-H} = 13.0\) Hz, 1H, IrH19F NMR (376.5 MHz, C6D6): \(\delta\) -141.76 (m), -155.25 (m), -166.61 (m). 13C{1H} NMR (125.8 MHz, C6D6): \(\delta\) 167.2 (C_q, vt, \(J_{P-C} = 5.8\) Hz, C3 and C5), 163.0 (C_q, s, CO), 144.5 (C_q, dm, \(J_{F-C} = 241.8\) Hz, C2' and C6'), 141.1 (C_q, dm, \(J_{F-C} = 254.3\) Hz, C4'), 137.7 (C_q, dm, \(J_{F-C} = 252.0\) Hz, C3' and C5'), 125.4 (CH, s, C1), 119.9 (C_q, m, C4), 116.2 (C_q, m, C1'), 104.7 (CH, t, vt, \(J_{P-H} = 5.3\) Hz, C2 and C6), 42.8 (Cq, vt, \(J_{P-H} = 12.1\) Hz, C(CH3)3), 39.8 (Cq, vt, \(J_{P-H} = 12.1\) Hz, C(CH3)3), 28.3 (CH3, vt, \(J_{P-H} = 3.3\) Hz, C(CH3)3), 27.6 (CH3, vt, \(J_{P-H} = 3.1\) Hz, C(CH3)3). Elemental analysis calculated for C29H41O3P2N1F5Ir (800.80): C: 43.50, H: 5.16, N: 1.75. Found: C: 43.70, H: 5.25, N: 1.71.
References and Notes


(39) Formed by reaction of *in situ* generated 14f followed by addition of PMe3 at -40°C. Key NMR resonances include 1H NMR (400 MHz, C7D8): δ -11.9 (dt, Ir-H, J_{P-H} = 149.1 Hz (trans), J_{P-H} = 23.4 Hz (cis), and 31P(162 MHz, C7D8): δ 169.6 (m, 2P), -57.1 (m, 1P).

(40) The stability of the aryl hydride complex can be dramatically altered by incorporation of fluorine substituents in the aromatic ring. In preliminary experiments we have shown that reaction of (POCOP)Ir, 10, with 2,3,5,6-tetrafluoroaniline yields solely the C-H activation product (POCOP)Ir(H)(C6F4NH2). Strengthening of the Re-aryl bond through fluorination of the aryl ring has been well-documented in earlier studies by Perutz et. al. *(Chem. Commun.*, **2003**, 490)


CHAPTER THREE

Reactions of electron-deficient cationic iridium hydride pincer complexes with hydrogen and olefins

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Introduction

Hydrocarbons, including alkenes, provide a large feedstock of inexpensive substrates that can be converted to more desirable compounds or materials. Therefore, new catalysts capable of converting olefins to more valuable products are highly sought-after. Two prominent areas of transition metal-catalyzed transformations of olefins include polymerization/copolymerization of olefins and functionalization of olefins through the formation of new C-X bonds. Transition metal catalyzed processes in general are desired because often they allow chemo-, regio-, or stereoselective control of the reaction. Additionally, these reactions have the potential of being atom economic, in which all the atoms in the starting substrates are found in the products. This provides an environmentally benign scenario as there is no waste formed at the end of the reaction.
There have been numerous reports of addition of a H-Nuc species across carbon-carbon triple and carbon-carbon double bonds with control of regioselectivity and stereoselectivity, depending on the catalyst, substrate and reaction conditions. A few examples include hydroformylation, hydroamination, hydrothiolation and hydrocyanation.

Although these reactions are all very different, they are initiated generally by one of two pathways. The first pathway involves nucleophilic attack of the reactant on a metal-olefin complex to form an alkyl species. The olefin, through binding with the metal, is activated for attack by the nucleophile. The second pathway involves insertion of the olefin into an M-H bond forming a metal alkyl species which provides an empty coordination site for the nucleophile to coordinate to the metal. Reductive elimination results in formation of the desired product. These processes are particularly facile when the olefin contains an electron-withdrawing functional group or is sterically strained in order to promote the reaction. Transformations involving common unactivated olefins such as ethylene or propylene are generally less facile and remain an important goal. A basic understanding of the behavior of new metal-olefin complexes should aid in developing new catalysts for these types of reactions.

As mentioned above, many of these transformations occur through a mechanism that involves an olefin insertion reaction. Previously in our laboratory it has been shown that (POCOP)IrH₂ (POCOP = 2,6-(OPtBu₂)₂C₆H₃) is capable of hydrogenation chemistry through insertion of an olefin into the Ir-H bond, followed by reductive elimination of the alkyl hydride fragment (Scheme 3.1).
Scheme 3.1. Hydrogenation of cyclooctene by (POCOP)IrH$_2$\textsuperscript{12,13}

It has also been shown that the 14-electron fragment [(POCOP)Ir] is able to oxidatively add anilines, preferentially electron-withdrawing anilines, to form (POCOP)Ir(H)(NHAr) (Scheme 3.2).\textsuperscript{14} However, when both ethylene and aniline were present, coordination of the ethylene occurred to form the stable ethylene complex. No C-N coupling occurred as might have been expected as shown in Scheme 3.3. Even when a more strained olefin, norbornene, was reacted with [(POCOP)Ir] and H$_2$N(3,5-bis(CF$_3$)C$_6$H$_3$) at 23-150°C, once again only the olefin complex was observed and no C-N bonds were formed.

Scheme 3.2. Activation of electron-withdrawing anilines by [(POCOP)Ir].

\[
\text{[(POCOP)Ir]} + \text{H}_2\text{NHAr} \rightarrow \text{[(POCOP)Ir]}\text{H}^+ \text{NHAr}
\]

\(\text{Ar} = -\text{C}_6\text{H}_4\rho\text{CF}_3, -\text{C}_6\text{F}_5, -3,5(\text{CF}_3)\text{C}_6\text{H}_3\)
We were interested in investigating how changing the POCOP pincer complexes from neutral to cationic would affect their reactivity. A cationic complex would render the iridium center even more electron-poor which might cause the olefin to bind less strongly since there would be less \( \pi \)-backdonation from the iridium to the \( \pi^* \) orbital of the olefin. This could activate the olefin to nucleophilic attack to form a new C-X bond or increase its ability to insert into a M-H or M-C bond. Therefore, the cationic complexes were developed with the goal to enhance the potential for these types of iridium systems to be involved in catalytic formation of C-X bonds. A possible reaction mechanism for this type of transformation is shown below in the Scheme 3.4.
Results and Discussion

I) Synthesis of (POCOP)Ir(H)(OTf) (2) and cationic [(POCOP)Ir(H)(L)][X] (X = SbF$_6$ (3), BAr$_F$ (4))

In order to synthesize cationic POCOP iridium complexes, various silver and sodium salts (AgOTf, AgSbF$_6$, and NaBAR$_F$) (Tf$^-$ = triflate, BAR$_F$ = tetrakis(3,5-bistri fluoromethylphenyl)borate) were used to abstract chloride from (POCOP)Ir(H)(Cl), 1, in methylene chloride (Scheme 3.5). When silver triflate was used as the chloride abstractor, it was found that the triflate anion coordinated to the iridium generating a neutral species.
Scheme 3.5. Synthesis of (POCOP)Ir(H)(OTf) and cationic [(POCOP)Ir(H)(L)][X] [X = SbF\textsubscript{6}, BAr\textsubscript{F}]

An X-ray quality crystal of 2 was obtained through slow crystallization from methylene chloride at -35°C under an argon atmosphere. An ORTEP diagram of the structure of 2 is shown in Figure 3.1. The triflate is bound in the coordination site trans to the ipso carbon of the ligand backbone. The hydride was not located, although one can assume it is in an axial position due to the \textsuperscript{1}H chemical shift of -43.1 ppm which is indicative of an apical hydride with an empty coordination site trans to the hydride.\textsuperscript{14,15} The C\textsubscript{ipso}-Ir-O angle is unable to be measured because there is some disorder in the position of the triflate.
Figure 3.1. ORTEP diagram $^{16}$ of (POCOP)Ir(H)(OTf), 2. The hydrogens have been excluded for clarity. Key bond distances (Å) and bond angles (degrees): Ir(1)–C(10) 1.993 Å, Ir(1)–P(1) 2.318 Å, Ir(1)–P(2) 2.296 Å, P(2)–Ir(1)–C(10) 80.41°, P(1)–Ir(1)–C(10) 80.08°

In order to test the lability of the bound triflate anion, a solution of 2 in methylene chloride-d$_2$ was exposed to one atmosphere of carbon monoxide. Initially, two products were formed ($^{31}$P NMR = 174.2 and 164.9 ppm). Both products bear a hydride with resonances downfield of the starting material at -10.5 and -7.3 ppm, respectively, which suggests a six-coordinate complex. When the solution is placed under a reduced pressure, the intensity of the resonance at 164.9 ppm ($^{31}$P NMR) decreases until the solution is comprised of only the complex represented by $^{31}$P = 174.2 ppm. These two complexes are proposed to be the mono- and di-carbon monoxide adducts, 5 and 6 (Scheme 3.6). The IR spectrum of complex
5 shows a stretching frequency of 2062 cm\(^{-1}\). Such a high frequency for a carbonyl stretch is not unexpected since the iridium center is electron poor, providing little backbonding into the \(\pi^*\) orbitals of the CO.

**Scheme 3.6.** Reaction of (POCOP)Ir(H)(OTf), 2, with carbon monoxide

Pentafluoroaniline was also added to solution of 2 in methylene chloride-d\(_2\). At room temperature, there was no reaction and only 2 and free pentafluoroaniline was observed in solution. After heating at 50\(^\circ\)C overnight, the \(^{31}\)P and \(^1\)H NMR spectra taken at room temperature showed 4% of a decomposition product that contained no aniline bound to iridium. Therefore, the triflate anion has a higher binding affinity for the [(POCOP)IrH]\(^+\) cation than aniline. Unfortunately, the results of both the above experiments indicate that the triflate ligand is coordinated more strongly than desired, and probably is not the optimum choice as counter-anion.

Reaction of 1 with AgSbF\(_6\) in CH\(_2\)Cl\(_2\) formed the H\(_2\)O complex 3 despite attempts to exclude water from the reaction mixture. (It was expected that methylene chloride might bind to the 14-electron [(POCOP)IrH]\(^+\) cation.) The \(^1\)H NMR spectrum shows the hydride resonance at -43.05 ppm, indicating a 5-coordinate species, as well as a very broad peak at ca. 4.05, spanning 1.5 ppm, for the coordinated water. An X-ray quality crystal was obtained through slow crystallization from methylene chloride at -35\(^\circ\)C under an argon atmosphere.
The ORTEP diagram of the structure is shown in Figure 3.2. Water is bound \textit{trans} to the \textit{ipso} carbon with a C\textit{ipso}-Ir-O angle of 178.2°. Similar to 2, the hydrogen was unable to be located but can be assumed to be in an axial position with an $^1$H chemical shift of -43.0 ppm.

**Figure 3.2.** ORTEP diagram\textsuperscript{16} of [(POCOP)Ir(H)(H$_2$O)][BAR$_F$], 3. The hydrogens have been excluded for clarity. Key bond distances (Å) and bond angles (degrees): Ir(1)–C(10) 1.991 Å, Ir(1)–O(31) 2.210 Å, Ir(1)–P(1) 2.301 Å, Ir(1)–P(2) 2.302 Å, P(1)–Ir(1)–C(10) 80.37°, P(2)–Ir(1)–C(10) 80.12°, C(10)–Ir(1)–O(31) 178.22°.

The reaction of 1 with NaBAR$_F$ was slower than the reactions with silver salts mentioned above. This is due the low solubility of NaBAR$_F$ in methylene chloride, and therefore the reaction had to be stirred overnight. The $^1$H iridium hydride chemical shift of the species formed is -41.92 ppm which indicates that there is no ligand \textit{trans} to the hydride. It seems likely that methylene chloride is coordinated \textit{trans} to the \textit{ipso} carbon in this species, but no clean NMR evidence nor crystal structure was obtained to support this. One can assume,
however, that the structure of 4 is analogous to 3. By adding a ligand that can strongly coordinate to the metal (such as an olefin), the cationic complex can be stabilized and the species of the type [(POCOP)Ir(H)(L)][BArF] can be fully characterized.

II. Synthesis and Dynamics of [(POCOP)Ir(H)(L)][BArF] (L = H2 (9), Ethylene (10), Propylene (11), Norbornene (12), and Methyl Acrylate (MA) (13))

a) Synthesis, Characterization and Dynamics of [(POCOP)Ir(H)(H2)][BArF] (9)

Formation of transition-metal dihydrogen complexes and their structures have been of interest since the first report of a stable M-(η2-H2) complex, (iPr3P)2(CO)3W(η2-H2), by Kubas.17 More recently, Crabtree,18-20 Heinekey,21-23 Parkin,24 and others have presented extensive work on elucidating the structures of various “trihydride” complexes. There are two possible structures that have been proposed in the literature, a classical trihydride complex and a non-classical dihydrogen/hydride complex. Two features have been employed to distinguish these two structures, T1(min) values and H/D coupling constants. Generally, small T1 values (4-100 ms) indicate the existence of a bound dihydrogen with a short H-H distance and therefore a dihydrogen/hydride structure. Examination of the H-D coupling constants in a partially deuterated substrate provides a way to differentiate the structures as well. The 1JH-D coupling constant for free HD is 43.2 Hz. However, when dihydrogen coordinates to a metal, the 1JH-D coupling constant lowers to around 30 Hz, for example 33.5 Hz in Kubas’ complex.17,25 The 2JH-D coupling constant between two terminal hydrides is much lower and tends to be less than 2 Hz.

Crabtree and coworkers synthesized a cationic iridium dihydrogen hydride complex [IrH3(bq)(PPh3)2][SbF6] (bq = benzoquinoline) (Scheme 3.7) by displacement of an aquo
ligand by H₂. The complex is thermally stable under an atmosphere of hydrogen gas, but if purged with nitrogen in the presence of water, the H₂ is displaced by the aquo ligand. A crystal of this complex could not be obtained to verify the structure because the H₂ was labile in the solid state. However, an H/D coupling constant of 29.5 Hz was measured, indicating that the structure was the dihydrogen/hydride, not the classical trihydride.

**Scheme 3.7.** Equilibrium between [IrH(H₂O)(bq)(PPh₃)₂][SbF₆] and [IrH₃(bq)(PPh₃)₂][SbF₆] by Crabtree et. al.

1H NMR studies on complex 8 performed by Crabtree et al. showed at room temperature a single resonance representing the weighted average of the three hydrogens bound to iridium. However at temperatures below 260 K, the exchange rate of the dihydrogen and hydride decreases and the two signals separate. The dihydrogen resonance appears at -2.9 ppm, integrating for 2 protons, while the hydride resonates at -15.3 ppm. Through line-broadening studies, the exchange rate between the hydrogens was estimated to be 350-500 s⁻¹ at 260 K. This corresponds to a ΔG‡ of ca. 12.0 kcal/mol. Possible mechanisms for exchange are presented later in this section.

Previously, Göttker-Schnetmann in our group prepared an anionic trihydride complex, [(POCOP)IrH₃][Na]. The ¹H{³¹P} NMR resonances for the hydrides appear as a triplet at -
13.33 and as a doublet at -13.55. The $^{2}J_{HH}$ coupling constant between the protons is 4.8 Hz ($J_{HH:D} = J_{HH}/7$), indicating that the structure is the classical trihydride and can be viewed as an 18-electron Ir(III) complex. Were this an $\eta^2$-H$_2$ complex [[(POCOP)Ir(H$_2$)H]] this would be a 16-electron anionic Ir(I) complex. It is not surprising that such an electron-rich, unsaturated system would prefer to undergo oxidative addition of hydrogen to form the classical tryhydride.

For comparison we were interested in generating a cationic iridium “trihydride” complex such as [[(POCOP)Ir(H$_3$)][BARF]], 9, and determining if the structure is a classical or nonclassical trihydride (Figure 3.3). Since this complex would be electron-deficient, it would be more likely to exist in the non-classical dihydrogen/hydride form.

![Figure 3.3. The non-classical dihydrogen/hydride vs. the classical trihydride for [(POCOP)IrH$_3$][BARF], 9](image)

Complex 9 was synthesized by two different routes. The first method involves the addition of HBAR$_F$ to a solution of (POCOP)IrH$_2$ in methylene chloride. However, HBAR$_F$ exists as a diethyl ether complex, [H(OEt$_2$)$_2$][BARF], where Et$_2$O is a potential ligand. To avoid the addition of ether to the reaction mixture, 9 can be produced by hydrogenation of the propylene complex [[(POCOP)Ir(H)(C$_3$H$_6$)][BARF]], 11, (for preparation see below) in methylene chloride (Scheme 3.8). The H$_3$ complex, 9, is cleanly generated and the only side product is one equivalent of propane which does not interfere with the NMR characterization.
While complex 9 can be quantitatively generated in situ, because the coordinated hydrogen is quite labile attempts to isolate this complex have been unsuccessful.

**Scheme 3.8.** Generation of [(POCOP)Ir(H)(H<sub>2</sub>)][BARF], 9, by hydrogenation of [(POCOP)Ir(H)(C<sub>3</sub>H<sub>6</sub>)][BARF], 11

At room temperature the proton NMR spectrum of 9 shows a broad iridium hydride band between -13 and -15 ppm integrating for three protons. However at temperatures below ca. 200 K, this resonance separates into two broad signals, 0.033 ppm and -41.9 ppm, in a two to one ratio, respectively. Both of these peaks were too broad to determine ³¹P coupling. The large difference in chemical shift of the two protons immediately suggests that this complex is a dihydrogen/hydride, as compared to a trihydride in analogy to the Crabtree complex, 8. Also, based on the resonance frequency of similar POCOP iridium pincer complexes, the very high upfield shift of -41.9 ppm is indicative of a hydride with an empty trans coordination site. However, more definitive proof of this structure was desired.

In order to obtain more detailed structural information, complex 9 was partially deuterated by purging both D<sub>2</sub> and H<sub>2</sub> through the solution. This generated a sample that contained a mixture of H<sub>3</sub>, H<sub>2</sub>D, HD<sub>2</sub>, and D<sub>3</sub> complexes. The <sup>1</sup>H NMR signal at δ 0.03 was too broad and complex to determine a <i>J</i><sub>HD</sub> coupling constant. In the normal <sup>2</sup>H NMR spectrum at 173 K, the peaks representing H-D and D-D coordinated to the iridium could be seen in approximately a 1:1 ratio. Although the H-D coupling could be observed (Figure...
it was difficult to obtain an accurate measurement of the H-D coupling constant. To circumvent this problem and accurately determine the coupling constant, a one-dimensional HMQC NMR experiment was performed in which the observed nucleus is deuterium. This experiment allowed only signals that contain H-D coupling to be visible, suppressing all signals that do not have coupling to $^1$H (i.e. the D$_2$ signal). This HMQC experiment is depicted in Figure 3.4 where the bottom spectrum shows the normal $^2$H-NMR spectrum, while the top spectrum shows the result of the one-dimensional $^2$H-HMQC experiment where the doublet resonance for the partially deuterated complex is clearly observable. The measured $J_{\text{HD}}$ coupling constant was 33.0 Hz, consistent with the $J_{\text{H-D}}$ of an $\eta^2$-HD ligand and supporting the assignment of 9 as an iridium(hydride)(dihydrogen).

Figure 3.4. Overlay of the $^2$H NMR spectrum of the dihydrogen region of a partially deuterated sample of [(POCOP)Ir(H)(H$_2$)][BAr$_F$], 9, in CH$_2$Cl$_2$. The top spectrum is a deuterium observed 1D-HMQC. The bottom spectrum is a $^2$H NMR. These spectra are not referenced but correlate to the $\sigma$-bound dihydrogen peak.
Similar to the Crabtree system, the three hydrogens on iridium interchange. Three possible mechanisms for the hydrogen exchange for [(POCOP)Ir(H)(H2)][BArF] 9 are shown in Scheme 3.9. In the first mechanism, A, the dihydrogen oxidatively adds to the iridium center forming the classical trihydride intermediate. From this intermediate, reductive coupling of H$_2$ can lead to the starting complex, where no site exchange has occurred, or the complex in which H$_a$, originally the terminal hydride, has been incorporated into the $\eta^2$-H$_2$ site. Mechanism B involves a proton transfer from the dihydrogen to the hydride through a transition state in which there is partial and symmetrical bonding of the migrating hydrogen to both remaining hydrogens. No trihydride intermediate is required. In the last mechanism, C, the exchange of the hydrogens occurs through a triangular H$_3^+$ intermediate in which all hydrogens become equivalent.

**Scheme 3.9.** Modes of hydrogen exchange for [(POCOP)Ir(H)(H2)][BArF], 9

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A

Classical Oxidative Addition

B

Proton Transfer

C

Triangular H$_3^+$ intermediate
The exchange rate for the dihydrogen/hydride complex was measured for both the trideutero \(9_\text{D}\) and triproteo \(9_\text{H}\) complexes by line-broadening techniques. For \(9_\text{D}\), the line-width of the \(\eta^2-\text{D}_2\) resonance was measured in the temperature range of 183.9-207.5 K. On the other hand, the rate for \(9_\text{H}\) was calculated by measuring the line-broadening of the hydride signal from 175.3 K to 196.8 K. The rate of exchange in the triproteo complex corresponded to \(\Delta G^\ddagger = 9.1\) kcal/mol (measured at 188 K, Appendix II, Scheme II.2 and Table II.2), while the rate in the trideuterated complex corresponded to \(\Delta G^\ddagger = 9.8\) kcal/mol (measured at 205 K, Appendix II, Scheme II.1 and Table II.1) for the exchange of the hydride with the proton on the \(\sigma\)-bound dihydrogen. Based on the energy barriers, the rate at 200 K was calculated for both \(9_\text{D}\) and \(9_\text{H}\). From these rates, an isotope effect of \(k_\text{H}/k_\text{D}\) ca. 6 was calculated (Appendix II, Table II.3). The existence of an isotope effect in which the energy barrier for the deuterated complex is higher was expected since the breaking of the H-H (or D-D) bond in the \(\eta^2-\text{H}_2\) (\(\eta^2-\text{D}_2\)) would have to be involved in the transition state and the zero point energy in \(\eta^2-\text{D-D}\) is lower than that in \(\eta^2-\text{H-H}\). There is no way, however, to distinguish between the three different mechanisms under these reaction conditions.

b) **Synthesis and Characterization of \[\{(\text{POCOP})\text{Ir(H)(L)}\}\text{[BArF]}\] L = \(\text{C}_2\text{H}_4\) (10), \(\text{C}_3\text{H}_6\) (11), norbornene (12), methyl acrylate (13)**

Similar to the cationic dihydrogen/hydride complexes, the cationic olefin hydride complexes can be synthesized by two methods (Scheme 3.10). The preferred method involves treatment of \((\text{POCOP})\text{Ir(H)(Cl)}\) 1 with NaBArF in the presence of olefin in methylene chloride. Alternatively, addition of HBArF to the isolated \((\text{POCOP})\text{Ir(olefin)}\) complexes produces the olefin hydride complexes.
Both the ethylene complex 10 and propylene complex 11 can be generated quickly and cleanly by purging a mixture of (POCOP)Ir(H)(Cl), 1, and NaBARF with either ethylene or propylene gas. Since the solution is saturated with olefin, and therefore, the olefin concentration is high, this reaction is complete within fifteen minutes as indicated by a color change from light red to pale orange. Removal of the salt by syringe filtration under argon and evaporation of the solvent yields the pure product as a pale orange powder (Scheme 3.11).
At room temperature the bound ethylene of 10 is rapidly rotating on an NMR timescale as evident by a single ethylene resonance in the $^1$H NMR spectrum at 4.15 ppm. The upfield shift of the hydride in the $^1$H NMR spectrum of -42.83 ppm, is consistent with a 5-coordinate complex where the hydride is situated in the apical position trans to an empty coordination site. This geometry requires the t-butyl groups cis to the iridium hydride be distinct from those trans to the hydride. In fact, two t-butyl signals, seen as virtual triplets due to strong phosphorus-phosphorus coupling, suggest the existence of a vertical mirror plans bisecting the ligand backbone. This is supported by a single $^{31}$P resonance at 182.0 ppm for the two equivalent phosphorus atoms.

The propylene complex 11 displays some characteristics similar to the ethylene complex 10 such as an $^1$H NMR hydride signal at -42.90 ppm. However, there are some very noticeable differences. Typically, in the $^1$H spectra of POCOP-pincer complexes, the aryl backbone of the ligand has two resonances associated with it, a triplet for the central hydrogen (para to the iridium-bound carbon) and a doublet for the two equivalent hydrogens adjacent to the central one. In the propylene complex 11, the two adjacent hydrogens are now inequivalent and are seen as two doublets in the $^1$H NMR spectrum at 6.90 and 6.86 ppm. There are also now four resonances for the t-butyl groups, indicating none of the t-butyl groups are related by symmetry. The $^{31}$P NMR also supports this as there are two doublet signals (182.7 ppm, 175.0 ppm, $J_{pp} = 260.1$ Hz) for the two inequivalent phosphorus nuclei that are strongly coupled with each other. It is likely that the propylene, similar to the ethylene, is also rotating rapidly at room temperature; however since none of the conformations possess a mirror plane bisecting the ligand backbone, rapid rotation does not result in averaging the $^{31}$P signals or the t-butyl pairs.
The structure of \([(\text{POCOP})\text{Ir(H)(C}_3\text{H}_6)]\text{[BAr}_\text{F}], 11\), was confirmed by X-ray analysis. A crystal was grown by slow diffusion of pentane into a solution of 11 in methylene chloride at room temperature under an argon atmosphere. An ORTEP diagram of 11 is shown in Figure 3.5 and supports the structure determined by NMR spectroscopy. The propylene is rotated slightly from alignment of the C-C double bond with the plane with the ligand backbone. This rotation likely occurs to decrease the steric interactions between the methyl groups of the propylene and the \(t\)-butyl groups.

**Figure 3.5.** ORTEP diagram\(^1\)\(^6\) of \([(\text{POCOP})\text{Ir(H)(C}_3\text{H}_6)]\text{[BAr}_\text{F}].\) The hydrogens and counterion have been excluded for clarity. Key bond distances (Å) and bond angles (degrees): Ir(1)–C(10) 2.046 Å, Ir(1)–P(1) 2.338 Å, Ir(1)–P(2) 2.338 Å, Ir(1)–C(1) 2.255 Å, Ir(1)–C(2) 2.276 Å, C(1)–C(2) 1.141 Å, P(1)–Ir(1)–C(10) 78.57°, P(2)–Ir(1)–C(10) 78.72°, C(2)–C(1)–Ir(1)–P(2) -39.78°
The norbornene complex 12 is synthesized in a similar manner as the ethylene and propylene complexes (Scheme 3.12). In order for this reaction to go to completion in a respectable time, excess norbornene must be added to the reaction mixture. After filtration and removal of the solvent, the crude product must be washed with pentane to remove the excess norbornene. A plane of symmetry passing through the plane of the POCOP ligand backbone is evident by both $^{31}$P NMR and $^1$H NMR spectroscopy. A single resonance is observed at 176.0 ppm in the $^{31}$P NMR spectrum and only two triplet $^1$H signals are seen for the $t$-butyl signals, one for the pair cis to the iridium hydride and one for the pair trans. The hydride resonance is located at -45.9 ppm as in the other olefin complexes, indicating a 5-coordinate complex with an empty coordination site trans to the hydride. The $^1$H olefinic signals and the methine protons are observed at 4.71 and 3.44 ppm, respectively, in the $^1$H NMR spectrum. The resonances for the two diastereotopic protons on the C7 methylene carbon are very distinct doublets at 0.90 and 0.22 ppm. The endo and exo protons are further downfield at 1.90 and 1.33 ppm.

Scheme 3.12. Synthesis of [(POCOP)Ir(H)(norbornene)][BArF], 12

The structure of [(POCOP)Ir(H)(norbornene)][BArF], 12, is confirmed by X-ray diffraction. The ORTEP diagram with key bond length and angles is shown in Figure 3.6.
The crystal was grown by slow diffusion of pentane in to a solution of 12 in methylene chloride under an argon atmosphere at room temperature. The carbon-carbon double bond is almost perfectly parallel with the plane of the ligand; however, it is slightly shifted above the plane. The hydride was not able to be located.

Figure 3.6. ORTEP diagram\textsuperscript{16} of [(POCOP)Ir(H)(norbornene)][BAR\textsubscript{F}], 12. The hydrogen and BAR\textsubscript{F} counterion have been omitted for clarity. Key bond distances (Å) and bond angles (degrees): Ir(1)–C(10) 2.051 Å, Ir(1)–P(1) 2.353 Å, Ir(1)–P(2) 2.348 Å, Ir(1)–C(25) 2.289 Å, Ir(1)–C(26) 2.287 Å, C(25)–C(26) 1.397 Å, P(1)–Ir(1)–C(10) 77.67°, P(2)–Ir(1)–C(10) 77.80°, C(25)–Ir(1)–C(10) 157.20°, C(26)–Ir(1)–C(10) 156.45°

Isolation of [(POCOP)Ir(H)(MA)][BAR\textsubscript{F}], 13, proved difficult. When NaBAR\textsubscript{F} and excess methyl acrylate were added to a solution of (POCOP)Ir(H)(Cl), 1, the final product was a sticky solid that was very difficult to purify. Therefore, 13 was generated \textit{in situ} by addition of HBAR\textsubscript{F} to (POCOP)Ir(MA) 14 (Scheme 3.13). (POCOP)Ir(MA) was cleanly prepared by
reaction of 1 with NaOrBu and methyl acrylate in benzene. Removal of solvent under vacuum yielded 14 as a brick red solid.

Scheme 3.13. Synthesis of [(POCOP)Ir(H)(MA)][BArF], 13

Upon mixing HBArF and (POCOP)Ir(MA), 14, in methylene chloride, the $^1$H NMR spectrum of the product 13 showed some distinctive peaks. At room temperature three broad resonances representing the methyl acrylate olefinic protons of the two rotamers, 13a and 13b, in fast exchange were observed at 3.33, 5.35 and 5.15 ppm. The $^{31}$P{^1}H spectrum exhibited two broad phosphorus doublets at 179.8 and 175.8 ($J_{pp} = 228.0$ Hz). A third complex is also observed in the reaction mixture that has one multiplet at 2.92 ppm and a triple resonance at 2.22 ppm in the $^1$H NMR spectrum. These two signals represent the methylene protons of the insertion product 15. It is believe that the insertion product is in slow equilibrium with the olefin hydride complexes, with an equilibrium constant of roughly 0.13, favoring the olefin hydride. The $^{31}$P chemical shift of the insertion product is 153.4 ppm which is significantly further upfield from the olefin hydride complexes. This upfield shift is likely indicative of an interaction of the carbonyl oxygen with the iridium as shown in Scheme 3.14. A similar upfield shift have been seen in the neutral POCOP system, (POCOP)Ir(H)(NH(CO)(C₆H₅)), reported in Chapter 2 which was also attributed to an
interaction of the carbonyl oxygen with Ir. Attempts to grow X-ray quality crystals of this complex were unsuccessful possible due to multiple complexes present in solution.

**Scheme 3.14.** Rotation and insertion of methyl acrylate in [(POCOP)Ir(H)(MA)][BArF], 13

\[
\begin{align*}
\text{Fast} & \quad \text{(tBu)}_2\text{P} & \quad \text{Ir} & \quad \text{(tBu)}_2\text{P} & \quad \text{Fast} \\
\text{Slow} & \quad \text{K}_{eq} = 0.13 & \quad \text{MeO} & \quad \text{OMe} & \quad \text{K}_{eq} = 0.13 \\
\end{align*}
\]

\text{13a} \quad \text{13b} \quad \text{15}

c. Dynamics of [(POCOP)Ir(H)(L)][BArF] L = C_2H_4 (10), C_3H_6 (11), norbornene (12), methyl acrylate (13)

In order to gain further understanding about the behavior of these cationic olefin hydride complexes 10-13, variable temperature NMR experiments were performed to observe any dynamic behavior. The dynamics were studied using both line-broadening and spin-saturation studies. Initially, it was believed that both rotation of the olefin and insertion of the olefin into the Ir-H bond were occurring. However, the NMR experiments are complicated and deserve an in-depth discussion.

**Low temperature studies to observe olefin rotation**

[(POCOP)Ir(H)(C_3H_6)][BArF] 11 was dissolved in methylene chloride-d_2 and cooled to 175.3 K in the NMR probe. Upon cooling, analysis of the ^1H NMR spectra show that the olefin and hydride signals broaden and shift slightly (resonances marked 1a-4a, Figure 3.7).
At temperatures below 205 K the resonances begin to sharpen and a second set of minor signals appear below ca. 184 K (resonances marked 1b-4b, Figure 3.7). The chemical shifts above at 205 K represent a weighted average between the two complexes in fast exchange.

**Figure 3.7.** Variable temperature stacked $^1$H NMR spectra of [(POCOP)Ir(H)(C$_3$H$_6$)][BAr$_F$].
There are two possible explanations for this behavior. The first is an equilibrium between two rotamers, 11a and 11b (Scheme 3.15), in which one rotamer is greatly favored over the other. The second possibility is an equilibrium between 11c, a solvated form of 11 (Scheme 3.16). The hydride chemical shifts of the two complexes are -42.56 and -43.20 ppm, both of which are characteristic for five-coordinate (POCOP) iridium pincer complexes. If solvent had coordinated to the complex, a significant down field $^1$H chemical shift for the hydride would be expected. Therefore, it seems most likely that the two complexes are rotamers.

**Scheme 3.15.** Propylene rotation in [(POCOP)Ir(H)(C$_3$H$_6$)][BAr$_F$]

![Scheme 3.15](image)

**Scheme 3.16.** Solvation in [(POCOP)Ir(H)(C$_3$H$_6$)][BAr$_F$]

![Scheme 3.16](image)

As shown in the $^1$H NMR spectra (Figure 3.7), the two rotamers 11a,b are of unequal populations. At 175 K, the two complexes, 11a and 11b, are exchanging slowly on an NMR timescale and can be observed as separate resonances (Scheme 3.15). The equilibrium constant was measured by integration of the three pairs of signals (1a vs. 1b, 2a vs. 2b, and 4a vs. 4b). The measured $K_{eq}$ values were 0.066, 0.063, and 0.069, with an average of 0.066.
at 175.3 K. It is not clear which rotamer is favored. Using linebroadening techniques along with the $K_{eq}$ shown above, energy barriers for the rotation from the major rotamer to the minor rotamer and vice versa have been calculated as 10.2 and 9.1 kcal/mol, respectively. (Line-broadening calculations for the rotation rate of the major isomer are shown in Appendix II, Table II.7)

A similar phenomenon is observed for [(POCOP)Ir(H)(C$_2$H$_4$)][BArF$_7$] 10 in which the ethylene and hydride signals broaden as the methylene chloride-$d_2$ solution of 10 is cooled in the NMR probe. However, at 175.3 K the ethylene resonance remains broad and does not sharpen (Figure 3.8) indicating that the coalescence between the two inequivalent ethylene protons occurs below 175.3 K. This is not unexpected as ethylene should have a lower energy barrier to rotation than propylene, and therefore, lower temperatures are needed to observe slow rotation. By assuming that the difference in frequency between the chemical shifts of the olefin protons is 25 Hz or greater, the ethylene rotation can be estimated as being less than 8.7 kcal/mol. (Calculations for this estimation are shown in Appendix II, Table II.4)
Figure 3.8. $^1$H NMR spectra of the ethylene resonance in [(POCOP)Ir(H)(C$_2$H$_4$)][BAr$_F$] 10 at variable temperatures

However, there are a couple of unusual characteristics observed in the [(POCOP)Ir(H)(C$_2$H$_4$)][BAr$_F$] spectra. First, if only simple rotation of the olefin was occurring, the hydride resonance should not broaden since both rotamers of ethylene are equivalent. Secondly, it is abnormal for the direction of the chemical shift drift to change, however this is seen for both the ethylene and hydride resonances (Figure 3.8 and Figure 3.9). One possible explanation that would explain both of the described characteristics is that there is both a temperature dependence of the chemical shifts of the ethylene and hydride resonances, as well as the existence of an equilibrium between 10 and a solvated complex as described above. If 10 were in equilibrium with the solvated complex, an upfield shift of the hydride would be expected as the two resonances decoalesce. This is what is observed at 175.3 K in Figure 3.9. There is, however, no resonance observed at 175.3 K for the hydride
of the solvated complex. This might be expected if the resonance is very broad and the solvated species is at low concentration. As the temperature is raised above 205 K, both the ethylene and hydride chemical shifts move in the opposite direction, the hydride drifts upfield while the ethylene resonance drifts downfield. This phenomenon might be explained by a temperature dependence of the chemical shifts or the fact that a rapid equilibrium between a solvated and unsolvated complex shifts in favor of the unsolvated complex as would be expected upon warming. This change in equilibrium would drive the shift average upfield as observed since the hydride signal of the solvated species should be downfield of that for the unsolvated species. (Scheme 3.17)

**Scheme 3.17.** Solvation in [(POCOP)Ir(H)(C$_2$H$_4$)][BARF]
Figure 3.9. $^1$H NMR spectra of the hydride resonance in [(POCOP)Ir(H)(C$_2$H$_4$)][BArF$_7$] 10 at variable temperatures

As [(POCOP)Ir(H)(norbornene)][BArF$_7$], 12, is cooled in the NMR probe the rotation of the norbornene, unlike the ethylene and propylene complexes, is clearly frozen out (Figure 3.10). The two rotamers exist in about a 50:50 ratio at 174 K (Scheme 3.19). This is expected since the steric interaction between the $t$-butyl groups and the coordinated norbornene are virtually the same for either rotamer. The room temperature $^{31}$P NMR spectrum shows a single resonance for the weighted average of the two rotamers at 177.8 ppm which decoalesces at about 200 K. Two equal intensity resonances are observed at 179.0 and 177.2 ppm (Appendix II, Figure II.2). The olefin, methine, hydride and the C$_7$ methylene protons all show decoalescence at low temperature in the $^1$H NMR spectrum.
(Figure 3.10). This data is consistent with the crystal structure shown in Figure 3.6 and the existence of two rotamers in which the olefin is parallel with the ligand backbone. If the two rotamers had a structure in which the olefin was bound perpendicular to the ligand plane, the C7 methylene protons would not broaden or show decoalescence since the rotamers would be mirror images of each other. Using line-broadening techniques in the \( ^1 \text{H} \) NMR spectra the rate of interconversion of the rotamers was calculated to be 167 s\(^{-1} \) at 190.8 K, corresponding to a \( \Delta G^\ddagger \) is 9.1 kcal/mol. The calculations are shown in Appendix II, Table II.10.

**Scheme 3.18.** Rotation of [(POCOP)Ir(H)(norbornene)][BARF], 12

![Scheme 3.18](image-url)
Low temperature NMR studies were also performed on [(POCOP)Ir(H)(methyl acrylate)][BARF] 13 in order to measure the rate of rotation of the methyl acrylate. As the sample is cooled in the NMR probe the broad olefin signals broaden, decoalesce, and then re-
sharpen at 196.8 K (Figure 3.11). Similar to the propylene complex 11, it is likely that the two complexes are the two rotamers in equilibrium. At 196.8 K, the equilibrium constant is 0.26 based on the $^1$H integration. It unclear which rotamer is the more favored isomer. The hydride signals for the two rotamers are at -30.0 ppm for the major isomer and -36.2 ppm for the minor one. This suggests that in both of these isomers there may be some interaction of the carbonyl oxygen with the coordination site trans to the hydride. Since chemical shift for the weight averaged hydride at room temperature is at -38.5 ppm, there must be a temperature dependence off the shifts causing the weighted average to drift downfield as the temperature lowers. Based on the relative intensities of the olefinic resonances in the $^1$H NMR spectrum for the coordinated methyl acrylate at 197 K, an equilibrium constant, $K_{eq} = 0.3$, was calculated. Line broadening techniques and the equilibrium constant allow for calculation of the rate of conversion from the major to the minor rotamer and the minor to the major rotamer. These rates correspond to free energy barriers of 11.0 kcal/mol and 10.5 kcal/mol, respectively. (Calculation are shown in Appendix II, Table II.11)
Figure 3.11. Stacked $^1\text{H}$ NMR spectra of [(POCOP)Ir(H)(MA)][BArF], 13, at low temperatures.

Kinetics of Migratory Insertion Processes

For [(POCOP)Ir(H)(C$_2$H$_4$)][BArF], 10, the rate of insertion of ethylene into the Ir-H bond to form [(POCOP)Ir(CH$_2$CH$_3$)][BArF] was measured by examining the exchange rate between the hydride and ethylene resonances using line-broadening techniques. As the temperature is raised to 320 K, both the ethylene and hydride resonances broaden (Figure 3.12 and 3.13). To verify that the observed broadening was due to insertion, a spin-saturation transfer experiment was performed. At 276.5 K, when the hydride signal was irradiated, the ethylene signal decreased 49%. Therefore, migration of the hydride to the ethylene followed by proton scrambling is occurring and can be attributed to the broadening of both the ethylene and the hydride signal at elevated temperatures. Interestingly, the two
resonances for the $t$-butyl signals do not average (Appendix II, Figure II.1). In other words, once the insertion occurs the alkyl chain resides on only one face of the complex and does not freely rotate to the opposite face.

Figure 3.12. High temperature $^1$H NMR stacked plots of the ethylene resonance of [(POCOP)Ir(H)(C$_2$H$_4$)][BAr$_F$], 10
Two possible pathways for exchange of the protons in the cationic ethylene complex are shown in Scheme 3.19; both account for restricted rotation after insertion. Pathway A is the direct insertion of the ethylene into the Ir-H′ bond to form a normal ethyl group (I → II). The three hydrogens can now exchange through rotation of the methyl moiety which should be very fast. However, rotation around the Ir-C₁ bond must be slower than return to Ir, otherwise the two sets of t-butyl signals would broaden and average. A second possibility involves the H′ migration to the bound ethylene to form the agostic complex III. In this case, “in-place” rotation of the agostic methyl group would achieve scrambling of the three hydrogens without averaging the two sets of t-butyl resonances. The transition state for scrambling would be the transition state for methyl rotation. Such an “in-place” rotation of an agostic methyl group to account for similar scrambling has been previously proposed.28 The free energy diagrams for these two processes are shown in Figure 3.14. The data do not allow distinction between the two mechanisms.
**Scheme 3.19.** Possible mechanism for the exchange of hydrogen in 
\[\text{[(POCOP)Ir(H)(C}_2\text{H}_4)[\text{BARF}], 10, (R = t\text{-butyl)}}\]
In mechanism A, there are three methyl protons that can β-hydride eliminate to reform the ethylene complex, however only 2/3 of the time will the exchange be observed since 1/3 of the time the same hydrogen that migrated will return to Ir. Therefore, the observed rate constant \( k_{obs} \) is 2/3 the actual rate constant \( k \). The rate, calculated as an average of the rate for both the line-broadening of the hydride and ethylene, is found to be 155 s\(^{-1}\) at 320K corresponds to \( \Delta G^\ddagger = 15.6 \text{ kcal/mol} \). (See Table II.5 and II.6 for calculations).

For the propylene complex 11, insertion of the propylene into the Ir-H bond could lead to two possible intermediates, the linear and the branched Ir-alkyls (Scheme 3.20). Spin-saturation transfer NMR experiments showed that proton exchange was occurring (Figure 3.15). Saturation of individual signals and observing a decrease in intensity of a companion signal indicates site exchange of these pairs. In line A of Figure 3.15, when the resonance at 3.3 ppm (H\(_c\)) was irradiated, only the signal at 5.5 ppm (H\(_b\)) showed a decrease in integration. Therefore, the only proton that H\(_b\) exchanges with is H\(_c\). Complementary results are seen if the signal at 5.5 ppm is irradiated as shown in line B. When H\(_a\) is saturated, only
the hydride H_d is observed to decrease in intensity. And similarly, if H_d is irradiated H_a decreases. Therefore, H_d only exchanges with H_a and vice versa. These results support the insertion of the propylene into the Ir-H bond forming only the linear product, as no exchange indicating formation of the branched product is observed.

**Scheme 3.20.** Insertion of the primary or secondary carbon of propylene into the Ir-H bond of [(POCOP)Ir(H)(C_3H_6)][BARF], 11.
As mentioned earlier, the propylene complex has both “top/bottom” and “side-to-side” inequivalence. However, insertion of the propylene into the Ir-H results in formation of a species with a mirror plane bisecting and perpendicular to the ligand plane. This can be observed in the $^1$H NMR spectra at 320 K; the meta hydrogens of the ligand backbone merges to one doublet from two, and the two pairs of t-butyl resonances broaden and merge into two triplets. Even at these elevated temperatures, the “top” and “bottom” do not equilibrate, as seen for [(POCOP)Ir(H)(C$_2$H$_4$)][BAr$_F$], 10. This hindered rotation can be attributed to steric restrictions between the propyl group and the t-butyl groups, or to an
agnostic interaction as described for the ethylene complex. These two mechanisms are indistinguishable by these studies.

As in the ethylene case, the proton exchange rates are used to measure the rate of insertion of propylene into the Ir-H bond. In this case however, the exchange rate was measured using spin saturation transfer NMR techniques. For this technique, one $^1\text{H}$ frequency is irradiated causing the intensity of any proton that exchanges with the irradiated proton to decrease. The rate of exchange of these pairs of protons is estimated as $2.8 \text{ s}^{-1}$ with a free energy barrier of 16.8 kcal/mol (calculations are shown in Appendix II, Tables II.8 and II.9).

In the case of $[(\text{POCOP})\text{Ir(H)(norbornene)}][\text{BAr}_F]$, 12, it is impossible to see evidence of insertion by NMR spectroscopy because the bicyclic structure of norbornene prohibits the exchange of the hydrogens. The hydrogen that migrates forming the $\sigma$-norbornyl species must be the same hydrogen that returns to Ir. In order to observe the behavior of 12 at higher temperatures, a NMR tube containing a solution of 12 in chlorobenzene-$d_5$ was prepared. At room temperature, however, free norbornene was observed in solution. An equilibrium, which favors dissociation of norbornene at higher temperature, was formed between $[(\text{POCOP})\text{Ir(H)(norbornene)}][\text{BAr}_F]$, 12 and $[(\text{POCOP})\text{Ir(H)(L)}][\text{BAr}_F]$ (L = solvent) 4. At 343 K the $K_{eq} (4/12) = 8.3 \times 10^{-4}$.

The insertion product $[(\text{POCOP})\text{Ir(CH}_2\text{CH}_2\text{(CO)OMe)}][\text{BAr}_F]$, 15 was described in Section II.b as in slow equilibrium with $[(\text{POCOP})\text{Ir(H)(MA)}][\text{BAr}_F]$, 13 with a $K_{eq}$ of 0.13 favoring the olefin complex when the reaction was carried out in methylene chloride. Similar results were observed initially when chlorobenzene-$d_5$ is used for a solvent. Chlorobenzene allows examination of this system at elevated temperatures. Initially, at room temperature similar results were observed as in methylene chloride, however after 2 days at
room temperature a new $^{31}$P NMR signal at 160.5 ppm appears. Further heating at 70°C for 5 hours, shows formation of additional complexes with $^{31}$P NMR signals at similar shifts to the cationic methyl acrylate complex 13, as well as an increase of the peak at 160.5 ppm. If the temperature is raised to 100°C overnight, all the signals for the starting complexes are gone and more unidentified complexes are observed. The major species now is found at δ 199.7 ppm which is consistent with the $^{31}$P chemical shift for (POCOP)Ir(CO). Although not conclusive, this suggests that decarbonylation of the methyl acrylate occurs.

III. Addition of Nucleophiles to [(POCOP)Ir(H)(norbornene)][BArF], 12

The ultimate goal of this chemistry is to use these cationic iridium olefin complexes in the formation of new C-X bonds. A few reactions were run to test the reactivity of these complexes towards nucleophiles. It is necessary to pick a nucleophile that has the appropriate balance of basicity and nucleophilicity. If the compound is either too basic or too nucleophilic, it might bind to the electron-deficient iridium center and prove unreactive to C-X formation. On the other hand, if the compound is not sufficiently nucleophilic, it will not react with the olefin. Two different nucleophiles were tested, aniline and 4-methylthiol. The norbornene complex was chosen since typically norbornene is more reactive due to its strained bicyclic structure. A negative feature is that it is also a more labile olefin.

When 12 was treated with aniline and norbornene (1:50:74 ratio, respectively) in chlorobenzene-$d_5$, aniline displaced the norbornene forming a new cationic aniline complexes, [(POCOP)Ir(H)(NH$_2$Ph)], 16. The $^1$H NMR of this complex shows a broad singlet at 5.7 ppm for the NH$_2$ protons of the coordinated aniline and a hydride resonance at
-42.6 ppm. This complex displays a 172.3 ppm $^{31}\text{P}$ chemical shift and is stable at elevated temperatures and no change in the $^1\text{H}$ spectrum is observed after 24 hours at 60°C. After two days at 100°C, new signals appear around $\delta$ 1.4, between $\delta$ 2.2 and 2.7, and $\delta$ 3.3 in the $^1\text{H}$ NMR spectra. The only iridium complex present is 16; no new peaks are observed in the $^{31}\text{P}$ NMR spectrum. It is unclear if the new $^1\text{H}$ resonances are due to formation of a C-N bond. The intensity of the new peaks is very low however, and therefore even if they do correspond to coupling products the turnover rate is extremely slow.

4-Methylthiophenol, which is less basic than aniline, was also shown to displace norbornene at room temperature. When 12 was treated with excess 4-methylthiophenol and norbornene (1 : 50 : 74, Ir : 4-methylthiophenyl: norbornene), an equilibrium was established between the norbornene complex and the 4-methylthiol complex (Scheme 3.21) with an equilibrium constant of 3.6 favoring the coordination of 4-methylthiol.

**Scheme 3.21.** Equilibrium between [(POCOP)Ir(H)(norbornene)][BArF] 12 and [(POCOP)Ir(H)(HSAr)][BArF] 17

![Scheme 3.21](image)

When this reaction mixture is heated to 60°C for 24 hours, peaks that correlate with the desired coupling product can be discerned. However, a control reaction consisting of only norbornene and 4-methylthiophenol in chlorobenzene showed similar results. In fact, in 1954
Cristol and Brindell showed that 4-methylthiophenyl adds to norbornene selectively to form the exo-norbornyl \( p \)-tolyl thioether by a radical process in chlorobenzene.\(^{29}\) Therefore, it is uncertain whether the above reaction was metal-catalyzed or radically induced.

**Summary**

Cationic POCOP iridium pincer complexes have been synthesized and characterized with the goal of gaining information that might lead to a new catalyst for the functionalization of alkenes. Investigations have included studies of the structure as well as the dynamic behavior of these complexes.

\[
[(\text{POCOP})\text{Ir}(\text{H})(\text{H}_2)][\text{BAR}_7], \quad 9, \quad \text{has been synthesized and shown to be a dihydrogen/hydride complex as compared to a classical trihydride. At room temperature, the hydrogens are in fast exchange and are seen as a broad singlet at ca. -14 ppm by} \quad ^1\text{H NMR. However, at 173 K, the exchange rate of the hydrogens is slow on the NMR time scale and are seen at 0.033 and -41.9 ppm in a 2:1 ratio in the} \quad ^1\text{H NMR spectrum. Using a one dimensional HMQC experiment at 173 K of a partially deuterated complex for the H-D ligand was observed which indicates that H-D is bound in an} \eta^2 \quad \text{fashion and the H-D coupling constant, 33 Hz. Typical} \eta^2\text{-dihydrogen H-D coupling constants are ca. 30 Hz, while dihydride H-D coupling constants are less than 1 Hz.}
\]

The exchange rate between the hydride and dihydrogen ligand in 9 was calculated \(^1\text{H NMR using line-broadening techniques and found to be 304.6 s}^{-1} \quad \text{(197 K) with} \quad \Delta G^\ddagger = 9.1 \quad \text{kcal/mol. The rate was also calculated for the deuterated complex using} \quad ^1\text{H NMR spectroscopy which had to a slightly higher} \Delta G^\ddagger \quad \text{of 9.8 kcal/mol. This result was expected since the energy barrier for breaking a D-D bond is higher than that for a H-H bond.}
Various cationic olefin hydride complexes of the type [(POCOP)Ir(H)(L)][BarF] (L = C2H4 10, C3H6 11, norbornene 12, and methyl acrylate 13) have been synthesized and characterized. All the complexes show dynamic behavior by NMR spectroscopy. Low temperature experiments were performed on all the complexes to examine their behavior more closely. At low temperatures, the cationic ethylene complex 10 is in equilibrium with the solvated complex. However, even at the 173K, the equilibrium is rapid and only broad signals for the averaged complexes are observed. As the temperature is raised the unsolvated complex is favored, seen as a upfield chemical shift of the average hydride resonance. The rotation of ethylene is too fast to be measured by 1H NMR spectroscopy.

The rotation of the olefin in the cationic propylene 11, norbornene 12, and methyl acrylate 13 complexes can all be observed by 1H NMR spectroscopy. The 1H spectrum for 11 shows a slow equilibrium (K_eq = 0.066) at 173 K in which one rotamer is present in significantly higher concentrations than the other. The methyl acrylate complex 13 also exhibits an equilibrium between the two rotamers of K_eq = 0.26 at 197 K. The two rotamers of the norbornene complex 12 are observed in a 1:1 ratio at 174 K. From the line broadening of the 1H NMR resonances of the two rotamers, the free energy barrier for rotation of the norbornene is calculated to be ΔG‡ = 9.1 kcal/mol.

The rates of migratory insertion of the cationic ethylene 10 and propylene 11 complexes were calculated using line-broadening and spin-saturation transfer NMR techniques. As expected the energy barrier for insertion is higher (ΔG‡ = 16.8 kcal/mol) for 11 than for 10 (ΔG‡ = 15.6 kcal/mol). It is not clear whether this barrier corresponds to the true migratory insertion rate of the olefin into the Ir-H bond or if it corresponds to the breaking of an agostic bond in an “in-place” rotation mechanism. Interestingly, the migratory insertion in propylene
complex 11 shows preference for the linear propyl intermediate. No rotation of the alkyl species is observed for either complex since “top/bottom” inequivalence is maintained at elevated temperatures.

Preliminary results on the reaction of [(POCOP)Ir(H)(norbornene)][BArF], 12, with the nucleophiles aniline and 4-methylthiophenyl was obtained. No attack of the nucleophiles on the coordinanted norbornene was observed and instead the norbornene was displaced by the nucleophile.

**Experimental Section**

**General Considerations:** All manipulations were carried out using standard Schlenk, high-vacuum, and glove box techniques. Argon was purified by passage through columns of BASF R3-11 (chemalog) and 4Å molecular sieves. Pentane and methylene chloride were passed through columns of activated alumina and deoxygenated by purging with N₂. Benzene was dried over 4Å molecular sieves and degassed to remove both oxygen and nitrogen. NMR spectra were recorded on Bruker DRX 400, AMX 300 and 500 MHz instruments and are referenced to residual protio solvent peaks. ³¹P chemical shifts are referenced to an external H₃PO₄ standard. Since there is a strong ³¹P-³¹P coupling in the pincer complexes, many of the ¹H and ¹³C signals exhibit virtual coupling and appear as triplets. These are specified as vt with the *apparent* coupling simply noted as J. IR spectra were recorded on an ASI ReactIR 1000 spectrometer. Elemental analyses were carried out by Atlantic Microlab, Inc. of Norcross, GA. All reagents, unless otherwise noted, were purchased from Sigma-Aldrich and used without further purification. Hydrogen and
Propylene was used as received from National Specialty Gases of Durham, NC. Deuterium was purchased from Sigma-Aldrich. Ethylene was purchased from Matheson. The synthesis of the phosphinite ligand, (POCOP)Ir(H)(Cl), 1, and (POCOP)IrH2 have been previously described in the literature.15 The abbreviation of BArF is used to represent the counterion tetrakis(3,5-trifluoromethylphenyl)borate. The 1H and 13C spectral data for BArF in CD2Cl2 is the same for all complexes listed as is therefore not reported in the characterizations below.

**BArF:** 1H NMR (CD2Cl2): δ 7.72 (s, 8H, H-o), 7.56 (s, 4H, H-p). 13C{1H} NMR (CD2Cl2): δ 162.2 (q, Jc-B = 37.4 Hz, C-ispo), 135.2 (C-o), 129.3 (q, Jc-F = 31.3 Hz, C-n), 125.0 (q, Jc-F = 272.5, CF3), 117.9 (C-p).

**Synthesis of (POCOP)Ir(H)(OTf) (2):** (POCOP)Ir(H)(Cl) (0.16 mmol, 100 mg), AgOTf (0.163 mmol, 41.9 mg) and 10 mL of methylene chloride were added to a Schlenk flask and allowed to stir for 2.5 hrs. The silver salts were removed by filtration through a 0.2 micron syringe filter under an argon atmosphere in the glove box. An orange powder was recovered after removal of the solvent under vacuum. (96 mg, 81 % yield)

\[
\begin{align*}
\text{O-P(tBu)}_2 & \quad \text{O-P(tBu)}_2 \\
\text{H} & \quad \text{Ir-OTf} \\
\text{1} & \quad 2, 3
\end{align*}
\]

1H NMR (400 MHz, CD2Cl2): δ 6.78 (t, JH-H = 8.2 Hz, 1H, 1-H), 6.52 (d, JH-H = 8.2 Hz, 2H, 2-H), 1.33 (m, 36H, P(tBu)2), -43.12 (t, Jp-H = 12.8 Hz, 1H, Ir/H). 31P{1H} NMR (162 MHz, CD2Cl2): δ 177.3.
Reaction of 2 with carbon monoxide (5 and 6): A NMR tube fitted with a septum was charged with a solution of 2 (15mg, 0.02 mmol) in CD$_2$Cl$_2$ (0.5 mL). Carbon monoxide was purged through the solution for 5 minutes until the color changed from yellow to nearly colorless. The $^{31}$P and $^1$H NMR showed two complexes in a 1:1 ratio, the mono- and dicarbonyl complexes (5 and 6). Under slight vacuum the solution turns yellow, and only one complex is observed, the monocarbonyl complex, 5.

\[
\begin{align*}
5: & 
\text{ $^1$H NMR (500 MHz, CD$_2$Cl$_2$): } \delta 7.14 \text{ (t, } J_{H-H} = 8.2 \text{ Hz, 1H, 1-H), 6.79 \text{ (d, } J_{H-H} = 8.3 \\
& \text{ Hz, 2H, 2-H), 1.57 \text{ (vt, } J = 8.8 \text{ Hz, 18H, P(tBu)$_2$), 1.36 \text{ (vt, } J = 8.2 \text{ Hz, 18H, P(tBu)$_2$), -10.463 \text{ (t, } J_{P-H} = 14.78 \text{ Hz, 1H, IrH). $^{31}$P \{^1H\} NMR (121 MHz, CD$_2$Cl$_2$): } \delta 174.2.}
\end{align*}
\]

\[
6: & 
\text{ $^1$H NMR (300 MHz, CD$_2$Cl$_2$): } \delta 6.83 \text{ (t, } J_{H-H} = 8.0 \text{ Hz, 1H, 1-H), 6.46 \text{ (d, } J_{H-H} = 8.0 \\
& \text{ Hz, 2H, 2-H), 1.58 \text{ (vt, overlapped with 5, 18H, P(tBu)$_2$), 1.37 \text{ (vt, overlapped with 5, 18H,} \\
& \text{ P(tBu)$_2$), -7.29 \text{ (t, } J_{P-H} = 16.1 \text{ Hz, 1H, IrH). $^{31}$P \{^1H\} NMR (162 MHz, C$_6$D$_6$): } \delta 164.9.}
\end{align*}
\]

Synthesis of [(POCOP)Ir(H)(H$_2$O)][SbF$_6$] (3): (POCOP)Ir(H)(Cl) (0.16 mmol, 100 mg), AgSbF$_6$ (0.163 mmol, 56 mg) and 10 mL of methylene chloride were added to a Schlenk flask and allowed to stir for 2.5 hrs. The silver salts were removed by filtration
through a 0.2 micron syringe filter under an argon atmosphere in the glove box. An orange powder was recovered after removal of the solvent under vacuum. (90 mg, 68 % yield)

\[
\begin{array}{c}
\text{[POCOP]Ir(H)Cl} \\
\text{[BArF]}
\end{array}
\]

\(3\)

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): $\delta$ 6.84 (t, $^3J_{H-H} = 8.1$ Hz, 1H, 1-H), 6.58 (d, $^3J_{H-H} = 8.1$ Hz, 2H, 2-H), 3.2-4.6 (b, 2H, H\(_2\)O), 1.35 (vt, $J = 7.6$ Hz, 36H, P(tBu)\(_2\)), -43.05 (t, $J_{P-H} = 12.6$ Hz, 1H, Ir\(H\)). \(^3\)P\(_{\{1\}H}\) NMR (162 MHz, CD\(_2\)Cl\(_2\)): $\delta$ 175.8.

**Synthesis of [(POCOP)Ir(H)(solvent)][BArF] (4):** (POCOP)Ir(H)(Cl) (0.32 mmol, 200 mg), NaBAr\(_F\) (0.35 mmol, 311.4 mg) and 20 mL of methylene chloride were added to a Schlenk flask and allowed to stir for overnight. The sodium salts were removed by filtration through a 0.2 micron syringe filter under an argon atmosphere in the glove box. The solid was washed with pentane three times and dried under vacuum. An orange powder was recovered after removal of the solvent under vacuum. (373 mg, 80.2% yield)

\[
\begin{array}{c}
\text{[POCOP]Ir(H)solv} \\
\text{[BArF]}
\end{array}
\]

\(4\)

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\)): $\delta$ 7.72 (s, 8H, BAr\(_F\)), 7.56 (s, 4H, BAr\(_F\)), 6.81 (t, $^3J_{H-H} = 7.6$ Hz, 1H, 1-H), 6.57 (d, $^3J_{H-H} = 7.6$ Hz, 2H, 2-H), 1.35 (m, 36H, P(tBu)\(_2\)), -41.92 (t, $J_{P-H} = 12.1$ Hz, 1H, Ir\(H\)). \(^3\)P\(_{\{1\}H}\) NMR (162 MHz, CD\(_2\)Cl\(_2\)): $\delta$ 175.5.
In Situ Generation of:

\[ [(POCOP)Ir(H(H_2)][BarF] \] (9H): A solution of \([(POCOP)Ir(H(C_3H_6)][BarF] \) (10 mg, 0.0066 mmol) in methylene chloride-\( d^2 \) (0.5 mL) was added to a medium-walled screw cap NMR tube. \( H_2 \) was purged through solution at -78 °C, shaking the tube occasionally for two minutes.

\[
\begin{align*}
\text{P} & \text{Bu}_2 \text{Ir} \\
\text{H} & \\
\text{O} & \text{P} \text{Bu}_2
\end{align*}
\]

\( 9 \)

\(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\), 173 K): \( \delta \) 7.16 (bs, 1H, 1-H), 6.82 (d, \( J_{H-H} = 6.0 \) Hz, 2H, 2-H), 1.17 (m, 36H, \( P\text{Bu}_2 \)), 0.033 (b, 2H, \( H_2 \)), -41.88 (t, \( J_{P-H} = 12.1 \) Hz, 1H, \( IrH \)). At 295 K, the hydride resonance is a broad singlet at -14 ppm. \(^{31}\)P{\(^1\)H} NMR (202 MHz, CD\(_2\)Cl\(_2\), 173 K): \( \delta \) 194.7.

\[ [(POCOP)Ir(D(D_2)][BarF] \] (9D): \([POCOP]Ir(D)(D_2)][BarF] \] was generated using the same procedure as \( 9H \) with the addition of deuterium gas instead of hydrogen gas.

**Partially deuterated sample of \([(POCOP)Ir(H/D)(H_2/HD/D_2)][BarF] \):** The partially deuterated sample was generated by the same procedure mentioned above, however \( H_2 \) was purged through the solution for one minute, followed by \( D_2 \) for one minute.

**General Procedure for the Synthesis of \([(POCOP)Ir(H)(olefin)][BarF] \) (10-12):** In a Schlenk flask under argon 1 equiv. of \((POCOP)Ir(H)(Cl) \) 1, 1.1 equiv. of NaBarF, and excess olefin were stirred in methylene chloride for 15 min. The reaction mixture was then filtered.
with a 0.2 micron syringe filter under an inert atmosphere in the glove box. The product was isolated after removal of the methylene chloride solvent under reduced pressure.

\[\text{[(POCOP)Ir(H)(C}_2\text{H}_4)\text{]}\text{[BArF]} (10):\] The general procedure was employed using \(\text{I} (0.08 \text{ mmol, 50 mg})\) and \(\text{NaBArF} (0.089 \text{ mmol, 77.9 mg})\) in \(\text{CH}_2\text{Cl}_2 (10\text{mL})\) and purging ethylene through the reaction mixture. The color changed from pale red to orange within 5 minutes indicating the completion of the reaction. Following filtration and solvent removal, the product was isolated as a pale orange solid (104 mg, 87.7% yield).

\[
\begin{array}{c}
\text{O} \\
\text{P(tBu)2} \\
\text{Ir} \\
\text{O} \\
\text{P(tBu)2}
\end{array}
\]

\[10\]

\(^1\text{H NMR} (500 \text{ MHz, CD}_2\text{Cl}_2): \delta 7.22 (t, J_{\text{H-H}} = 8.0 \text{ Hz, 1H, 1-H}), 6.92 (d, J_{\text{H-H}} = 8.0 \text{ Hz, 2H, 2-H}), 4.15 (s, 4H, \text{C}_2\text{H}_4), 1.34 (\text{vt, } J = 7.5 \text{ Hz, 18H, P(tBu)2}), 1.27 (\text{vt, } J = 8.0 \text{ Hz, 18H, P(tBu)2}), -42.83 (\text{b, 1H, IrH}). \]

\(^31\text{P} \{^1\text{H}\} \text{ NMR (162 MHz, CD}_2\text{Cl}_2): \delta 182.0. \]

\(^{13}\text{C} \{^1\text{H}\} \text{ NMR (125.8 MHz, CD}_2\text{Cl}_2): \delta 167.0 (\text{C}, \text{vt, } J = 5.6 \text{ Hz, 2C, 3-C}), 133.8 (\text{C}, \text{m, 1C, 4-C}), 132.3 (\text{CH, s, 1C, 1-C}), 107.1 (\text{CH, t, } J_{\text{P-C}} = 6.0 \text{ Hz, 2C, 2-C}), 55.1 (\text{CH}_2, \text{s, 2C, C}_2\text{H}_4), 45.7 (\text{C}, \text{vt, } J = 12.1 \text{ Hz, C(CH}_3)_3), 42.8 (\text{C}, \text{vt, } J = 13.5 \text{ Hz, C(CH}_3)_3), 28.9 (\text{CH}_3, \text{vt, } J = 2.1 \text{ Hz, C(CH}_3)_3), 28.1 (\text{CH}_3, \text{vt, } J = 1.9 \text{ Hz, C(CH}_3)_3). \]

Elemental analysis calculated for \(\text{C}_{56}\text{H}_{56}\text{BF}_{24}\text{IrO}_2\text{P}_2\) (1481.98): C: 45.39, H: 3.81. Found: C: 45.18, H: 3.69.

\[\text{[(POCOP)Ir(H)(C}_3\text{H}_6)\text{]}\text{[BArF]} (11):\] The general procedure was employed using \(\text{I} (0.08 \text{ mmol, 50 mg})\) and \(\text{NaBArF} 0.087 \text{ mmol, 77.8 mg})\) in \(\text{CH}_2\text{Cl}_2 (10\text{mL})\) and purging propylene through the reaction mixture. The color changed from pale red to orange within five minutes.
indicating the completion of the reaction. Following filtration and solvent removal, the product was isolated as a pale orange solid (103 mg, 86% yield).

\[
\text{O-P(tBu)}_2 \text{Ir} \text{O-P(tBu)}_2 \text{][BARF]}
\]

\[\text{H NMR (500 MHz, CD}_2\text{Cl}_2): \delta 7.21 (t, \; J_{\text{H-H}} = 8.1 \text{ Hz, 1H, 1-H}), 6.90 (d, \; J_{\text{H-H}} = 7.9 \text{ Hz, 1H, 2-H}), 6.86 (d, \; J_{\text{H-H}} = 8.2 \text{ Hz, 1H, 6-H}), 6.43 (m, 1H, 8-H), 5.5 (dd, \; J_{\text{H-H}} = 12.0 \text{ Hz, J}_{\text{P-H}} = 8.5 \text{ Hz 1H, 7-H}_{\text{trans}}), 3.3 (d, \; J_{\text{H-H}} = 8.0 \text{ Hz, 1H, 7-H}_{\text{cis}}), 1.9 (d, \; J_{\text{H-H}} = 5.5 \text{ Hz, 3H, 9-H}), 1.46 (d, \; J_{\text{P-H}} = 15.3 \text{ Hz, 9H, P(tBu)}_2), 1.35 (d, \; J_{\text{P-H}} = 14.6 \text{ Hz, 9H, P(tBu)}_2), 1.34 (d, \; J_{\text{P-H}} = 15.3 \text{ Hz, 9H, P(tBu)}_2), 1.17 (d, \; J_{\text{P-H}} = 14.6 \text{ Hz, 9H, P(tBu)}_2), -42.9 (t, \; J_{\text{P-H}} = 11.6 \text{ Hz, 1H, IrH}). \]

\[\text{P}^1\text{NMR (162 MHz, CD}_2\text{Cl}_2): \delta 182.7 (dd, \; J_{\text{PP}} = 260.1 \text{ Hz}), 175.0 (dd, \; J_{\text{P-P}} = 260.1 \text{ Hz}). \]

\[\text{C}^1\text{NMR (125.8 MHz, CD}_2\text{Cl}_2): \delta 167.2 (C_q, m, 2C, 3-C and 5-C), 132.4 (CH, s, 1C, 1-C), 131.3 (C_q, m, 1C, 4-C), 106.9 (CH, m, 2C, 2-C and 6-C), 77.8 (CH, s, 1C, 7-C), 66.2 (CH_2, s, 1C, 8-C), 45.6 (C_q, d, \; J_{\text{P-H}} = 22.3 \text{ Hz, 2C, C(CH}_3)_3), 42.5 (C_q, d, \; J_{\text{P-H}} = 20.5 \text{ Hz, 1C, C(CH}_3)_3), 41.9 (C_q, d, \; J_{\text{P-H}} = 20.9 \text{ Hz, 1C, C(CH}_3)_3), 29.4 (CH_3, d, \; J_{\text{P-H}} = 3.5 \text{ Hz, C(CH}_3)_3), 29.2 (CH_3, d, \; J_{\text{P-H}} = 3.5 \text{ Hz, C(CH}_3)_3), 28.4 (CH_3, d, \; J_{\text{P-H}} = 2.9 \text{ Hz, C(CH}_3)_3), 28.11 (CH_3, d, \; J_{\text{P-H}} = 3.5 \text{ Hz, C(CH}_3)_3). \]

Elemental analysis calculated for C_{57}H_{58}BF_{24}IrO_2P_2 (1496.01): C: 45.76, H: 3.91. Found: C: 45.64, H: 3.84.

\[\([(POCOP)\text{Ir(H)(C}_7\text{H}_{10})\][\text{BARF}]\ (12): \] The general procedure was employed using 1 (0.16 mmol, 100 mg), NaBARF 0.176 mmol, 156 mg), and norbornene (1.6 mmol, 150 mg) in CH_2Cl_2 (7 mL). Excess norbornene is necessary for the reaction to proceed at a reasonable rate. The product was a pale orange solid (194mg, 78.4% yield).
$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.16 (t, $^3$J$_{H-H}$ = 8.0 Hz, 1H, 1-H), 6.87 (d, $^3$J$_{H-H}$ = 8.0 Hz, 2H, 2-H), 4.71 (7, $^3$J$_{H-H}$ = 4.2 Hz, 2H, 5-H), 3.44 (s, 2H, 6-H), 1.90 (d, $^3$J$_{H-H}$ = 8.2 Hz, 2H, 8-H), other pair of 8-H protons is overlapped with P(tBu)$_2$, 1.41 (vt, $J = 7.7$ Hz, 18H, P(tBu)$_2$), 1.33 (vt, $J = 7.5$ Hz, 18H, P(tBu)$_2$), 0.90 (d, $^3$J$_{H-H}$ = 10.0 Hz, 1H, 7-H), 0.22 (d, $^3$J$_{H-H}$ = 10.1 Hz, 1H, 7-H), -45.9 (t, $J_{P-H}$ = 11.2 Hz, 1H, Ir). $^{31}$P{$_^1$H} NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ 176.0.

$^{13}$C{$_^1$H} NMR (125.8 MHz, CD$_2$Cl$_2$): $\delta$ 166.0 ($C_q$, t, $J_{P-H}$ = 5.4 Hz, 2C, 3-C), 131.5 (CH, s, 1C, 1-C), 130.4 ($C_q$, m, 1C, 4-C), 106.7 (CH, t, $J_{P-H}$ = 5.9 Hz, 2C, 2-C), 78.0 (CH, s, 2C, 5-C), 47.1 (CH, s, 2C, 6-C), 46.4 ($C_q$, vt, $J = 11.4$ Hz, 2C, C(CH$_3$)$_3$), 43.7 ($C_q$, vt, $J = 13.0$ Hz, 2C, C(CH$_3$)$_3$), 40.6 (CH$_2$, s, 1C, 7-H), 29.5 (CH$_3$, vt, $J = 2.1$ Hz, C(CH$_3$)$_3$), 28.6 (CH$_3$, vt, $J = 2.0$ Hz, C(CH$_3$)$_3$), 27.9 (CH$_2$, s, 2C, 8-C). Elemental analysis calculated for C$_{61}$H$_{62}$BF$_2$IrO$_2$P$_2$ (1548.36): C: 47.33, H: 4.04. Found: C: 47.46, H: 3.93.

$^{(POCOP)}$Ir(C$_3$H$_3$(CO)OCH$_3$) (14): 1 (100 mg, 0.16 mmol), NaOtBu (18.4 mg, 0.19 mmol) and benzene (10 mL) were added to a Schlenk flask under argon. The reaction mixture was stirred for one hour at 75°C. The reaction mixture was cooled to room temperature and methyl acrylate (19 µL, 0.23 mmol) was syringed into the flask and stirred for 20 minutes. After filtering the mixture through a 0.2 micron syringe filter under argon, the solvent was removed under vacuum yielding a brick red solid (71 mg, 65.7% yield).

$^{1}$H{$_^{31}$P} NMR (400 MHz, C$_6$D$_6$): $\delta$ 6.963 (t, $^3$J$_{H-H}$ = 8.0 Hz, 1H, 1-H), 6.85 (d, $^3$J$_{H-H}$ = 8.0 Hz, 2H, 2-H), 4.40 (dd, $^3$J$_{cis}$ = 6.8 Hz, $^3$J$_{trans}$ = 10.0 Hz, 1H), 4.17 (dd, $^3$J$_{gem}$ = 0.8 Hz, $^3$J$_{trans}$ = 10.0 Hz 1H), 3.45 (s, 3H, -OME), 2.64 (dd, $^3$J$_{cis}$ = 6.8 Hz, $^3$J$_{gem}$ = 0.8 Hz, 1H), 1.43 (s, 18H,
$\text{P(tBu)$_2$, 1.18 (s, 18H, P(tBu)$_2$).} \quad \text{ } ^{31}\text{P} \{^1\text{H}\} \text{ NMR (162 MHz, C}_6\text{D}_6\): } \delta 175.7. \quad \text{Elemental analysis calculated for C}_{26}\text{H}_{45}\text{IrO}_4\text{P}_2 (675.80): C: 46.21, H: 6.71. \quad \text{Found: C: 45.99, H: 6.74.}

**In situ generation of \[(\text{POCOP})\text{Ir(H)(C}_2\text{H}_3(\text{CO})\text{OCH}_3)\][\text{BArF}] (13) and \[(\text{POCOP})\text{Ir(C}_2\text{H}_4(\text{CO})\text{OCH}_3)\][\text{BArF}] (15):**

\[13 \quad \text{(10 mg, 0.015 mmol), } [\text{H(OEt)$_2$}]\text{[BArF]} \text{ (16.5 mg, 0.016 mmol), and and CD}_2\text{Cl}_2 \text{ (0.5 mL) were added to a screw cap NMR tube. After mixing, a color change was observed from brick red to light orange. 13: } ^1\text{H} \text{ NMR (500 MHz, ClC}_6\text{D}_5\): } \delta 8.41 \text{ (s, 8H, BAr$_F$), 7.78 (s, 4H, BAr$_F$), } \text{para H on ligand backbone is underneath other peaks, 6.91 (b, 2H), 5.20 (bs, 1H, olefinic), 4.94 (bs, 1H, olefinic), 3.12 (s, 3H, -O\text{Me}), 2.96 (bs, 1H, olefinic), 1.16 (b, 36 H, tButyls), -39.2 (bs, 1H, Ir-H).} \quad ^{31}\text{P} \{^1\text{H}\} \text{ NMR (162 MHz, ClC}_6\text{D}_5\): } \delta 179.2 \text{ (d, } J = 182.4 \text{ Hz), 176.90 (d, } J = 213.6 \text{ Hz). 14: } ^1\text{H} \text{ NMR (500 MHz, ClC}_6\text{D}_5\): } \delta 8.41 \text{ (s, 8H, BAr$_F$), 7.78 (s, 4H, BAr$_F$), } \text{para H on ligand backbone is underneath other peaks, 6.79 (d, 2H, } ^3J = 8.2 \text{ Hz), 3.78 (s, 3H, -O\text{Me}), 2.69 (m, 2H), 1.93 (t, } ^3J = 7.2 \text{ Hz, 2H), tbutyls are overlapping with 13.} \quad ^{31}\text{P} \{^1\text{H}\} \text{ NMR (162 MHz, ClC}_6\text{D}_5\): } \delta 153.4.

**In situ (POCOP)\text{Ir(H)(NH}_2\text{C}_6\text{H}_5)\][\text{BArF}] (16):**

\[16 \quad \text{In a J. Young NMR Tube, 12 (10 mg, 0.0064 mmol), aniline (29.16 } \mu\text{L, 0.32 mmol), and norbornene (44.6 mg, 0.474 mmol) was dissolved in chlorobenzene-d$^5 \text{ (0.5 mL). The product 16 was observed by NMR spectroscopy.}

\[\begin{array}{c}
\text{O} \\
\text{P(tBu)$_2$} \\
\text{1} \\
\text{H} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{P(tBu)$_2$} \\
\text{Ir-NH$_2$Ph} \\
\text{O} \\
\text{BAr$_F$}
\end{array}\]
\(^1\)H NMR (400 MHz, ClC\(_6\)D\(_5\)): \(\delta\) 8.41 (s, 8H, BAr\(_F\)), 7.78 (s, 4H, BAr\(_F\)), 6.11 (s, 2H, NH\(_2\)), -43.73 (s, 1H, Ir-\(H\)), other peaks are overlapped with free norbornene and anilines signals. \(^{31}\)P\(_{\{^1\}H}\) NMR (162 MHz, ClC\(_6\)D\(_5\)): 172.5 (s).

**In situ [(POCOP)Ir(H)(HSC\(_6\)H\(_4\)-pMe)][BAr\(_F\)] (17):** In a J. Young NMR tube, 1 (10 mg, 0.016 mmol), NaBAr\(_F\) (15.6 mg, 0.018 mmol), and 4-methylthiophenyl (2.2 mg, 0.018 mmol) were dissolved in chlorobenzene-\(d^5\) (0.5 mL). 17 was observed by NMR.

\[
\begin{array}{c}
\text{O-P(tBu)}_2 \\
\text{H} \\
\text{Ir} \\
\text{S} \\
\text{O-P(tBu)}_2
\end{array}
\]

\[
\text{[BAr}_F\text{]}_1
\]

\(^1\)H NMR (400 MHz, ClC\(_6\)D\(_5\)): \(\delta\) 8.41 (s, 8H, BAr\(_F\)), 7.78 (s, 4H, BAr\(_F\)), 7.38 (m, 3H, Ar), 7.15 (m, 2H, Ar), 7.10 (t, 1H, \(^3\)J\(_{HH}\) = 8.0 Hz, 1-H), 6.83 (d, 2H, \(^3\)J\(_{HH}\) = 8.0 Hz, 2-H), 5.19 (s, 1H, SH), -41.69 (t, \(^3\)J\(_{PH}\) = 13 Hz, 1H, Ir-\(H\)). \(^{31}\)P\(_{\{^1\}H}\) NMR (162 MHz, ClC\(_6\)D\(_5\)): 176.7 (s).
References and Notes


(27) A similar phenomena was observed with [(POCOP)Ir(H)(H2)(H2O)][SbF6] except initially the exchange between bound and free water occurred than the decoalescence of the dihydrogen/hydride.


APPENDIX I

Supporting Information for Chapter Two

Conversion of 13d to 14d at -12°

Figure I.1  First-order plot for the conversion of 13d to 14d
Figure I.2  First-order plot of the rate of reductive elimination of pentafluoroaniline from (POCOP)Ir(H)(NHC₆F₅)
Figure I.3. First-order plot of the dissociation of H$_2$NC$_6$H$_4$-pOMe 11a from (POCOP)Ir(NH$_2$C$_6$H$_4$-pOMe) 13a at -8°C

\[ y = 2.65E-04x + 4.25E+00 \]
\[ R^2 = 9.99E-01 \]
\[ \Delta G^\ddagger = 19.8 \text{ kcal/mol} \]
Reductive Elimination of Benzamide 21a from (POCOP)Ir(H)(NH(CO)C₆H₅) 22a at 100°C

\[ \text{Keq} = 0.18 \ (22a) \]
\[ 0.07 \ (22b) \]

**Figure I.4.** First-order plot of the reductive elimination of benzamide 21a from (POCOP)Ir(H)(NH(CO)C₆H₅) 22a at 100°C
APPENDIX II

Supporting Information for Chapter Three

Calculations and NMR spectra for dynamic process in [(POCOP)Ir(H)(L)][BArF] complexes 9-13

I. [(POCOP)Ir(H)(H2)][BArF] 9

Scheme II.1. Deuterium exchange with [(POCOP)Ir(D)(D2)][BArF] 9D

Table II.1. Line-broadening experiment based on the dideuterium resonance to measure the deuterium exchange rate in 9D

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$W_{1/2}$ (Hz)</th>
<th>$\Delta W$ (Hz)</th>
<th>k (s$^{-1}$) = $2\pi\Delta W$</th>
<th>$\Delta G^\ddagger$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>183.9</td>
<td>10.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>201.1</td>
<td>26.8</td>
<td>26.8</td>
<td>50.6</td>
<td>9.8</td>
</tr>
<tr>
<td>205.4</td>
<td>34.0</td>
<td>34.0</td>
<td>73.2</td>
<td>9.8</td>
</tr>
<tr>
<td>207.5</td>
<td>39.0</td>
<td>39.0</td>
<td>88.9</td>
<td>9.9</td>
</tr>
</tbody>
</table>
Scheme II.2. Hydrogen exchange with \(((\text{POCOP})\text{Ir}(\text{H})(\text{H}_2))[\text{BArF}] \, 9_{\text{H}}\)

Table II.2. Line-broadening experiment based on the hydride resonance to measure the hydrogen exchange rate of \(9_{\text{H}}\).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>(W_{1/2}) (Hz)</th>
<th>(\Delta W) (Hz)</th>
<th>(k) (s(^{-1})) = (\pi \Delta W)</th>
<th>(\Delta G^\ddagger) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>175.3</td>
<td>30.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>188.2</td>
<td>59.4</td>
<td>29.4</td>
<td>92.3</td>
<td>9.2</td>
</tr>
<tr>
<td>192.5</td>
<td>83.4</td>
<td>53.4</td>
<td>167.7</td>
<td>9.1</td>
</tr>
<tr>
<td>196.8</td>
<td>127.0</td>
<td>97.0</td>
<td>304.6</td>
<td>9.1</td>
</tr>
</tbody>
</table>

Table II.3 Calculation for \(k_{\text{H}}/k_{\text{D}}\) of hydrogen exchange in \(((\text{POCOP})\text{Ir}(\text{H})(\text{H}_2))[\text{BArF}] \, 9\)

<table>
<thead>
<tr>
<th>(\Delta G^\ddagger) (kcal/mol)</th>
<th>(k) (s(^{-1}))</th>
<th>(k_{\text{H}}/k_{\text{D}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H)(H(_2))</td>
<td>9.1</td>
<td>474.1</td>
</tr>
<tr>
<td>(D)(D(_2))</td>
<td>9.8</td>
<td>81.5</td>
</tr>
</tbody>
</table>
II. [(POCOP)Ir(H)(C₂H₄)][BArF]

Table II.4. Estimation of the free energy barrier for the rotation of ethylene in [(POCOP)Ir(H)(C₂H₄)][BArF]

<table>
<thead>
<tr>
<th>T (K)</th>
<th>δυ (Hz)</th>
<th>k (s⁻¹) = π(δυ)/(√2)</th>
<th>ΔG (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>175.3</td>
<td>25</td>
<td>55.51</td>
<td>8.68</td>
</tr>
</tbody>
</table>

Figure II.1. ¹H NMR spectra of t-butyl resonances in [(POCOP)Ir(H)(C₂H₄)][BArF] at variable temperatures
Table II.5. Rate and energy barrier of the insertion of ethylene into the Ir-H bond of [(POCOP)Ir(H)(C2H4)][BArF] based on line-broadening of the ethylene resonance

<table>
<thead>
<tr>
<th>T (K)</th>
<th>W1/2 (Hz)</th>
<th>ΔW</th>
<th>k = 4*(3/2)πΔW (s⁻¹)</th>
<th>ΔG‡(kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>257.7</td>
<td>4.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>310.4</td>
<td>8.4</td>
<td>3.6</td>
<td>67.3</td>
<td>15.6</td>
</tr>
<tr>
<td>319.8</td>
<td>13.4</td>
<td>8.5</td>
<td>160.9</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Table II.6. Rate and energy barrier of the insertion of ethylene into the Ir-H bond of [(POCOP)Ir(H)(C2H4)][BArF] based on line-broadening of the hydride resonance

<table>
<thead>
<tr>
<th>T (K)</th>
<th>W1/2 (Hz)</th>
<th>ΔW</th>
<th>k = (3/2)πΔW (s⁻¹)</th>
<th>ΔG‡(kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>257.7</td>
<td>26.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>310.4</td>
<td>38.8</td>
<td>12.4</td>
<td>58.3</td>
<td>15.7</td>
</tr>
<tr>
<td>319.8</td>
<td>57.9</td>
<td>31.4</td>
<td>148.0</td>
<td>15.6</td>
</tr>
</tbody>
</table>

III. [(POCOP)Ir(H)(C3H6)][BArF]

Table II.7. Rate and free energy barrier for the rotation of propylene in [(POCOP)Ir(H)(C3H6)][BArF] based on line-broadening of the major isomer in the 1H NMR spectra

<table>
<thead>
<tr>
<th>T (K)</th>
<th>W1/2 (Hz)</th>
<th>ΔW</th>
<th>k = πΔW (s⁻¹)</th>
<th>ΔG‡(kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>175.3</td>
<td>15.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>201.1</td>
<td>30.6</td>
<td>14.7</td>
<td>46.2</td>
<td>10.1</td>
</tr>
<tr>
<td>205.4</td>
<td>37.0</td>
<td>21.1</td>
<td>66.3</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Table II.8. T1 values for the olefinic and hydridic resonances of [(POCOP)Ir(H)(C3H6)][BArF] at 296.5 K in the 1H NMR spectrum

<table>
<thead>
<tr>
<th>Resonance</th>
<th>T1 (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-42</td>
<td>1.34</td>
</tr>
<tr>
<td>6.5</td>
<td>1.13</td>
</tr>
<tr>
<td>5.6</td>
<td>0.81</td>
</tr>
<tr>
<td>3.4</td>
<td>0.84</td>
</tr>
</tbody>
</table>
Table II.9. Rate of insertion and energy barrier for the insertion of propylene into the Ir-H bond of [(POCOP)Ir(H)(C₃H₆)][BARF] at 296.5K using spin-saturation transfer techniques

<table>
<thead>
<tr>
<th>Irradiated</th>
<th>Affected</th>
<th>Mo</th>
<th>M₀</th>
<th>kobs (s⁻¹) = (1/T₁)(Mo/M₀²)⁻¹</th>
<th>k = 2kobs (s⁻¹)</th>
<th>ΔG‡ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4</td>
<td>5.6</td>
<td>1</td>
<td>0.52</td>
<td>1.12</td>
<td>2.25</td>
<td>16.88</td>
</tr>
<tr>
<td>5.6</td>
<td>3.4</td>
<td>1</td>
<td>0.50</td>
<td>1.19</td>
<td>2.39</td>
<td>16.84</td>
</tr>
<tr>
<td>6.5</td>
<td>-42</td>
<td>1</td>
<td>0.33</td>
<td>1.29</td>
<td>2.57</td>
<td>16.80</td>
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<tr>
<td>-42</td>
<td>6.5</td>
<td>1</td>
<td>0.31</td>
<td>1.96</td>
<td>3.91</td>
<td>16.55</td>
</tr>
</tbody>
</table>

average = 16.76

IV. [(POCOP)Ir(H)(norbornene)][BARF]

Figure II.2. Stacked ³¹P NMR spectra of [(POCOP)Ir(H)(norbornene)][BARF] at variable temperatures
Table II.10. Rotation rate of norbornene in [(POCOP)Ir(H)(norbornene)][BARF] based on line-broadening in the $^1$H NMR spectra

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$W_{1/2}$ (Hz)</th>
<th>$\Delta W$</th>
<th>$k = \pi \Delta W$ (s$^{-1}$)</th>
<th>$\Delta G^\ddagger$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>173.6</td>
<td>27.8</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>182.2</td>
<td>47.2</td>
<td>19.4</td>
<td>60.9</td>
<td>9.0</td>
</tr>
<tr>
<td>190.8</td>
<td>100.4</td>
<td>53.2</td>
<td>167.0</td>
<td>9.1</td>
</tr>
</tbody>
</table>

V. [(POCOP)Ir(H)(MA)][BARF]

Table II.11. Rate of rotation of methyl acrylate in [(POCOP)Ir(H)(MA)][BARF] based on line-broadening of the major isomer in the $^1$H NMR spectra

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$W_{1/2}$ (Hz)</th>
<th>$\Delta W_{1/2}$</th>
<th>$k$ (s$^{-1}$) = $\pi \Delta W$</th>
<th>$\Delta G^\ddagger$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>196.8</td>
<td>25.2</td>
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<td></td>
</tr>
<tr>
<td>214.0</td>
<td>29</td>
<td>3.8</td>
<td>11.93</td>
<td>11.33</td>
</tr>
<tr>
<td>222.6</td>
<td>46.6</td>
<td>21.4</td>
<td>67.20</td>
<td>11.04</td>
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</tbody>
</table>