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OXIDATIVE ADDITION TO IRIIDIUM(I) COMPLEXES

by

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ABSTRACT OF THE DISSERTATION
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Understanding the fundamental processes underlying the activation of small molecules by metal complexes is a continuing goal of organometallic chemistry. This thesis aims to better understand the processes and interactions of small molecules with organometallic complexes.

DFT calculations were performed on an extensive series of $(\text{PH}_3)_2\text{IrX}$ complexes to investigate the thermodynamics of C-H and N-H oxidative addition. Electronic substituent effects were decomposed into their σ and π effects and individually parameterized; the resulting σ_X and π_X parameters were used to fit the energies of oxidative addition of methane to a series of 3- and 4-coordinate Ir(I) complexes. Regression analysis indicates that oxidative addition of methane to 3-coordinate Ir(I) complexes generally is favored by a less σ -donating ligand *trans* to the vacant coordination site.

DFT calculation was used to investigate the oxidative addition of chlorobenzene and fluorobenzene to pincer iridium complexes. Activation of the aryl C-H bonds

proximal to the electron-withdrawing atom is favored. The kinetic barriers were calculated and correlate with the relative steric interactions in the transition state leading to the oxidative addition product.

CO stretching frequencies for a series of $\text{Ni}(\text{CO})_3\text{L}$ complexes were calculated using DFT calculations. NBO analysis of these complexes yielded parameters that reflect the extent of backbonding in the π^* orbitals of the CO ligands and polarization of the π^b orbitals of the CO ligands. The effects of a point charge on free CO were calculated.

Experimentally, reactions of small molecules with pincer iridium complexes were investigated. The kinetic barriers for olefin dissociation from (pincer)Ir(olefin) complexes were measured. The ($^t\text{BuPOCOP}$)Ir-catalyzed olefin isomerization of 1-octene was investigated and shows an apparent 2nd order dependence on 1-octene concentration.

A synthesis scheme for $^t\text{Bu}^3\text{MePCP}$ ligand was developed. While H_2 did not add to $^t\text{Bu}^4\text{PCPIr}(\text{CO})$, three isomers were observed when H_2 was added to $^t\text{Bu}^3\text{MePCPIr}(\text{CO})$, and the isomers were assigned using an isotopic labeling experiment and NMR spectroscopy.

The thermodynamic and kinetic products of tropone addition to ($^t\text{BuPCP}$)IrH₂ were synthesized and characterized. The formation of a tropone dimer was investigated.

The product of methyl fluoride addition to ($^t\text{BuPCP}$)IrH₂ was characterized through NMR spectroscopy, LIFDI mass spectrometry, and elemental analysis.

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Dedication

To Amy, Mom, Dad, and Frank

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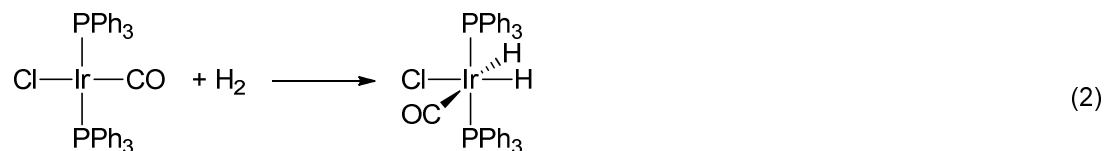
Chapter 1

Introduction to the Thesis

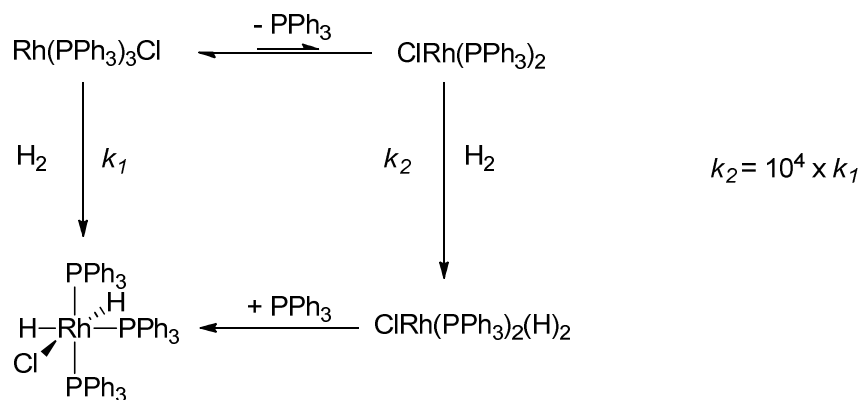
Selective bond activation using metal complexes has been a fundamental transformation of organometallic chemistry and is vital to many metal-catalyzed transformations. These bond activation processes typically involve oxidative addition to a metal center. Oxidative addition with a mononuclear metal complex implies a formal two electron oxidation of the metal and involves the cleavage of an X-Y bond with the concomitant formation of M-X and M-Y bonds.¹ Given its fundamental role in bond activation, many reports have focused on oxidative addition and its microscopic reverse, reductive elimination, in the activation and functionalization of small molecules.²⁻¹²

The history of activation of small molecules by metals extends more than sixty years. In 1955, Halpern reported the catalytic hydrogenation of dichromic anion ($\text{Cr}_2\text{O}_7^{2-}$) by catalytic Cu(II) and proposed in subsequent work that Cu(II) heterolytically cleaves the H_2 bond to give $[\text{Cu-H}]^+$ and H^+ (eq. 1).^{13,14} In 1962, Vaska reported the oxidative addition of H_2 to his eponymous complex, *trans*-(PPh_3)₂Ir(Cl)(CO)(PPh_3)₂ (eq. 2),¹⁵ and the following year he reported its use in the catalytic hydrogenation of ethylene and acetylene.¹⁶ The mechanism and utility of the addition of H_2 to Vaska's complex has been extensively studied.¹⁷⁻²⁸ In 1965, Wilkinson reported the oxidative addition of H_2 to $\text{RhCl}(\text{PPh}_3)_3$ (Wilkinson's catalyst) for the catalytic hydrogenation of olefins and acetylenes.²⁹ Extensive investigations into the mechanistic aspects of the oxidative

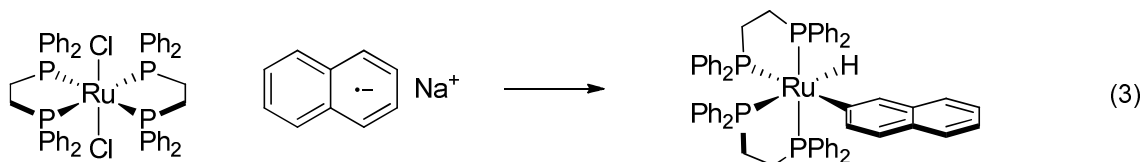
addition of H_2 to Wilkinson's catalyst showed that addition of H_2 occurs predominantly after initial dissociation of a PPh_3 ligand to give the highly active 14-electron complex $\text{RhCl}(\text{PPh}_3)_2$ (Scheme 1.1).^{30,31}



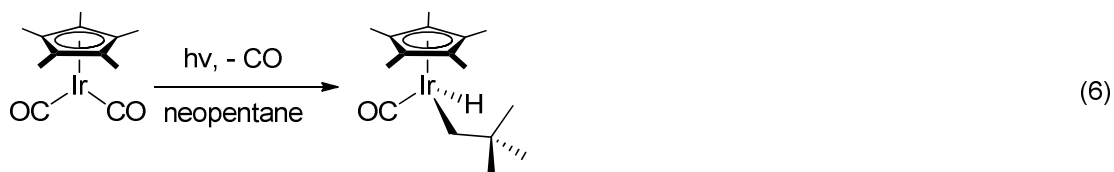
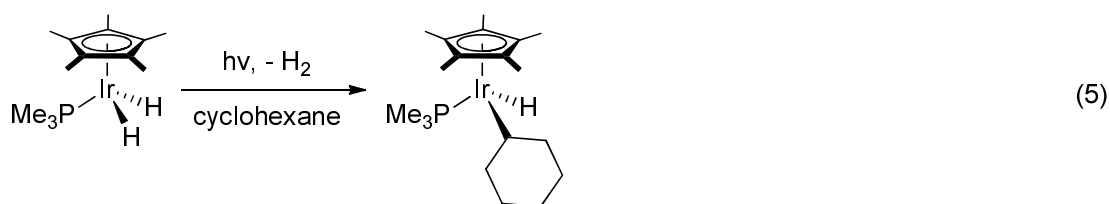
Scheme 1.1. Mechanistic aspects of H_2 addition to Wilkinson's catalyst.^{30,31}



The activation of C-H bonds by transition metal complexes was first reported by Chatt and Davidson in 1965, where $\text{Ru}(0)(\text{dmpe})_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) was found to activate a C-H bond of naphthalene to yield a naphthyl hydride complex (eq. 3).³² Similarly, Green and co-workers reported the oxidative addition of benzene following the photolysis of H_2 from Cp_2WH_2 (eq. 4).³³⁻³⁵

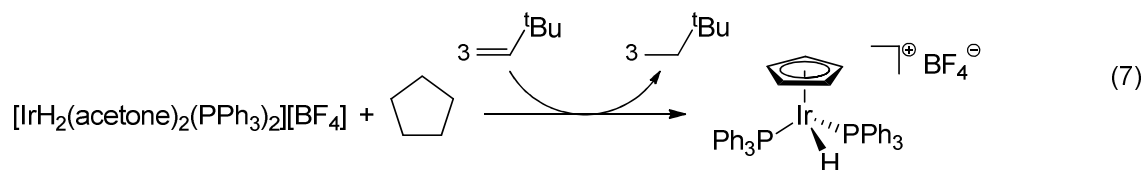


While the oxidative addition of alkanes was thought to be more difficult to achieve than arenes despite the lower C-H bond strength of alkanes, Bergman³⁶ and Graham³⁷ independently reported the isolation and characterization of iridium alkyl hydride complexes in 1982. Bergman reported that the irradiation of $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{H})_2$ in cyclohexane and neopentane led to loss of H_2 and formation of the respective alkyl hydride complexes (eq. 5).³⁶ Graham reported the formation of a neopentyl hydride complex following photolytic loss of CO from $\text{Cp}^*\text{Ir}(\text{CO})_2$ (eq. 6).³⁷ In 1984, Jones reported arene and alkane oxidative addition to Rh analogous to Bergman's work.³⁸

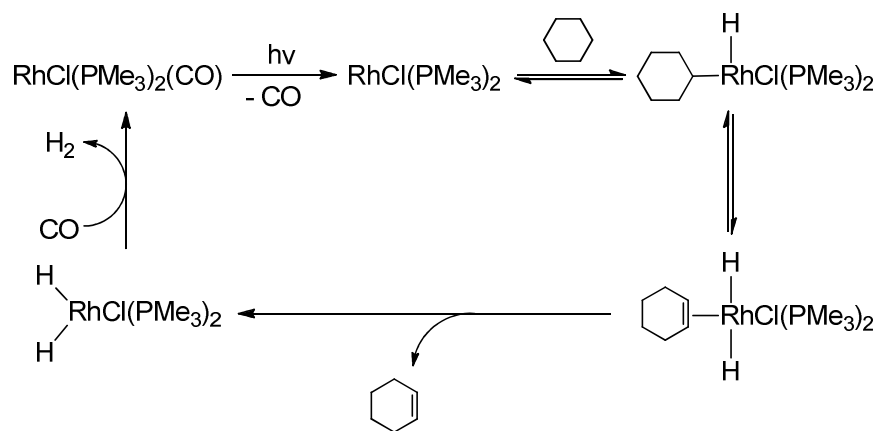


Investigations into the selectivity of alkane oxidative addition found a surprising thermodynamic preference for activation of the stronger C-H bonds of alkanes. Independent investigations by Bergman,³⁹ Bercaw,⁴⁰ and Jones⁴¹ showed a clear preference for C-H activation of alkanes at the strongest C-H bonds (i.e. $1^\circ > 2^\circ > 3^\circ$) despite widely differing metal-ligand complexes. By contrast, hydrogen atom abstraction by radical reactions occurs preferentially at the more substituted position.⁴² While the selectivity of alkane oxidative addition to metal complexes was initially ascribed in part to steric effects,³⁹ more recent work have shown that metal-X bond strength correlates with H-X bond strength, implying an electronic basis for selectivity.^{40,41,43-49}

Oxidative addition of C-H bonds is particularly important in catalytic alkane dehydrogenation. While dehydrogenation is an enthalpically uphill process ($\Delta H \sim 30$ kcal/mol),^{50,51} the process is positive entropically. As a result, some systems under elevated temperatures can overcome the enthalpic barrier and achieve catalytic turnover. To achieve catalytic dehydrogenation under less forcing condition, the dehydrogenation reaction can be coupled with the thermodynamically downhill hydrogenation reaction of a sacrificial hydrogen acceptor, often *tert*-butylethylene (tbe) or norbornene. In 1979, Crabtree reported the first example of transfer dehydrogenation in which $[\text{IrH}_2(\text{acetone})_2(\text{PPh}_3)_2] [\text{BF}_4]$ reacted with cycloalkanes in conjunction with tbe to yield cyclic diene iridium complexes (eq. 7).⁵² In 1987, Crabtree reported catalytic alkane dehydrogenation using *trans*-($\text{P}(p\text{-C}_6\text{H}_5\text{F})_3$)₂Ir(H)₂($\kappa^2\text{-O}_2\text{CCF}_3$) under thermal transfer dehydrogenation and acceptorless photochemical conditions.⁵³ In 1989, our group reported the first example of efficient alkane functionalization, the photochemical dehydrogenation of alkanes catalyzed by $\text{RhCl}(\text{PMe}_3)_2(\text{CO})$ (Scheme 1.2).^{54,55}

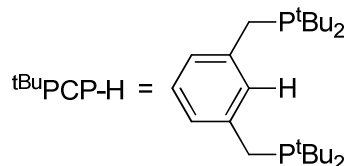


Scheme 1.2. Mechanism of photochemical catalytic cyclohexane dehydrogenation by $\text{RhCl}(\text{PMe}_3)_2\text{CO}$.^{54,55}

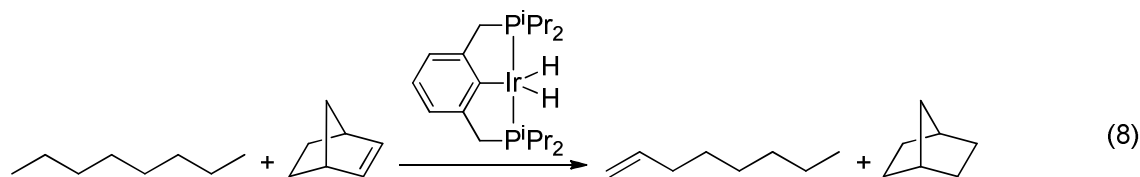


More recently, many groups have investigated the use of pincer ligand metal complexes to effect reactions with small molecules. The “pincer” ligand was first introduced by Moulton and Shaw in 1976 to describe complexes bearing κ^3 -2,6- $(^t\text{Bu}_2\text{PCH}_2)_2\text{C}_6\text{H}_3$ ($^t\text{Bu}_2\text{PCP}$), a meridionally-bound, benzene-based, tridentate ligand (Figure 1.1).⁵⁶ Since then, the term “pincer” has been extended to any meridionally-bound tridentate ligand, and many different pincer ligand motifs have been reported.⁵⁷⁻⁶³

Figure 1.1. Protonated ^tBuPCP ligand.



Iridium⁶⁴⁻⁶⁶ and rhodium⁶⁷ pincer complexes were investigated as catalysts toward alkane dehydrogenation. While the rhodium pincer complexes displayed low activity for catalytic alkane dehydrogenation,⁶⁷ iridium pincer complexes (^tBuPCP)IrH₂ and (ⁱPrPCP)IrH₂ were found to exhibit high rates and turnover number for both acceptorless and transfer dehydrogenation of cyclic alkanes.^{64-66,68} More significantly, regioselective catalytic alkane dehydrogenation was reported by Goldman in 1999 in which (ⁱPrPCP)IrH₂ selectively dehydrogenates *n*-alkanes to α -olefins (eq. 8).⁶⁹



Many modifications have been made to the pincer ligand first introduced by Moulton and Shaw in an effort to improve catalytic dehydrogenation activity and to investigate new reactivity. The phosphine substituents have been modified such that methyl, isopropyl, adamantyl, and trifluoromethyl groups have replaced one or more of the *t*-butyl groups (Figure 1.2).^{62,68-73} Substitution of OMe,⁷⁴⁻⁷⁶ CO₂Me,⁷⁴ and NMe₂⁷⁷ groups at the *para* position of the aryl ring of the PCP ligand have been reported (Figure 1.2). Replacement of the methylene linkers with nitrogen⁶⁰ or oxygen^{57,78,79} atoms has been reported (Figure 1.3). The benzene ring has also been modified to give new ligand

motifs such as a pyridyl-PNP ligand,^{58,80-82} an amido-PNP ligand,^{59,83} and a PSiP ligand (Figure 1.3).⁶¹

Figure 1.2. Synthesized variations of the PCP ligand, shown coordinated to Ir.

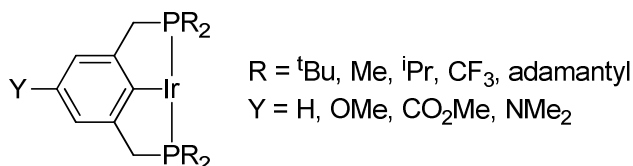
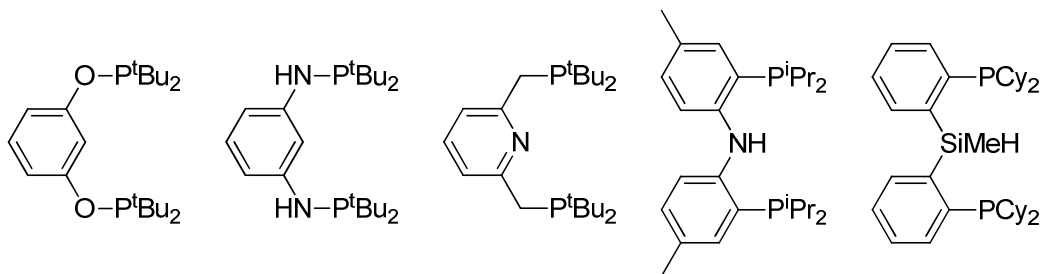


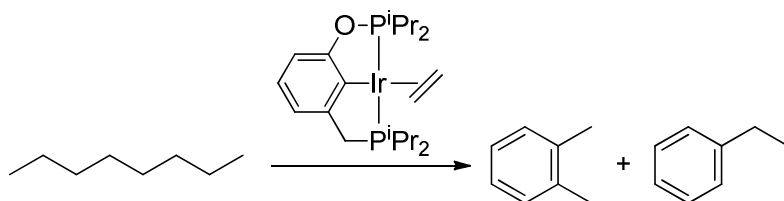
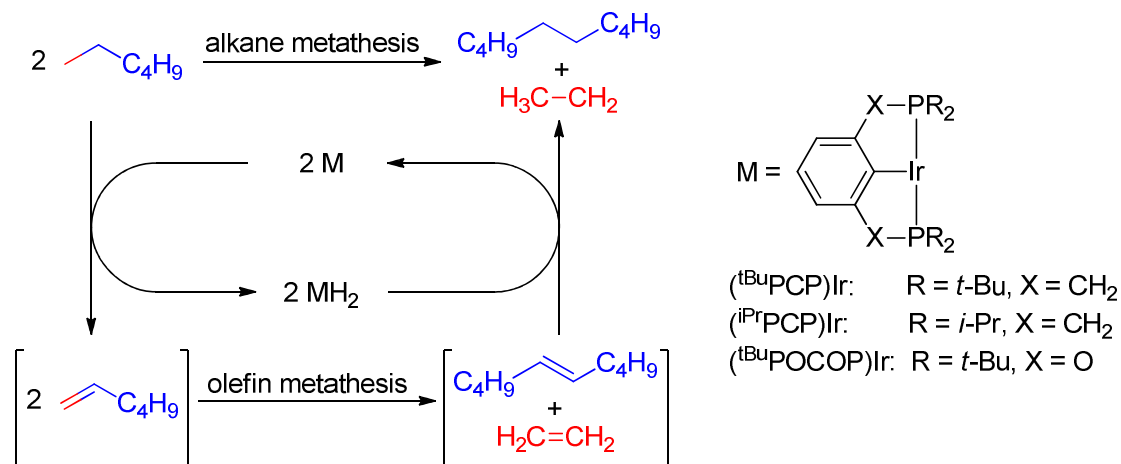
Figure 1.3. Various pincer ligand motifs.



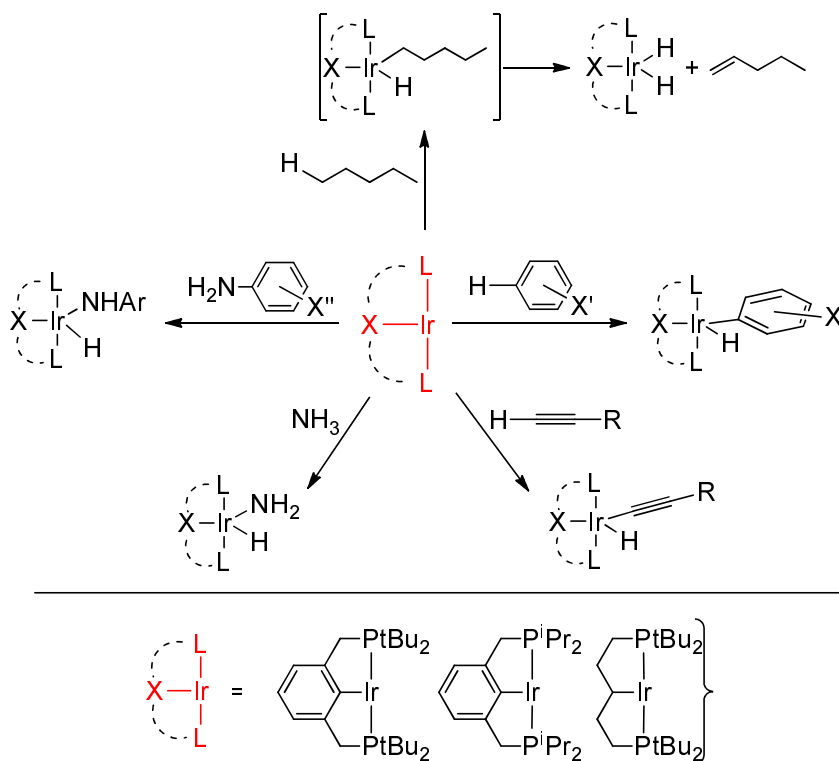
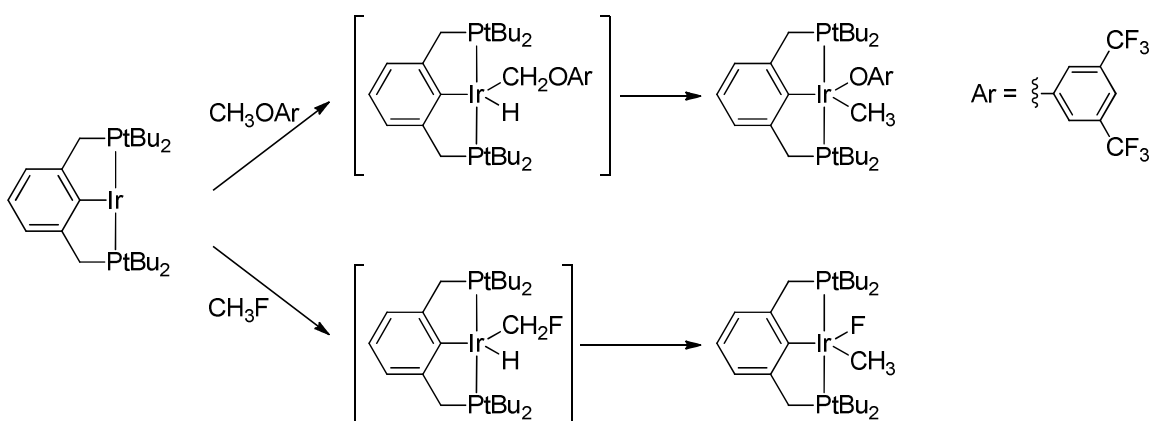
Our group has reported the use of pincer iridium complexes in the activation of a wide variety of small molecules. As noted before in the context of dehydrogenation, the oxidative addition of alkanes has been reported,⁶⁹ and this reaction is utilized as part of multistep reactions like alkane metathesis (Scheme 1.3)^{84,85} and dehydroaromatization (eq. 9).⁸⁶ Activation of other hydrocarbons, arenes⁸⁷ and alkynes,⁸⁸ was also reported (Scheme 1.4). Bonds other than C-H bonds have also been reported by our group to oxidatively add to pincer iridium complexes. Aniline⁸⁹ and ammonia⁹⁰ have been reported to undergo N-H oxidative addition (Scheme 1.4). The oxidative addition of C-

O⁹¹ and C-F⁹² bonds have also been reported, although the mechanism for both reactions proceeds through an initial C-H activation step (Scheme 1.5).

Scheme 1.3. Mechanism of alkane metathesis.



(9)

Scheme 1.4. Oxidative addition of various bonds to PCP pincer iridium complexes.**Scheme 1.5.** Oxidative addition of C-O and C-F bonds through an initial C-H oxidative addition step.

1. 2 Research Goals of This Thesis

Understanding the fundamental processes underlying the activation of small molecules by metal complexes is a continuing goal of organometallic chemistry. This thesis aims to better understand the processes and interactions of small molecules with organometallic complexes. The remaining chapters of this thesis can be organized into two parts. The first part comprises Chapters 2 through 4 and covers work that primarily utilizes DFT calculations. The second part comprises Chapters 5 through 8 and covers my experimental work.

Chapter 2 presents a combined computational and experimental study of electronic factors affecting C-H and N-H bond addition to Ir(I) complexes. DFT calculations were performed on an extensive series of $(\text{PH}_3)_2\text{IrX}$ complexes to investigate the thermodynamics of C-H and N-H oxidative addition. Electronic substituent effects were decomposed into their σ and π effects and individually parameterized; the resulting σ_X and π_X parameters were used to fit the energies of oxidative addition of methane to a series of 3- and 4-coordinate Ir(I) complexes. Regression analysis indicates that oxidative addition of methane to 3-coordinate Ir(I) complexes generally is favored by a less σ -donating ligand *trans* to the vacant coordination site, although this preference is reversed in the special case where the geometry of the 5-coordinate product is square pyramidal with the X ligand in the apical position.

Chapter 3 presents a computational study into the oxidative addition of chlorobenzene and fluorobenzene to $^{\text{H}}\text{PCPIr}$, $^{\text{Me}}\text{PCPIr}$, and $^{\text{tBu}}\text{PCPIr}$. The thermodynamics of addition were found to favor activation of the C-H bond proximal to the electron-withdrawing Cl atom (ΔG : *para* addition > *meta* addition > *ortho* addition).

The kinetic barriers were also calculated and correlated with the relative steric interactions in the transition state leading to the oxidative addition product. Both calculations for thermodynamic and kinetic preferences were found to be in accord with experimental results.

Chapter 4 describes an investigation into the contributions of backbonding and through-space effects on the stretching frequency of metal-bound CO. CO stretching frequencies for a series of $\text{Ni}(\text{CO})_3\text{L}$ complexes were calculated using DFT calculations. NBO analysis of these complexes yielded parameters that reflected backbonding in the π^* orbitals of the CO ligands and polarization of the π^b orbitals of the CO ligands. We found that a linear two-variable model fit the data better than the traditional one-variable model of solely back-bonding effects. A close look at rotamers of anisoyl phosphine complexes highlighted the dominant effect of polarization in some cases. In the course of our investigation, we also calculated the effects of a point charge on free CO, which was consistent with previous work.

Chapter 5 presents experimental work relevant to the mechanism of olefin isomerization. The reaction kinetics of olefin coordination to $(^t\text{BuPCP})\text{Ir}$ and $(^t\text{BuPOCOP})\text{Ir}$ were quantified and discussed in the context of olefin isomerization. Additionally, the $(^t\text{BuPOCOP})\text{Ir}$ -catalyzed olefin isomerization of 1-octene was investigated and found to show an apparent 2nd order dependence on 1-octene concentration.

Chapter 6 describes investigations into the synthesis and reactivity of $^t\text{Bu}_3\text{MePCPIr}(\text{CO})$. A revised synthesis scheme for the synthesis of the $^t\text{Bu}_3\text{MePCP}$ ligand was developed. The revised synthesis scheme was found to be amenable for the

synthesis of a variety of unsymmetrical pincer ligands. With the $^{\text{tBu}^3\text{Me}}\text{PCP}$ ligand, addition of H_2 to $^{\text{tBu}^3\text{Me}}\text{PCPIr}(\text{CO})$ was investigated. Addition of H_2 was not observed to add to $^{\text{tBu}^4}\text{PCPIr}(\text{CO})$. However, when H_2 was added to $^{\text{tBu}^3\text{Me}}\text{PCPIr}(\text{CO})$, three isomers were observed and assigned using an isotopic labeling experiment and NMR spectroscopy.

Chapter 7 discusses the reactivity of tropone with $(^{\text{tBu}}\text{PCP})\text{IrH}_2$. The thermodynamic and kinetic products have been synthesized and characterized. One of the tropone addition adducts was previously found to catalyze the dimerization of tropone to give a fused tricyclic dihydrodicycloheptafulanol; the formation of this compound was investigated.

Chapter 8 details the addition of methyl fluoride's $\text{C}(\text{sp}^3)\text{-F}$ bond to an iridium center via the initial, reversible cleavage of a C-H bond. The structure was characterized through NMR spectroscopy, LIFDI mass spectrometry, and elemental analysis.

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Chapter 2

A Computational and Experimental Study of Electronic Factors Affecting ‘Oxidative Addition’ of C-H and N-H Bonds to Iridium Complexes

Abstract

A combined computational and experimental study of electronic factors affecting C-H and N-H bond addition to Ir(I) complexes has been carried out. DFT calculations were performed on an extensive series of $(\text{PH}_3)_2\text{IrX}$ complexes to investigate the thermodynamics of C-H and N-H oxidative addition. Electronic substituent effects were decomposed into their σ and π effects and individually parameterized; the resulting σ_X and π_X parameters were used to fit the energies of oxidative addition of methane to a series of 3- and 4-coordinate Ir(I) complexes. Regression analysis indicates that oxidative addition of methane to 3-coordinate Ir(I) complexes generally is favored by a less σ -donating ligand *trans* to the vacant coordination site, although this preference is reversed in the special case where the geometry of the 5-coordinate product is square pyramidal with the X ligand in the apical position. The oxidative addition of methane to 4-coordinate Ir(I) was found to be analogous in its electronic preferences to the 3-coordinate case. Rates of reductive elimination from a series of isoelectronic Ir(III) phenyl hydride complexes were measured and found to be consistent with the computational analysis. The regression analysis was extended to investigate NH_3

oxidative addition to 3-coordinate Ir(I) complexes. While more σ -donating ligands are unfavorable for N-H oxidative addition (analogous to methane oxidative addition), they are even more unfavorable for NH_3 coordination. An orbital rationale is proposed for the results obtained.

2.1 Introduction

Oxidative addition is a fundamental transformation of metal complexes and is a key step in various processes including catalytic dehydrogenation¹ and arylation reactions.² Oxidative addition implies a formal two-electron oxidation of a metal center and involves the cleavage of an X-Y bond with concomitant formation of metal-X and metal-Y bonds. As suggested by its name and according to textbooks and conventional wisdom, oxidative addition is commonly thought to be favored by more electron-rich metal centers that can facilitate the formal two-electron loss during this transformation.³⁻⁵ Consequently, there have been reports of electron-donating ligands around a metal center promoting oxidative addition.^{6,7} Conversely, there are also reports of the use of electron-withdrawing ligands around a metal center to promote reductive elimination,⁸⁻¹⁰ the microscopic reverse of oxidative addition.

The addition of C-H and N-H bonds to metal centers form highly desirable subsets of oxidative addition reactions. Many reports of C-H oxidative addition to late-metal complexes, particularly Ir(I) and Rh(I) complexes, can be found.¹¹⁻¹⁴ While our group has primarily investigated reactions involving 3-coordinate Ir(I) and Rh(I) complexes,¹ many reports of additions to analogous 4-coordinate complexes covering a wide breadth of ligand motifs have been published.^{1,5}

There are only a few recent examples of N-H oxidative addition of ammonia (NH₃).¹⁵⁻²⁰ Among the reports of NH₃ oxidative addition, our group reported that a change in the type of pincer ligand from an aryl-PCP type to an aliphatic-PCP ligand results in a change in thermodynamic selectivity from 4-coordinate NH₃ coordination (aryl-PCP type) to the 5-coordinate amido hydride product (aliphatic-PCP type).¹⁵ This

change in selectivity was attributed to increased electron density on the metal center afforded by the more electron-donating aliphatic-PCP ligand, a hypothesis consistent with the conventional wisdom regarding oxidative addition.

While the concept of oxidative addition being oxidative at the metal seems intuitively appealing, there have been reports that suggest that oxidative addition may not be oxidative at all with respect to the metal and, correspondingly, that electron-donating ligands do not necessarily favor oxidative addition. Saillard and Hoffman cautioned against interpreting the oxidative addition formalism as a literal picture of oxidation at the metal; rather, these authors proposed that a better description of oxidative addition involved the formation of covalent bonds in which electron density in ligand-localized and metal-localized orbitals moves in both ligand-to-metal and metal-to-ligand directions during the course of the reaction.²¹ Similarly, investigations by Low and Goddard²² and Koga and Morokuma²³ concluded that covalency, rather than oxidation, is a better description of oxidative addition products.

Various theoretical calculations of oxidative addition to 3-coordinate Ir(I) and Rh(I) complexes have also suggested that electron-donating ligands do not necessarily favor the reaction. Cundari calculated that the energy of methane oxidative addition to *trans*-(PH₃)₂IrX (X = H, Cl) was significantly more favorable for (PH₃)₂IrCl ($\Delta H = -41.6$ kcal/mol) than (PH₃)₂IrH ($\Delta H = -12.8$ kcal/mol).²⁴ Similarly, we reported that oxidative addition of H₂ to *trans*-(PH₃)₂MX complexes (X = Cl, Ph, M = Rh, Ir) was significantly more favorable for X = Cl than X = Ph ($\Delta\Delta E = 24.3$ kcal/mol and 31.1 kcal/mol for M = Rh and Ir, respectively).²⁵ In both cases, the more strongly electron-donating ligands (i.e. H⁻ and Ph⁻) result in *less* favorable oxidative addition than the weakly donating Cl⁻ ligand.

In a substituent effect study on oxidative addition of H-H and C-Y (Y = H, C, and F) bonds to $(\text{PH}_3)_2\text{IrX}$ (X = H, F, Cl, and Ph) complexes, we noted that π -donation by the ancillary ligand X favored the addition reaction, whereas σ -donation from X was unfavorable.²⁶ We concluded that, at least for the limited set of substrates considered, substituent effects in oxidative addition reactions were dominated by individual orbital interactions rather than transfer of charge.

Other groups have reported similar counter-intuitive results in which oxidative addition is promoted by less electron-donating ligands. Su and Chu reported C-F oxidative addition of CH_3F to $(\text{PH}_3)_2\text{MX}$ (X = Cl, H, Me; M = Rh, Ir);²⁷ Macgregor reported NH_3 oxidative addition to $(\text{PH}_3)_2\text{MX}$ (X = Cl, H; M = Rh, Ir);²⁸ and Diggle, Macgregor, and Whittlesey reported the oxidative addition of H_2 , CH_4 , and C_2H_4 to $\text{Ru}(\text{CO})(\text{IR})_{3-n}(\text{PH}_3)_n$ (R = H = 1,3-imidazol-2-ylidene and R = Me = 1,3-dimethylimidazol-2-ylidene).²⁹ In each case, the less electron-donating ligands were calculated to favor the oxidative addition reaction.

Thus, to date, no comprehensive review of electronic effects on the thermodynamics of oxidative addition has been performed. Here, we report a systematic approach through DFT calculations to probe the electronic factors that influence the thermodynamics of C-H (methane) and N-H (ammonia) oxidative addition to both 3- and 4-coordinate Ir(I) complexes. Computed electronic substituent effects have been decomposed into their σ - and π -components and individually parameterized. The resulting parameters are used to investigate ligand characteristics favorable for the oxidative addition of methane to a series of 3- and 4-coordinate Ir(I) complexes. Rates of benzene reductive elimination from a series of isoelectronic Ir(I) phenyl hydride

complexes have been experimentally determined to verify the conclusions drawn from the electronic structure calculations. The factors that influence the thermodynamics of ammonia oxidative addition were investigated through calculations analogously to methane. Finally, an orbital rationale is proposed for the results obtained.

2.2 Computational Methods

All calculations used DFT methodology³⁰ as implemented in the Gaussian 03 and 09 series of computer programs.^{31,32} We employed the Perdew–Burke–Ernzerhof exchange-correlation functional (PBE) in all calculations.³³ For the model complexes (**1-3**), we applied the SDD relativistic, small-core effective potential and corresponding basis set to the Ir atom³⁴ and all-electron, valence triple- ζ plus polarization and diffuse function 6-311+G(d,p) basis sets to all non-metal atoms.³⁵⁻³⁸ For the calculations of actual complexes **4-7** and related species, we used the LANL2DZ relativistic, small-core effective potential and the LANL2TZ basis set augmented by a diffuse d-type function (exponent = 0.07645) for Ir^{39,40} and 6-311+G(d,p) basis sets for atoms bonded to Ir or contained in substrate molecules (e.g. CH₄, NH₃, or benzene); all other atoms were treated with valence double- ζ plus diffuse function 6-31+G basis sets. All complexes underwent geometry optimization, and stationary points were subjected to normal mode analysis. Electronic population indices were derived from the Natural Bond Orbital (NBO) analysis scheme developed by Weinhold et al.^{41,42} and calculated using NBO 5.G and Gaussian 03.⁴³

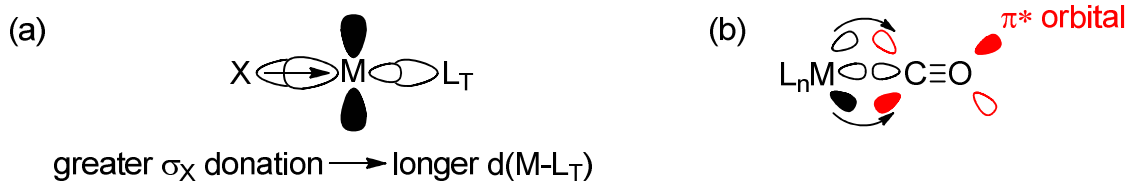
2.3 Parameterization of Electronic Substituent Effects

Electronic substituent effects on oxidative addition of C-H and N-H bonds to Ir complexes were determined from a series of comparative calculations on small model complexes. To investigate solely the electronic substituent effects, we chose to minimize steric contributions by focusing on complexes that have a $(\text{PH}_3)_2\text{IrX}$ substructure, with the PH_3 groups held mutually *trans* (X = various monodentate ligands). Provided that the X ligand and any additional ligands are not unusually large, we can assume that steric interactions with the PH_3 groups are negligible and that perturbations to the calculated reaction energies between complexes with different X ligands are strictly attributable to electronic effects. The electronic effects of various X ligands were further separated into σ and π effects and separately parameterized yielding σ_{X} and π_{X} parameters. The X ligands investigated feature a range of σ -type and π -type electronic properties: strongly σ -donating ligands (H^- , Li^- , Ph^- , Me^-), weakly σ -donating ligands (pyrrolide), strongly σ -donating and π -donating ligands (O^{2-} , BH_3^{2-}), strongly σ -donating and π -accepting ligands (BH_2^-), weakly σ -donating and π -donating ligands (NH_2^- , F^- , OH^- , OMe^-), and weakly σ -donating and π -accepting ligands (NH_3 , NO_2^-). The orientations of some ligands (BH_2^- , NH_2^- , NO_2^- , OH^- , OMe^- , Ph^- , and pyrrolide) were also constrained to be coplanar with or orthogonal to the plane of the molecule.

Trans influence was used to isolate the σ effects of different X ligands. The *trans* influence is a ground-state phenomenon in which the strength of a ligand-metal bond inversely affects the length of the ligand-metal bond located *trans* to it;⁴⁴⁻⁴⁶ that is, if a particular X ligand forms a comparatively strong and short bond with the metal center, then a bond situated *trans* to it will tend to be correspondingly weak and long (Scheme

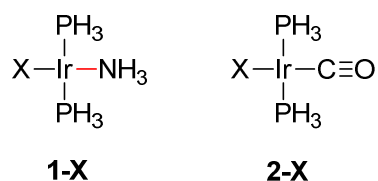
2.1a). If the *trans* ligand (L_T) bonds solely to a metal center through σ interactions, then the *trans* influence produced by an X ligand directly reflects the effective σ -donating ability of X.

Scheme 2.1. (a) *Trans* Influence of an X Ligand on the $M-L_T$ Distance. (b) π -Back-bonding of Electron Density from a Metal to Vacant π^* Antibonding Orbitals of CO.



Thus, the geometries of a series of *trans*-(PH_3)₂Ir(NH_3)(X) complexes (**1-X**) were optimized, and the resulting equilibrium Ir-N bond distances were measured (Figure 2.1). It was assumed that NH_3 exhibits exclusively σ -type bonding interactions with the Ir atom; consequently, variations in Ir-N bond distances were attributed to variations in the σ -donation characteristics of X. The complexes were constrained to rigorously maintain square planar geometries (angles between ligands equal to 90°) to eliminate unusual perturbations to the geometry about the metal center. In addition, the orientation of certain X ligands (e.g. BH_2^-) were constrained to be coplanar with or orthogonal to the plane of the molecule to control for differences in X ligand orientation.⁴⁷ All other geometrical variables were allowed to freely optimize. The differences in the Ir-N bond distances between complexes constrained (as described above) and unconstrained are relatively small, and thus the applied geometry constraints exert only a minor effect on the measured Ir-N bond distances.⁴⁸

Figure 2.1. Complexes used for the determination of electronic substituent effect parameters (σ_X , π_X).



The σ_X parameter was referenced relative to the Ir-N bond distance for **1-H**, as shown in equation 1. Ligands with a positive σ_X parameter have engendered elongations in the Ir-N bonds *trans* to X and are hence considered stronger σ donors than hydride, whereas ligands with a negative σ_X value are considered weaker σ donors than hydride. The series of calculated ligands and corresponding derived σ_X parameters are shown in Table 2.1. The series follows what one would traditionally expect: strong σ -donating ligands such methyl and phenyl exert large *trans* influences comparable to that of hydride are found to have σ_X values near zero (-0.015 and -0.012, respectively), while weakly σ -donating substituents like fluoride and hydroxide possess relatively more negative σ_X values (-0.146 and -0.110, respectively). As expected, hydride is among the most strongly σ -donating ligands, as only BH_3^{2-} , O^{2-} , Li^- , and BH_2^- are calculated to have positive σ_X values, indicating more strongly σ -donating properties than hydride.

$$\sigma_X = (\text{Ir-N bond distance; } \text{\AA})_X - (\text{Ir-N bond distance; } \text{\AA})_{\text{H}} \quad (1)$$

Table 2.1. Calculated Electronic Substituent Parameters (σ_X , π_X).

X ligand	σ_X	π_X
BH_2^- , $\perp$	0.115	-0.038
BH_2^- , $\parallel$	0.139	-0.036
BH_3^{2-}	0.235	0.114
CF_3^-	-0.033	-0.031
CH_3^-	-0.015	0.018
F^-	-0.146	0.076
H^-	0.000	0.000
Li^-	0.128	0.010
NH_2^- , $\perp^1$	-0.072	0.037
NH_2^- , $\parallel^2$	-0.072	0.072
NH_3	-0.153	-0.064
NO_2^- , $\perp$	-0.081	0.001
NO_2^- , $\parallel$	-0.071	-0.023
O^{2-}	0.023	0.312
OH^- , $\perp$	-0.110	0.064
OH^- , $\parallel$	-0.113	0.083
OMe^- , $\perp$	-0.106	0.059
OMe^- , $\parallel$	-0.113	0.072
Ph^- , $\perp$	-0.012	0.002
pyrrolide, $\perp$	-0.108	0.017
$\parallel$ = coplanar with P-Ir-P axis $\perp$ = orthogonal to P-Ir-P axis ¹ H-N-Ir-P dihedrals set to 58.5° ² H-N-Ir-P dihedrals set to 31.5°		

We gauge π -effects from consideration of metal(d_π)-ligand(p_π) backbonding using a series of 4-coordinate *trans*-(PH_3)₂Ir(CO)(X) complexes **2-X** (Figure 2.1). The extent to which electron density is transferred from occupied metal d-orbitals into formally vacant CO(π^*) orbitals (Scheme 2.1b)⁵ was quantified via NBO analyses to determine the occupancies of Lewis-type bonding and antibonding orbitals.^{41,42}

First, the geometries of **2-X** were fully optimized without any imposed symmetry constraints, and the *average* Ir-CO bond distance was found to be 1.86796 Å. Geometries of **2-X** were then constrained to be rigorously square planar in the same manner as **1-X** described above and, additionally, the Ir-CO bond distance was constrained to the length 1.86796 Å. This latter constraint was imposed due to the concern that the *trans*-influence of ligand X would affect the Ir-CO bond distance and influence, accordingly, Ir(d_{π})-CO(π^*) orbital overlap. A change in overlap due to variation in the Ir-CO bond distance affects the π^* bond occupancies independent of the π donating or accepting characteristics of ligand X, thus introducing a σ -type component to the occupancy values of the virtual CO(π^*) orbitals. The effect is illustrated in Table 2.2, where varying the Ir-CO distance of complex **2-F** changes the CO(π^*) bond occupancy. By constraining the C-O bond distance to a common value for all complexes, this effect is eliminated, and the differences in orbital occupancies reflect therefore solely differences in the π -donating and accepting abilities of ligands X.

Table 2.2. Effect of the Ir-CO Bond Distance on the CO(π^*) Orbital Occupancy of **2-F**.

d(Ir-CO) (Å)	CO(π^*) orbital occupancy
1.850	0.585
1.855	0.582
1.860	0.579
1.865	0.576
1.86796 ^a	0.574
1.870	0.573
1.875	0.569
1.880	0.566
1.885	0.563
1.890	0.560

^aAverage C-O bond length from fully optimized **2-X** geometries, see text.

The total $\text{CO}(\pi^*)$ orbital occupancy is the sum of the NBO populations in the two orthogonal $\text{CO}(\pi^*)$ antibonding orbitals. Analogously to the σ_X parameter, the π_X substituent parameter is referenced to the $\text{CO}(\pi^*)$ occupancy for **2-H** and defined as shown in equation 2. Ligands with a positive π_X parameter are considered π donors, whereas ligands with a negative π_X value are considered π acceptors. The trend in the π_X values (Table 2.1) is as expected: π donating ligands like amido and methoxide have positive π_X values (both 0.072), while a π accepting ligand like BH_2^- has a negative π_X value (-0.036). The relative orientation of the ligands, while not significantly influencing σ_X values, does have a more significant effect on the value of the π_X parameter. The amido ligand shows very different π_X values when oriented coplanar with the P-Ir-P axis (0.072) or orthogonal to the axis (0.037). Additionally, while ligands like NH_3 and BH_3 are not expected to interact significantly in a hyperconjugative π sense with a metal d orbital, the charge that the ligand imparts on the complexes affects the effective π characteristics of the metal center,⁴⁹ and as such, they are effectively considered as a π acceptor and π donor, respectively.

$$\pi_X = (\text{CO } \pi^* \text{ bond occupancy; e})_X - (\text{CO } \pi^* \text{ bond occupancy; e})_H \quad (2)$$

2.4 Oxidative Addition of CH_4 to 3-Coordinate *trans*-(PH_3)₂IrX

The energy of oxidative addition of methane to $(\text{PH}_3)_2\text{IrX}$ was calculated for a variety of X ligands (ΔE_X , Table 2.3). Structures for the 3-coordinate reactants and the 5-coordinate products were optimized both with and without imposed geometry restrictions. When the geometries were restricted, the P-Ir-P angles were fixed at 180° ,

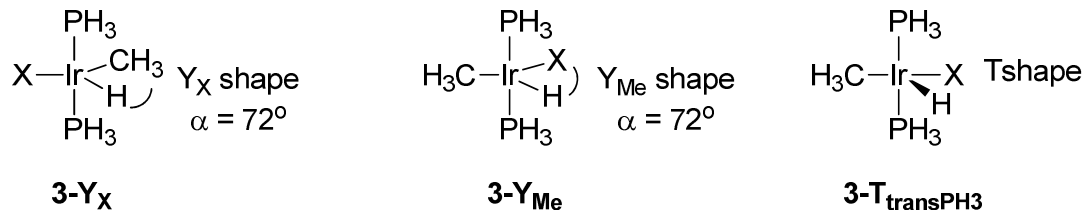
and the remaining ligands were held rigorously perpendicular to the P-Ir-P axis. Selected X ligands were constrained to be coplanar with or orthogonal to the P-Ir-P axis, and the Ir-C-H angles of the methyl group of the 5-coordinate products were set to tetrahedral values (109.47°). We found that the unconstrained geometries of the 5-coordinate products fell into three general categories: square pyramidal and two types of distorted trigonal bi-pyramidal.⁵⁰⁻⁵² These geometries were then standardized into three model geometries that are described by the local coordination in the equatorial plane: T-shape (square pyramidal, **3-T_{trans}PH₃**), Y_{Me} shape (where the X-Ir-H angle is set to 72° , **3-Y_{Me}**), and Y_X shape (where the Me-Ir-H angle is set to 72° , **3-Y_X**)(Figure 2.2). For both constrained and unconstrained geometries, the computed data (reaction energies, bond distances and orbital populations) was treated in the same manner. The numerical fits of the regression analyses were better when constrained geometries were used, but, overall, the same conclusions may be drawn from either set of geometries and regression analyses. Because the geometry variations of specific complexes are perturbations to the calculated reaction energies independent of the underlying electronic factors of the X ligands, and since the overall conclusions remain the same regardless of geometry restrictions, only the geometry constrained data will be presented below.

Table 2.3. Calculated Reaction Energies (ΔE_X , kcal/mol) of CH_4 Addition to $(\text{PH}_3)_2\text{IrX}$ for Different Equatorial Plane Geometries, cf. Figure 2.2.^a

$\begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{M} \\ \\ \text{PH}_3 \end{array} + \text{CH}_4 \longrightarrow \begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{M}-\text{CH}_3 \\ \quad \\ \text{PH}_3 \quad \text{H} \end{array}$			
	ΔE_X (kcal/mol)		
X ligand	Y_{Me}	Y_X	T
BH_2^- , $\perp$	3.8	14.8	15.2
BH_2^- , $\parallel$	-2.0	32.6	18.6
BH_3^{2-}	0.3	9.3	15.9
CF_3^-	-3.4	3.9	-2.5
CH_3^-	-4.9	-4.6	-1.3
F^-	-15.1	-35.1	-28.8
H^-	-6.9	1.7	-0.7
Li^-	-5.4	14.6	15.0
NH_2^- , $\perp^1$	-6.3	-10.4	-8.5
NH_2^- , $\parallel^2$	-10.2	-24.6	-14.4
NH_3	-16.1	-28.9	-32.7
NO_2^- , $\perp$	-3.6	-6.6	-10.9
NO_2^- , $\parallel$	-2.4	-0.5	-6.5
O^{2-}	0.3	-23.1	-7.5
OH^- , $\perp$	-12.2	-22.8	-18.4
OH^- , $\parallel$	-10.2	-30.6	-20.9
OMe^- , $\perp$	-9.3	-19.4	-15.8
OMe^- , $\parallel$	-9.0	-28.4	-20.2
Ph^- , $\perp$	-1.6	2.9	1.6
pyrrolide, $\perp$	-9.0	-14.7	-16.3
$\parallel$ = coplanar with P-Ir-P axis $\perp$ = orthogonal to P-Ir-P axis ¹ H-N-Ir-P dihedrals set to 58.5° ² H-N-Ir-P dihedrals set to 31.5°			

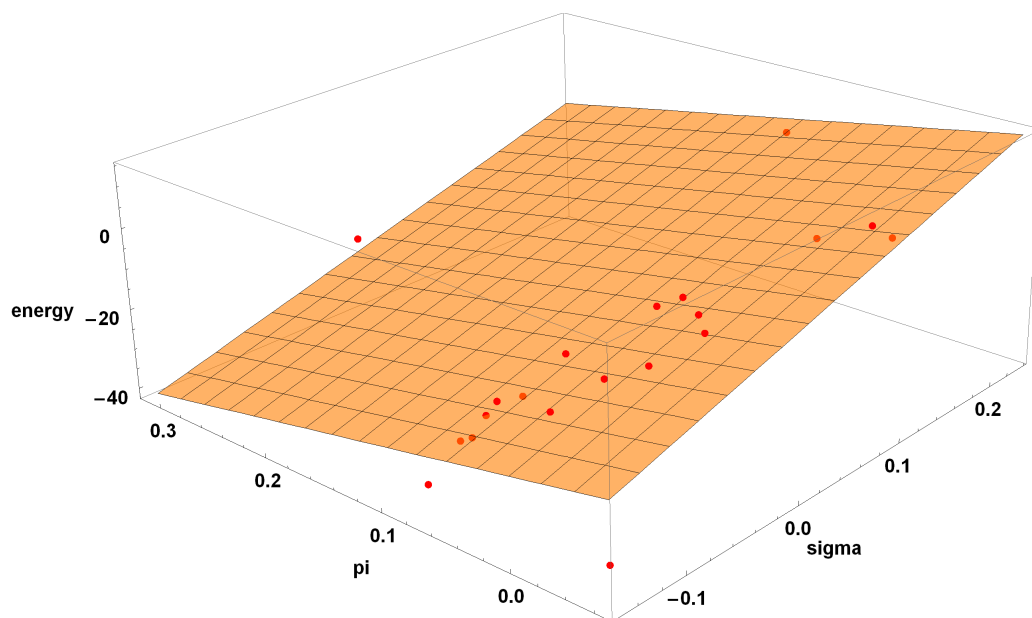
^aFor each ligand X, the lowest calculated ΔE_X is in bold font.

Figure 2.2. Three general geometries appropriate for *trans*-(PH₃)₂Ir(X)(H)(CH₃).



We propose that the differences in reaction energies ($\Delta\Delta E$) arise from differences in σ and π effects exerted by the X ligands. A 2-variable linear regression was performed in which the σ_X and π_X parameters were simultaneously fit to the data set comprised of the lowest calculated reaction energy for each X ligand (bold font values shown in Table 2.3; Figure 2.3). Inspection of the sign and magnitude of the coefficients obtained in the regression equation reveals which X ligand characteristics are favorable for oxidative addition. The large positive coefficient for the σ_X parameter (86.1) indicates that *weaker* σ donating ligands favor oxidative addition. The large negative coefficient for the π_X parameter indicates that oxidative addition is favored by π -donating ligands (-60.8). Given that conventional wisdom suggests that oxidative addition is generally favored by more electron-donating ligands, the result obtained for the σ_X parameter was surprising, since it clearly suggests that oxidative addition should not be regarded simply as an oxidative event at the metal.

Figure 2.3. 2-Variable linear regression fit of calculated ΔE_X to σ_X and π_X parameters for the constrained, lowest energy conformers of CH_4 addition to *trans*-(PH_3)₂IrX.



$$\Delta E_X = (86.1 \pm 14.9) \sigma_X + (-60.8 \pm 19.7) \pi_X + (-9.4 \pm 1.8)$$

$$R^2 = 0.709$$

While the above regression analysis utilizes the lowest reaction energy for each X ligand, each singular geometry case (Y_{Me} , Y_X , T_{transPH_3}) may, of course, be treated separately. Although the use of constrained geometries results in higher ΔE_X values, it does allow for the direct comparison of ligands with controlled geometries. Computed ΔE_X values for each of the three constrained geometry cases are presented in Table 2.3, and the resulting regression equations are given in Table 2.4. In all three cases (Y_{Me} , Y_X , T_{transPH_3}), the σ_X parameter coefficient is large and positive, indicating that oxidative addition is favored by less σ -donating ligands, independent of geometry. The π_X parameter coefficient varies, from negative in the case of Y_X to close to or effectively zero for T_{transPH_3} and Y_{Me} .

Table 2.4. Regression Equations Using Restricted Geometries for **3-Y_{Me}**, **3-Y_X**, and **3-T_{transPH3}**.

	regression equation	std. dev. of σ effects (kcal/mol)	std. dev. of π effects (kcal/mol)
$\begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir} \\ \\ \text{PH}_3 \\ \mathbf{1} \end{array} + \text{CH}_4 \longrightarrow \begin{array}{c} \text{PH}_3 \\ \\ \text{H}_3\text{C}-\text{Ir} \begin{array}{l} \nearrow \text{X} \\ \searrow \text{H} \end{array} \\ \\ \text{PH}_3 \\ \mathbf{3-Y_{Me}} \end{array} \quad \begin{array}{l} \text{Y}_{\text{Me}} \text{ shape} \\ \alpha = 72^\circ \end{array}$	$\Delta E_X = (37 \pm 8)\sigma_X + (2 \pm 10)\pi_X + (-5.2 \pm 0.9)$ $R^2 = 0.570$	4.0	0.2
$\begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir} \\ \\ \text{PH}_3 \\ \mathbf{1} \end{array} + \text{CH}_4 \longrightarrow \begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{H} \end{array} \\ \\ \text{PH}_3 \\ \mathbf{3-Y_X} \end{array} \quad \begin{array}{l} \text{Y}_X \text{ shape} \\ \alpha = 72^\circ \end{array}$	$\Delta E_X = (143 \pm 15)\sigma_X + (-106 \pm 19)\pi_X + (-0.5 \pm 1.7)$ $R^2 = 0.876$	15.3	8.5
$\begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir} \\ \\ \text{PH}_3 \\ \mathbf{1} \end{array} + \text{CH}_4 \longrightarrow \begin{array}{c} \text{PH}_3 \\ \\ \text{H}_3\text{C}-\text{Ir} \begin{array}{l} \nearrow \text{X} \\ \searrow \text{H} \end{array} \\ \\ \text{PH}_3 \\ \mathbf{3-T} \end{array} \quad \text{Tshape}$	$\Delta E_X = (131 \pm 10)\sigma_X + (-34 \pm 13)\pi_X + (-2.0 \pm 1.2)$ $R^2 = 0.911$	14.0	2.8

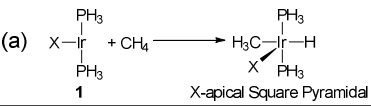
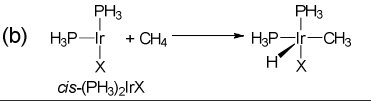
Because the σ_X and π_X parameters refer to widely different properties, it was unclear from casual inspection of a particular regression equation what the relative contributions of σ and π effects were on the overall energy of oxidative addition over the set of X ligands. To provide a sense of relative contributions, standard deviations were calculated for both σ and π effects by first multiplying the sets of individual computed σ_X and π_X parameters (Table 2.1) by the regression coefficients for the respective parameters (Table 2.4). The resulting two sets of energies correspond to the (σ , π) energy contributions for each ligand. The standard deviation of each set was then calculated, reflecting the relative significance of σ and π effects for that particular oxidative addition geometry (Y_{Me}, Y_X, T_{transPH3}).

Across all three geometry types, σ effects are more significant for the energy of oxidative addition than π effects. For the **3-T_{transPH3}** and **3-Y_{Me}** geometries, the standard deviation of σ effects are significantly larger than the standard deviation of π effects (14.0 and 4.0 kcal/mol vs. 2.8 and 0.2 kcal/mol, respectively), suggesting that the energy of

oxidative addition is predominantly governed by σ effects. While the standard deviation of σ effects remains larger than the standard deviation of π effects for the **3-Y_X** geometry (15.3 vs. 8.5 kcal/mol), π effects more significantly influence the energy of oxidative addition in this geometry than in the other geometries.

In the rare cases when the X ligand exerts a stronger *trans* influence than hydride or methyl,^{16,50,53} the 5-coordinate complex may adopt a square pyramidal geometry in which the X ligand is found in the apical position as opposed to an equatorial position (**3-T_{X-apical}**). In the regression equation for this geometry, a reversal of preference for σ effects is observed (Table 2.5a). The σ_X parameter coefficient is negative, suggesting that a more σ -donating ligand is favorable for oxidative addition. Like the **3-Y_{Me}** geometry, the standard deviation of σ effects for **3-T_{X-apical}** is significantly larger than the standard deviation of π effects (4.1 vs. 0.1 kcal/mol, respectively), suggesting that the energy of oxidative addition in the **3-T_{X-apical}** geometry is predominantly governed by σ effects.

Table 2.5. Regression Equations Using Restricted Geometries for **(a)** the X-apical Square Pyramidal Geometry (**3-T_{X-apical}**) and **(b)** the Oxidative Addition of Methane to *cis*-(PH₃)₂IrX (**3-T_{cisPH3}**).

	regression equation	std. dev. of σ effects (kcal/mol)	std. dev. of π effects (kcal/mol)
(a) 	$\Delta E_X = (-38 \pm 7)\sigma_X + (1 \pm 18)\pi_X + (2.3 \pm 0.9)$ $R^2 = 0.643$	4.1	0.1
(b) 	$\Delta E_X = (0 \pm 14)\sigma_X + (33 \pm 18)\pi_X + (-16 \pm 2)$ $R^2 = 0.241$	0.0	3.1

Given the variety of pincer ligand motifs,⁵⁴ we were also interested in the energetic effect of varying the ligand occupying the position *cis* to the vacant coordination site. Consequently, the energy of oxidative addition of CH₄ to *cis*-(PH₃)IrX complexes was calculated. The 5-coordinate structures were restricted to a square pyramidal geometry with the hydride located in the apical position (**3-T_{cis}PH₃**), and a 2-variable linear regression was performed analogously to the treatment for the *trans*-(PH₃)₂IrX complexes described above (Table 2.5b). The coefficient of determination for the regression is very low ($R^2 = 0.241$), suggesting that the energy of oxidative addition does not correlate significantly with σ or π effects of the X ligand in this geometry. To the extent that the σ and π effects correlate with the energy of oxidative addition, the σ_X parameter coefficient is zero, suggesting that with that ligand position only π effects correlate with the energy of oxidative addition. As a practical consequence in ligand design, this result suggests that modification of a pincer ligand at the positions *cis* to the vacant coordination site should not strongly influence the thermodynamics of oxidative addition to 3-coordinate Ir(I); instead, the position of the pincer ligand *trans* to the vacant coordination site strongly influences the thermodynamics of oxidative addition.

2.5 Orbital Rationale

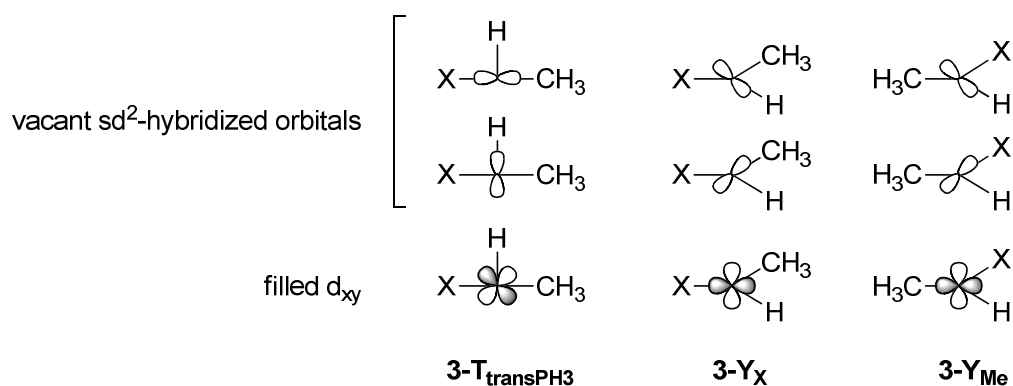
These results can be rationalized from a consideration of orbital interactions in both the reactant 3-coordinate d⁸ Ir(I) complexes and the product 5-coordinate d⁶ Ir(III) complexes. In the 3-coordinate *trans*-(PH₃)₂IrX complexes, the d⁸ Ir(I) atom can be visualized as having filled d_{xy}, d_{xz}, and d_{yz} orbitals and a filled d_{z2}-hybridized orbital that

lies on the axis perpendicular to the plane containing the P, X, and Ir atoms (cf. Scheme 2.2).

In the 5-coordinate d^6 Ir(III) complexes, the d_{xy} , d_{xz} , and d_{yz} orbitals remain filled, and two d orbitals are vacant. A traditional analysis of the orbital interactions involves σ -bonding of the PH_3 groups, the X ligand, and the Me group with the $d_{x^2-y^2}$ orbital on Ir. In that orbital picture, the X ligand and the PH_3 groups interact equivalently with the $d_{x^2-y^2}$ orbital, and no distinction is made between the positions *cis* and *trans* to the Me group. However, given the differences in the regression equations for the **3-T_{trans}PH₃** and **3-T_{cis}PH₃** geometries (cf. Tables 2.4 and 2.5), it is necessary to invoke Landis's representation of sd-hybridized metal orbitals in order to differentiate the two ligand positions.^{45,55} Here, three sd^2 -hybridized orbitals arise from the combination of the $5d_{x^2-y^2}$, $5d_{z^2}$, and 6s orbitals on Ir. One of these sd^2 -hybridized orbital is oriented along the P-Ir-P axis, while the other two are oriented in the plane perpendicular to the P-Ir-P axis; for the **3-T_{trans}PH₃** geometry, the sd^2 -hybridized orbitals are oriented along the Ir-X, Ir-P, and Ir-H axes.

If we examine σ interactions in the plane containing X, Ir, H, and Me, then the orbital picture can be simplified to contain just three orbitals: a filled d_{xy} orbital and two empty sd^2 -hybridized orbitals that, when considered together, resemble the $d_{x^2-y^2}$ orbital in the shapes of the orbital lobes (Scheme 2.2). In the case of the square pyramidal geometry (**3-T_{trans}PH₃**), the X, Me, and H groups interact directly with the two empty sd^2 -hybridized orbitals. Because the σ orbital of the X ligand “shares” one of the sd^2 orbitals with the Me group *trans* to it (3c-4e interaction), a less σ -donating X ligand will be favorable for oxidative addition.

Scheme 2.2. Orientation of sd^2 -hybridized Orbitals and d_{xy} in **3-T_{trans}PH₃**, **3-Y_X**, and **3-Y_{Me}**.^a



^aThe depictions of **3-Y_X** and **3-Y_{Me}** have coordinate axes that are rotated 45 degrees counterclockwise relative to that shown for **3-T_{trans}PH₃**.

The orbital picture is different for the **Y_X** and **Y_{Me}** shapes. For the **Y_X** geometry, the Me and H groups, which are strong *trans*-influence ligands, interact maximally with the two empty sd^2 -hybrid orbitals. The σ orbital of the X ligand then interacts directly with the filled d_{xy} orbital, an interaction that again is favored by a less σ -donating X ligand. For the **Y_{Me}** shape, the Me group and the X ligand switch places. The σ orbital of the X ligand is now oriented to interact primarily with the empty sd^2 -hybridized orbital, although orbital overlap is reduced because the ligand is positioned ca. 9° off the axis. Additionally, the Me group has a slight interaction with the filled d_{xy} orbital, although the geometry limits the angular overlap. Taken together, oxidative addition is slightly favored by less σ -donating X ligands in the **Y_{Me}** geometry, though not to the extent encountered in the **3-T_{trans}PH₃** or **3-Y_X** geometries.

While the **3-T_{X-apical}** geometry is similar to the **3-T_{trans}PH₃** geometry with the only difference being the positions of the X ligand and hydride in the 5-coordinate complex,

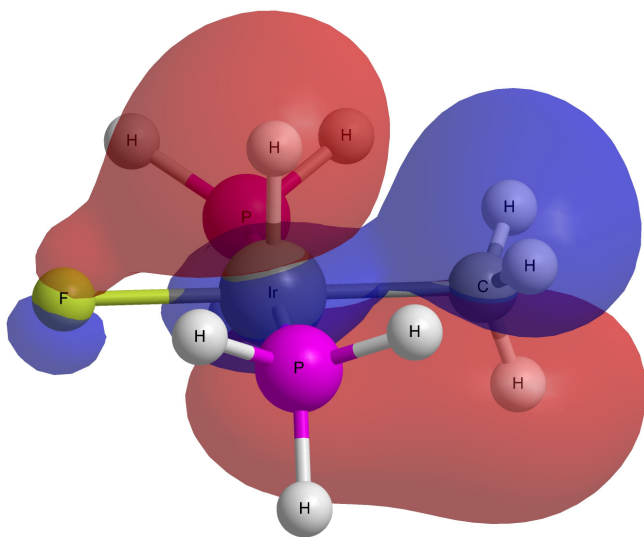
the regression equation for the **3-T_{X-apical}** geometry suggests a reversal in preference for σ effects; the coefficient of the σ_X parameter is negative (Table 2.5a), suggesting that more σ -donating ligands now are favorable for oxidative addition. In this geometry, the σ orbital of the X ligand would not need to “share” an sd^2 -hybridized orbital with a strong *trans*-influence ligand like Me or hydride as is the case for the **3-T_{transPH3}** geometry. Additionally, the favorability of more σ -donating ligands could arise in part from the antibonding interaction of X with the torus of the filled $5d_{z^2}$ orbital in the 3-coordinate complex.

The proposed orbital picture also correlates with the conclusions drawn from the coefficient of the π_X parameter. In the 3-coordinate *trans*-(PH₃)₂IrX complexes, the π -type orbitals would interact with the corresponding filled off-axis d orbital (d_{xy} , d_{xz} , or d_{yz}). However, in the 5-coordinate d^6 Ir(III) complexes, the π interactions are not as simple. For the **3-Y_X** geometry, the π interactions of X in the plane containing X, Ir, H, and Me would be with the empty sd^2 -hybridized orbitals. Additionally, the π interactions in the plane containing the PH₃ groups would be with a rotated filled d-orbital, resulting in a decrease in the angular overlap integral by ca. 30% from its optimal value. Both of these orbital effects would result in oxidative addition being strongly favored by π donating ligands, which corresponds nicely with the obtained π_X coefficient from the **3-Y_X** regression equation, which is large and negative (-106, Table 2.4).

For the **3-T_{transPH3}** geometry, the X-Ir π interactions would be approximately the same as those in the 3-coordinate complexes (overlap with two filled d orbitals), suggesting little to no influence of π effects on the energy of oxidative addition. However, the π_X coefficient of the **3-T_{transPH3}** regression equation is relatively small and

negative (-34, Table 2.4), suggesting that oxidative addition should be favored by slightly π donating ligands. This result could arise from π interactions between a π -type orbital on X and the vacant sd^2 -hybridized orbital oriented along the Ir-H axis. In the 3-coordinate complex, this type of interaction would be entirely non-bonding due to the symmetry of the orbitals. However, mixing of the 1s orbital of the hydride with this sd^2 -hybridized orbital would polarize the sd^2 -hybridized orbital such that net overlap with the π -type orbital of X could occur. Examination of the relevant MO for the *trans*-(PH_3)₂Ir(F)(H)(Me) complex in the **3-T_{transPH3}** geometry reveals this π -type interaction (Figure 2.4).

Figure 2.4. The HOMO(-8) orbital of *trans*-(PH_3)₂Ir(F)(H)(Me) in the **3-T_{transPH3}** geometry (isovalue = 0.015) showing how polarization of the metal sd^2 -hybridized orbital may create favorable overlap with the π -system of ligand X.



In contrast, the regression equation for the **3-T_{X-apical}** geometry suggests little to no influence of π effects on oxidative addition; the coefficient of the π_X parameter is effectively zero within the error of the regression (1 ± 18 , Table 2.5). The π interactions in the 5-coordinate complex are expected to be similar to those in the **3-T_{transPH3}**. However, the polarization of the sd^2 -hybridized orbital that arose from mixing with the 1s orbital of the hydride would be attenuated by equivalent mixing with the σ orbital of the Me group. As a result, the interaction between the π -type orbital on the X ligand and the vacant sd^2 -hybridized orbital oriented along the Me-Ir-H axis remains a non-bonding due to orbital symmetry.

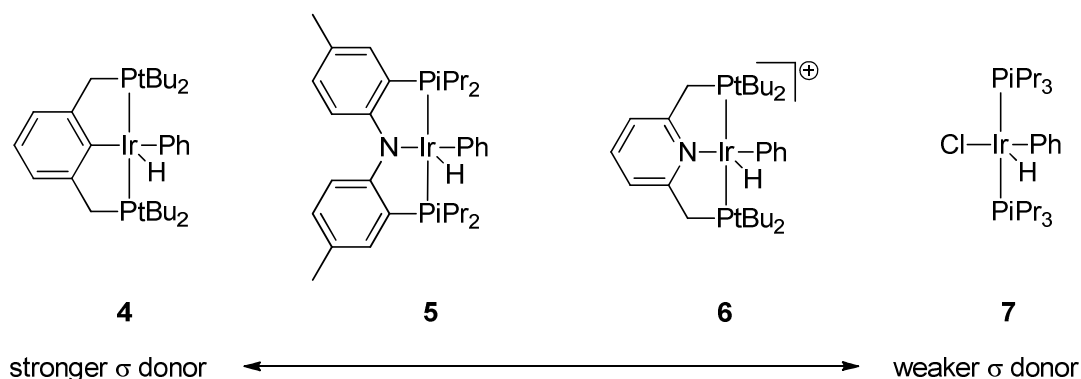
In the **3-Y_{Me}** geometry, the π interactions would be again approximately the same as those in the 3-coordinate complexes (albeit with slightly decreased overlap due to the 9° off-axis location of the X ligand). Consequently, the expected result that π effects have little to no influence on the energy of oxidative addition is reflected in the computed π_X coefficient that is zero within the error of the regression (2 ± 10 , Table 2.4).

2.6 Experimental Verification

A series of iridium complexes were investigated computationally and experimentally to further investigate the unexpected result that oxidative addition to 3-coordinate Ir(I) complexes should be favored by less σ -donating ligands. Four isoelectronic 5-coordinate Ir(III) phenyl hydride complexes have been previously reported in the literature: (PCP)Ir(H)(Ph) (**4**) (PCP = κ^3 -C₆H₃-2,6-(CH₂P^tBu₂)₂)⁵⁶, (^{Am}PNP)Ir(H)(Ph) (**5**) (^{Am}PNP = κ^3 -bis(2-diisopropylphosphino-4-methylphenyl)amide)^{57,58}, (^{Py}PNP)Ir(H)(Ph)⁺PF₆⁻ (**6**) (^{Py}PNP = κ^3 -C₅H₃N-2,6-

$(\text{CH}_2\text{P}^t\text{Bu}_2)_2$)^{59,60}, and *trans*-(P^iPr_3)₂-Ir(Cl)(H)(Ph) (**7**).^{61,62} Aside from the differences in the phosphine steric bulk and the variations in the P-Ir-P angles of the pincer-ligand frameworks, the series of complexes feature equatorial ligands with varying σ -donating abilities (Scheme 2.3). Complex **4** possesses a strongly σ -donating aryl carbon, while complex **7** has a less σ -donating chloride. Complexes **5** and **6** feature an amido nitrogen and a pyridyl nitrogen, respectively, and are hence expected to have intermediate σ -donating abilities.

Scheme 2.3. Several Ir(III) Phenyl Hydride Complexes and the Relative σ -donating Abilities of the Ligand at the Position *trans* to the Phenyl Moiety.



The σ_X and π_X parameters for the X ligands in complexes **4-7** were calculated from the corresponding 4-coordinate (ligand)Ir(NH₃) and (ligand)Ir(CO) complexes (Table 2.6). The values of the σ_X parameter were consistent with the expected σ -donating properties of these complexes, whereas the π_X parameter values indicate the X ligands in complexes **4**, **5**, and **7** to be moderate π -donors (**4** < **5** < **7**) and cationic **6** to be neither π accepting or donating. With these σ_X and π_X parameters, ΔE for the oxidative addition of methane were calculated from the regression equation presented in Table 4 for the Y_X

geometry. The calculated ΔE_{OA} values become more favorable with increasingly negative σ_X parameters, except for the two PNP-pincer complexes. Complex **5** ($\pi_X = 0.088$) is calculated to be a stronger π -donor than complex **6** ($\pi_X = 0.008$). This difference in π contribution results in oxidative addition being more favorable to complex **5** than complex **6**, despite complex **5** being a stronger σ -donor. Actual DFT calculations (see Computational Methods) for the energies of benzene and methane oxidative addition (Table 2.7) are consistent with the regression-equation-derived trend (Table 2.6) of increasingly favorable oxidative addition across the series in Scheme 3 (ΔE_{OA} : **4** > **6** > **5** > **7**).

Table 2.6. Calculated σ_X and π_X Parameters for Complexes **4-7**.

	σ_X	π_X	Calculated ΔE_{OA} for Y_X Geometry
4	0.017	0.070	-5.4
5	-0.097	0.088	-23.7
6	-0.107	0.008	-16.8
7	-0.137	0.106	-31.4

Table 2.7. Calculated Energies of Benzene and Methane Oxidative Addition to Complexes **4-7**.^a

M + benzene → M(H)(Ph)				
M(H)(Ph)	ΔE	ΔH	ΔS	ΔG
4	-11.7	-11.9	-43.7	1.2
5	-37.9	-38.4	-37.3	-27.2
6	-30.8	-31.1	-41.3	-18.7
7	-42.1	-41.7	-49.6	-26.9

M + methane → M(H)(CH ₃)				
M(H)(Ph)	ΔE	ΔH	ΔS	ΔG
4	-2.1	-2.4	-34.3	7.8
5	-28.6	-28.7	-33.3	-18.8
6	-23.6	-23.7	-30.9	-14.5
7	-35.4	-35.1	-33.5	-25.1

^aUnits for ΔE, ΔH, and ΔG are kcal/mol; units for ΔS are eu. Standard state for ΔG is T = 298.15 K and P = 1 atm for each species participating in the reaction.

The transition states for oxidative C-H cleavage of benzene were located via DFT calculations, and the calculated kinetic parameters for reductive coupling are given in Table 2.8. The ΔE[‡] and ΔH[‡] values for reductive coupling from complexes **5** and **6** were found to be lower than the thermodynamic barriers for reductive elimination. This suggests that the overall kinetic barriers to reductive elimination for complexes **5** and **6** correspond to the transition state for σ-coordination of a benzene C-H bond. Since coordination of benzene to the 3-coordinate Ir(I) complexes is expected to be a barrierless or near-barrierless process on the potential energy surface, the overall kinetic barrier for the reductive elimination of benzene from complexes **5** and **6** can be approximated by the thermodynamic barriers shown in Table 2.7.

Table 2.8. Calculated Kinetic Parameters for Reductive Cleavage of Benzene for Complexes **4-7**.

M(H)(Ph) → M + benzene				
M(H)(Ph)	$\Delta E^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
4	14.1	13.9	-3.2	14.8
5	25.3	20.3	-22.7	27.1
6	16.8	16.4	-3.0	17.3
7	33.3	32.1	0.7	31.9

Direct experimental determination of the oxidative addition energies is difficult because the 3-coordinate complexes leading to the oxidative addition products are not directly observable. However, the microscopically reverse process – reductive elimination – can be observed, and the rates can be measured (Table 2.9). Although caution must be taken when drawing thermodynamic conclusions from kinetic data, the kinetic barrier to oxidative addition is expected to be small relative to the much larger thermodynamic differences. EXSY NMR experiments were performed with complex **4** at a range of temperatures from -54 °C to -27 °C and yielded activation parameters for reductive elimination of 13.2 kcal/mol and -1.7 eu for $\Delta H^\ddagger$ and $\Delta S^\ddagger$, respectively. The rate of reductive elimination for complexes **5** was measured at a range of temperatures from 85 °C to 114 °C by monitoring the rate of disappearance of the hydride signal upon exchange with toluene- d_8 ; the enthalpic and entropic contributions to the barrier were determined to be 31.2 kcal/mol and 6.3 eu, respectively. The rate of reductive elimination for complex **6** at 84 °C was measured to be $1.3 \times 10^{-4} \text{ s}^{-1}$, which corresponds to a kinetic barrier ($\Delta G^\ddagger$) of 27.4 kcal/mol. A conservative upper limit for the rate of

benzene loss from complex **7** at 120 °C was previously reported to be $5 \times 10^{-5} \text{ s}^{-1}$, corresponding to a kinetic barrier ($\Delta G^\ddagger$) of 30.9 kcal/mol.⁶²

Table 2.9. Experimentally Determined Kinetic Parameters for the Reductive Elimination of Benzene for Complexes **4-7**.

M(H)(Ph) → M + benzene				
M	ΔH [‡]	ΔS [‡]	ΔG [‡] (at 84 °C)	ΔG [‡] (120 °C)
4	13.2 (±0.9)	-1.7 (±3.7)	13.8 ^a	13.9 ^a
5	31.2 (±1.9)	6.3 (±5.1)	29.0 ^a	28.7 ^a
6	k = 1.25 x 10 ⁻⁴ s ⁻¹ (84 °C)		27.4	27.5 ^b
7	k ≤ 5.0 x 10 ⁻⁵ (120 °C)		≥ 31.2 ^c	≥ 30.9
ΔH [‡] and ΔG [‡] values given in kcal/mol. ΔS [‡] values given in eu. ^a Extrapolated values. ^b Calculated with ΔS [‡] = -1.7 eu. ^c Calculated with ΔS [‡] = 6.3 eu.				

The trend for the relative rates of reductive elimination correlates well with the expected trends from both DFT calculation (Tables 2.7 and 2.8) as well as from the regression equation (Table 2.6). Complex **4** bearing the strongly σ -donating aryl ligand was found to have the smallest barrier to reductive elimination, while complex **7** bearing the weakly σ -donating chloride ligand was found to have the largest barrier. Complexes **5** and **6** that have ligands of relatively intermediate σ -donating ligands were found to have intermediate rates of reductive elimination (vs. complexes **4** and **7**).

2.7 Oxidative Addition of Methane to 4-Coordinate Ir(I) Complexes

We find that the principles of *trans* influence effects can also be more generally applied to 4-coordinate Ir(I) complexes. Oxidative addition to 4-coordinate 16-electron

Ir(I) complexes is well known in the literature.^{13,63-67} Upon applying the same 2-variable linear regression analysis method to the oxidative addition of methane to 4-coordinate Ir(I) complexes, three regression equations were obtained, corresponding to the three possible 6-coordinate isomeric complexes (Table 2.10). The regression analysis of the two oxidative addition reactions that proceed in a *cis* fashion yield regression equations that have positive σ_X coefficients and negative π_X coefficients, which is consistent with the analysis of oxidative addition to 3-coordinate Ir(I). Analogously to the **3-T** square pyramidal geometry, the ligands of the 6-coordinate oxidative addition products may be considered again as interacting with sd^2 -hybridized orbitals that are oriented along the three metal-ligand bond axes. Less σ -donating X ligands favor oxidative addition, due to the presence of a strong *trans*-influence ligand (hydride or methyl) *trans* to the X ligand in the 6-coordinate product (3c-4e bonding interaction).

Table 2.10. Regression Equations Based on Constrained Geometries.

	regression equation	std. dev. of σ effects (kcal/mol)	std. dev. of π effects (kcal/mol)
$\begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir}-\text{NH}_3 + \text{CH}_4 \longrightarrow \begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir}-\text{CH}_3 \\ \\ \text{H}_3\text{N} \end{array} \end{array}$ cis addition H/NH₃ trans	$\Delta E_X = (44 \pm 7)\sigma_X + (-20 \pm 9)\pi_X + (-1 \pm 1)$ $R^2 = 0.686$	4.5	1.5
$\begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir}-\text{NH}_3 + \text{CH}_4 \longrightarrow \begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir}-\text{CH}_3 \\ \\ \text{H}_3\text{N} \end{array} \end{array}$ cis addition H/NH₃ cis	$\Delta E_X = (52 \pm 10)\sigma_X + (-31 \pm 13)\pi_X + (1 \pm 1)$ $R^2 = 0.683$	5.7	2.5
$\begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir}-\text{NH}_3 + \text{CH}_4 \longrightarrow \begin{array}{c} \text{PH}_3 \\ \\ \text{X}-\text{Ir}-\text{NH}_3 \\ \\ \text{H}_3\text{C} \end{array} \end{array}$ trans addition	$\Delta E_X = (-32 \pm 6)\sigma_X + (28 \pm 8)\pi_X + (2 \pm 1)$ $R^2 = 0.676$	3.4	2.2

The opposite preference is observed when oxidative addition proceeds in a *trans*-fashion. The σ_X coefficient is negative (-32), while the π_X coefficient is positive (28).

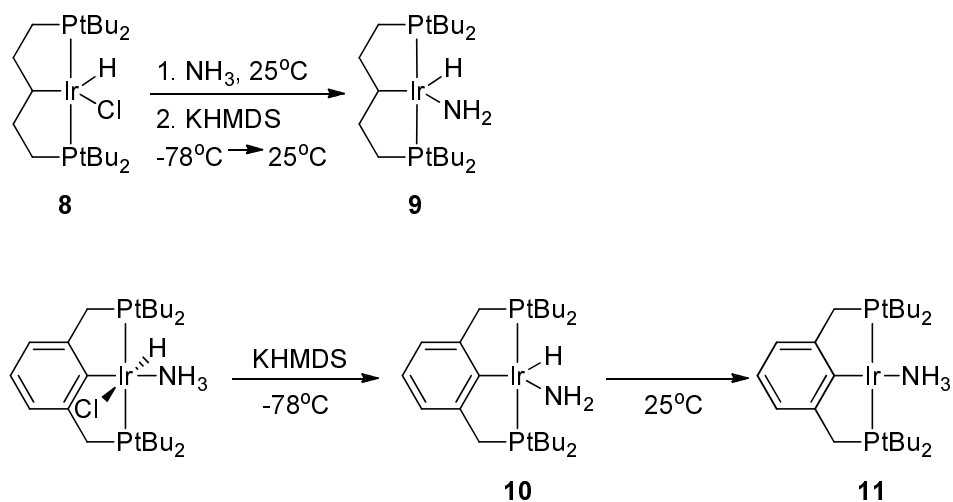
This reversal of preference, however, is still consistent with the orbital rationale given above for oxidative addition to 3-coordinate Ir(I) complexes; in the present case, the analogous 5-coordinate complex is the X-apical square pyramidal geometry. In the 6-coordinate case, the NH_3 group is positioned *trans* to the X ligand throughout the transformation, akin to the vacant coordination site in the analogous 3-/5-coordinate case. Again, we would not expect less σ -donating ligands to favor oxidative addition, and, indeed, the 2-variable linear regression nicely mirrors the 5-coordinate case. The coefficient for the σ_X parameter is again small and negative (Table 2.10), suggesting that a strong σ donor slightly favors oxidative addition.

2.8 Oxidative Addition of Ammonia to 3-Coordinate Ir(I) Complexes

In addition to C-H oxidative addition, we were interested in investigating the electronic effects influencing N-H addition, in particular NH_3 oxidative addition. There are relatively few examples of oxidative addition of ammonia that yield an amido hydride complex,¹⁵⁻²⁰ and only two examples of N-H oxidative addition of ammonia to a single, well-defined, late transition metal center have been reported – one from our group in 2005¹⁵ and one by Turculet and co-workers in 2009.¹⁶ In 2005, we reported that aliphatic PCP pincer Ir complex **8** reacts with ammonia and a base to give amido hydride **9** at 25 °C (Scheme 2.4).¹⁵ However, we found that when the aryl PCP pincer Ir amido hydride complex **10** was synthesized, it underwent isomerization to the 4-coordinate NH_3 coordination complex **11** at 25 °C. We had proposed that the more electron-donating aliphatic PCP pincer ligand of complex **9** should favor oxidative addition more than the aryl PCP pincer ligand of complex **10** in accordance with the conventional wisdom that a

more electron-rich metal center should favor oxidative addition. This hypothesis seemed to be confirmed by the recent report from the Turculet group in which oxidative addition of ammonia is observed with an iridium pincer complex featuring a highly σ -donating P-Si-P ligand.¹⁶ However, this reasoning is *contrary* to the conclusions of the work reported above for methane oxidative addition, where less σ -donating ligands should favor oxidative addition; thus, ammonia oxidative addition was investigated in the same manner as the methane addition presented above.

Scheme 2.4. Formation and Subsequent Reactivity of (PCP)Ir Amido Hydride Complexes.



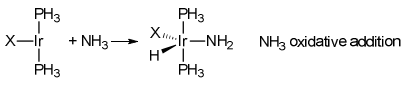
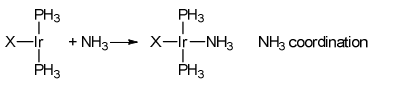
The reaction energies for oxidative addition of NH_3 to a variety of 3-coordinate Ir(I) complexes were calculated (Table 2.11),⁶⁸ and a 2-variable linear regression was performed to fit the σ_X and π_X parameters to the reaction energies (Table 2.12). We found that the coefficient of the σ_X parameter was positive (68.4), again indicating that oxidative addition is favored by less σ -donating ligands. Although this result appeared

contrary to the observed reactivity of complexes **9** and **10**, N-H oxidative addition of ammonia was then considered in the context relative to the commonly-favored NH_3 coordination.^{69,70}

Table 2.11. Calculated ΔE_X for NH_3 Oxidative Addition and Coordination to $(\text{PH}_3)_2\text{IrX}$.

X ligand	ΔE_{NH_3} oxidative addition	ΔE_{NH_3} coordination
BH_2^- , $\perp$	-7.3	-12.8
BH_2^- , $\parallel$	-15.6	-12.5
BH_3^{2-}	-9.1	-0.2
CF_3^-	-21.5	-25.2
CH_3^-	-20.1	-21.8
F^-	-35.4	-39.3
H^-	-22.9	-21.6
Li^-	-12.9	-4.3
NH_2^- , $\perp^1$	-24.2	-26.4
NH_2^- , $\parallel^2$	-19.2	-28.1
NH_3	-40.9	-53.1
NO_2^- , $\perp$	-21.2	-26.5
NO_2^- , $\parallel$	-22.1	-28.0
O^{2-}	-7.5	-11.9
OH^- , $\perp$	-27.9	-32.4
OH^- , $\parallel$	-27.8	-32.8
OMe^- , $\perp$	-27.3	-30.0
OMe^- , $\parallel$	-26.9	-32.3
Ph^- , $\perp$	-18.0	-21.3
pyrrolide, $\perp$	-29.6	-33.4
$\parallel$ = coplanar with P-Ir-P axis $\perp$ = orthogonal to P-Ir-P axis ¹ H-N-Ir-P dihedrals set to 58.5° ² H-N-Ir-P dihedrals set to 31.5°		

Table 2.12. Regression Equations for the Oxidative Addition and Coordination of Ammonia to *trans*-(PH₃)₂IrX Using Constrained Geometries.

	regression equation	std. dev. of σ effects (kcal/mol)	std. dev. of π effects (kcal/mol)
	$\Delta E_X = (68 \pm 9)\sigma_X + (27 \pm 13)\pi_X + (-21 \pm 1)$ $R^2 = 0.777$	7.3	2.2
	$\Delta E_X = (105 \pm 9)\sigma_X + (30 \pm 12)\pi_X + (-23 \pm 1)$ $R^2 = 0.897$	11.2	2.4

Reaction energies for the coordination of NH₃ to a variety of 3-coordinate Ir(I) complexes were calculated (Table 2.11), and a 2-variable linear regression was performed (Table 2.12). The π_X coefficient in the regression equation for NH₃ coordination (30) was equivalent within the error limits of the regression to the π_X coefficient of the regression equation for NH₃ oxidative addition (27). This suggests that π effects exert no significant control over the favorability of NH₃ coordination vs. oxidative addition. By contrast, a large difference is seen in the magnitude of the σ_X coefficients of the two regression equations. The coefficient of the σ_X parameter in the regression equation for NH₃ coordination was again positive (104.8), indicating that coordination is favored by less σ -donating ligands. However, the σ_X coefficient for the NH₃ coordinating regression equation has a *larger magnitude* than the σ_X coefficient for N-H oxidative addition (68.4). This suggests that while a more σ -donating ligand is unfavorable for oxidative addition, it is even more unfavorable for NH₃ coordination. As a result, complexes with a more σ -donating ligand like complex **9** or Turculet's PSiP-pincer Ir complex disfavor NH₃ coordination relative to N-H oxidative addition, to such an extent that the amido hydride complex is observed.

2.9 Summary

DFT calculations were performed on a series of Ir(I) complexes to investigate the electronic factors that affect the thermodynamics of C-H and N-H oxidative addition. Electronic substituent effects were decomposed into their σ and π effects and parameterized, and these parameters were used to fit the energies of oxidative addition of methane to a series of 3- and 4-coordinate Ir(I) complexes. Regression analysis indicates that oxidative addition to 3-coordinate Ir(I) complexes is generally favored in most cases by a less σ -donating ligand trans to the vacant coordination site, although this preference reverses in the special case where the geometry of the 5-coordinate product is square pyramidal with the X ligand in the apical position. The oxidative addition of methane to 4-coordinate Ir(I) was found to be analogous in its electronic preferences to the 3-coordinate case.

Given that conventional wisdom suggests that oxidative addition is favored by more electron-donating ligands, the surprising result that less σ -donating ligands are usually favorable for oxidative addition to Ir(I) suggests that oxidative addition should not be regarded simply as an oxidative event at the metal. Instead, an orbital rationale was proposed which invokes sd^2 -hybridized orbitals and the strong role of *trans* influence. Importantly, rates of reductive elimination from a series of isoelectronic Ir(III) phenyl hydride complexes were measured and found to be fully consistent with the computational analysis.

The regression analysis was extended to investigate NH_3 oxidative addition to 3-coordinate Ir(I) complexes. While a more σ -donating ligand is unfavorable for oxidative addition (analogous to methane oxidative addition), it is even more unfavorable for NH_3

coordination. This result explains the observed reactivity in which a more σ -donating ligand disfavors NH_3 coordination relative to N-H oxidative addition and hence affords the amido hydride complex.

2.10 Acknowledgments

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Chapter 3

DFT Computational Study of the Oxidative Addition of Chlorobenzene and Fluorobenzene to ^RPCPIr Complexes

Abstract

The oxidative addition reactions of chlorobenzene and fluorobenzene to ^HPCPIr, ^{Me}PCPIr, and ^{tBu}PCPIr were calculated. The thermodynamics of addition favor activation of the C-H bond proximal to the electron-withdrawing Cl atom (ΔG : *para* addition > *meta* addition > *ortho* addition). The kinetic barriers were also calculated and correlated with the relative steric interactions in the transition state leading to the oxidative addition product. Both calculations for thermodynamic and kinetic preferences were found to be in accord with experimental results.

3.1 Introduction

Regioselective C-H bond activation is an important area of investigation in organometallic chemistry. Many groups have utilized various strategies for achieving regioselective C-H bond activation.^{1,2} In a common strategy that was popularized by Murai, precoordination of a metal to a functional group of an arene can lead to the preferential activation of arene C-H bonds at positions *ortho* to the functional group.³

The Milstein and Ozerov groups have reported regioselective C-H bond activation of haloarenes by PNP-type pincer iridium complexes.^{4,5} Although Milstein has attributed the regioselectivity primarily to haloatom coordination to the metal center,⁶ it is likely that electronic effects of the haloatom on the neighboring C-H bonds of the arene also play a role in the observed regioselectivity.^{7,8} An electronic basis for regioselectivity follows principles first set forth by Bergman, which indicates the key role electronegativity has on the selectivity of C-H bonds by metal complexes.^{9,10}

Our group has likewise been interested in understanding the mechanism of C-H activation to metal complexes, in particular to ^tBuPCPIr pincer complexes (^tBuPCP = κ^3 -C₆H₃-2,6-(CH₂P^tBu₂)₂).¹¹⁻¹³ The low-valent, 14-electron complex is highly active to oxidative addition of C-H bonds and has been utilized for dehydrogenation and small molecule activation.¹⁴⁻¹⁸ In analogy to the reports from Milstein and Ozerov, our group has been interested in the kinetic and thermodynamic selectivity of haloarene addition to ^tBuPCPIr. While the experimental work has been performed by David Laviska,¹⁹ this chapter will detail computational investigations into this reaction.

3.2 Basis Set Determination

All calculations used DFT methodology²⁰ as implemented in the Gaussian 03 and 09 series of computer programs.^{21,22} We employed the Perdew–Burke–Ernzerhof exchange-correlation functional (PBE) in all calculations.²³ We applied the SDD relativistic, small-core effective potential and corresponding basis set to the Ir atom.²⁴ A survey of various basis set combinations was conducted for non-metal atoms to assess the optimal basis set for this study.²⁵⁻²⁷ In the interest of computational speed, the basis sets for atoms more distant from the metal center were generally made smaller than for atoms closer to the metal center. The various basis set combinations can be seen in Table 3.1.

Table 3.1. Basis set combinations used for DFT calculations.

	Basis Set 1	Basis Set 2	Basis Set 3
Ir	sdd	sdd	sdd
atoms bonded to Ir	6-31+G(d)	6-311+G(d,p)	6-311+G(d,p)
remaining PCP ligand C's	6-31G ^a	6-31G ^a	6-31G
PCP ligand H's	STO-3G	STO-3G	STO-3G
ClPh's H's, remaining C's, and Cl	6-31G ^b	6-311+G(d,p)	6-311+G(d,p)
number of basis functions	382	512	560

	Basis Set 4	Basis Set 5	Basis Set 6
Ir	sdd	sdd	sdd
atoms bonded to Ir	6-311+G(d,p)	6-311+G(d,p)	6-311+G(d,p) ^c
remaining PCP ligand C's	6-31G	6-31+G	6-31+G
PCP ligand H's	6-31G	6-31+G	6-31+G
ClPh's H's, remaining C's, and Cl	6-311+G(d,p)	6-311+G(d,p)	6-311++G(d,p)
number of basis functions	603	695	700

	Basis Set 7	Basis Set 8	Basis Set 9
Ir	sdd	sdd	sdd
atoms bonded to Ir	6-311++G(d,p)	6-311+G(d,p)	6-311+G(d,p)
remaining PCP ligand C's	6-31++G	6-31+G(d)	6-31+G(d,p)
PCP ligand H's	6-31++G	6-31+G(d)	6-31+G(d,p)
ClPh's H's, remaining C's, and Cl	6-311++G(d,p)	6-311+G(d,p)	6-311+G(d,p)
number of basis functions	743	810	939

^aSTO-3G for tBu primary C's. ^bSTO-3G for H's. ^c6-311++G(d,p) for hydride.

The energy of chlorobenzene oxidative addition to ^tBuPCPIr to yield the *ortho,trans*-isomer (Scheme 3.1) was calculated for each basis set. As can be seen in Table 3.2, increasing basis set size from Basis Set 1 to Basis Set 5 significantly influences ΔE , ΔH , and ΔG . However, further increases in basis set size beyond that of Basis Set 5 do not appear to significantly impact the calculated energies, despite requiring considerably longer computational time. As a result, Basis Set 5 was used as the basis set for all further calculations.

Scheme 3.1. Oxidative addition of chlorobenzene to ^tBuPCPIr to yield the *ortho,trans*-isomer.

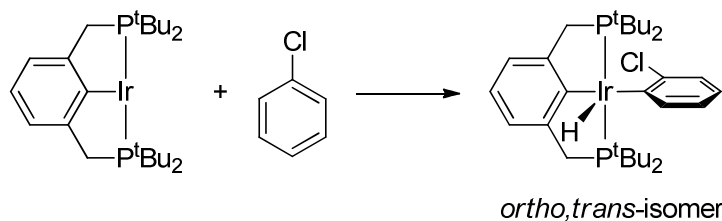


Table 3.2. Calculated parameters for the oxidative addition of chlorobenzene to ^tBuPCPIr to yield the *ortho,trans*-isomer.

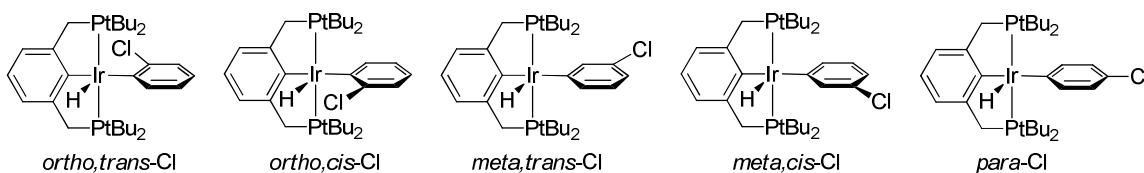
	ΔE (kcal/mol)	ΔH (kcal/mol)	ΔS (eu)	ΔG (kcal/mol)
Basis Set 1	-18.3	-19.1	-49.1	-4.5
Basis Set 2	-28.7	-31.3	-49.5	-16.5
Basis Set 3	-15.9	-16.5	-50.1	-1.6
Basis Set 4	-12.2	-12.3	-48.3	2.1
Basis Set 5	-9.8	-9.9	-47.5	4.3
Basis Set 6	-9.8	-9.8	-47.4	4.3
Basis Set 7	-9.9	-10.0	-47.5	4.2
Basis Set 8	-9.8	-9.8	-47.4	4.3
Basis Set 9	-9.8	-9.9	-47.1	4.1

3.3 Results

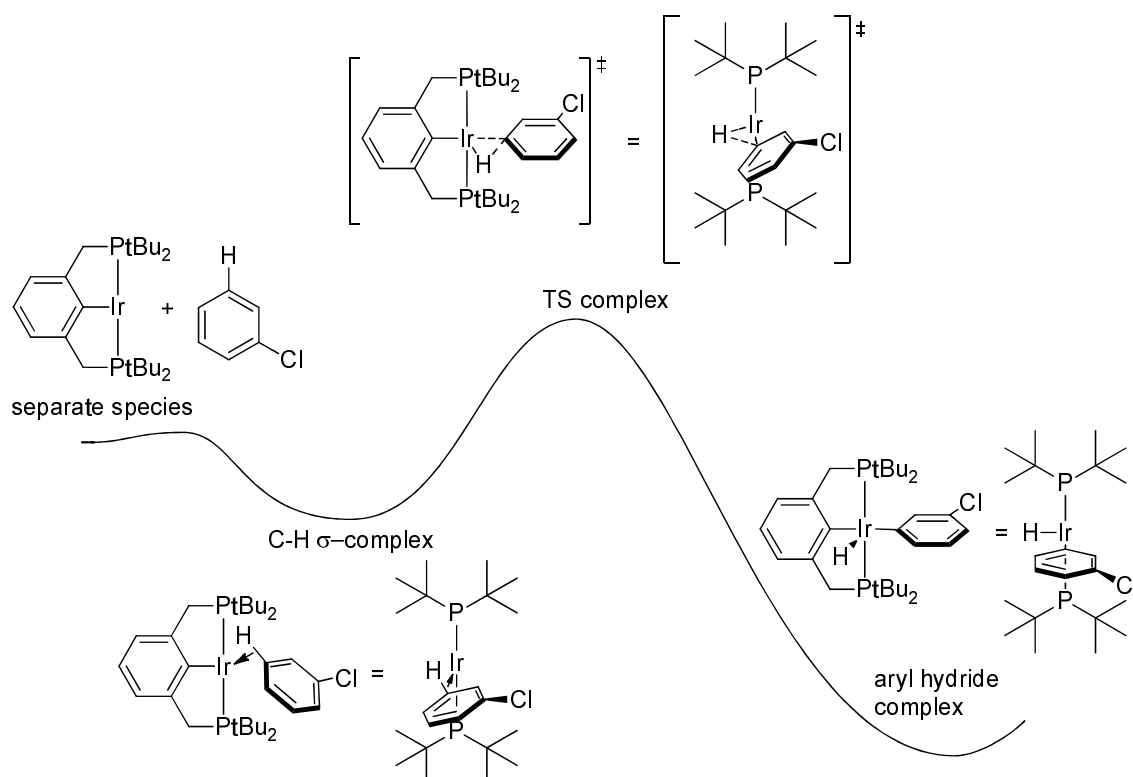
3.3.1 Chlorobenzene Activation

Addition of chlorobenzene to PCPIr can result in five possible aryl hydride isomers that vary in the location of the Cl atom and the relative orientation of the Cl atom and the hydride (Fig. 3.1). Addition is thought to proceed via initial C-H coordination to form a σ -complex, followed by oxidative cleavage to yield the aryl hydride product (Scheme 3.2).⁶ The barrier to formation of the σ -complex is generally considered to be very small or non-existent; this TS was not calculated. Similarly, the energies of C-H coordination are similar among the isomers, with the exception of the *ortho,trans* isomer, which could not be located. Geometry optimization of the *ortho,trans* isomer results in the migration of the Ir from the side of the Cl atom substituent to the opposite side, which corresponds to the *ortho,cis* isomer. It is unclear from computation whether the potential energy surface for the *ortho,cis* C-H coordination complex is extremely shallow, or whether that intermediate does not exist and formation of the *ortho,trans* isomer proceeds from the C-H complex that is more generally assigned to the *ortho,cis* isomer.

Figure 3.1. Isomers of the oxidative addition of chlorobenzene to PCPIr.



Scheme 3.2. Representative reaction coordinate diagram for the oxidative addition of chlorobenzene to $^{\text{tBu}}\text{PCPIr}$. The pathway that yields the *meta,trans*-isomer is shown.



The energies for the addition of chlorobenzene to $^{\text{H}}\text{PCPIr}$, $^{\text{Me}}\text{PCPIr}$, and $^{\text{tBu}}\text{PCPIr}$ were calculated (Table 3.3). The thermodynamics of chlorobenzene addition to $^{\text{H}}\text{PCPIr}$ and $^{\text{Me}}\text{PCPIr}$ favor activation of the C-H bond proximal to the electron-withdrawing Cl atom (ΔG : *para* addition > *meta* addition > *ortho* addition), analogous to previously reported results.^{10,28,29} The difference in energies between the *meta* isomers is very small ($\Delta\Delta G < 0.3$ kcal/mol), which is consistent with the Cl being directed away from the metal center and incurring minimal interactions with the metal center and PCP ligand. By contrast, the energy difference between the *ortho* isomers is considerably larger ($\Delta\Delta G > 4.4$ kcal/mol), consistent with interactions of the Cl atom occurring with the ligand

substituents or the Ir atom. For the *ortho* isomers, the *ortho,cis*-isomer is higher in energy than the *ortho,trans*-isomer, due to unfavorable steric interactions between the bulky Cl atom and the hydride. Additionally, the *ortho,trans*-isomer may benefit from interactions between the Ir atom and the Cl atom.

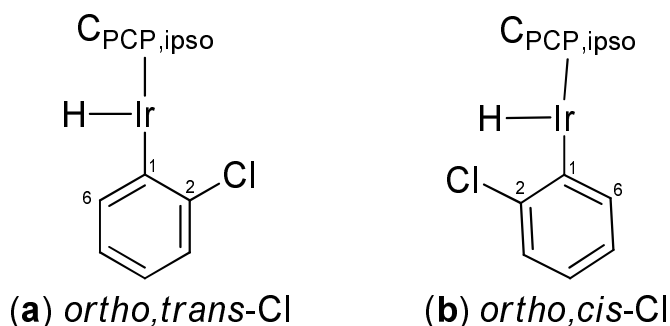
However, the calculated ΔG values for ^tBuPCPIr do not follow this trend, contrary to experimental results.¹⁹ While the calculated ΔG values for the *meta* and *para* isomers of chlorobenzene addition to ^tBuPCPIr follow the same trends observed for ^HPCPIr and ^{Me}PCPIr, the values for the *ortho* isomers for ^tBuPCPIr are much larger than expected, such that they are no longer the thermodynamically favored products. This discrepancy likely arises due to the calculations overstating the steric interactions between the Cl atom and the phosphine substituents of the *ortho* isomers, which are largest for ^tBuPCPIr.

Table 3.3. Calculated ΔG (kcal/mol) for the various complexes in the reaction coordinate for the oxidative addition of chlorobenzene to ^tBuPCPIr, ^{Me}PCPIr, and ^HPCPIr.

ΔG					
R = tBu	R4PCPIr + ClPh	C-H σ -complex	TS (barrier to OA)	aryl hydride	barrier to RE
2-ClPh-Cltrans	0.0	not located	23.4	4.2	19.2
2-ClPh-Clcis	0.0	11.7	18.1	5.5	12.6
3-ClPh-Cltrans	0.0	10.3	17.1	2.9	14.2
3-ClPh-Clcis	0.0	11.1	16.9	3.3	13.6
4-ClPh	0.0	11.4	18.1	4.2	13.9
R = Me	R4PCPIr + ClPh	C-H σ -complex	TS	aryl hydride	barrier to RE
2-ClPh-Cltrans	0.0	not located	7.5	-10.4	17.9
2-ClPh-Clcis	0.0	2.7	3.6	-6.0	9.6
3-ClPh-Cltrans	0.0	3.2	2.1	-4.5	6.6
3-ClPh-Clcis	0.0	3.4	2.3	-4.2	6.5
4-ClPh	0.0	3.5	2.7	-2.8	5.5
R = H	R4PCPIr + ClPh	C-H σ -complex	TS	aryl hydride	barrier to RE
2-ClPh-Cltrans	0.0	not located	4.6	-7.9	12.5
2-ClPh-Clcis	0.0	1.7	3.1	-2.7	5.8
3-ClPh-Cltrans	0.0	0.3	1.4	-1.2	2.6
3-ClPh-Clcis	0.0	0.4	1.2	-1.3	2.5
4-ClPh	0.0	0.7	1.8	-0.4	2.2

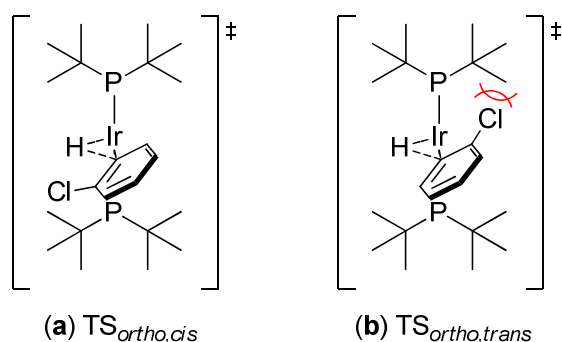
The differences in steric interactions between the *ortho,cis*-isomer and the *ortho,trans*-isomer can be seen in the DFT calculated geometries of the 5-coordinate aryl hydride complexes (Fig. 3.2). The *ortho,trans*-isomer displays a square pyramidal geometry. The aryl group of the *ortho,trans*-isomer displays normal coordination; the angles of the two carbons (C2, C6) ortho to the ipso carbon (C1) relative to the Ir atom are essentially identical (124.1° and 123.3° , respectively). By contrast, the *ortho,cis*-isomer displays rotation of the aryl group consistent with the presence of steric interactions between the chlorine atom and the hydride. The aryl group displays rotation about the ipso carbon (C1) such that the Cl atom is found farther away from the hydride. The angles Ir-C2-C6 (129.5°) and Ir-C1-C6 (117.9°) clearly illustrate this rotation. Additionally, the distance between the hydride and the chlorine atom ($2.588 \text{ \AA}$) is smaller than the sum of the van der Waals radii for hydrogen and chlorine ($2.95 \text{ \AA}$), suggesting steric interactions between the atoms.³⁰

Figure 3.2. Abbreviated DFT-optimized geometries of *ortho,trans*-Cl (**a**) and *ortho,cis*-Cl (**b**) complexes. Selected distances ($\text{\AA}$) and angles ($^\circ$): (**a**) $C_{\text{PCP,ipso}}\text{-Ir-H}$, 89.0; H-Ir-C1 , 89.0; Ir-C1-C2 , 124.1; Ir-C1-C6 , 123.3; Ir-Cl , 3.441. (**b**) $C_{\text{PCP,ipso}}\text{-Ir-H}$, 100.8; H-Ir-C1 , 84.7; Ir-C1-C2 , 129.5; Ir-C1-C6 , 117.9; Ir-Cl , 2.588.



Kinetically, the transition state leading to the *ortho,cis*-isomer is lower in energy than the transition state leading to the *ortho,trans*-isomer. This result can be rationalized by examining the approach trajectory of the metal center to the *ortho* C-H bond. As shown in Figure 3.3, a trajectory in which the Ir atom approaches the C-H bond on the side opposite to the Cl substituent will lead to the *ortho,cis*-isomer; conversely, a trajectory in which the Ir atom approaches the C-H bond on the same side as the Cl substituent will lead to the *ortho,trans*-isomer. In TS_{*ortho,cis*}, the Cl atom is directed farther away from the metal center than in TS_{*ortho,trans*}, which results in a decrease in unfavorable steric interactions between the Cl atom and the phosphine substituents of the PCP ligand. Comparing ^HPCPIr, ^{Me}PCPIr, and ^{tBu}PCPIr, the bulk of the phosphine substituents successively increases, and the $\Delta\Delta G^\ddagger$ between the transition states leading to the two *ortho* isomers correspondingly increases.

Figure 3.3. Transition state interactions leading to (a) the *ortho,cis*-isomer and (b) the *ortho,trans*-isomer.



Presumably, interconversion of isomers proceeds via reductive coupling to give the C-H coordination complex, whereupon the complex decoordinates or “walks” along

the chlorobenzene ring to another C-H bond.³¹⁻³⁴ Direct interconversion of isomers via rotation of the aryl ring about the Ir-ipsoC bond was calculated to be too high in energy to be viable ($\Delta G^{\ddagger}_{ortho,cis \rightarrow ortho,trans} = 41.3$ kcal/mol).

Coordination of chlorobenzene to 3-coordinate PCPIr through the Cl atom was also calculated for ^tBuPCPIr. While the energy of Cl coordination is calculated to be lower than the formation of the C-H coordination complex ($\Delta G = 6.5$ kcal/mol vs. 11 kcal/mol), oxidative addition is still considerably more favorable than Cl coordination, which suggests that Cl coordination may be kinetically relevant but not thermodynamically relevant. Experimental confirmation of this complex is likely to be difficult, since the Cl coordination complex is expected to be transient and would lack the diagnostic hydride signal that accompanies C-H oxidative addition.

3.3.2 Fluorobenzene Activation

The oxidative addition of fluorobenzene to ^HPCPIr, ^{Me}PCPIr, and ^tBuPCPIr was calculated (Table 3.4). Again, the C-H coordination complex leading to the *ortho,trans*-isomer was not located for any of the three metal-ligand complexes calculated. Additionally, the transition state for the *ortho,trans*-isomer in the ^tBuPCPIr complex was not located.

Table 3.4. Calculated ΔG (kcal/mol) for the various complexes in the reaction coordinate for the oxidative addition of fluorobenzene to $^t\text{BuPCPIr}$, $^{\text{Me}}\text{PCPIr}$, and $^{\text{H}}\text{PCPIr}$.

ΔG (kcal/mol)						
R = tBu	R4PCPIr + FPh	C-H σ -complex	TS (barrier to OA)	aryl hydride		barrier to RE
2-FPh-Ftrans	0.0	not located	18.5	0.4		18.1
2-FPh-Fcis	0.0	11.3	17.5	3.3		14.2
3-FPh-Ftrans	0.0	9.8	17.1	4.5		12.6
3-FPh-Fcis	0.0	10.7	17.6	4.3		13.3
4-FPh	0.0	10.7	18.0	5.0		13.0

R = Me	R4PCPIr + FPh	C-H σ -complex	TS (barrier to OA)	aryl hydride		barrier to RE
2-FPh-Ftrans	0.0	not located	4.6	-8.0		12.6
2-FPh-Fcis	0.0	3.4	1.6	-6.4		8.0
3-FPh-Ftrans	0.0	1.6	2.3	-3.6		5.9
3-FPh-Fcis	0.0	3.6	2.8	-3.6		6.4
4-FPh	0.0	3.8	4.8	-2.7		7.5

R = H	R4PCPIr + FPh	C-H σ -complex	TS (barrier to OA)	aryl hydride		barrier to RE
2-FPh-Ftrans	0.0	0.1	not located	-4.8		#VALUE!
2-FPh-Fcis	0.0	0.1	0.9	-3.7		4.6
3-FPh-Ftrans	0.0	0.3	1.8	-1.1		2.9
3-FPh-Fcis	0.0	0.4	1.6	-1.0		2.6
4-FPh	0.0	0.7	2.6	0.4		2.2

The general trends for the thermodynamics of fluorobenzene oxidative addition proceed in exactly the same fashion as seen for chlorobenzene. *Ortho* addition is more favorable than *meta*, which is more favorable than *para* addition. The *ortho,trans* isomers were calculated to be lower in energy than the *ortho,cis* isomers.

Kinetically, the barriers for fluorobenzene oxidative addition also correlate with the extent of steric interactions at the transition state. The fluorine atom is smaller than chlorine ($R_{\text{F, van der Waals}} = 1.47 \text{ \AA}$ vs. $R_{\text{Cl, van der Waals}} = 1.75 \text{ \AA}$) and thus suffers fewer unfavorable steric interactions with the phosphine substituents of the pincer ligand than the corresponding chlorobenzene complexes.³⁰ As such, the kinetic barriers for the oxidative addition of fluorobenzene were smaller than for the analogous chlorobenzene oxidative addition, but remain in the same relative order. This result serves to further

emphasize the role of steric interactions in determining the kinetic barrier to oxidative addition.

3.3.3 Comparison to Experimental Data

The calculated results were found to be in complete agreement with experimental data.¹⁹ Experiments performed by David Laviska in our lab demonstrated that the *ortho* isomers were thermodynamically more favorable than the *meta* and *para* isomers. Of the *ortho* isomers, the less favorable kinetic product (*ortho,trans*) was found to be the more favorable thermodynamic product. Assignment of the isomers was confirmed through a series of NMR experiments, which showed possible metal-halide interactions for the *ortho,trans*-isomers.

3.4 Summary

The oxidative addition of chlorobenzene and fluorobenzene to ^HPCPIr, ^{Me}PCPIr, and ^{tBu}PCPIr were calculated. The thermodynamics of addition were found to favor activation of the C-H bond proximal to the electron-withdrawing Cl atom (ΔG : *para* addition > *meta* addition > *ortho* addition). The kinetic barriers were also calculated and correlated with the relative steric interactions in the transition state leading to the oxidative addition product. Both calculations for thermodynamic and kinetic preferences were in accord with experimental results.

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Chapter 4

Investigation of Bonding and Through-Space Effects on CO Stretching Frequencies

Abstract

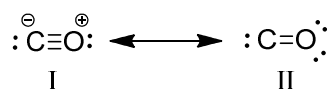
Calculations were performed to investigate the contributions of backbonding and through-space effects on the CO stretching frequency. CO stretching frequencies for a series of $\text{Ni(CO)}_3\text{L}$ complexes were calculated using DFT calculations. NBO analysis of these complexes yielded parameters that reflected backbonding to the π^* orbitals of the CO ligands and polarization of the π^b orbitals of the CO ligands. We found that a linear two-variable model fit the data better than the traditional one-variable model of solely back-bonding effects. A close look at rotamers of anisoyl phosphine complexes highlighted the dominant effect of polarization in some cases. In the course of our investigation, we also calculated the effects of a point charge on free CO, which was consistent with previous work.

4.1 Introduction

Carbon monoxide C-O stretching frequencies (ν_{CO}) have long been used to assess the electronic environment of a metal center in organometallic complexes. The perturbation of C-O stretching frequencies has been traditionally rationalized as a result of $\text{M} \rightarrow \text{CO}$ π -back-bonding, where more electron-rich metal centers exhibit a greater extent of π -back-bonding and thus induce a decrease in ν_{CO} .¹ As such, ν_{CO} has been used as a parameter in the determination of several ligand electronic series.²⁻⁵ Tolman parameterized the electronic effects of phosphorus ligands using the frequency of the A_1 carbonyl vibrational mode of $\text{Ni}(\text{CO})_3\text{L}$ in CH_2Cl_2 ,² and this approach has been extended to different ligand types and complexes.^{3,4}

While Tolman defined the electronic effect as a change in molecular properties by through-bond interactions, several groups have investigated the perturbation of ν_{CO} by through-space effects.⁶⁻¹² Notably, their work has shown that placement of bound CO in an electrostatic field induces a change in ν_{CO} .¹⁰ These through-space effects can be most easily understood by looking at the nature of the bonding orbitals in free CO. The bonding orbitals of free CO are polarized toward the oxygen atom. Introduction of a positive charge near the carbon atom would oppose this polarization, increase the covalency of the molecule, and increase the value of the stretching force constant.⁶ When depicted as valence bond structures (Figure 4.1), a positive charge near the C-terminus should preferentially stabilize the triply-bonded resonance form (I).

Figure 4.1. Resonance forms of CO.



In the course of our group's work, we have found that some of our organometallic complexes exhibit C-O stretching frequencies that are not easily explained by traditional $M \rightarrow CO$ π -back-bonding rationales.¹³ Instead, we have found that a consideration of through-space effects gives a better *prima facie* explanation.¹³ Herein, we report calculations of several organometallic carbonyl complexes that aim to separate and quantify through-space and through-bond factors that influence ν_{CO} . The data suggests that while through-bond effects ($M \rightarrow CO$ π -back-bonding) are significant, through-space effects (electrostatic effects) are also significant and, in some cases, the dominant effects governing the perturbation of ν_{CO} .

4.2 Computational Methods

4.2.1 Computational Details

All calculations used DFT methodology¹⁴ as implemented in the Gaussian03, version C.02, series of computer programs.¹⁵ We have made use of the Perdew–Burke–Ernzerhof exchange-correlation functional (PBE).¹⁶ The relativistic, small-core ECP and corresponding basis sets of Dolg et al. (SDD model) were used for all metal atoms (Ir, Ni, Co, V, Cr).¹⁷ We used split valence plus polarization and diffuse functions 6-31+G(d) basis sets¹⁸⁻²¹ for all carbonyls and all atoms directly bonded to the metal center in organometallic complexes. Split valence plus polarization function 6-31G(d) basis sets were used for all remaining atoms. All complexes underwent initial geometry optimization and subsequent frequency calculation. To increase numerical accuracy, the complexes were then subjected again to geometry optimization using the analytical force constants obtained from the initial frequency calculation. Electronic population analysis

(natural bond order analysis^{22,23}) and a final frequency calculation were performed on the re-optimized geometries.

4.2.2 Natural Bond Orbital Analysis

In order to evaluate the separate contributions of through-space and through-bond effects, we utilized Natural Bond Orbital (NBO) analysis as implemented in the NBO 3.1 software package.^{22,23} Very generally speaking, NBO analysis proceeds by initially generating a basis set of atom-localized orbitals. This basis set of atomic orbitals is then used to generate localized electron-pair orbitals for Lewis-like bonding, antibonding, and lone-pair orbitals. In this manner, NBO analysis allows the determination of orbital occupancy (population analysis) as well as the determination of the percentage contribution of each atomic orbital that constitutes the natural bond orbital.

When using this computational model in the context of evaluating perturbations to the CO molecule, through-bond effects (namely π -back-bonding) should principally influence the occupancy of the carbonyl π^* orbitals. Complexes with greater π -back-bonding should see higher orbital occupancy values for the carbonyl π^* orbitals. Through-space effects (electrostatic effects) should induce changes in polarization and should be reflected in the atomic orbital composition of the bonding carbonyl π^b orbitals. Thus, in systems where through-space effects are the only factor, the orbital occupancies of the carbonyl π^b and π^* orbitals should remain constant (e.g. essentially 2.0 and 0.0, respectively, for free CO) while the percent-composition of the π^b orbitals coming from their constituent carbon and oxygen p-orbitals should change.

4.3 Calculation of Selected Tolman-type Complexes

A series of vibrational frequency and NBO calculations were performed on complexes of the general form $\text{Ni}(\text{CO})_3\text{L}$, where L is a two-electron donor ligand. These pseudo-tetrahedral complexes include many of the phosphine ligands used by Tolman in his review² and also include both anionic and cationic ligands. The calculated stretching frequencies (Table 4.1) show similar trends when compared to literature stretching frequencies, though the absolute values are about 25 cm^{-1} smaller. A similar computational method applied by Crabtree *et al.* shows a similar general trend, and their calculated values also deviate slightly from experimental values.³

Table 4.1. Computational Results for Ni(CO)₃L Complexes: Calculated and Experimental ν_{CO} Values and NBO Analysis.

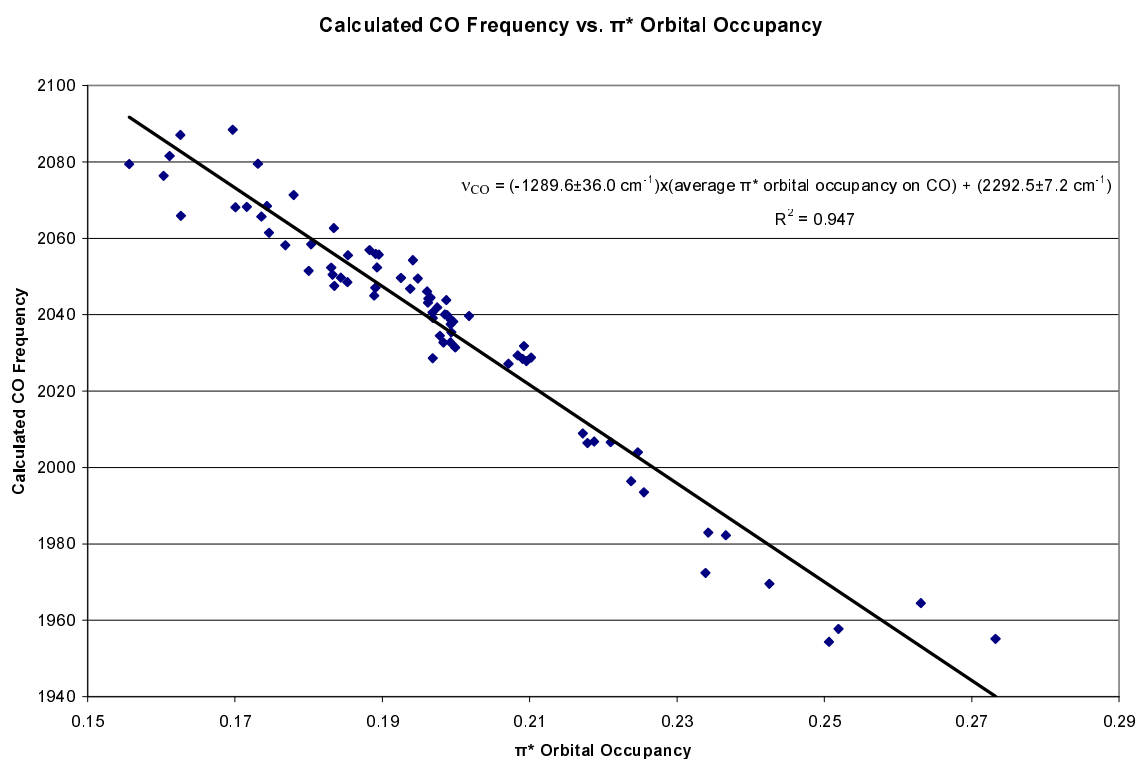
Ligand	Literature ν_{CO}^a (cm ⁻¹)	Calculated ν_{CO} (cm ⁻¹)	π^* Orbital Occupancy (backbonding effects)	% of π^* on the Carbon Atom (polarization effects)
PHu ₃	2056.1	2031.4	0.19989	25.68
PEt ₃	2061.7	2039.7	0.20176	25.47
P(NMe ₂) ₃	2061.9	2039.9	0.19880	25.52
PMe ₃	2064.1	2043.8	0.19868	25.50
PPH ₃	2068.9	2044.2	0.19626	25.53
P(vinyl) ₃	2069.5	2046.8	0.19379	25.57
NMe ₃	2067.6 ^b	2047.1	0.18905	25.63
PHMe ₂	2069.6	2049.5	0.19482	25.55
PPH ₂ OMe	2072.0	2046.1	0.19607	25.60
NH ₃	2073.3 ^b	2052.4	0.18926	25.64
PH ₂ Me	2075.3	2055.7	0.18952	25.62
PH ₂ Ph	2077.0	2055.9	0.18909	25.64
P(OMe) ₃	2079.5	2054.3	0.19414	25.74
PClPh ₂	2080.7	2055.6	0.18533	25.68
PMe ₂ CF ₃	2080.9	2056.9	0.18826	25.65
PH ₃	2083.2	2062.7	0.18341	25.69
PCl ₂ Ph	2092.1	2068.5	0.17435	25.85
PH ₂ F	2090.9	2071.4	0.17795	25.84
PHF ₂	2100.8	2079.5	0.17310	25.96
PCl ₃	2097 (2107) ^b	2081.6	0.16111	26.05
PF ₃	2110.8	2088.4	0.16970	26.04
PHPh ₂	2073.3	2049.6	0.19253	25.58
PPh ₂ (anisyl), <i>o</i> -OMe toward Ni	2066.1	2039.1	0.19685	25.41
PPh ₂ (anisyl), <i>o</i> -OMe away from Ni	2066.1	2040.6	0.19681	25.52
P(anisyl) ₃ , <i>o</i> -OMe, 0 OMe toward Ni	2058.3	2037.5	0.19928	25.47
P(anisyl) ₃ , <i>o</i> -OMe, 1 OMe toward Ni	2058.3	2035.4	0.19935	25.36
P(anisyl) ₃ , <i>o</i> -OMe, 2 OMe toward Ni	2058.3	2032.7	0.19829	25.24
P(anisyl) ₃ , <i>o</i> -OMe, 3 OMe toward Ni	2058.3	2028.6	0.19683	25.10
P(anisyl) ₃ , <i>m</i> -OMe, 0 OMe toward Ni		2043.2	0.19619	25.50
P(anisyl) ₃ , <i>m</i> -OMe, 1 OMe toward Ni		2041.9	0.19746	25.49
P(anisyl) ₃ , <i>m</i> -OMe, 2 OMe toward Ni		2040.1	0.19850	25.50
P(anisyl) ₃ , <i>m</i> -OMe, 3 OMe toward Ni		2038.2	0.19960	25.50
P(anisyl) ₃ with <i>p</i> -OMe	2066.1	2038.7	0.19926	25.46
IME (NHC)		2031.8	0.20922	25.33
IPr (NHC)	2051.5 ^c	2027.8	0.20955	25.18
ICy (NHC)	2049.6 ^c	2027.2	0.20711	25.43
IMes (NHC)	2050.7 ^c	2028.5	0.20904	25.24

Ligand	Literature ν_{CO} (cm ⁻¹)	Calculated ν_{CO} (cm ⁻¹)	π^* Orbital Occupancy (backbonding effects)	% of π^* on the Carbon Atom (polarization effects)
SiMe (NHC)		2032.8	0.19923	25.65
SiPr (NHC)	2052.2 ^c	2028.8	0.21020	25.23
SiMes (NHC)	2051.5 ^c	2029.3	0.20839	25.25
BiMe (NHC)		2034.5	0.19782	25.68
OH ₂		2065.7	0.17358	25.88
OMe ₂		2061.5	0.17461	25.82
OPh ₂		2065.9	0.16267	26.04
FMe		2076.4	0.16031	26.01
FPh		2079.5	0.15562	26.10
ClMe		2068.2	0.17159	25.83
ClPh		2088.1	0.17007	25.62
MeCN		2058.2	0.17883	25.54
MeNC		2058.4	0.18033	25.56
pyridine		2048.5	0.18526	25.62
pyridine with <i>o</i> -F		2051.5	0.18000	25.67
pyridine with <i>m</i> -F		2050.5	0.18326	25.67
pyridine with <i>p</i> -F		2049.7	0.18437	25.65
pyridine with <i>bis-m</i> -F		2052.4	0.18305	25.68
PhicycloB		2044.5	0.19656	25.52
PadamantB3		2047.6	0.18346	25.73
NbicycloB		2045.0	0.18888	25.63
CbicycloNH		1996.4	0.22376	25.10
PbicycloBH-		2004.0	0.22469	24.98
NbicycloBH-		2009.0	0.21719	24.78
CbicycloN-		1954.3	0.25060	24.55
Br ⁻		2006.8	0.21874	24.45
Cl ⁻		2006.4	0.21785	24.38
F ⁻		1993.5	0.22550	24.25
H ⁻		1964.5	0.26307	24.59
Ph ⁻		1972.4	0.23386	24.80
Me ⁻		1957.7	0.25189	24.52
NMe ₂ ⁻		1969.5	0.24254	24.35
MeO ⁻		1983.0	0.23423	24.26
OH ⁻		1982.3	0.23660	24.22
CN ⁻		2006.6	0.22098	24.70
Ni(CO) ₄ with 1 heavy CO		2087.0	0.16257	25.94
Co(CO) ₄ with 1 heavy CO		1955.2	0.27322	24.08

^a ref. 2, unless otherwise noted; ^b ref. 3; ^c ref. 5.

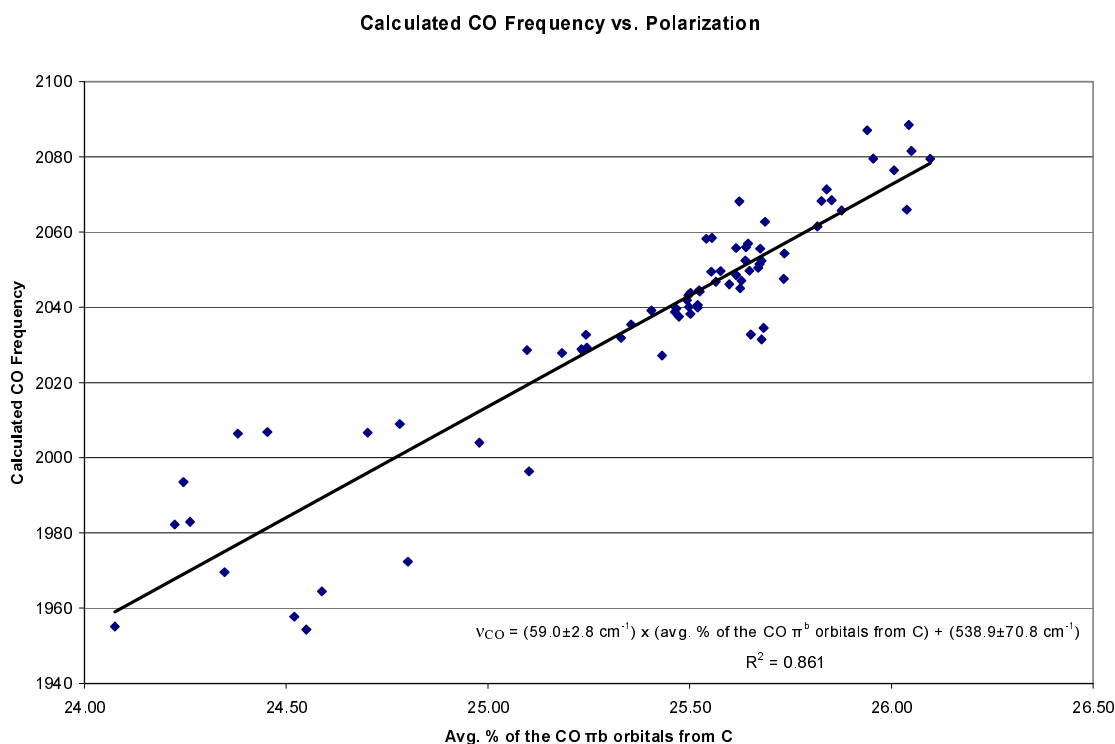
A plot of calculated ν_{CO} vs. average π^* orbital occupancy (Figure 4.2) does show a strong linear correlation between ν_{CO} and average π^* orbital occupancy. This plot, consistent with the Tolman-type backbonding explanation for perturbations to the CO stretching frequency, should be linear with a negative slope; as backbonding increases, the CO stretching frequency should decrease. The coefficient of determination for a least-squares one-variable linear regression ($R^2 = 0.947$) indicates a strong correlation between backbonding and CO stretching frequency.

Figure 4.2. Plot of calculated ν_{CO} vs. average CO π^* orbital occupancy for $\text{Ni}(\text{CO})_3\text{L}$ Complexes.



Similarly, the CO frequency is also expected to correlate with orbital polarization. Polarization was quantified by percent-composition of the CO π^b orbitals coming from their constituent carbon atom. A plot of calculated ν_{CO} vs. this measure of polarization (Figure 4.3) does show a linear correlation between ν_{CO} and average π^* orbital occupancy. While the coefficient of determination for a least-squares one-variable linear regression ($R^2 = 0.861$) is not high, it does indicate some correlation between polarization and CO stretching frequency.

Figure 4.3. Plot of calculated ν_{CO} vs. average percentage of CO π^b orbital from the C atom for $\text{Ni}(\text{CO})_3\text{L}$ Complexes.



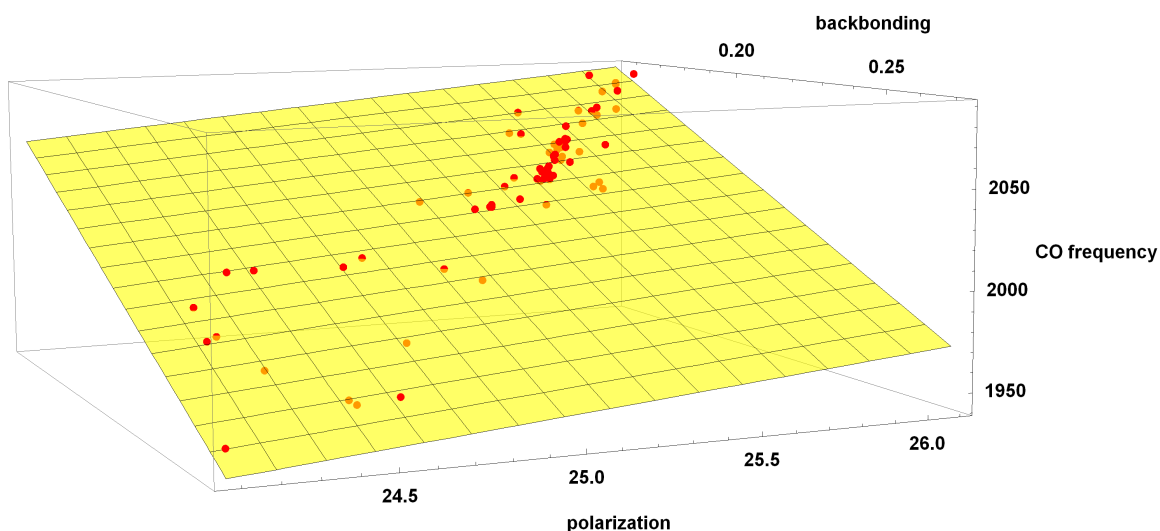
Phosphine ligands bearing anisoyl substituents highlight the contribution of through-space effects (Table 4.2). These ligands can exist in different rotamer conformations, where the methoxy moieties are oriented proximal or distal to the carbonyl groups. Within both the anisoyldiphenylphosphine and trianisoylphosphine series, the extent of back-bonding is relatively constant in both cases. By contrast, the polarization changes depending on the proximal or distal orientation of the methoxy moieties to the carbonyl groups. Given more methoxy moieties oriented farther away from the carbonyl groups, the extent of polarization toward the carbon increases, and ν_{CO} similarly increases.

Table 4.2. NBO data for Selected $\text{Ni}(\text{CO})_3\text{L}$ Complexes.

Ligand	Calculated ν_{CO} (cm^{-1})	π^* Orbital Occupancy (back-bonding effects)	% of π^b on the Carbon Atom (polarization effects)
$\text{PPh}_2(\text{anisoyl})$, o-OMe away from Ni	2040.6	0.19681	25.52
$\text{PPh}_2(\text{anisoyl})$, o-OMe toward Ni	2039.1	0.19685	25.41
$\text{P}(\text{anisoyl})_3$, o-OMe, 0 OMe toward Ni	2037.5	0.19928	25.47
$\text{P}(\text{anisoyl})_3$, o-OMe, 1 OMe toward Ni	2035.4	0.19935	25.36
$\text{P}(\text{anisoyl})_3$, o-OMe, 2 OMe toward Ni	2032.7	0.19829	25.24
$\text{P}(\text{anisoyl})_3$, o-OMe, 3 OMe toward Ni	2028.6	0.19683	25.10

Instead of separate treatment of polarization and backbonding parameters with calculated CO stretching frequencies, a two-variable least-squares fit was performed in which both parameters were simultaneously fit to the data set comprised of calculated CO stretching frequencies (Figure 4.4). The coefficient of determination for the regression plane of best-fit (Figure 4.4, $R^2 = 0.956$) suggests that the two-variable fit is better than either of the one-variable fits.

Figure 4.4. Two-variable linear regression fit of calculated CO stretching frequency to polarization and backbonding parameters for Ni(CO)₃L Complexes.



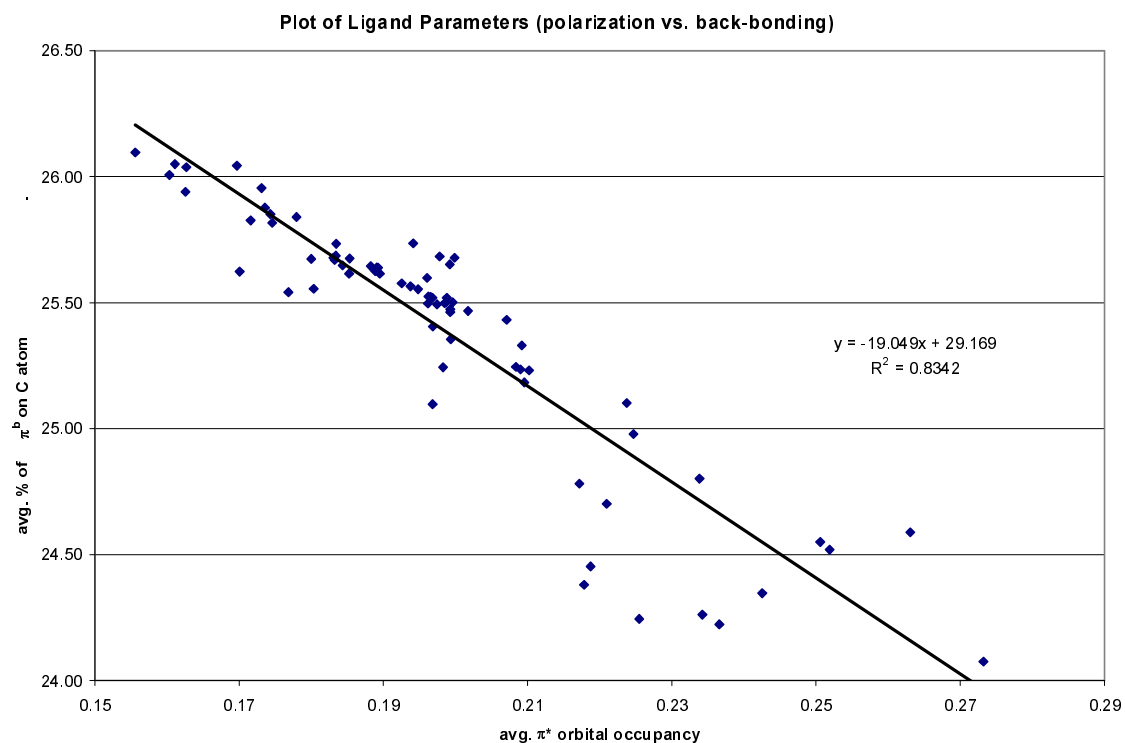
$$\nu_{\text{CO}} = (-1001.0 \pm 80.8 \text{ cm}^{-1}) \times (\text{avg } \pi^* \text{ orbital occupancy on CO}) + (15.1 \pm 3.9 \text{ cm}^{-1}) \times (\text{average percentage of the CO } \pi^b \text{ orbitals lying on the C atom}) + (1850.4 \pm 113.3 \text{ cm}^{-1})$$

Because the polarization and the backbonding parameters refer to widely different properties, it was unclear from inspection of the regression equation what the relative contributions of polarization and backbonding were on the calculated CO stretching frequencies over the set of ligands used. To provide a sense of relative contributions, a standard deviation was calculated for both polarization and backbonding effects by first multiplying the sets of polarization and backbonding parameters by the regression coefficients for the respective parameters. The resulting two sets of values correspond to the frequency contribution of each effect for each ligand on the calculated CO stretching frequency. The standard deviation of each set was then calculated, which reflected the relative significance of polarization and backbonding effects on the perturbations to the CO stretching frequency. The standard deviation of backbonding effects was calculated

to be 23.8 cm^{-1} , while the standard deviation of polarization effects was calculated to be 7.5 cm^{-1} , suggesting that backbonding effects are approximately 3 times more significant for the perturbations to CO stretching frequency over the set of calculated ligands.

Although both backbonding and polarization parameters independently correlate with CO stretching frequency, the perturbations to CO stretching frequency may not be dependent on both variables. If polarization correlates with backbonding, one or the other may be the underlying factor responsible for perturbations to CO stretching frequency. A plot of polarization vs. backbonding (Figure 4.5) does show a rough correlation between the two parameters. While there are a few points that lie off the best-fit line, two quadrants of the graph are clearly under-populated. Ligands that exhibit high backbonding and high polarization of the CO π^b orbital toward the C atom (upper right quadrant) and ligands that exhibit low backbonding and low polarization of the CO π^b orbital toward the C atom (lower left quadrant) are not represented or under-represented. In contrast, ligands are generally aligned along the line connecting the quadrant representing high backbonding and low polarization of the CO π^b orbital toward the C atom (upper left) and its opposite quadrant (lower right). While this arises from the specific ligand set, it is unsurprising as ligands that polarize the CO toward the C atom are usually relatively more electronegative, which decreases the propensity for that particular ligand-metal complex to exhibit backbonding. Future investigations to identify such ligands that lie in the under-represented regimes would further help to support the two-variable regression and more strongly establish independent correlation of the two parameters with CO stretching frequency.

Figure 4.5. Plot of average percentage of CO π^b orbital from the C atom vs. average CO π^* orbital occupancy for Ni(CO)₃L Complexes.

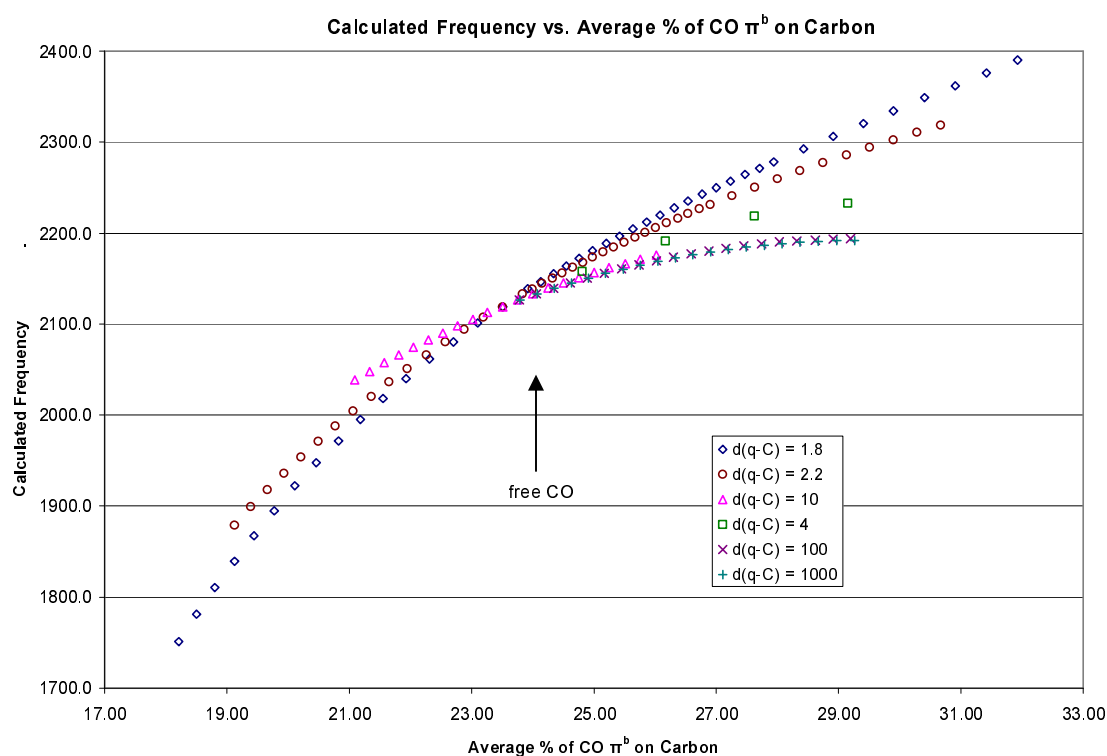


4.4 Perturbation of CO with a Point Charge

The stretching frequencies of free CO in the presence of a point charge were also computed. Assuming that the geometry of the M-(CO)₃ fragment is relatively constant across all complexes, through-space perturbations to ν_{CO} can be roughly approximated as the effect of a point charge at a fixed distance away from the CO; different overall perturbations are approximated as different point charges. Several series of data were generated for different metal-point charge distances by varying the magnitude of the charges at a particular distance (Figure 4.6). Moving left to right in Figure 4.6 corresponds to a greater polarization of the π^b orbitals toward the carbon atom, and

variation of ν_{CO} with the change in polarization clearly shows that stretching frequency is perturbed by the presence of a point charge, which is consistent with previous work from our group.⁶ While the plot is roughly linear across the range of polarization for Tolman's ligands (25.13% to 25.82%), deviations from linearity are observed at high polarization away from free CO. The plots change in the curvature as the distance of the point charge from the CO changes (i.e. $d(\text{q-C}) = 2.2 \text{ \AA}$ vs. $d(\text{q-C}) = 1000 \text{ \AA}$). This result is not unexpected, since the carbon and oxygen atom lie at different distances from the point charge and thus the relative electrostatic field felt by them scales differently as well.

Figure 4.6. Plot of calculated ν_{CO} vs. the average percentage of the CO π^{b} orbitals lying on the carbon atom for free CO in the presence of a point charge.



4.5 Summary

Calculations were performed to investigate the contributions of through-space effects on CO stretching frequency. We found that a linear two-variable model fit the data better than the traditional one-variable model of solely back-bonding effects. A close look at the data gave a few examples that highlighted the dominant effect of polarization in some cases. In the course of our investigation, we also calculated the effects of a point charge on free CO, which was consistent with previous work.

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Chapter 5

Kinetic Study of (^tBuPCP)Ir and (^tBuPOCOP)Ir

Complexes: Olefin Coordination and Isomerization

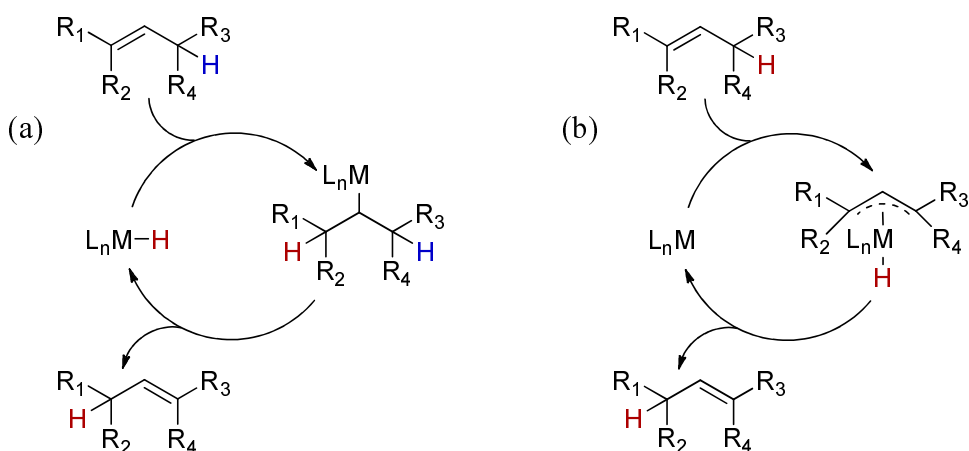
Abstract

Olefin isomerization is particularly relevant to the selectivity of alkane dehydrogenation and alkane metathesis reactions. In our investigations to better understand the mechanism of olefin isomerization, the reaction kinetics of olefin coordination to (^tBuPCP)Ir and (^tBuPOCOP)Ir were quantified and discussed in the context of olefin isomerization. Additionally, the (^tBuPOCOP)Ir-catalyzed olefin isomerization of 1-octene was investigated and found to show an apparent 2nd order dependence on 1-octene concentration.

5.1 Introduction

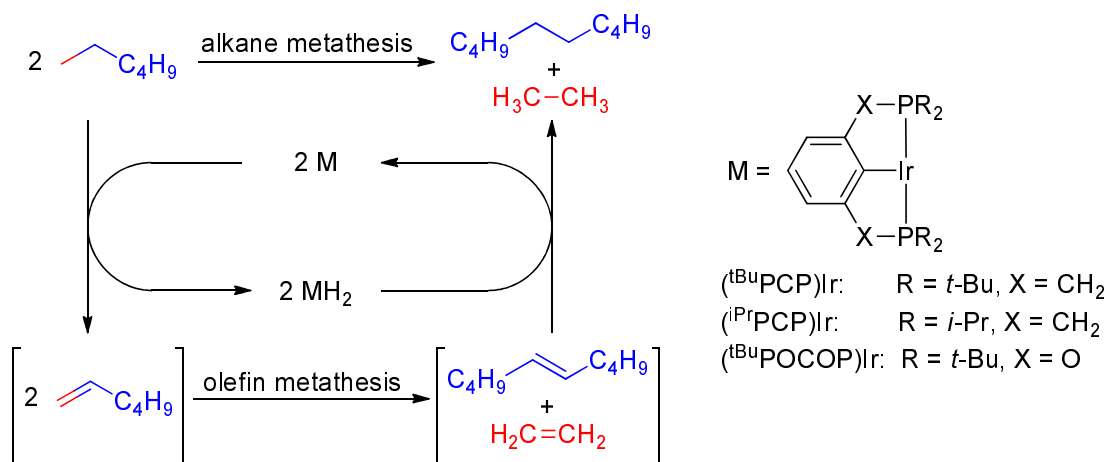
Examples of transition metal-catalyzed olefin isomerization are widespread and play a key role in numerous important chemical processes.¹⁻⁹ The mechanism most commonly accepted for olefin isomerization involves initial addition of a metal-H bond across the olefin double bond. If the resulting metal alkyl has a β -carbon atom that is inequivalent to the carbon to which the hydride was added, β -elimination of hydrogen from that carbon will result in olefin isomerization (Scheme 5.1a). An alternative pathway, less commonly proposed and less well studied, involves the intermediacy of a π -allyl complex (Scheme 5.1b) through which olefin isomerization occurs via a formal 1,3-hydride shift.^{1,2,10-14} If a coordinatively unsaturated metal complex bears a metal-bound hydride, the hydride addition pathway is believed to be the preferred mechanism for olefin isomerization.¹

Scheme 5.1. Schematic illustration of the two mechanism classes proposed for olefin isomerization: (a) “hydride” mechanism, (b) π -allyl mechanism.



Olefin isomerization is particularly relevant to the selectivity of alkane dehydrogenation and alkane metathesis reactions. Iridium pincer catalysts, including (^RPCP)Ir (^RPCP = κ^3 -C₆H₃-2,6-(CH₂PR₂)₂) and (^RPOCOP)Ir (^RPOCOP = κ^3 -C₆H₃-2,6-(OPR₂)₂) have been found to effect alkane dehydrogenation. Of these, (^tBuPCP)Ir and (ⁱPrPCP)Ir complexes have been found to dehydrogenate *n*-alkanes with kinetic selectivity to form α -olefins.¹⁵ These alkane dehydrogenation catalysts, when coupled with a Schrock-type olefin metathesis catalyst, can yield alkane metathesis (Scheme 5.2). The alkane metathesis system might be expected to selectively produce ethane and C_{2n-2} species as shown in the example in Scheme 2 (metathesis of *n*-hexane to yield ethane and *n*-decane); in fact, AM of *n*-hexane generates a range of C₂ to C₁₅ *n*-alkanes.^{16,17} Significantly, the (^tBuPCP)Ir system gives moderate selectivity for the formation of *n*-decane (ca. 50 mol% of the C_n products where n>6), whereas the (^tBuPOCOP)Ir system gives an essentially stochastic distribution of *n*-alkanes.^{16,17} The most obvious explanation for the initial formation of C₃₋₅ and C₇₋₉ products from *n*-hexane is based upon isomerization/metathesis of the olefin intermediates prior to hydrogenation. A significant degree of isomerization of 1-alkenes has indeed been previously reported when pincer-Ir complexes are used for either acceptorless or transfer-dehydrogenation of *n*-alkanes.¹⁸ In consideration of these issues, we initiated a study of pincer-iridium catalyzed olefin isomerization with an emphasis on the comparison between the (^tBuPCP)Ir and (^tBuPOCOP)Ir systems.¹⁹

Scheme 5.2. Tandem catalytic alkane metathesis with pincer-ligated iridium complexes and olefin metathesis catalysts (shown for reaction of *n*-hexane)



A kinetic study of the isomerization of 1-octene catalyzed by (^tBuPCP)IrH₂ (**1**) was previously conducted by Soumik Biswas.¹⁹ Addition of 1-octene (100 mM) to **1** (5 mM) in either *n*-octane or *p*-xylene results in apparently quantitative conversion to (^tBuPCP)Ir(1-octene) within 10 min at 25 °C. The turnover frequency (*k*) for eq 1 in either solvent is 4.2 × 10⁻³ s⁻¹ at 125 °C (rate = *k*[(^tBuPCP)Ir], Δ*G*[‡] ~ 27.9 kcal/mol), suggesting that a “hydride” mechanism for olefin isomerization is not operative.²⁰ A zero-order dependence on [1-octene] is observed (Figure 5.1), which is consistent with an intramolecular π-allyl mechanism in which (^tBuPCP)Ir(1-octene) is the major resting state (as observed by NMR spectroscopy), and the rate-determining step lies within segments (a), (b), or (c) of the cycle indicated in Scheme 5.3. (We define these as “segments” of the cycle since each of them, and particularly (a) or (b), could involve more than one elementary reaction step).

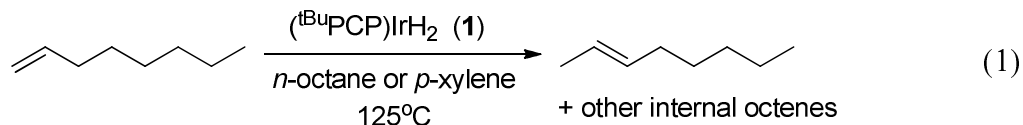
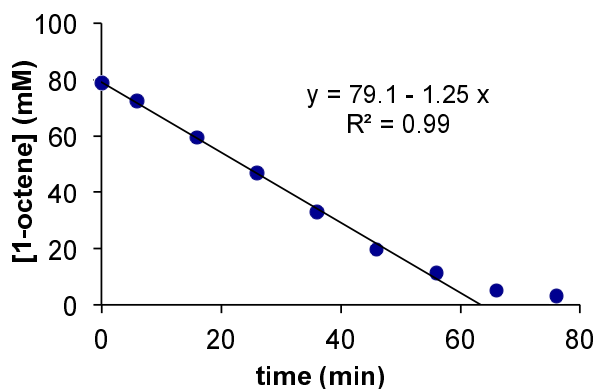
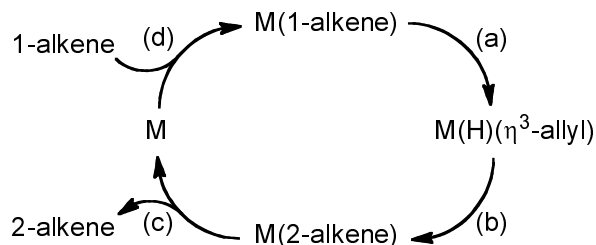


Figure 5.1. Catalytic isomerization of 1-octene to internal octenes by **1** (5 mM) at 125 °C in *n*-octane solvent.



Scheme 5.3. Schematic π -allyl pathway for 1-alkene isomerization with dissociative olefin exchange (detailed mechanism not specified).



These kinetic experiments were repeated with $(\text{t}^{\text{Bu}}\text{POCOP})\text{IrH}_2$ (**2**) as the catalyst precursor. As was the case with $(\text{t}^{\text{Bu}}\text{PCP})\text{IrH}_2$, $(\text{t}^{\text{Bu}}\text{POCOP})\text{Ir}(1\text{-octene})$ was formed rapidly and apparently quantitatively, and remained the major species in solution during the catalysis, as determined by *in situ* ^{31}P NMR spectroscopy. While no significant

difference in isomerization rates was found using *n*-octane as solvent vs. *p*-xylene, the reaction kinetics showed a clear positive dependence on 1-octene concentration. This result is discussed below in greater detail.

In this chapter, I will discuss my contributions to the study published as reference 20, with regards to quantifying the kinetics of olefin coordination to (^tBuPCP)Ir and (^tBuPOCOP)Ir as well as discuss olefin isomerization by (^tBuPOCOP)Ir.

5.2 Results and Discussion

5.2.1 Kinetics of Olefin Dissociation from (*pincer*)Ir(*alkene*) Complexes

Consistent with Scheme 5.3, loss of alkene from (^tBuPCP)Ir(*alkene*) is rapid and dissociative. Exchange spectroscopy (EXSY) experiments reveal that at 25 °C the rate of 1-hexene dissociation is 0.51 s⁻¹ and independent of the concentration of added 1-hexene. An Eyring plot based on rates measured at temperatures between 20 °C and 46 °C affords activation parameters $\Delta H^\ddagger = 21.4 \pm 0.8$ kcal/mol and $\Delta S^\ddagger = 12 \pm 3$ eu for loss of 1-hexene (Figure 5.2). Dissociation of *trans*-2-hexene, as would be expected of a dissociative process with a bulkier ligand, is even faster; at 4 °C the rate is 3.1 s⁻¹, independent of the concentration of added *trans*-2-hexene, with activation parameters determined to be $\Delta H^\ddagger = 15.4 \pm 0.4$ kcal/mol and $\Delta S^\ddagger = -0.7 \pm 1.5$ eu (from rates measured at temperatures ranging from -17 °C to 6 °C, Figure 5.3). Extrapolation to 125 °C yields a value (2×10^4 s⁻¹) that is orders of magnitude greater than the overall rate of isomerization. Thus, the rate determining step of the cycle indicated in Scheme 5.3 lies within segments (a) or (b).

Figure 5.2. Eyring plot for the rate of dissociative 1-hexene exchange of (^tBuPCP)Ir(1-hexene) with free 1-hexene in *p*-xylene-*d*₁₀ in the temperature interval 20 °C to 46 °C.

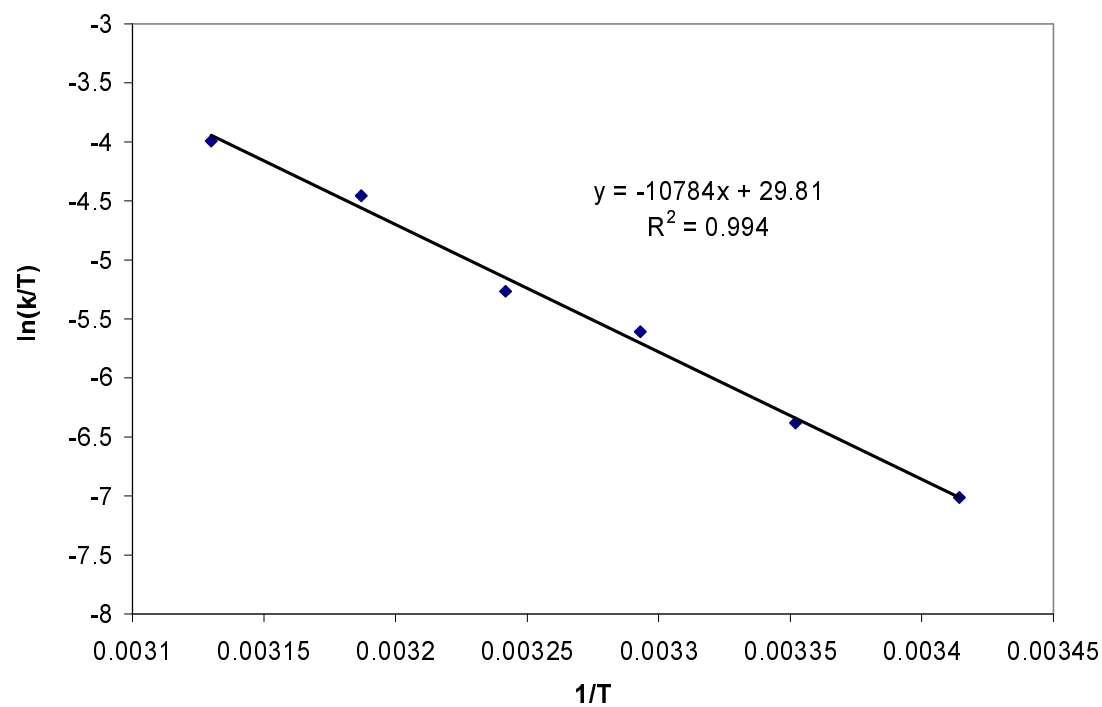
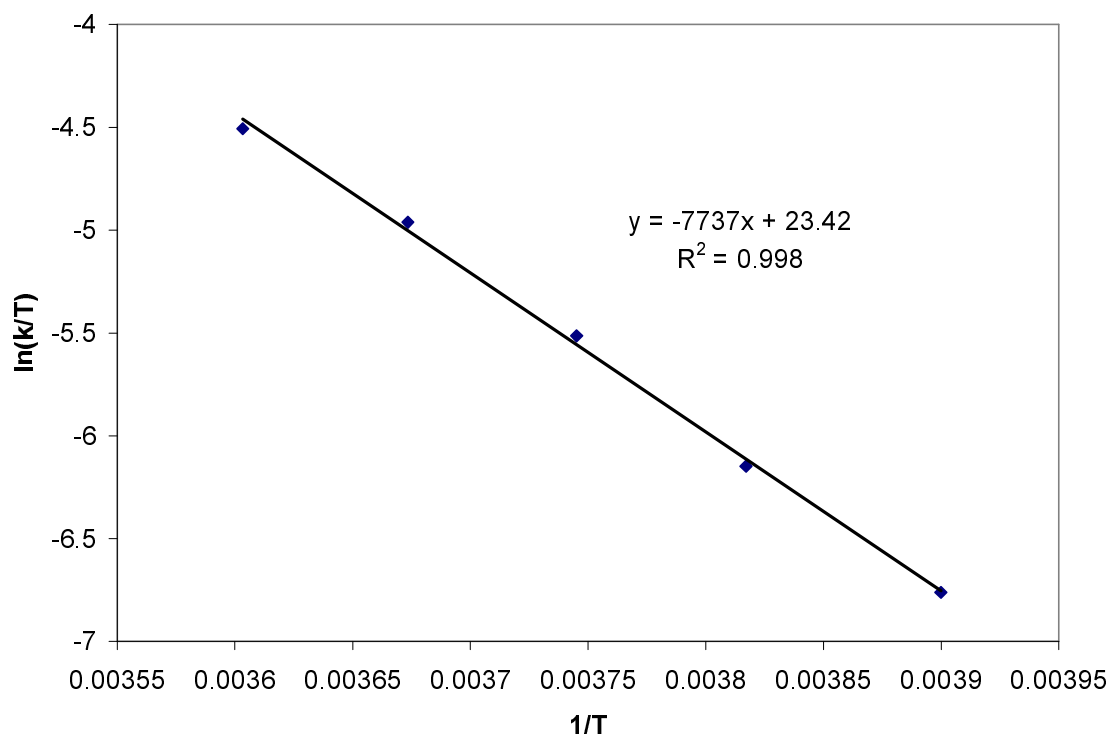


Figure 5.3. Eyring plot for the rate of dissociative *trans*-2-hexene exchange of $(^t\text{BuPCP})\text{Ir}(\text{trans-2-hexene})$ with free *trans*-2-hexene in mesitylene- d_{12} in the temperature interval -17 °C to 6 °C.



Reaction kinetics for self-exchange for $(^t\text{BuPOCOP})\text{Ir}(\text{olefin})$ were also determined by EXSY spectroscopy. Similar to loss of alkene from $(^t\text{BuPCP})\text{Ir}(\text{alkene})$, loss of alkene from $(^t\text{BuPOCOP})\text{Ir}(\text{alkene})$ is rapid and dissociative. From Eyring plots shown in Figures 5.4 and 5.5, the activation enthalpy for $(^t\text{BuPOCOP})\text{Ir}(\text{olefin})$ was found to be 29.4 ± 1.2 and 26.0 ± 1.2 kcal/mol for 1-hexene and *trans*-2-hexene, respectively, while the respective activation entropies were found to be 15 ± 3 and 17 ± 3 eu (from rates measured at temperatures between 107 °C and 126 °C, and 57 °C to 79 °C, respectively). These olefin dissociation rates for $(^t\text{BuPOCOP})\text{Ir}(\text{olefin})$ are in fact much slower than those of the corresponding $(^t\text{BuPCP})\text{Ir}$ complexes, as would be expected from

the decrease in steric demand of the arrangement of the tBu substituents in the ^tBuPOCOP ligand relative to the ^tBuPCP ligand. This decrease in unfavorable steric repulsions for (^tBuPOCOP)Ir results in an increase in olefin binding affinity. Nevertheless, extrapolation to 125 °C for *trans*-2-hexene self-exchange (experimentally determined at increments from 57 °C to 79 °C) affords a rate of $2.1 \times 10^2 \text{ s}^{-1}$, which is still much faster than the reported rate of isomerization of (^tBuPOCOP)Ir(*trans*-2-hexene) to (^tBuPOCOP)Ir(1-hexene),²⁰ suggesting that olefin exchange is a fast step in (^tBuPOCOP)Ir-catalyzed olefin isomerization.

Figure 5.4. Eyring plot for the rate of dissociative 1-hexene exchange of (^tBuPOCOP)Ir(1-hexene) with free 1-hexene in *p*-xylene-*d*₁₀ in the temperature interval 107 °C to 126 °C.

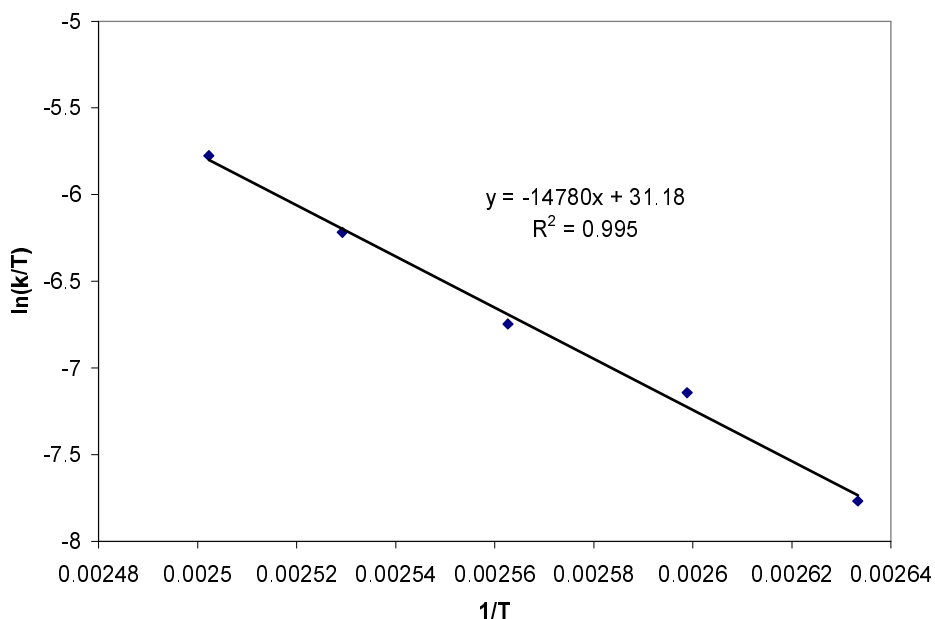
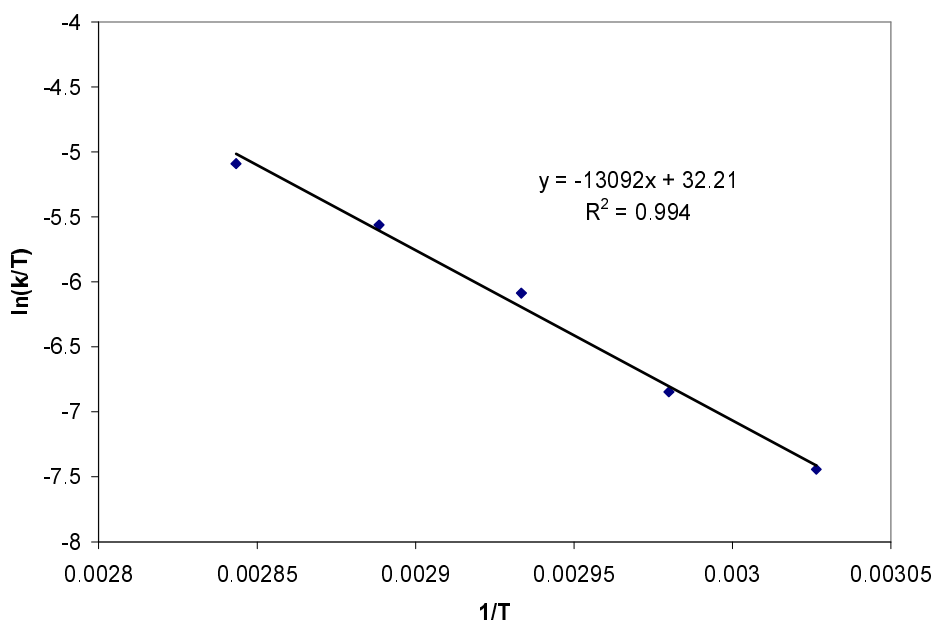


Figure 5.5. Eyring plot for the rate of dissociative *trans*-2-hexene exchange of (^tBuPOCOP)Ir(*trans*-2-hexene) with free *trans*-2-hexene in *p*-xylene-*d*₁₀ in the temperature interval 57 °C to 79 °C.

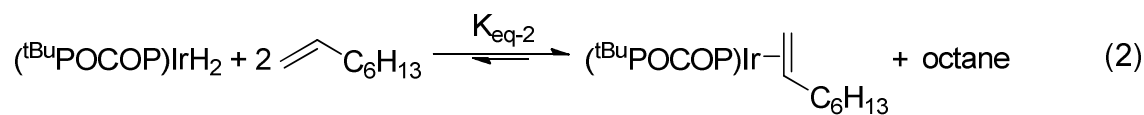
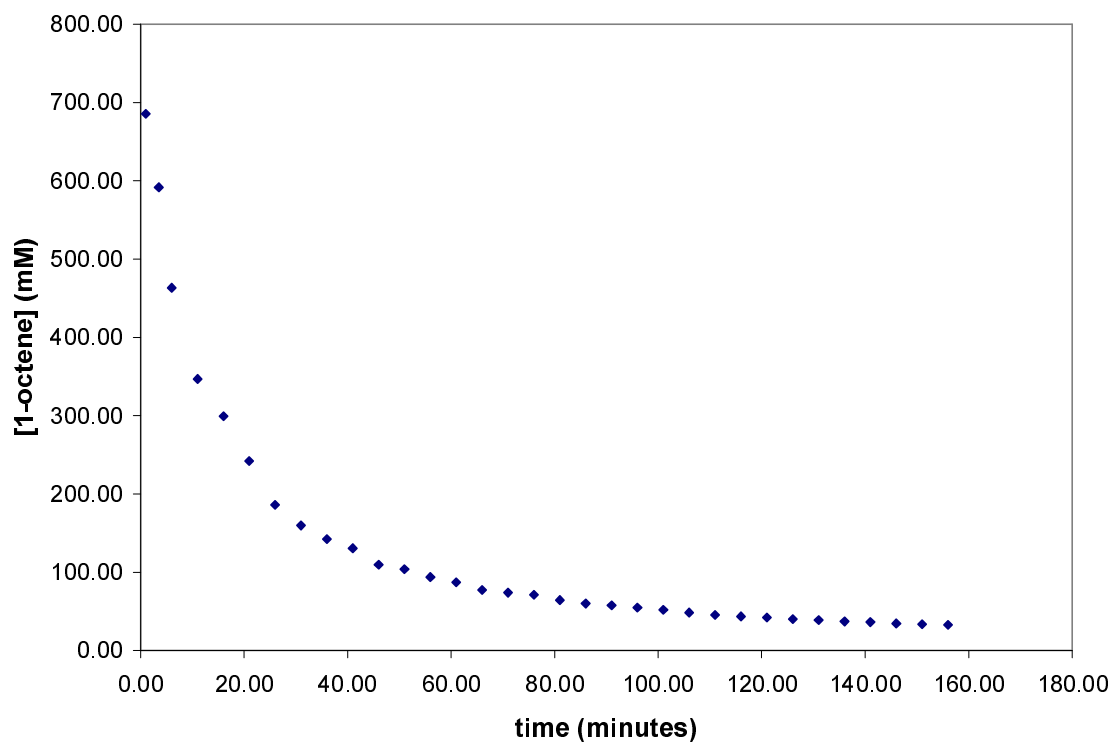


5.2.2 (^tBuPOCOP)Ir-Catalyzed Olefin Isomerization of 1-Octene

The (^tBuPOCOP)Ir-catalyzed olefin isomerization of 1-octene to internal octenes was investigated analogously to (^tBuPCP)Ir. In contrast with the (^tBuPCP)Ir-catalyzed reaction, the reaction kinetics of (^tBuPOCOP)Ir-catalyzed olefin isomerization show a clear positive dependence on 1-octene concentration (Figure 5.6). Given that the 1-octene complex is observed to be the major species in solution, this is not easily reconciled with a hydride-insertion mechanism, since the steady-state concentration of (^tBuPOCOP)IrH₂ should be *inverse-second-order* in [1-octene] (and first-order in *n*-octane) (eq 2). This positive dependence on [1-octene] is, however, also inconsistent with a π -allyl mechanism operating with (^tBuPOCOP)Ir(1-octene) as the resting state, unless

the rate-determining step involves an additional equivalent of 1-octene. While this would be the case if loss of 2-alkene (step c in Scheme 5.3) were reversible and the back-reaction with 2-octene were fast relative to addition of 1-alkene, these conditions seem highly unlikely given the lesser bulkiness and initially higher concentration of 1-alkenes.

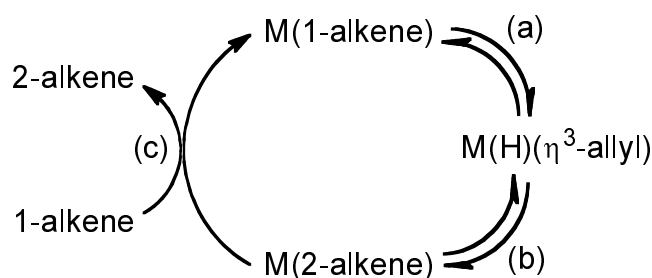
Figure 5.6. Catalytic isomerization of 1-octene to internal octenes by (^tBuPOCOP)IrH₂ (5 mM) at 125 °C.



$$[(\text{tBuPOCOP})\text{IrH}_2] = K_{\text{eq-2}} \cdot [n\text{-octane}] \cdot [(\text{tBuPOCOP})\text{Ir}(1\text{-octene})] / [1\text{-octene}]^2$$

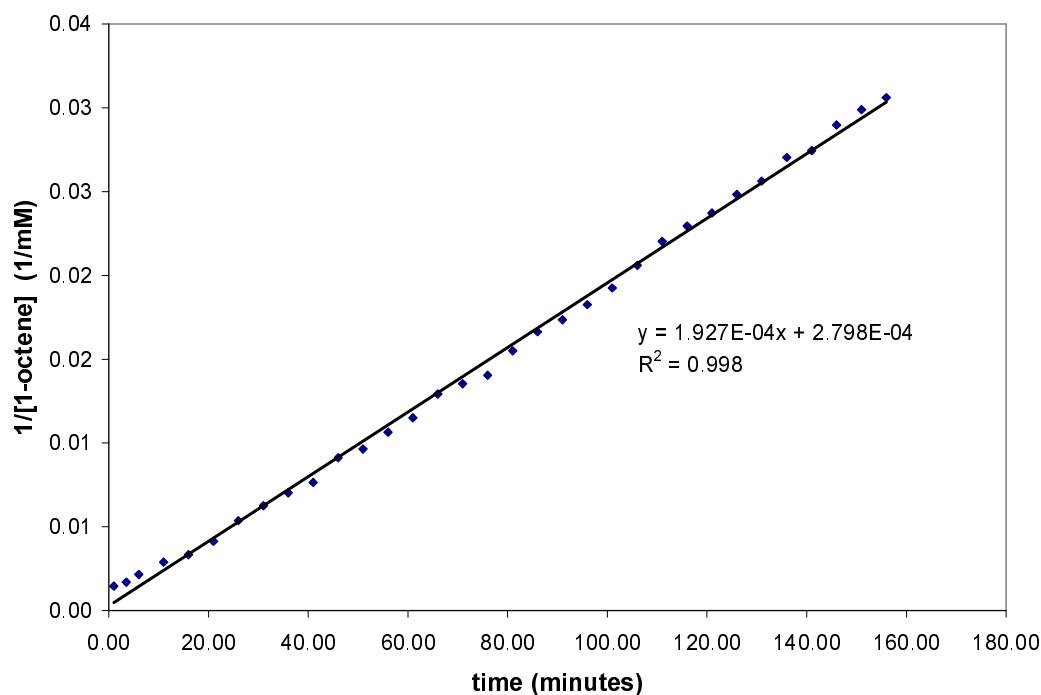
An alternative explanation for the positive dependence of rate on [1-alkene] is that formation of $(^t\text{BuPOCOP})\text{Ir}(2\text{-alkene})$ is reversible, and that displacement of coordinated 2-alkene by 1-alkene proceeds through an *associative* rate-determining step; such a pathway is indicated in Scheme 5.4. However, as noted above, the rate of *trans*-2-hexene self exchange is much faster than isomerization of $(^t\text{BuPOCOP})\text{Ir}(\text{trans-2-alkene})$ to $(^t\text{BuPOCOP})\text{Ir}(1\text{-alkene})$, which argues against such a mechanism.

Scheme 5.4. Alternative π -allyl pathway for 1-alkene isomerization, involving associative displacement of 2-alkene by 1-alkene.



Closer examination of the reaction kinetics appears to show that the reaction is 2nd order in [1-octene] (Figure 5.7). Given that the resting state of the catalyst is the $(^t\text{BuPOCOP})\text{Ir}(1\text{-octene})$ complex, this suggests that *two* additional equivalents of 1-octene bind to the complex in the rate determining step. Speculatively, one could envision a rate determining transition state in which the phosphinite arms of the pincer ligand decoordinate and are replaced by olefin ligands, resulting in the active olefin isomerization catalyst. However, we currently have no data to support or refute such a hypothesis.

Figure 5.7. 2nd order plot of the catalytic isomerization of 1-octene to internal octenes by **2** (5 mM) at 125 °C.



5.3 Summary

The reaction kinetics of olefin coordination to (^tBuPCP)Ir and (^tBuPOCOP)Ir were quantified and were found to be rapid relative to olefin isomerization. The kinetics of olefin exchange was inversely related to the steric bulk of the olefin and pincer ligand; less bulky olefins and ligands resulted in slower exchange rates. Accordingly, 1-hexene underwent olefin exchange more slowly than *trans*-2-hexene, and (^tBuPOCOP)Ir-bound olefins underwent olefin exchange more slowly than (^tBuPCP)Ir-bound olefins. The (^tBuPOCOP)Ir-catalyzed olefin isomerization of 1-octene was found to show an apparent 2nd order dependence on 1-octene concentration.

5.4 Experimental

5.4.1 General Considerations.

All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. Anhydrous *p*-xylene-*d*₁₀ was dried over Na/K and collected by vacuum transfer. 1-hexene and trans-2-hexene were degassed and used without further purification. Complexes **1**²¹ and **2**²² were synthesized as previously reported.

5.4.2 EXSY Experiments.

10.0 mg of a pincer-iridium dihydride complex (17 μmol) and 10.0 μL of olefin were dissolved in 0.7 mL of *p*-xylene-*d*₁₀. Conversion to the pincer-iridium olefin complex was complete after 30 min at 25 °C for most pincer-ligand-olefin combinations. Formation of the (^tBuPCP)Ir(*trans*-2-hexene) complex required heating at 50 °C for 30 min to effect complete conversion to the olefin complex, and the rapid rate of olefin exchange for this complex necessitated a change in solvent to mesitylene-*d*₁₂. After formation of the olefin complex, a vinyl proton of the bound olefin complex was selectively irradiated in a 1D EXSY experiment, and magnetization transfer to free olefin was observed at different mixing times. The rate of olefin dissociation was determined from a plot of magnetization transfer vs. mixing time.²³ NMR spectroscopy acquisition temperatures were determined by measuring an external ethylene glycol or methanol reference sample. These 1D EXSY experiments were performed at different temperatures, and an Eyring plot yielded activation energy parameters ΔH[‡] and ΔS[‡]. Olefin exchange was confirmed to proceed via a dissociative mechanism by repeating the

EXSY experiment with a much larger excess of free olefin (4 to 10-fold excess) and observing negligible change in the rate.

5.4.3 Catalytic 1-Octene Isomerization.

3.0 mg of a pincer-iridium dihydride complex (5.1 mM, (^tBuPCP)IrH₂ or (^tBuPOCOP)IrH₂) was dissolved with 1-octene (17.0 μL, 108 mM) and mesitylene (5.0 μL, 36 mM, internal standard) in a volume of *n*-octane or *p*-xylene solvent such that the total volume of the reaction solution was 1 mL. The reaction solution was transferred into an air-tight, septa-sealed vial. An initial aliquot was taken before heating the reaction to 125 °C. Reaction data was obtained via GC analysis of aliquots taken at various times during the reaction.

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Chapter 6

Investigations of the (^tBu³MePCP)Ir(CO) Complex: Synthesis and Oxidative Addition of H₂

Abstract

A revised synthesis scheme for the synthesis of the ^tBu³MePCP ligand was developed. The revised synthesis scheme was found to be amenable for the synthesis of a variety of unsymmetrical pincer ligands. With the ^tBu³MePCP ligand, addition of H₂ to ^tBu³MePCPIr(CO) and ^tBu⁴PCPIr(CO) was investigated. Addition of H₂ was not observed to add to ^tBu⁴PCPIr(CO). However, when H₂ was added to ^tBu³MePCPIr(CO), three isomers were observed and assigned using an isotopic labeling experiment and NMR spectroscopy. The kinetic products were the two possible isomers of *cis*-H₂ addition. The thermodynamic product was the result of *trans*-H₂ addition.

6.1 Introduction

Oxidative addition of small molecules has been a longstanding fundamental transformation of organometallic chemistry. Both steric and electronic factors have been investigated regarding the favorability of small molecule addition.¹⁻⁸ The simplest small molecule to undergo oxidative addition, H₂, has been reported from the beginnings of organometallic chemistry.^{9,10} While the effects of sterics on the reactivity and selectivity of oxidative addition of larger molecules to metal centers has been explored, investigations into the oxidative addition of H₂ have generally focused on electronic effects, given the small size of H₂.¹¹⁻¹³ There are comparatively fewer investigations of steric effects on the oxidative addition reaction of H₂.^{14,15} Selective catalytic reactions that involve the oxidative addition of hydrogen such as asymmetric hydrogenation have been achieved, but most strategies utilize bulky ligand frameworks to bias the coordination and reactivity of the much larger substrate being hydrogenated rather than control the addition of H₂.¹³ As such, steric considerations for the oxidative addition reaction of H₂ tend to be scant.

Our group has reported the synthesis of several PCP pincer Ir complexes, which are identical save for the substituents on the phosphine atoms.¹⁶ Our previous studies have examined the reactivity of these complexes for catalytic transfer dehydrogenation, and have found that a very large difference in reactivity is observed between ^tBu³MePCPIrH₂ and ^tBu⁴PCPIrH₂. It appears that replacing one sterically large tBu group for a methyl group results in drastically improved activity.

In this chapter, I detail a very large change in reactivity for the oxidative addition of H₂ when changing the ligand from ^tBu⁴PCPIrH₂ to ^tBu³MePCPIrH₂. In addition, the

synthesis route for $^{\text{tBu3Me}}\text{PCPIrH}_2$ was revised; the new route was found to be useful for the generation of a variety of unsymmetrical PCP pincer ligands.

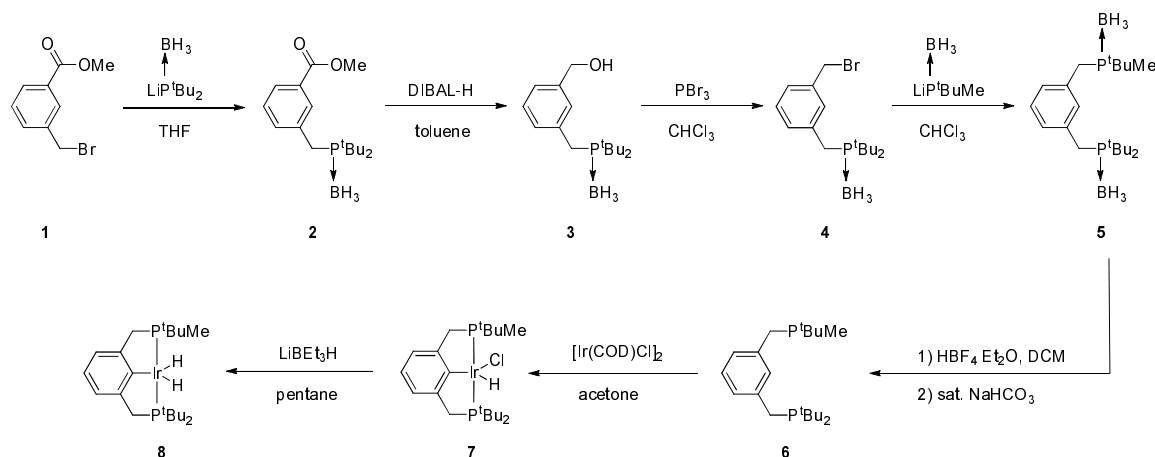
6.2 Revised Synthesis of $^{\text{tBu3Me}}\text{PCPIrH}_2$

$^{\text{tBu3Me}}\text{PCPIr}(\text{CO})$ is obtained from $^{\text{tBu3Me}}\text{PCPIrH}_2$ by reaction with CO. However, the previously reported synthesis route of $^{\text{tBu3Me}}\text{PCPIrH}_2$ by our group is somewhat inelegant.¹⁶ The reported route uses *m*-xylylene dibromide as the starting point and requires desymmetrization of the two benzyl bromide arms as the phosphine groups are introduced successively. The desymmetrization and initial mono-phosphonation of *m*-xylylene dibromide was achieved by utilizing a very large excess of the dibromide (5 fold excess of dibromide vs. phosphine). Separation of the desired mono-phosphine product from the excess starting material required multiple cycles of reprecipitation by the addition of diethyl ether to an acetone solution of the reaction mixture. Addition of the second phosphine group, completion of the ligand, and metallation all proceeded analogously to the well-established procedure for $^{\text{tBu4}}\text{PCPIrHCl}$ synthesis.

Similarly, Jensen *et al.* reported a synthesis scheme to generate unsymmetrical diphosphine pincer ligands by initial desymmetrization of the resorcinol starting material to (2-chloromethyl)benzyl alcohol.¹⁷ Initial phosphonation was achieved by reaction of the benzylic chloride with diphenylphosphine. Completion of the ligand was achieved following BH_3 -protection of the phosphine, conversion of the remaining benzylic alcohol to a chloride, addition of the second phosphine group, and deprotection of the phosphine groups. Although Jensen utilized this synthesis scheme to generate PCP

pincer ligands with a diphenylphosphine moiety, this scheme can be easily adapted to the synthesis of unsymmetrical alkyl-phosphine pincer ligands such as the $^t\text{Bu}^3\text{MePCP}$ ligand.

In contrast to the previous synthesis of the $^t\text{Bu}^3\text{MePCP}$ ligand and Jensen's unsymmetrical diphosphine PCP ligand synthesis, the revised synthesis scheme (Scheme 6.1) utilizes methyl (3-bromomethyl)benzoate as the starting point, which obviates the need for desymmetrization. Synthesis of the $^t\text{Bu}^3\text{MePCP}$ ligand began with the phosphonation of methyl (3-bromomethyl)benzoate with $\text{Li}^t\text{Bu}_2\text{P}\cdot\text{BH}_3$ to generate compound **2**. The BH_3 -protected phosphine is easily synthesized and has the advantage of being stable under ambient conditions.^{18,19} The ester moiety of compound **2** was reduced with diisobutylaluminum hydride to yield benzylic alcohol **3** and then converted to benzylic bromide **4** via reaction with PBr_3 . The second phosphonation reaction was achieved using another lithiated BH_3 -protected phosphine, $\text{Li}^t\text{BuMeP}\cdot\text{BH}_3$, to yield BH_3 -protected ligand **5**. Deprotection of the phosphines under conditions reported by Jensen afforded the desired $^t\text{Bu}^3\text{MePCP}$ pincer ligand **6**.¹⁷ Metallation of the ligand onto Ir to yield hydrido chloride complex **7** and subsequent reduction to dihydride complex **8** followed previously reported procedures for $^t\text{Bu}^3\text{MePCPIrH}_2$.

Scheme 6.1. Revised Synthesis Scheme for $^{t\text{Bu}^3\text{Me}}\text{PCPIrH}_2$ (**8**).

While the original aim of this revised synthesis scheme was to obtain the $^{t\text{Bu}^3\text{Me}}\text{PCP}$ ligand, this scheme can be easily modified to generate a large variety of unsymmetrical PCP-type pincer ligands through the installation of different phosphine groups during the second phosphination step. In addition, this scheme is scalable; compound **4** was easily synthesized in multigram quantities and can serve as a precursor for various unsymmetrical or chiral pincer ligands. While our group has not yet undertaken an extensive investigation of the ligand variants, this synthesis scheme was successfully utilized by our group in the synthesis of $^{t\text{Bu}^2}\text{PCP}^{i\text{Pr}^2}\text{Ir}$ complexes from compound **4**.²⁰

6.3 Addition of H_2 to $^{t\text{Bu}^3\text{Me}}\text{PCPIrCO}$

With the $^{t\text{Bu}^4}\text{PCPIr}(\text{CO})$ and $^{t\text{Bu}^3\text{Me}}\text{PCPIr}(\text{CO})$ complexes in hand, we turned to investigating the addition of H_2 to these complexes. (Milstein *et al.* reported the analogous addition of H_2 to $^{i\text{Pr}^4}\text{PCPIrCO}$.²¹) Addition of H_2 to $^{t\text{Bu}^4}\text{PCPIrCO}$ does not show any reaction after several weeks at elevated temperature (40 °C). By contrast,

addition of H_2 to $^{\text{tBu}_3\text{Me}}\text{PCPIrCO}$ at room temperature immediately displays signals in the hydride region of the ^1H NMR spectrum, corresponding to 6-coordinate dihydride complexes. The three isomers of H_2 addition are possible and are shown in Figure 6.1: *cis* addition of H_2 to the bis- $^{\text{tBu}}$ side, *cis* addition of H_2 to the $^{\text{tBu}}$ Me side, and *trans* addition of H_2 . After 8 h at room temperature, six hydride signals were observed in the ^1H NMR spectrum corresponding to the three isomers. The assignment of the observed isomers was achieved through the use of ^{13}C -labeled CO in the formation of $^{\text{tBu}_3\text{Me}}\text{PCPIr}(^{13}\text{CO})$. Two hydride signals display large ^1H - ^{13}C coupling constants ($J_{\text{HC}} = 38 \text{ Hz}$ and 39.5 Hz) for one of the hydride signals, consistent with a relative *trans* arrangement between the hydride and CO group (Figure 6.2). The remaining hydride signals display small ^1H - ^{13}C coupling constants (J_{HC} around 5 Hz), consistent with hydrides mutually *cis* to the CO group. Given the integration ratios, the two most-downfield hydride signals could be assigned to the *trans* addition isomer, while the remaining hydride signals correspond to *cis* addition of H_2 to $^{\text{tBu}_3\text{Me}}\text{PCPIr}(\text{CO})$.

Figure 6.1. Isomers of $^{\text{tBu}_3\text{Me}}\text{PCPIr}(\text{CO})(\text{H})_2$ complexes.

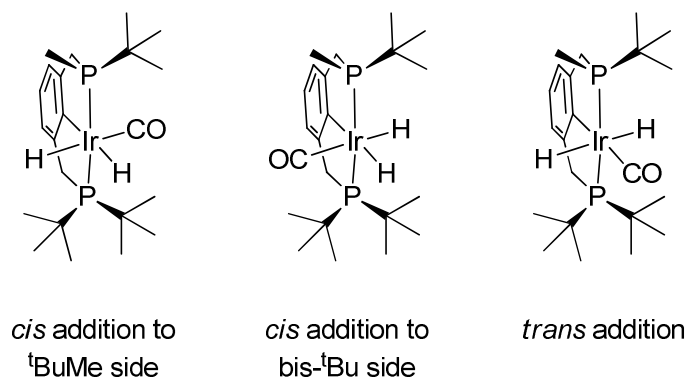
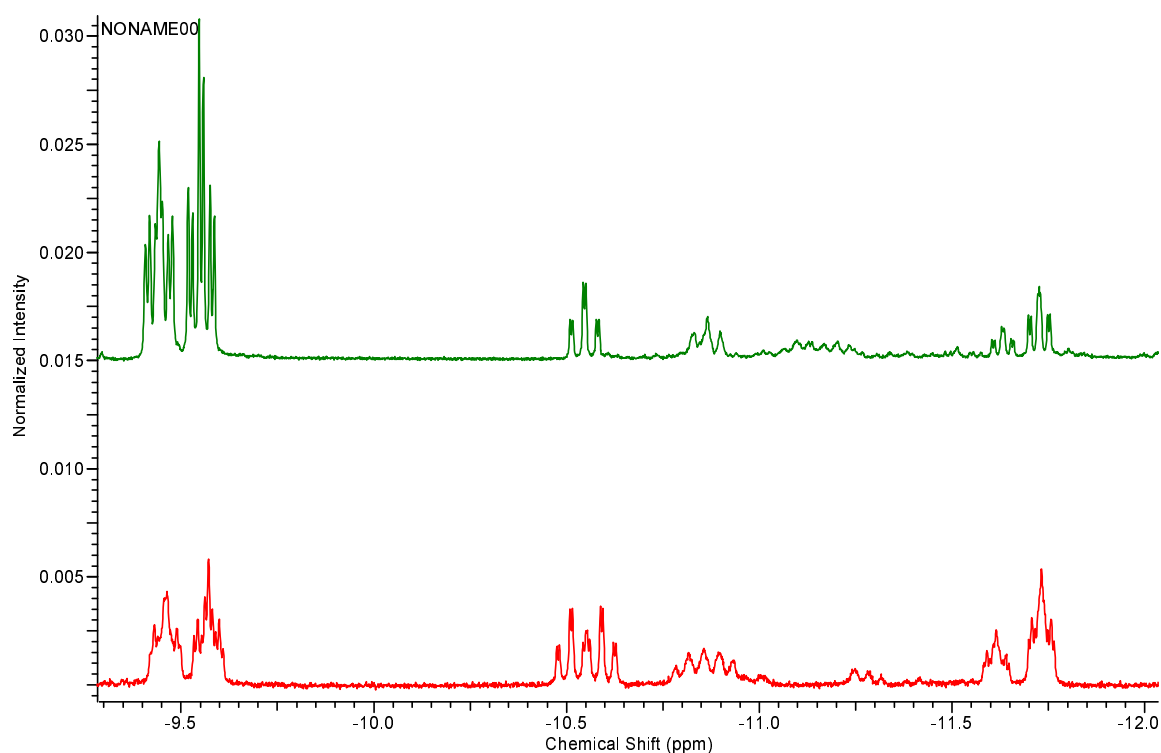
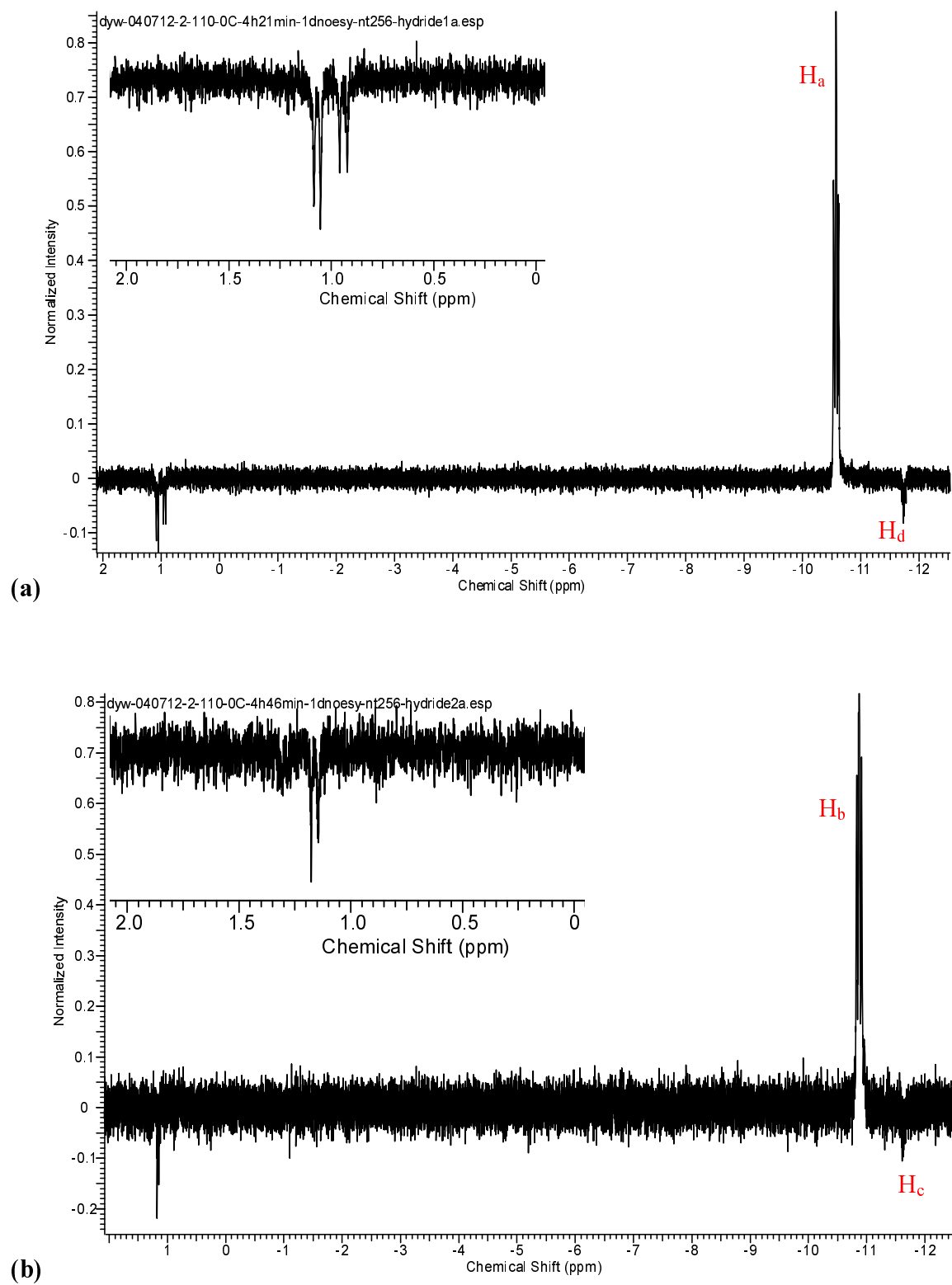


Figure 6.2. ^1H NMR spectrum of H_2 addition to $^t\text{Bu}_3\text{MePCIr}(\text{CO})$ (top, green) and $^t\text{Bu}_3\text{MePCIr}(^{13}\text{CO})$ (bottom, red).



Low temperature experiments clearly showed that the *cis* isomers are the kinetic products of H_2 addition. After 3 h at $0\text{ }^\circ\text{C}$, only the *cis* isomers were observed. The assignment of the *cis* isomers was performed using 1D NOESY experiments for the hydride signals *trans* to the CO group (Figure 6.3). Selective excitation of the hydride H_a at $\delta = -10.6\text{ ppm}$ resulted in a NOE correlation with two ^tBu groups as well as hydride H_d . By contrast, hydride H_b at $\delta = -10.9\text{ ppm}$ has a NOE correlation signal with only one ^tBu group. Thus the kinetically preferred isomer was determined to be *cis* addition of the H_2 to the bis- ^tBu side.

Figure 6.3. 1D NOESY spectra of $t\text{Bu}_3\text{Me}_c\text{PCPIr}(\text{CO})$ with the selective excitation of hydride **(a)** H_a and **(b)** H_b .



The integration ratio of the hydride signals for the *cis* isomers was found to be 1.9 at low temperature (<30 °C) at early reaction times, and the same ratio is observed as the reaction progresses and as the reaction is allowed to warm to room temperature. This suggests that the kinetic selectivity and thermodynamic selectivity for the two *cis* isomers are coincidentally the same ($\Delta\Delta G^\ddagger = \Delta\Delta G$).

The *cis* isomers convert completely to the *trans* isomer at room temperature after 17 d. Upon heating to 120 °C in vacuo overnight, the *trans* isomer does undergo partial conversion back to the 4-coordinate complex (22 % conversion by integration of the ^{31}P NMR signals).

6.4 Discussion

It is remarkable that a slight change in substitution on the ligand results in a drastic change in reactivity for the addition of H_2 . With ^tBu groups exclusively on the ligand for $^{t\text{Bu}}_4\text{PCIr}(\text{CO})$, there is effectively no H_2 addition, presumably because the ^tBu groups are a large steric presence which inhibits access to the metal center. However, it is not the mere presence of two ^tBu on one side of the complex that prevents H_2 addition. Given that H_2 addition to *both* sides of the $^{t\text{Bu}^3\text{Me}}\text{PCIr}(\text{CO})$ complex is kinetically facile, and given that addition of H_2 to the side with bis- ^tBu groups is the kinetically (and thermodynamically) favored isomer, it is clear that the kinetic picture is more complicated than simply the presence of sterically large groups on one side of the complex. It is likely that the lone methyl group in $^{t\text{Bu}^3\text{Me}}\text{PCIr}(\text{CO})$ allows the ligand's phosphine substituents to reorganize in the direction of the less-hindered quadrant to relieve steric strain.

6.5 Summary

A revised synthesis scheme for the synthesis of the $^{\text{tBu3Me}}\text{PCP}$ ligand was developed. The revised synthesis scheme was found to be amenable for the synthesis of a variety of unsymmetrical pincer ligands. With the $^{\text{tBu3Me}}\text{PCP}$ ligand, addition of H_2 to $^{\text{tBu3Me}}\text{PCPIr}(\text{CO})$ and $^{\text{tBu4}}\text{PCPIr}(\text{CO})$ was investigated. Addition of H_2 was not observed to add to $^{\text{tBu4}}\text{PCPIr}(\text{CO})$. However, when H_2 was added to $^{\text{tBu3Me}}\text{PCPIr}(\text{CO})$, three isomers were observed and assigned using an isotopic labeling experiment and NMR spectroscopy. The kinetic products were the two possible isomers of *cis*- H_2 addition. The thermodynamic product resulted from *trans*- H_2 addition.

6.6 Experimental

All reactions, recrystallizations, and routine manipulations were conducted under argon using an argon-filled glove box or by using standard Schlenk techniques. Reagent grade solvents were used and dried according to established methods, then degassed with argon. All NMR solvents were dried using Na/K alloy, vacuum-transferred, and stored in an argon-filled glove box. Column chromatography was performed as described by Still *et al.* using Silicycle 40-63 μm 60 Å silica gel (SilaFlash P60).²² TLC analysis of reaction mixtures was performed on Silicycle silica gel 60 Å F₂₅₄ TLC plates and visualized using p-anisaldehyde, KMnO_4 , and 254 nm UV light. ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained on 400-MHz or 500-MHz Varian Spectrometers. ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and were referenced to residual protiated (^1H) or deuterated solvent (^{13}C). $^{31}\text{P}\{^1\text{H}\}$ NMR

chemical shifts are referenced to an external standard, Me₃P in mesitylene-*d*₁₂ solvent (δ - 62.4 ppm), in a capillary tube.

X-ray diffraction data were collected on a Bruker Smart APEX CCD diffractometer with graphite monochromatized Mo K α radiation (λ = 0.71073 Å) at 100 K. Crystals were immersed in Paratone oil, placed on a glass needle, and examined at 100 K. The data were corrected for Lorentz effects, polarization, and absorption, the latter by a multiscan (SADABS) method.²³ The structures were solved by direct methods (SHELXS86).²⁴ All non-hydrogen atoms were refined (SHELXL97)²⁵ based upon F_{obs} .²⁴ All hydrogen atom coordinates were calculated with idealized geometries (SHELXL97). Scattering factors (f_o , f' , f'') are as described in SHELXL97.²⁵

Synthesis and characterization of ^tBu⁴PCPIrCO and compounds **7**, **8**, and **9** matched previously reported procedures.^{16,26} Compound **6** was prepared from compound **5** using the deprotection procedure detailed by Jensen *et al.*,¹⁷ and its spectral data was previously reported by our group.¹⁶ ^tBuMePH was prepared as previously reported by our group.¹⁶ BH₃-protection of ^tBu₂PH and ^tBuMePH was performed as reported by Higham *et al.*¹⁹

Representative procedure for the formation of lithiated phosphine-boranes (Li^tBu₂P·BH₃, Li^tBuMeP·BH₃). A solution of ^tBu₂PH·BH₃ (2.2000 g, 13.7461 mmol) in 20 mL of THF was cooled to 0 °C. A solution of ⁿBuLi in hexanes (2.5 M, 5.5 mL, 13.75 mmol) was added via syringe. The reaction solution was allowed to warm to room temperature and stir for 1 h.

Compound 2. Methyl 3-(bromomethyl)benzoate (3.00 g, 13.10 mmol) was dissolved in 10 mL of THF and cooled to 0 °C. This solution was transferred via cannula to a flask charged with a solution of $\text{Li}^t\text{Bu}_2\text{P}\cdot\text{BH}_3$ (13.75 mmol) in 20 mL of THF that was prepared separately and cooled to 0 °C. After 90 min, 20 mL of water was added. The aqueous layer was extracted with dichloromethane (3 x 10 mL), and the combined organic layers were dried over magnesium sulfate, filtered, and concentrated. Column chromatography (20:1 hexanes:ethyl acetate) afforded the product as a white solid (3.66 g, 11.88 mmol) in 91 % yield. Crystals suitable for single-crystal X-ray analysis were obtained from the slow evaporation of a solution of compound **2** in pentane. An ORTEP diagram of this complex is shown in Figure 6.4. X-ray crystallography refinement parameters and various x-ray crystal structure parameters are listed in Tables 6.1 – 6.6.

$^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 500 MHz): δ 47.58 (q). ^1H NMR (CDCl_3 , 500 MHz): δ 8.03 (d, J = 1.5 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 7.3 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 3.91 (s, 3H), 3.18 (d, J = 12.1 Hz, 2H), 1.26 (d, 12.1 Hz, 18H), 0.54 (br q, J = 91.3 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 500 MHz): δ 167.12 (s), 135.50 (d, J = 3.3 Hz), 135.41 (d, J = 2.8 Hz), 131.63 (d, J = 4.7 Hz), 130.10 (s), 128.34 (d, J = 1.9 Hz), 128.06 (d, J = 2.3 Hz), 52.32 (s), 33.04 (d, J = 24.7 Hz), 28.42 (d, J = 1.4 Hz), 25.98 (d, J = 24.7 Hz).

Compound 3. A flask was charged with compound **2** (1.5077 g, 4.8919 mmol) and 20 mL of toluene and cooled to 0 °C. This solution was transferred via cannula to a flask containing a solution of di-isobutyl aluminum hydride (12.5 mL, 1.0 M in cyclohexane, 12.5 mmol) that was diluted with 20 mL of toluene and cooled to 0 °C. The reaction solution was allowed to slowly warm to room temperature and stir for 6 h. Diethyl ether

(40 mL) was added, and the reaction solution was cooled to 0 °C. Water (0.5 mL), a 15% sodium hydroxide solution (0.5 mL), and a second portion of water (1.25 mL) were added successively. The reaction mixture was then allowed to warm to room temperature and stir for an additional 15 min. The reaction mixture was dried over magnesium sulfate, filtered, and concentrated. Column chromatography (20:1 hexanes:ethyl acetate) afforded the product as a white solid (1.2059 g, 4.3038 mmol) in 88% yield. Crystals suitable for single-crystal X-ray analysis were obtained from the slow evaporation of a solution of compound **3** in ethyl acetate. Compound **3** was also obtained in a one-pot reaction via the addition of di-isobutyl aluminum hydride directly to the reaction solution of compound **2** without isolation and purification of compound **2** (80 % yield from the methyl 3-(bromomethyl)benzoate starting material). An ORTEP diagram of this complex is shown in Figure 6.5. X-ray crystallography refinement parameters and various x-ray crystal structure parameters are listed in Tables 6.7 – 6.12. **³¹P{¹H} NMR (CDCl₃, 500 MHz):** δ 47.11 (q). **¹H NMR (CDCl₃, 500 MHz):** δ 7.45 (d, J = 1.1 Hz, 1H), 7.36 (dd, J = 1.3 Hz, J = 7.5 Hz, 1H), 7.26 (t, J = 7.5 Hz, 1H), 7.20 (dd, J = 0.7 Hz, J = 7.7 Hz, 1H), 4.66 (s, 2H), 3.14 (d, J = 12.1 Hz, 2H), 1.83 (s, 1H), 1.25 (d, J = 12.5 Hz, 18H), 0.53 (br q, J = 92.6 Hz, 3H). **¹³C{¹H} NMR (CDCl₃, 500 MHz):** δ 140.90 (d, J=1.9 Hz), 135.12 (d, J=3.7 Hz), 129.98 (d, J=4.2 Hz), 129.43 (d, J=4.2 Hz), 128.39 (d, J=1.9 Hz), 125.33 (d, J=1.8 Hz), 65.29 (s), 32.96 (d, J=25.2 Hz), 28.41 (d, J=1.4 Hz), 26.02 (d, J=24.7 Hz).

Compound 4. Compound **3** (1.2059 g, 4.3038 mmol) was dissolved in 40 mL of chloroform and cooled to 0 °C. Phosphorus tribromide (0.42 mL, 4.4686 mmol) was added, and the reaction mixture was allowed to stir for 15 min. Water (1 mL) was added.

The reaction mixture was then dried over magnesium sulfate, filtered, and concentrated. Column chromatography (20:1 hexanes:ethyl acetate) afforded the product as a white solid (1.2312 g, 3.5885 mmol) in 83% yield. Crystals suitable for single-crystal X-ray analysis were obtained from the slow evaporation of a solution of compound **2** in chloroform. An ORTEP diagram of this complex is shown in Figure 6.6. X-ray crystallography refinement parameters and various x-ray crystal structure parameters are listed in Tables 6.13 – 6.18. **³¹P NMR (CDCl₃, 500 MHz):** δ 47.29 (q). **¹H NMR (CDCl₃, 500 MHz):** δ 7.46 (s, 1H), 7.36 (m, 1H), 7.19–7.24 (m, 2H), 4.45 (s, 2H), 3.11 (d, J = 12.1 Hz, 2H), 1.22 (d, J = 12.5 Hz, 18H), 0.52 (br q, J = 93.1, 3H). **¹³C NMR (CDCl₃, 500 MHz):** δ 137.73 (d, J = 1.9 Hz), 135.50 (d, J = 2.8 Hz), 131.52 (d, J = 4.2 Hz), 130.86 (d, J = 3.7 Hz), 128.62 (d, 1.4 Hz), 127.39 (d, J = 1.9 Hz), 33.64 (s), 32.96 (d, J = 24.66 Hz), 28.38 (d, J = 0.9 Hz), 25.99 (d, J = 24.19 Hz).

Compound 5. Compound **4** (0.7305 g, 2.1291 mmol) was dissolved in 10 mL of THF and cooled to 0 °C. This solution was transferred via cannula to a flask that was charged with a solution of compound Li^tBuMeP·BH₃ (1.15 mmol) in 10 mL of THF and cooled to 0 °C. The reaction was stirred at 0 °C for 1 h and then warmed to room temperature. An aqueous solution of hydrochloric acid (1 M, 10 mL) was added. The aqueous layer was extracted with diethyl ether (3 x 10 mL) and ethyl acetate (10 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated. Column chromatography (40:1 hexanes:ethyl acetate) afforded the product as a white solid (0.4972 g, 1.3079 mmol) in 61% yield. **³¹P NMR (CDCl₃, 500 MHz):** δ 47.55 (br d, J = 73 Hz), 29.14 (br d, J = 73 Hz). **¹H NMR (CDCl₃, 500 MHz):** δ 7.30–7.35 (m, 2H), 7.20

(t, $J = 7.5$ Hz, 1H), 7.14 (bd, $J = 7.7$ Hz, 1H), 3.11 (d, $J = 12.5$ Hz, 2H), 3.02 (dd, $J = 8.8$ Hz, $J = 13.6$ Hz, 1H), 2.93 (t, $J = 13.9$ Hz, 1H), 1.26 (d, $J = 12.1$ Hz, 9H), 1.23 (d, $J = 12.5$ Hz, 9H), 1.19 (d, $J = 13.6$ Hz, 9H), 1.05 (d, $J = 9.5$ Hz, 3H), 0–1.0 (br m, 6H). **^{13}C NMR (CDCl_3 , 500 MHz):** δ 135.14 (dd, $J = 2.6$ Hz, $J = 3.5$ Hz), 133.17 (dd, $J = 1.6$ Hz, $J = 5.4$ Hz), 132.13 (t, $J = 4.0$ Hz), 129.31 (dd, $J = 2.8$ Hz, $J = 4.2$ Hz), 128.65 (dd, $J = 2.1$ Hz, $J = 4.0$ Hz), 128.27 (dd, $J = 1.6$ Hz, $J = 2.4$ Hz), 33.05 (d, $J = 16.3$ Hz), 32.85 (d, $J = 17.2$ Hz), 29.00 (d, $J = 28.4$ Hz), 28.4 (d, $J = 0.9$ Hz), 28.35 (d, $J = 0.9$ Hz), 27.92 (d, $J = 31.6$ Hz), 26.00 (d, $J = 24.7$ Hz), 25.31 (d, $J = 1.9$ Hz), 4.87 (d, $J = 34.9$ Hz).

Representative procedure for the addition of H_2 to $\text{PCPIr}(\text{CO})$ complexes. $\text{PCPIr}(\text{CO})$ (20 μmol) was dissolved in 0.7 mL of toluene- d_8 in a J Young NMR tube. The reaction solution was degassed and cooled to -78 $^\circ\text{C}$, and 1 atm of H_2 was added. Signals corresponding to the formation of *cis* isomers were first observed to appear upon heating the reaction to -10 $^\circ\text{C}$. After 15 h at 0 $^\circ\text{C}$, only *cis* isomers were observed by NMR spectroscopy. Heating the reaction mixture to 50 $^\circ\text{C}$ for 2 d resulted in complete conversion of both *cis* isomers to the *trans* H_2 addition isomer.

Selected NMR spectral data for $^t\text{Bu}^3\text{MePCPIr}(\text{CO})(\text{H}_2)$ complexes. **$^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8 , 400 MHz):** δ 31.8 (*cis* addition to $^t\text{BuMe}$ side isomer, d, $J_{\text{PP}} = 285.5$ Hz), 33.7 (*cis* addition to bis- ^tBu side isomer, d, $J_{\text{PP}} = 283.0$ Hz), 38.4 (*trans* addition isomer, d, $J_{\text{PP}} = 288.1$ Hz), 73.6 (*cis* addition to bis- ^tBu side isomer, d, $J_{\text{PP}} = 283.0$ Hz), 75.4 (*cis* addition to $^t\text{BuMe}$ side isomer, d, $J_{\text{PP}} = 285.5$ Hz), 76.4 (*trans* addition isomer, d, $J_{\text{PP}} = 288.1$ Hz). **^1H NMR (toluene- d_8 , 400 MHz):** δ -9.46 (*trans* addition isomer, m, $J_{\text{HP1}} =$

12.8 Hz, $J_{\text{HP2}} = 16.8$ Hz, $J_{\text{HH}} = 5.5$ Hz), -9.58 (*trans* addition isomer, dt, $J_{\text{HP1}} = J_{\text{HP2}} = 14.0$ Hz, $J_{\text{HH}} = 5.5$ Hz), -10.57 (*cis* addition to bis-^tBu side isomer– hydride *trans* to CO, dt, $J_{\text{HP1}} = J_{\text{HP2}} = 17.0$ Hz, $J_{\text{HH}} = 3.1$ Hz), -10.86 (*cis* addition to ^tBuMe side isomer – hydride *trans* to CO, dt, $J_{\text{HP1}} = J_{\text{HP2}} = 12.4$ Hz, $J_{\text{HH}} = 3.4$ Hz), -11.63 (*cis* addition to ^tBuMe side isomer – hydride *cis* to CO, dt, $J_{\text{HP1}} = J_{\text{HP2}} = 12.4$ Hz, $J_{\text{HH}} = 3.4$ Hz), -11.74 (*cis* addition to bis-^tBu side isomer – hydride *cis* to CO, dt, $J_{\text{HP1}} = J_{\text{HP2}} = 14.5$ Hz, $J_{\text{HH}} = 3.1$ Hz).

Figure 6.4. ORTEP diagram of compound **2**.

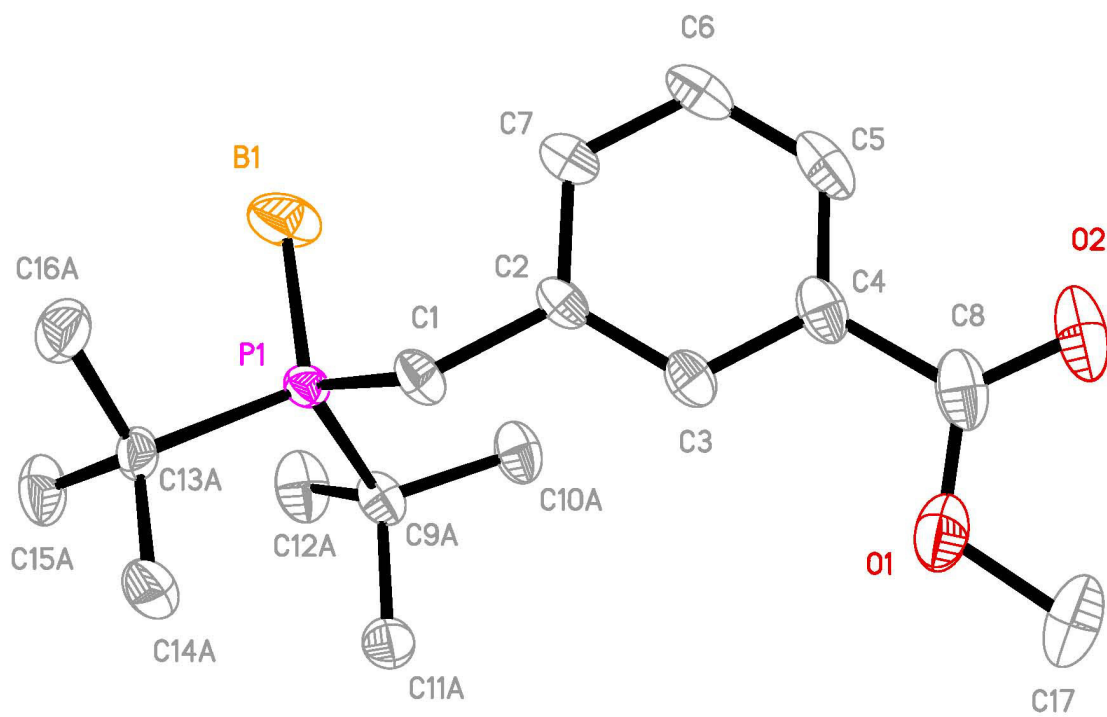


Table 6.1. Crystal data and structure refinement for **2**.

Identification code	dyw2-139	
Empirical formula	C17 H30 B O2 P	
Formula weight	308.19	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 14.5265(11) Å	$\alpha = 90^\circ$.
	b = 6.8077(5) Å	$\beta = 99.530(1)^\circ$.
	c = 18.7924(14) Å	$\gamma = 90^\circ$.
Volume	1832.8(2) Å ³	
Z	4	
Density (calculated)	1.117 Mg/m ³	
Absorption coefficient	0.152 mm ⁻¹	
F(000)	672	
Crystal size	0.40 x 0.25 x 0.22 mm ³	
Theta range for data collection	1.94 to 32.03°.	
Index ranges	-20 ≤ h ≤ 21, -10 ≤ k ≤ 10, -27 ≤ l ≤ 28	
Reflections collected	28942	
Independent reflections	6340 [R(int) = 0.0248]	
Completeness to theta = 32.03°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9674 and 0.9417	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6340 / 502 / 241	
Goodness-of-fit on F ²	1.006	
Final R indices [I > 2sigma(I)]	R1 = 0.0470, wR2 = 0.1178	
R indices (all data)	R1 = 0.0571, wR2 = 0.1247	
Largest diff. peak and hole	0.630 and -0.210 e.Å ⁻³	

Table 6.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
P(1)	9568(1)	3810(1)	2553(1)	20(1)
B(1)	9131(1)	1196(2)	2351(1)	46(1)
O(1)	8765(1)	9842(2)	-41(1)	46(1)
O(2)	7588(1)	8852(2)	-892(1)	50(1)
C(1)	8718(1)	5698(2)	2182(1)	24(1)
C(2)	8268(1)	5562(2)	1399(1)	24(1)
C(3)	8398(1)	7060(2)	922(1)	25(1)
C(4)	7937(1)	7034(2)	208(1)	29(1)
C(5)	7337(1)	5492(2)	-32(1)	38(1)
C(6)	7211(1)	3996(2)	436(1)	42(1)
C(7)	7669(1)	4025(2)	1150(1)	34(1)
C(8)	8057(1)	8651(2)	-302(1)	35(1)
C(9A)	10663(2)	4127(5)	2166(2)	26(1)
C(10A)	10431(8)	4040(13)	1332(3)	32(1)
C(11A)	11159(2)	6061(5)	2376(1)	37(1)
C(12A)	11324(2)	2398(6)	2424(1)	45(1)
C(13A)	9706(3)	4436(5)	3537(1)	24(1)
C(14A)	9853(2)	6639(4)	3708(1)	31(1)
C(15A)	10518(2)	3284(6)	3972(1)	34(1)
C(16A)	8799(4)	3807(12)	3802(6)	35(1)
C(9B)	10635(3)	4515(9)	2175(4)	26(1)
C(10B)	10390(15)	3850(20)	1380(6)	32(1)
C(11B)	10853(3)	6716(6)	2209(2)	30(1)
C(12B)	11509(3)	3385(8)	2522(2)	31(1)
C(13B)	9742(6)	4070(9)	3560(2)	24(1)
C(14B)	10168(4)	6042(7)	3820(2)	32(1)
C(15B)	10361(3)	2377(9)	3901(2)	36(1)
C(16B)	8775(7)	3850(20)	3785(11)	35(1)
C(17)	8946(2)	11434(3)	-509(1)	58(1)

Table 6.3. Bond lengths (Å) and angles (°) for **2**.

P(1)-C(1)	1.8375(10)	C(5)-C(6)	1.378(2)
P(1)-C(9A)	1.867(2)	C(6)-C(7)	1.3966(17)
P(1)-C(9B)	1.871(3)	C(9A)-C(11A)	1.521(4)
P(1)-C(13B)	1.876(3)	C(9A)-C(12A)	1.545(4)
P(1)-C(13A)	1.876(2)	C(9A)-C(10A)	1.549(4)
P(1)-B(1)	1.9057(14)	C(13A)-C(15A)	1.536(4)
O(1)-C(8)	1.3376(18)	C(13A)-C(16A)	1.544(4)
O(1)-C(17)	1.4467(18)	C(13A)-C(14A)	1.541(3)
O(2)-C(8)	1.2097(15)	C(9B)-C(11B)	1.531(6)
C(1)-C(2)	1.5104(13)	C(9B)-C(12B)	1.535(6)
C(2)-C(7)	1.3910(15)	C(9B)-C(10B)	1.546(6)
C(2)-C(3)	1.3919(15)	C(13B)-C(14B)	1.525(6)
C(3)-C(4)	1.3971(14)	C(13B)-C(15B)	1.535(6)
C(4)-C(5)	1.3898(18)	C(13B)-C(16B)	1.539(6)
C(4)-C(8)	1.4882(18)		
		C(7)-C(2)-C(1)	121.30(10)
C(1)-P(1)-C(9A)	109.49(12)	C(3)-C(2)-C(1)	120.00(9)
C(1)-P(1)-C(9B)	102.9(2)	C(2)-C(3)-C(4)	121.02(10)
C(9A)-P(1)-C(9B)	8.2(3)	C(5)-C(4)-C(3)	119.75(11)
C(1)-P(1)-C(13B)	106.6(2)	C(5)-C(4)-C(8)	118.95(11)
C(9A)-P(1)-C(13B)	113.6(3)	C(3)-C(4)-C(8)	121.29(11)
C(9B)-P(1)-C(13B)	112.1(3)	C(6)-C(5)-C(4)	119.58(11)
C(1)-P(1)-C(13A)	99.78(12)	C(5)-C(6)-C(7)	120.68(12)
C(9A)-P(1)-C(13A)	113.47(19)	C(2)-C(7)-C(6)	120.41(12)
C(9B)-P(1)-C(13A)	110.8(3)	O(2)-C(8)-O(1)	123.39(13)
C(13B)-P(1)-C(13A)	7.9(3)	O(2)-C(8)-C(4)	124.39(14)
C(1)-P(1)-B(1)	113.42(6)	O(1)-C(8)-C(4)	112.20(10)
C(9A)-P(1)-B(1)	107.90(14)	C(11A)-C(9A)-C(12A)	109.6(3)
C(9B)-P(1)-B(1)	115.7(2)	C(11A)-C(9A)-C(10A)	108.0(4)
C(13B)-P(1)-B(1)	105.9(2)	C(12A)-C(9A)-C(10A)	108.0(4)
C(13A)-P(1)-B(1)	112.72(13)	C(11A)-C(9A)-P(1)	113.4(2)
C(8)-O(1)-C(17)	115.89(12)	C(12A)-C(9A)-P(1)	108.34(19)
C(2)-C(1)-P(1)	118.78(7)	C(10A)-C(9A)-P(1)	109.4(6)
		C(15A)-C(13A)-C(16A)	107.9(4)
C(7)-C(2)-C(3)	118.56(10)	C(15A)-C(13A)-C(14A)	108.6(3)

C(16A)-C(13A)-C(14A)	107.4(4)	C(10B)-C(9B)-P(1)	102.7(10)
C(15A)-C(13A)-P(1)	110.9(2)	C(14B)-C(13B)-C(15B)	110.4(5)
C(16A)-C(13A)-P(1)	107.3(5)	C(14B)-C(13B)-C(16B)	109.7(7)
C(14A)-C(13A)-P(1)	114.54(18)	C(15B)-C(13B)-C(16B)	108.1(7)
C(11B)-C(9B)-C(12B)	108.8(4)	C(14B)-C(13B)-P(1)	112.8(4)
C(11B)-C(9B)-C(10B)	109.9(7)	C(15B)-C(13B)-P(1)	108.8(3)
C(12B)-C(9B)-C(10B)	107.8(7)	C(16B)-C(13B)-P(1)	106.9(9)
C(11B)-C(9B)-P(1)	114.5(3)		
C(12B)-C(9B)-P(1)	112.9(4)		

Table 6.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	19(1)	19(1)	21(1)	0(1)	-1(1)	0(1)
B(1)	47(1)	21(1)	63(1)	1(1)	-16(1)	-2(1)
O(1)	58(1)	41(1)	39(1)	15(1)	2(1)	4(1)
O(2)	47(1)	75(1)	28(1)	13(1)	2(1)	22(1)
C(1)	23(1)	26(1)	22(1)	-2(1)	-4(1)	5(1)
C(2)	18(1)	29(1)	22(1)	-2(1)	-3(1)	3(1)
C(3)	20(1)	29(1)	24(1)	-1(1)	-1(1)	6(1)
C(4)	24(1)	38(1)	23(1)	0(1)	1(1)	12(1)
C(5)	31(1)	55(1)	24(1)	-7(1)	-7(1)	5(1)
C(6)	35(1)	51(1)	35(1)	-8(1)	-11(1)	-11(1)
C(7)	28(1)	39(1)	31(1)	-1(1)	-5(1)	-8(1)
C(8)	35(1)	46(1)	26(1)	4(1)	6(1)	20(1)
C(9A)	20(1)	36(1)	23(1)	-4(1)	2(1)	6(1)
C(10A)	30(1)	42(2)	22(1)	0(1)	6(1)	7(1)
C(11A)	26(1)	55(2)	30(1)	2(1)	5(1)	-14(1)
C(12A)	32(1)	63(2)	38(1)	8(1)	6(1)	25(1)
C(13A)	22(1)	30(1)	19(1)	8(1)	0(1)	-1(1)
C(14A)	35(1)	35(1)	21(1)	-6(1)	1(1)	-2(1)
C(15A)	34(1)	43(2)	25(1)	10(1)	-1(1)	6(1)
C(16A)	29(1)	47(1)	30(1)	8(1)	8(1)	-3(1)
C(9B)	20(1)	36(1)	23(1)	-4(1)	2(1)	6(1)
C(10B)	30(1)	42(2)	22(1)	0(1)	6(1)	7(1)
C(11B)	26(2)	32(2)	33(2)	7(1)	9(1)	-1(1)
C(12B)	22(1)	37(2)	34(2)	2(2)	1(1)	9(1)
C(13B)	22(1)	30(1)	19(1)	8(1)	0(1)	-1(1)
C(14B)	42(2)	33(2)	20(2)	-2(1)	1(1)	-5(2)
C(15B)	43(2)	34(2)	27(2)	12(2)	-3(1)	12(2)
C(16B)	29(1)	47(1)	30(1)	8(1)	8(1)	-3(1)
C(17)	76(1)	47(1)	52(1)	24(1)	15(1)	10(1)

Table 6.5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**.

	x	y	z	U(eq)
H(1B1)	8504	1060	2473	70
H(2B1)	9555	269	2639	70
H(3B1)	9110	915	1837	70
H(1A)	8213	5700	2476	29
H(1B)	9034	6989	2253	29
H(3)	8807	8116	1083	30
H(5)	7017	5471	-516	46
H(6)	6807	2934	271	51
H(7)	7572	2989	1468	40
H(10A)	10112	2801	1184	47
H(10B)	11010	4121	1130	47
H(10C)	10023	5144	1154	47
H(11A)	11291	6171	2903	56
H(11B)	10759	7155	2177	56
H(11C)	11746	6104	2184	56
H(12A)	11000	1153	2297	67
H(12B)	11513	2472	2949	67
H(12C)	11878	2474	2191	67
H(14A)	9345	7396	3427	46
H(14B)	10450	7062	3581	46
H(14C)	9858	6860	4224	46
H(15A)	10427	1876	3877	52
H(15B)	10540	3537	4488	52
H(15C)	11107	3703	3829	52
H(16A)	8262	4415	3498	53
H(16B)	8822	4231	4303	53
H(16C)	8738	2374	3774	53
H(10D)	9858	4612	1136	47
H(10E)	10229	2450	1362	47
H(10F)	10929	4062	1137	47
H(11D)	10297	7454	1994	45
H(11E)	11364	6989	1941	45

H(11F)	11039	7115	2713	45
H(12D)	11626	3633	3043	47
H(12E)	12047	3825	2311	47
H(12F)	11412	1975	2434	47
H(14D)	10739	6261	3617	48
H(14E)	10318	6038	4348	48
H(14F)	9720	7095	3663	48
H(15D)	10077	1120	3731	53
H(15E)	10420	2446	4428	53
H(15F)	10980	2483	3762	53
H(16D)	8427	2804	3501	53
H(16E)	8432	5092	3698	53
H(16F)	8852	3523	4299	53
H(17A)	8385	12250	-625	86
H(17B)	9110	10894	-954	86
H(17C)	9463	12235	-264	86

Table 6.6. Torsion angles (°) for **2**.

C(9A)-P(1)-C(1)-C(2)	70.72(17)	C(13B)-P(1)-C(9A)-C(10A)	-175.8(4)
C(9B)-P(1)-C(1)-C(2)	75.9(3)	C(13A)-P(1)-C(9A)-C(10A)	-167.2(4)
C(13B)-P(1)-C(1)-C(2)	-166.0(3)	B(1)-P(1)-C(9A)-C(10A)	67.1(4)
C(13A)-P(1)-C(1)-C(2)	-169.97(16)	C(1)-P(1)-C(13A)-C(15A)	-170.3(2)
B(1)-P(1)-C(1)-C(2)	-49.85(12)	C(9A)-P(1)-C(13A)-C(15A)	-53.9(3)
P(1)-C(1)-C(2)-C(7)	65.92(13)	C(9B)-P(1)-C(13A)-C(15A)	-62.4(3)
P(1)-C(1)-C(2)-C(3)	-118.48(10)	C(13B)-P(1)-C(13A)-C(15A)	39(3)
C(7)-C(2)-C(3)-C(4)	0.26(15)	B(1)-P(1)-C(13A)-C(15A)	69.1(3)
C(1)-C(2)-C(3)-C(4)	-175.46(9)	C(1)-P(1)-C(13A)-C(16A)	72.1(4)
C(2)-C(3)-C(4)-C(5)	0.01(16)	C(9A)-P(1)-C(13A)-C(16A)	-171.5(4)
C(2)-C(3)-C(4)-C(8)	178.69(10)	C(9B)-P(1)-C(13A)-C(16A)	-180.0(4)
C(3)-C(4)-C(5)-C(6)	-0.53(18)	C(13B)-P(1)-C(13A)-C(16A)	-79(3)
C(8)-C(4)-C(5)-C(6)	-179.24(12)	B(1)-P(1)-C(13A)-C(16A)	-48.5(4)
C(4)-C(5)-C(6)-C(7)	0.8(2)	C(1)-P(1)-C(13A)-C(14A)	-47.0(3)
C(3)-C(2)-C(7)-C(6)	-0.02(18)	C(9A)-P(1)-C(13A)-C(14A)	69.3(3)
C(1)-C(2)-C(7)-C(6)	175.65(11)	C(9B)-P(1)-C(13A)-C(14A)	60.9(4)
C(5)-C(6)-C(7)-C(2)	-0.5(2)	C(13B)-P(1)-C(13A)-C(14A)	162(3)
C(17)-O(1)-C(8)-O(2)	0.39(19)	B(1)-P(1)-C(13A)-C(14A)	-167.7(2)
C(17)-O(1)-C(8)-C(4)	178.66(12)	C(1)-P(1)-C(9B)-C(11B)	43.8(5)
C(5)-C(4)-C(8)-O(2)	9.03(18)	C(9A)-P(1)-C(9B)-C(11B)	-172(3)
C(3)-C(4)-C(8)-O(2)	-169.67(11)	C(13B)-P(1)-C(9B)-C(11B)	-70.4(5)
C(5)-C(4)-C(8)-O(1)	-169.22(11)	C(13A)-P(1)-C(9B)-C(11B)	-62.1(5)
C(3)-C(4)-C(8)-O(1)	12.09(15)	B(1)-P(1)-C(9B)-C(11B)	168.1(4)
C(1)-P(1)-C(9A)-C(11A)	63.9(3)	C(1)-P(1)-C(9B)-C(12B)	169.0(4)
C(9B)-P(1)-C(9A)-C(11A)	26(2)	C(9A)-P(1)-C(9B)-C(12B)	-47(2)
C(13B)-P(1)-C(9A)-C(11A)	-55.1(3)	C(13B)-P(1)-C(9B)-C(12B)	54.8(5)
C(13A)-P(1)-C(9A)-C(11A)	-46.5(3)	C(13A)-P(1)-C(9B)-C(12B)	63.1(5)
B(1)-P(1)-C(9A)-C(11A)	-172.2(2)	B(1)-P(1)-C(9B)-C(12B)	-66.8(5)
C(1)-P(1)-C(9A)-C(12A)	-174.2(2)	C(1)-P(1)-C(9B)-C(10B)	-75.2(7)
C(9B)-P(1)-C(9A)-C(12A)	148(3)	C(9A)-P(1)-C(9B)-C(10B)	69(3)
C(13B)-P(1)-C(9A)-C(12A)	66.7(3)	C(13B)-P(1)-C(9B)-C(10B)	170.6(7)
C(13A)-P(1)-C(9A)-C(12A)	75.3(3)	C(13A)-P(1)-C(9B)-C(10B)	178.9(6)
B(1)-P(1)-C(9A)-C(12A)	-50.4(3)	B(1)-P(1)-C(9B)-C(10B)	49.0(7)
C(1)-P(1)-C(9A)-C(10A)	-56.7(4)	C(1)-P(1)-C(13B)-C(14B)	-63.5(5)
C(9B)-P(1)-C(9A)-C(10A)	-94(3)	C(9A)-P(1)-C(13B)-C(14B)	57.2(5)

C(9B)-P(1)-C(13B)-C(14B)	48.4(5)	B(1)-P(1)-C(13B)-C(15B)	52.5(5)
C(13A)-P(1)-C(13B)-C(14B)	-34(2)	C(1)-P(1)-C(13B)-C(16B)	57.1(6)
B(1)-P(1)-C(13B)-C(14B)	175.4(4)	C(9A)-P(1)-C(13B)-C(16B)	177.8(6)
C(1)-P(1)-C(13B)-C(15B)	173.6(4)	C(9B)-P(1)-C(13B)-C(16B)	169.0(6)
C(9A)-P(1)-C(13B)-C(15B)	-65.7(5)	C(13A)-P(1)-C(13B)-C(16B)	87(3)
C(9B)-P(1)-C(13B)-C(15B)	-74.5(5)	B(1)-P(1)-C(13B)-C(16B)	-64.0(6)
C(13A)-P(1)-C(13B)-C(15B)	-156(3)		

Figure 6.5. ORTEP diagram of compound **3**.

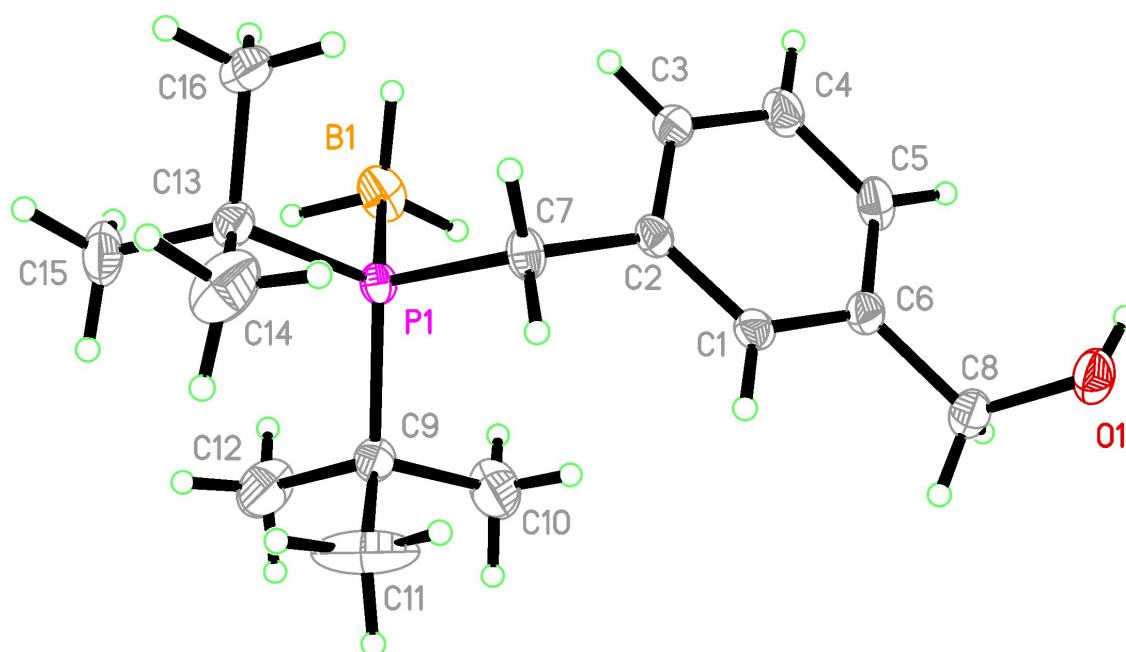


Table 6.7. Crystal data and structure refinement for **3**.

Identification code	dyw153	
Empirical formula	C16 H30 B O P	
Formula weight	280.18	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.119(5) Å	$\alpha = 90^\circ$.
	b = 13.889(9) Å	$\beta = 99.253(11)^\circ$.
	c = 15.007(10) Å	$\gamma = 90^\circ$.
Volume	1670.2(18) Å ³	
Z	4	
Density (calculated)	1.114 Mg/m ³	
Absorption coefficient	0.156 mm ⁻¹	
F(000)	616	
Crystal size	0.31 x 0.27 x 0.21 mm ³	
Theta range for data collection	2.01 to 31.00°.	
Index ranges	-11 ≤ h ≤ 11, -20 ≤ k ≤ 20, -21 ≤ l ≤ 21	
Reflections collected	20000	
Independent reflections	5320 [R(int) = 0.0218]	
Completeness to theta = 31.00°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.9680 and 0.9532	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5320 / 0 / 188	
Goodness-of-fit on F ²	1.014	
Final R indices [I > 2σ(I)]	R1 = 0.0454, wR2 = 0.1152	
R indices (all data)	R1 = 0.0506, wR2 = 0.1192	
Largest diff. peak and hole	0.641 and -0.516 e.Å ⁻³	

Table 6.8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
P(1)	768(1)	9696(1)	2481(1)	16(1)
O(1)	6012(1)	8385(1)	-902(1)	27(1)
C(1)	3499(1)	9059(1)	661(1)	19(1)
C(2)	1858(1)	9099(1)	834(1)	18(1)
C(3)	757(2)	8371(1)	497(1)	24(1)
C(4)	1297(2)	7610(1)	19(1)	28(1)
C(5)	2943(2)	7562(1)	-124(1)	26(1)
C(6)	4059(1)	8292(1)	191(1)	21(1)
C(7)	1265(2)	9938(1)	1343(1)	21(1)
C(8)	5845(2)	8253(1)	23(1)	28(1)
C(9)	2782(1)	9801(1)	3279(1)	21(1)
C(10)	3951(2)	9032(1)	3024(1)	45(1)
C(11)	3622(2)	10776(1)	3248(2)	60(1)
C(12)	2518(2)	9601(2)	4246(1)	57(1)
C(13)	-739(1)	10681(1)	2630(1)	22(1)
C(14)	-109(2)	11686(1)	2430(1)	42(1)
C(15)	-1187(2)	10664(1)	3583(1)	38(1)
C(16)	-2340(2)	10478(1)	1960(1)	36(1)
B(1)	-233(2)	8454(1)	2613(1)	29(1)

Table 6.9. Bond lengths (Å) and angles (°) for **3**.

P(1)-C(7)	1.8484(15)	C(10)-H(10A)	0.9800
P(1)-C(9)	1.8705(15)	C(10)-H(10B)	0.9800
P(1)-C(13)	1.8719(14)	C(10)-H(10C)	0.9800
P(1)-B(1)	1.9313(17)	C(11)-H(11A)	0.9800
O(1)-C(8)	1.4271(17)	C(11)-H(11B)	0.9800
O(1)-H(1O)	0.8400	C(11)-H(11C)	0.9800
C(1)-C(6)	1.3924(17)	C(12)-H(12A)	0.9800
C(1)-C(2)	1.3987(17)	C(12)-H(12B)	0.9800
C(1)-H(1)	0.9500	C(12)-H(12C)	0.9800
C(2)-C(3)	1.3905(16)	C(13)-C(15)	1.532(2)
C(2)-C(7)	1.5126(17)	C(13)-C(14)	1.533(2)
C(3)-C(4)	1.3871(18)	C(13)-C(16)	1.5359(19)
C(3)-H(3)	0.9500	C(14)-H(14A)	0.9800
C(4)-C(5)	1.389(2)	C(14)-H(14B)	0.9800
C(4)-H(4)	0.9500	C(14)-H(14C)	0.9800
C(5)-C(6)	1.3908(18)	C(15)-H(15A)	0.9800
C(5)-H(5)	0.9500	C(15)-H(15B)	0.9800
C(6)-C(8)	1.5128(19)	C(15)-H(15C)	0.9800
C(7)-H(7A)	0.9900	C(16)-H(16A)	0.9800
C(7)-H(7B)	0.9900	C(16)-H(16B)	0.9800
C(8)-H(8A)	0.9900	C(16)-H(16C)	0.9800
C(8)-H(8B)	0.9900	B(1)-H(1B)	1.09(2)
C(9)-C(10)	1.5186(19)	B(1)-H(2B)	1.127(19)
C(9)-C(11)	1.520(2)	B(1)-H(3B)	1.12(2)
C(9)-C(12)	1.526(2)		

C(7)-P(1)-C(9)	106.19(7)	C(10)-C(9)-C(11)	108.57(15)
C(7)-P(1)-C(13)	102.82(6)	C(10)-C(9)-C(12)	107.45(13)
C(9)-P(1)-C(13)	112.82(6)	C(11)-C(9)-C(12)	108.87(15)
C(7)-P(1)-B(1)	114.48(6)	C(10)-C(9)-P(1)	107.52(10)
C(9)-P(1)-B(1)	110.08(7)	C(11)-C(9)-P(1)	113.62(9)
C(13)-P(1)-B(1)	110.29(8)	C(12)-C(9)-P(1)	110.60(10)
C(8)-O(1)-H(10)	109.5	C(9)-C(10)-H(10A)	109.5
C(6)-C(1)-C(2)	121.55(10)	C(9)-C(10)-H(10B)	109.5
C(6)-C(1)-H(1)	119.2	H(10A)-C(10)-H(10B)	109.5
C(2)-C(1)-H(1)	119.2	C(9)-C(10)-H(10C)	109.5
C(3)-C(2)-C(1)	118.60(11)	H(10A)-C(10)-H(10C)	109.5
C(3)-C(2)-C(7)	120.34(11)	H(10B)-C(10)-H(10C)	109.5
C(1)-C(2)-C(7)	121.01(10)	C(9)-C(11)-H(11A)	109.5
C(4)-C(3)-C(2)	120.29(11)	C(9)-C(11)-H(11B)	109.5
C(4)-C(3)-H(3)	119.9	H(11A)-C(11)-H(11B)	109.5
C(2)-C(3)-H(3)	119.9	C(9)-C(11)-H(11C)	109.5
C(3)-C(4)-C(5)	120.53(11)	H(11A)-C(11)-H(11C)	109.5
C(3)-C(4)-H(4)	119.7	H(11B)-C(11)-H(11C)	109.5
C(5)-C(4)-H(4)	119.7	C(9)-C(12)-H(12A)	109.5
C(4)-C(5)-C(6)	120.19(11)	C(9)-C(12)-H(12B)	109.5
C(4)-C(5)-H(5)	119.9	H(12A)-C(12)-H(12B)	109.5
C(6)-C(5)-H(5)	119.9	C(9)-C(12)-H(12C)	109.5
C(5)-C(6)-C(1)	118.79(11)	H(12A)-C(12)-H(12C)	109.5
C(5)-C(6)-C(8)	120.42(11)	H(12B)-C(12)-H(12C)	109.5
C(1)-C(6)-C(8)	120.78(11)	C(15)-C(13)-C(14)	109.48(12)
C(2)-C(7)-P(1)	117.49(8)	C(15)-C(13)-C(16)	107.78(11)
C(2)-C(7)-H(7A)	107.9	C(14)-C(13)-C(16)	108.23(12)
P(1)-C(7)-H(7A)	107.9	C(15)-C(13)-P(1)	110.97(9)
C(2)-C(7)-H(7B)	107.9	C(14)-C(13)-P(1)	113.39(10)
P(1)-C(7)-H(7B)	107.9	C(16)-C(13)-P(1)	106.78(10)
H(7A)-C(7)-H(7B)	107.2	C(13)-C(14)-H(14A)	109.5
O(1)-C(8)-C(6)	113.64(10)	C(13)-C(14)-H(14B)	109.5
O(1)-C(8)-H(8A)	108.8	H(14A)-C(14)-H(14B)	109.5
C(6)-C(8)-H(8A)	108.8	C(13)-C(14)-H(14C)	109.5
O(1)-C(8)-H(8B)	108.8	H(14A)-C(14)-H(14C)	109.5
C(6)-C(8)-H(8B)	108.8	H(14B)-C(14)-H(14C)	109.5
H(8A)-C(8)-H(8B)	107.7	C(13)-C(15)-H(15A)	109.5

C(13)-C(15)-H(15B)	109.5	H(16A)-C(16)-H(16C)	109.5
H(15A)-C(15)-H(15B)	109.5	H(16B)-C(16)-H(16C)	109.5
C(13)-C(15)-H(15C)	109.5	P(1)-B(1)-H(1B)	108.0(10)
H(15A)-C(15)-H(15C)	109.5	P(1)-B(1)-H(2B)	104.8(10)
H(15B)-C(15)-H(15C)	109.5	H(1B)-B(1)-H(2B)	110.8(14)
C(13)-C(16)-H(16A)	109.5	P(1)-B(1)-H(3B)	109.0(10)
C(13)-C(16)-H(16B)	109.5	H(1B)-B(1)-H(3B)	112.3(14)
H(16A)-C(16)-H(16B)	109.5	H(2B)-B(1)-H(3B)	111.5(14)
C(13)-C(16)-H(16C)	109.5		

Table 6.10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	19(1)	17(1)	13(1)	2(1)	5(1)	0(1)
O(1)	31(1)	27(1)	28(1)	-2(1)	14(1)	-6(1)
C(1)	20(1)	22(1)	14(1)	1(1)	3(1)	-3(1)
C(2)	21(1)	20(1)	13(1)	1(1)	4(1)	-1(1)
C(3)	20(1)	31(1)	20(1)	-4(1)	5(1)	-6(1)
C(4)	31(1)	30(1)	25(1)	-10(1)	10(1)	-12(1)
C(5)	34(1)	24(1)	22(1)	-5(1)	12(1)	-3(1)
C(6)	21(1)	25(1)	16(1)	2(1)	5(1)	1(1)
C(7)	28(1)	20(1)	16(1)	3(1)	8(1)	2(1)
C(8)	22(1)	37(1)	24(1)	0(1)	7(1)	3(1)
C(9)	20(1)	26(1)	18(1)	2(1)	3(1)	4(1)
C(10)	39(1)	60(1)	32(1)	-11(1)	-6(1)	30(1)
C(11)	40(1)	40(1)	87(2)	16(1)	-31(1)	-14(1)
C(12)	30(1)	124(2)	16(1)	6(1)	2(1)	11(1)
C(13)	19(1)	25(1)	21(1)	0(1)	4(1)	4(1)
C(14)	37(1)	22(1)	71(1)	5(1)	14(1)	8(1)
C(15)	39(1)	53(1)	23(1)	-4(1)	10(1)	18(1)
C(16)	20(1)	59(1)	28(1)	-3(1)	2(1)	6(1)
B(1)	41(1)	23(1)	24(1)	2(1)	11(1)	-9(1)

Table 6.11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**.

	x	y	z	U(eq)
H(1O)	5620	7904	-1202	41
H(1)	4249	9566	868	23
H(3)	-370	8395	593	28
H(4)	534	7118	-212	34
H(5)	3308	7030	-439	31
H(7A)	254	10207	969	25
H(7B)	2136	10443	1400	25
H(8A)	6497	8758	389	33
H(8B)	6330	7622	229	33
H(10A)	4177	9153	2412	68
H(10B)	3428	8398	3045	68
H(10C)	5000	9047	3450	68
H(11A)	4720	10761	3631	90
H(11B)	2931	11273	3469	90
H(11C)	3757	10923	2626	90
H(12A)	1880	9004	4262	85
H(12B)	1901	10136	4462	85
H(12C)	3604	9534	4635	85
H(14A)	-1017	12153	2417	64
H(14B)	276	11681	1844	64
H(14C)	818	11867	2903	64
H(15A)	-211	10854	4021	56
H(15B)	-1532	10012	3723	56
H(15C)	-2104	11114	3616	56
H(16A)	-2775	9842	2085	54
H(16B)	-2091	10492	1343	54
H(16C)	-3176	10971	2026	54
H(1B)	700(20)	7900(15)	2542(12)	43
H(2B)	-540(20)	8455(14)	3318(13)	43
H(3B)	-1380(20)	8382(14)	2095(13)	43

Table 6.12. Torsion angles (°) for **3**.

C(6)-C(1)-C(2)-C(3)	-2.46(16)	C(13)-P(1)-C(9)-C(10)	-174.07(10)
C(6)-C(1)-C(2)-C(7)	-179.82(10)	B(1)-P(1)-C(9)-C(10)	62.26(12)
C(1)-C(2)-C(3)-C(4)	1.68(17)	C(7)-P(1)-C(9)-C(11)	57.99(14)
C(7)-C(2)-C(3)-C(4)	179.06(11)	C(13)-P(1)-C(9)-C(11)	-53.90(15)
C(2)-C(3)-C(4)-C(5)	0.3(2)	B(1)-P(1)-C(9)-C(11)	-177.56(13)
C(3)-C(4)-C(5)-C(6)	-1.6(2)	C(7)-P(1)-C(9)-C(12)	-179.23(12)
C(4)-C(5)-C(6)-C(1)	0.87(18)	C(13)-P(1)-C(9)-C(12)	68.88(13)
C(4)-C(5)-C(6)-C(8)	-178.91(12)	B(1)-P(1)-C(9)-C(12)	-54.78(13)
C(2)-C(1)-C(6)-C(5)	1.19(17)	C(7)-P(1)-C(13)-C(15)	-174.70(10)
C(2)-C(1)-C(6)-C(8)	-179.03(10)	C(9)-P(1)-C(13)-C(15)	-60.75(11)
C(3)-C(2)-C(7)-P(1)	70.84(13)	B(1)-P(1)-C(13)-C(15)	62.80(11)
C(1)-C(2)-C(7)-P(1)	-111.85(11)	C(7)-P(1)-C(13)-C(14)	-51.01(12)
C(9)-P(1)-C(7)-C(2)	85.78(10)	C(9)-P(1)-C(13)-C(14)	62.94(12)
C(13)-P(1)-C(7)-C(2)	-155.52(9)	B(1)-P(1)-C(13)-C(14)	-173.51(11)
B(1)-P(1)-C(7)-C(2)	-35.89(12)	C(7)-P(1)-C(13)-C(16)	68.10(10)
C(5)-C(6)-C(8)-O(1)	69.06(16)	C(9)-P(1)-C(13)-C(16)	-177.95(9)
C(1)-C(6)-C(8)-O(1)	-110.71(13)	B(1)-P(1)-C(13)-C(16)	-54.40(11)
C(7)-P(1)-C(9)-C(10)	-62.18(12)		

Figure 6.6. ORTEP diagram of compound **4**.

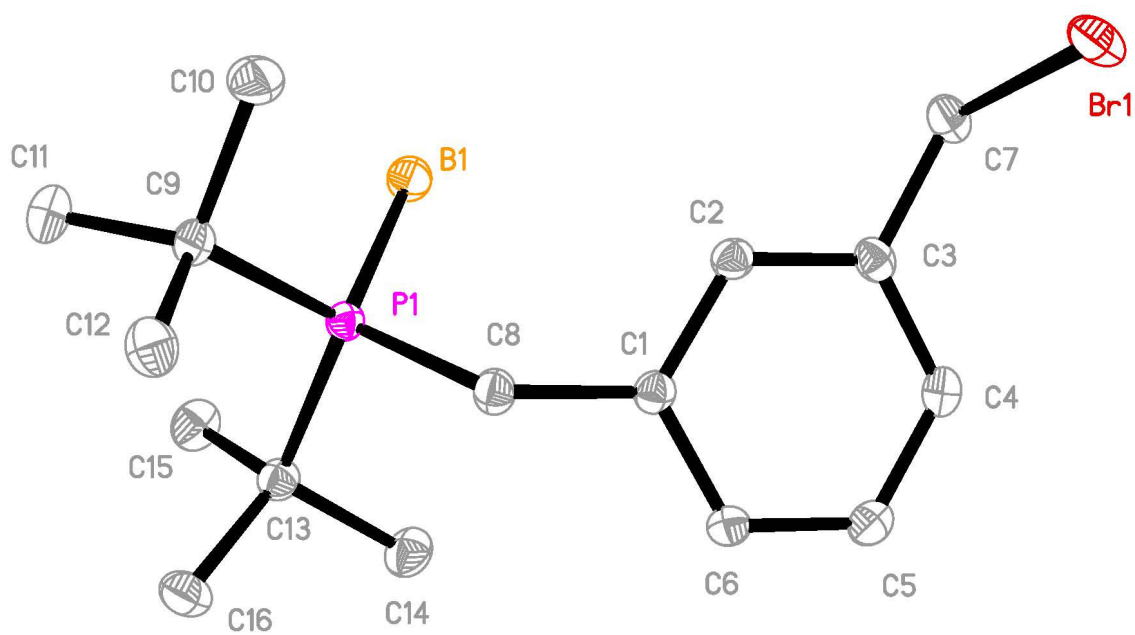


Table 6.13. Crystal data and structure refinement for **4**.

Identification code	dyw1149	
Empirical formula	C ₁₆ H ₂₉ B Br P	
Formula weight	343.08	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.9157(6) Å	α = 81.703(1)°.
	b = 8.5216(7) Å	β = 79.170(1)°.
	c = 14.9218(12) Å	γ = 62.750(1)°.
Volume	876.94(12) Å ³	
Z	2	
Density (calculated)	1.299 Mg/m ³	
Absorption coefficient	2.422 mm ⁻¹	
F(000)	360	
Crystal size	0.44 x 0.20 x 0.20 mm ³	
Theta range for data collection	2.69 to 30.03°.	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 11, -20 ≤ l ≤ 21	
Reflections collected	10125	
Independent reflections	5040 [R(int) = 0.0193]	
Completeness to theta = 30.03°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.444 and 0.333	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5040 / 0 / 288	
Goodness-of-fit on F ²	1.004	
Final R indices [I > 2σ(I)]	R1 = 0.0314, wR2 = 0.0790	
R indices (all data)	R1 = 0.0360, wR2 = 0.0816	
Largest diff. peak and hole	0.929 and -0.253 e.Å ⁻³	

Table 6.14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Br(1)	-3676(1)	3992(1)	-6348(1)	23(1)
P(1)	-128(1)	2694(1)	-2140(1)	13(1)
B(1)	-1213(3)	1089(3)	-2190(1)	20(1)
C(1)	576(2)	3058(2)	-4121(1)	14(1)
C(2)	-865(2)	2857(2)	-4432(1)	15(1)
C(3)	-564(2)	2170(2)	-5269(1)	15(1)
C(4)	1214(2)	1666(2)	-5815(1)	17(1)
C(5)	2648(2)	1891(2)	-5524(1)	18(1)
C(6)	2331(2)	2593(2)	-4686(1)	16(1)
C(7)	-2137(2)	1942(2)	-5565(1)	18(1)
C(8)	178(2)	3909(2)	-3236(1)	16(1)
C(9)	-1782(2)	4543(2)	-1392(1)	16(1)
C(10)	-3790(2)	5206(2)	-1667(1)	24(1)
C(11)	-1863(3)	3850(2)	-387(1)	22(1)
C(12)	-1289(3)	6110(2)	-1508(1)	21(1)
C(13)	2295(2)	1453(2)	-1759(1)	16(1)
C(14)	3689(2)	433(2)	-2570(1)	23(1)
C(15)	2240(3)	95(2)	-970(1)	23(1)
C(16)	3061(3)	2635(2)	-1471(1)	22(1)

Table 6.15. Bond lengths (Å) and angles (°) for **4**.

Br(1)-C(7)	1.9744(16)	C(9)-C(11)	1.532(2)
P(1)-C(8)	1.8437(16)	C(9)-C(12)	1.534(2)
P(1)-C(13)	1.8699(16)	C(9)-C(10)	1.539(2)
P(1)-C(9)	1.8734(15)	C(10)-H(10A)	0.97(2)
P(1)-B(1)	1.9344(18)	C(10)-H(10B)	0.93(3)
B(1)-H(1A)	1.07(2)	C(10)-H(10C)	0.95(2)
B(1)-H(1B)	1.14(2)	C(11)-H(11A)	0.95(2)
B(1)-H(1C)	1.11(2)	C(11)-H(11B)	0.97(3)
C(1)-C(2)	1.395(2)	C(11)-H(11C)	0.97(3)
C(1)-C(6)	1.397(2)	C(12)-H(12A)	0.97(2)
C(1)-C(8)	1.510(2)	C(12)-H(12B)	0.97(2)
C(2)-C(3)	1.390(2)	C(12)-H(12C)	0.91(3)
C(2)-H(2)	0.94(2)	C(13)-C(16)	1.533(2)
C(3)-C(4)	1.394(2)	C(13)-C(14)	1.537(2)
C(3)-C(7)	1.495(2)	C(13)-C(15)	1.537(2)
C(4)-C(5)	1.386(2)	C(14)-H(14A)	0.96(2)
C(4)-H(4)	0.90(2)	C(14)-H(14B)	0.98(3)
C(5)-C(6)	1.394(2)	C(14)-H(14C)	0.92(2)
C(5)-H(5)	0.92(2)	C(15)-H(15A)	0.99(2)
C(6)-H(6)	0.90(2)	C(15)-H(15B)	0.95(3)
C(7)-H(7A)	0.95(2)	C(15)-H(15C)	0.97(2)
C(7)-H(7B)	0.96(2)	C(16)-H(16A)	0.95(3)
C(8)-H(8A)	0.94(2)	C(16)-H(16B)	0.95(2)
C(8)-H(8B)	0.93(2)	C(16)-H(16C)	0.97(2)
C(8)-P(1)-C(13)	106.80(7)	H(1A)-B(1)-H(1C)	115.7(17)
C(8)-P(1)-C(9)	101.81(7)	H(1B)-B(1)-H(1C)	110.7(17)
C(13)-P(1)-C(9)	111.91(7)	C(2)-C(1)-C(6)	118.17(14)
C(8)-P(1)-B(1)	114.64(8)	C(2)-C(1)-C(8)	120.47(13)
C(13)-P(1)-B(1)	110.17(8)	C(6)-C(1)-C(8)	121.13(13)
C(9)-P(1)-B(1)	111.23(7)	C(3)-C(2)-C(1)	121.48(14)
P(1)-B(1)-H(1A)	107.9(13)	C(3)-C(2)-H(2)	118.9(13)
P(1)-B(1)-H(1B)	104.7(12)	C(1)-C(2)-H(2)	119.6(13)
H(1A)-B(1)-H(1B)	109.7(18)	C(2)-C(3)-C(4)	119.64(14)
P(1)-B(1)-H(1C)	107.5(11)	C(2)-C(3)-C(7)	119.58(14)

C(4)-C(3)-C(7)	120.76(14)	C(9)-C(11)-H(11B)	111.5(14)
C(5)-C(4)-C(3)	119.57(14)	H(11A)-C(11)-H(11B)	109.3(19)
C(5)-C(4)-H(4)	117.8(15)	C(9)-C(11)-H(11C)	110.3(15)
C(3)-C(4)-H(4)	122.6(15)	H(11A)-C(11)-H(11C)	107.3(19)
C(4)-C(5)-C(6)	120.44(15)	H(11B)-C(11)-H(11C)	104(2)
C(4)-C(5)-H(5)	120.1(13)	C(9)-C(12)-H(12A)	106.3(14)
C(6)-C(5)-H(5)	119.4(13)	C(9)-C(12)-H(12B)	113.3(14)
C(5)-C(6)-C(1)	120.66(14)	H(12A)-C(12)-H(12B)	107.5(19)
C(5)-C(6)-H(6)	121.1(13)	C(9)-C(12)-H(12C)	112.9(16)
C(1)-C(6)-H(6)	118.2(13)	H(12A)-C(12)-H(12C)	110(2)
C(3)-C(7)-Br(1)	111.92(11)	H(12B)-C(12)-H(12C)	107(2)
C(3)-C(7)-H(7A)	111.1(14)	C(16)-C(13)-C(14)	108.25(14)
Br(1)-C(7)-H(7A)	103.5(14)	C(16)-C(13)-C(15)	109.71(14)
C(3)-C(7)-H(7B)	114.2(14)	C(14)-C(13)-C(15)	107.95(13)
Br(1)-C(7)-H(7B)	100.8(15)	C(16)-C(13)-P(1)	114.07(11)
H(7A)-C(7)-H(7B)	114(2)	C(14)-C(13)-P(1)	107.14(11)
C(1)-C(8)-P(1)	119.51(11)	C(15)-C(13)-P(1)	109.51(11)
C(1)-C(8)-H(8A)	108.6(14)	C(13)-C(14)-H(14A)	111.8(13)
P(1)-C(8)-H(8A)	101.9(14)	C(13)-C(14)-H(14B)	113.6(16)
C(1)-C(8)-H(8B)	110.6(13)	H(14A)-C(14)-H(14B)	107(2)
P(1)-C(8)-H(8B)	105.0(14)	C(13)-C(14)-H(14C)	108.4(15)
H(8A)-C(8)-H(8B)	110.9(19)	H(14A)-C(14)-H(14C)	110(2)
C(11)-C(9)-C(12)	109.93(13)	H(14B)-C(14)-H(14C)	106(2)
C(11)-C(9)-C(10)	107.77(14)	C(13)-C(15)-H(15A)	109.4(14)
C(12)-C(9)-C(10)	108.22(14)	C(13)-C(15)-H(15B)	107.3(15)
C(11)-C(9)-P(1)	110.31(11)	H(15A)-C(15)-H(15B)	110(2)
C(12)-C(9)-P(1)	114.30(11)	C(13)-C(15)-H(15C)	113.3(14)
C(10)-C(9)-P(1)	106.01(11)	H(15A)-C(15)-H(15C)	110.4(19)
C(9)-C(10)-H(10A)	112.5(15)	H(15B)-C(15)-H(15C)	106(2)
C(9)-C(10)-H(10B)	111.3(15)	C(13)-C(16)-H(16A)	108.3(16)
H(10A)-C(10)-H(10B)	109(2)	C(13)-C(16)-H(16B)	115.1(14)
C(9)-C(10)-H(10C)	108.6(14)	H(16A)-C(16)-H(16B)	110(2)
H(10A)-C(10)-H(10C)	107(2)	C(13)-C(16)-H(16C)	112.6(13)
H(10B)-C(10)-H(10C)	108(2)	H(16A)-C(16)-H(16C)	108(2)
C(9)-C(11)-H(11A)	113.8(12)	H(16B)-C(16)-H(16C)	102.3(19)

Table 6.16. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	22(1)	24(1)	29(1)	7(1)	-13(1)	-13(1)
P(1)	13(1)	14(1)	13(1)	-2(1)	-1(1)	-7(1)
B(1)	23(1)	23(1)	19(1)	-4(1)	0(1)	-16(1)
C(1)	16(1)	14(1)	14(1)	0(1)	-2(1)	-7(1)
C(2)	13(1)	15(1)	15(1)	0(1)	-2(1)	-6(1)
C(3)	18(1)	14(1)	15(1)	2(1)	-6(1)	-8(1)
C(4)	21(1)	16(1)	13(1)	-1(1)	-2(1)	-8(1)
C(5)	17(1)	19(1)	17(1)	-1(1)	0(1)	-8(1)
C(6)	16(1)	20(1)	16(1)	0(1)	-2(1)	-10(1)
C(7)	22(1)	19(1)	18(1)	3(1)	-7(1)	-12(1)
C(8)	18(1)	16(1)	14(1)	-1(1)	-2(1)	-9(1)
C(9)	16(1)	16(1)	15(1)	-4(1)	-1(1)	-6(1)
C(10)	15(1)	25(1)	28(1)	-8(1)	-2(1)	-4(1)
C(11)	26(1)	24(1)	15(1)	-4(1)	0(1)	-10(1)
C(12)	24(1)	17(1)	22(1)	-4(1)	-3(1)	-9(1)
C(13)	15(1)	16(1)	16(1)	-1(1)	-2(1)	-5(1)
C(14)	17(1)	23(1)	21(1)	-3(1)	0(1)	-3(1)
C(15)	24(1)	21(1)	20(1)	4(1)	-4(1)	-7(1)
C(16)	19(1)	26(1)	25(1)	-1(1)	-6(1)	-11(1)

Table 6.17. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**.

	x	y	z	U(eq)
H(1A)	-2430(30)	1780(30)	-2546(16)	30(6)
H(1B)	-1700(30)	780(30)	-1444(17)	34(6)
H(1C)	-50(30)	-120(30)	-2498(15)	24(5)
H(2)	-2070(30)	3210(30)	-4076(15)	21(5)
H(4)	1460(30)	1230(30)	-6364(16)	24(5)
H(5)	3810(30)	1610(30)	-5892(14)	18(5)
H(6)	3250(30)	2760(30)	-4494(14)	15(5)
H(7A)	-3050(30)	1910(30)	-5055(16)	26(6)
H(7B)	-1700(30)	1000(30)	-5965(17)	34(6)
H(8A)	-1010(30)	4920(30)	-3217(15)	26(5)
H(8B)	1150(30)	4200(30)	-3189(15)	21(5)
H(10A)	-4230(30)	4300(30)	-1567(17)	31(6)
H(10B)	-3820(30)	5640(30)	-2273(18)	34(6)
H(10C)	-4680(30)	6150(30)	-1296(17)	33(6)
H(11A)	-710(30)	3520(30)	-137(14)	17(5)
H(11B)	-2180(30)	2860(30)	-296(16)	30(6)
H(11C)	-2900(40)	4750(30)	-13(18)	38(7)
H(12A)	-2260(30)	6980(30)	-1102(16)	29(6)
H(12B)	-1330(30)	6670(30)	-2121(16)	29(6)
H(12C)	-100(40)	5810(30)	-1362(17)	32(6)
H(14A)	3880(30)	1210(30)	-3064(16)	25(5)
H(14B)	3260(40)	-310(40)	-2823(19)	41(7)
H(14C)	4840(40)	-320(30)	-2371(16)	31(6)
H(15A)	3540(30)	-610(30)	-795(16)	30(6)
H(15B)	1830(30)	-650(30)	-1184(16)	31(6)
H(15C)	1330(30)	630(30)	-443(17)	30(6)
H(16A)	4360(40)	1930(30)	-1389(17)	36(7)
H(16B)	2370(30)	3250(30)	-938(16)	23(5)
H(16C)	2990(30)	3600(30)	-1926(16)	25(5)

Table 6.18. Torsion angles (°) for **4**.

C(6)-C(1)-C(2)-C(3)	1.7(2)	C(13)-P(1)-C(9)-C(11)	-53.19(13)
C(8)-C(1)-C(2)-C(3)	176.27(14)	B(1)-P(1)-C(9)-C(11)	70.52(13)
C(1)-C(2)-C(3)-C(4)	0.0(2)	C(8)-P(1)-C(9)-C(12)	-42.44(13)
C(1)-C(2)-C(3)-C(7)	178.64(14)	C(13)-P(1)-C(9)-C(12)	71.29(13)
C(2)-C(3)-C(4)-C(5)	-1.4(2)	B(1)-P(1)-C(9)-C(12)	-165.00(12)
C(7)-C(3)-C(4)-C(5)	-179.98(15)	C(8)-P(1)-C(9)-C(10)	76.67(12)
C(3)-C(4)-C(5)-C(6)	1.0(2)	C(13)-P(1)-C(9)-C(10)	-169.60(11)
C(4)-C(5)-C(6)-C(1)	0.8(2)	B(1)-P(1)-C(9)-C(10)	-45.89(14)
C(2)-C(1)-C(6)-C(5)	-2.2(2)	C(8)-P(1)-C(13)-C(16)	69.20(13)
C(8)-C(1)-C(6)-C(5)	-176.67(14)	C(9)-P(1)-C(13)-C(16)	-41.41(14)
C(2)-C(3)-C(7)-Br(1)	94.58(15)	B(1)-P(1)-C(13)-C(16)	-165.71(12)
C(4)-C(3)-C(7)-Br(1)	-86.83(16)	C(8)-P(1)-C(13)-C(14)	-50.58(13)
C(2)-C(1)-C(8)-P(1)	72.03(17)	C(9)-P(1)-C(13)-C(14)	-161.19(11)
C(6)-C(1)-C(8)-P(1)	-113.59(15)	B(1)-P(1)-C(13)-C(14)	74.52(13)
C(13)-P(1)-C(8)-C(1)	91.58(13)	C(8)-P(1)-C(13)-C(15)	-167.42(11)
C(9)-P(1)-C(8)-C(1)	-150.94(12)	C(9)-P(1)-C(13)-C(15)	81.98(12)
B(1)-P(1)-C(8)-C(1)	-30.75(15)	B(1)-P(1)-C(13)-C(15)	-42.32(13)
C(8)-P(1)-C(9)-C(11)	-166.91(11)		

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Chapter 7

Addition of Tropone to (^tBuPCP)IrH₂: Formation of a Dimerization Product

Abstract

Adducts of tropone with (PCP)IrH₂ (PCP = κ^3 -C₆H₃-2,6-(CH₂P^tBu₂)₂) have been observed. The thermodynamic and kinetic products have been synthesized and characterized. The thermodynamic product was previously found to catalyze the dimerization of tropone to give a fused tricyclic dihydrodicycloheptafuranol. The formation of this tropone dimer was investigated. A possible mechanism for the dimerization reaction is suggested in which tropone, normally an electrophile, acts as a nucleophile upon activation by C-H oxidative addition to the iridium(I) center.

7.1 Introduction

α,β -unsaturated ketones are of great utility in a wide variety of organic transformations, arising from the ability to activate and functionalize the carbonyl moiety and positions α , β , and γ to the carbonyl group. Classically, α,β -unsaturated ketones can be prepared via aldol condensation,¹ allylic oxidation,²⁻⁴ and elimination reactions from α -substituted ketones.⁵ These methods often require several steps or may be complicated by low yields and unwanted byproducts. A simple one-step reaction to introduce the double bond into an aliphatic molecular framework would be a desirable synthetic tool.

Direct dehydrogenation of ketones has been one strategy to approach α,β -unsaturated ketones. Dehydrogenation of ketone substrates by palladium complexes in both stoichiometric and catalytic amounts have been reported, although efforts at catalytic reactions have been hampered by low conversions and yields.⁶⁻⁹ The use of substituted iodoxybenzoic acids with Oxone has been reported to effect the formation of α,β -unsaturated ketones from alcohols, presumably via initial alcohol oxidation and subsequent ketone dehydrogenation; however, the formation of α,β -unsaturated ketones by this method is limited to cyclic substrates.¹⁰

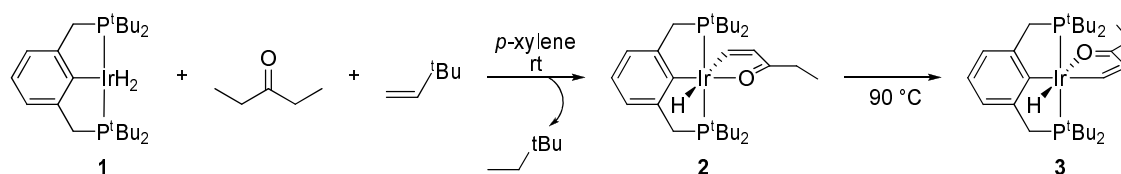
Pincer-ligated iridium complexes, specifically derivatives of “(PCP)Ir” (PCP = κ^3 -C₆H₃-2,6-(CH₂PR₂)₂; R = t-Bu in this chapter) (**1**), are the most successful class of catalysts for the dehydrogenation of aliphatic linkages reported to date.^{11,12} In addition to the dehydrogenation of alkanes, the catalytic dehydrogenation of THF¹³ and amines¹⁴ has been reported with selectivity for the α,β -position. Work performed by Xiawei Zhang, a previous graduate student in our group, had shown that ketone dehydrogenation occurs readily but in general the resulting enones, or products of further dehydrogenation, tend

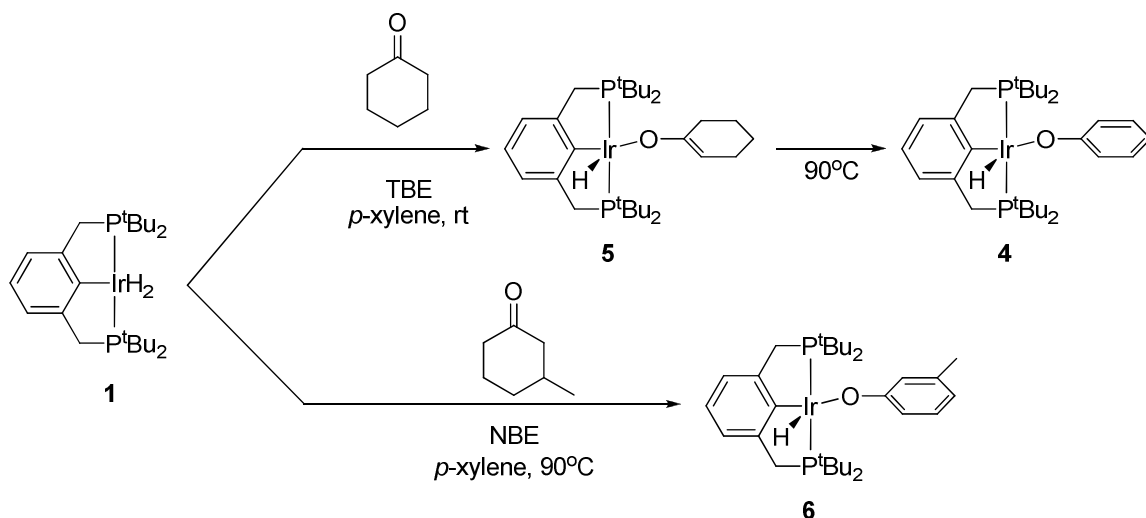
to strongly inhibit catalysis.^{15,16} In the case of a simple acyclic enone, a conjugated metallacyclic species is formed which is remarkably stable. In the particular case of cycloheptanone, a very unusual conjugated [5.2.0] metallabicyclic species is formed, apparently resulting from the triple dehydrogenation (transfer of 6 H atoms) of the ring to give tropone, followed by C-H addition and O-coordination. Accordingly this complex can be generated directly by the reaction of “(PCP)Ir” with tropone. Remarkably, this species acts as a catalyst for the dimerization of tropone to give a fused tricyclic dihydrodicycloheptafuranol, a reaction which to our knowledge is without reported precedent.

7.2 Previous Investigations: Reactions of Ketones with (^tBuPCP)Ir

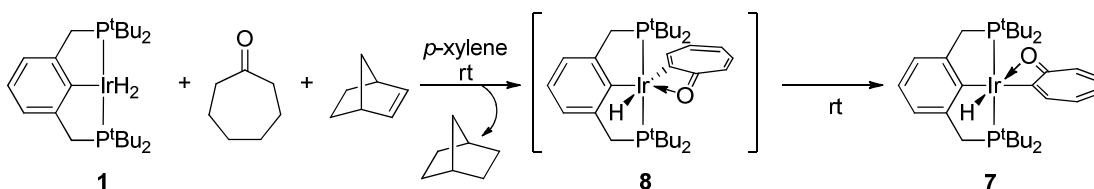
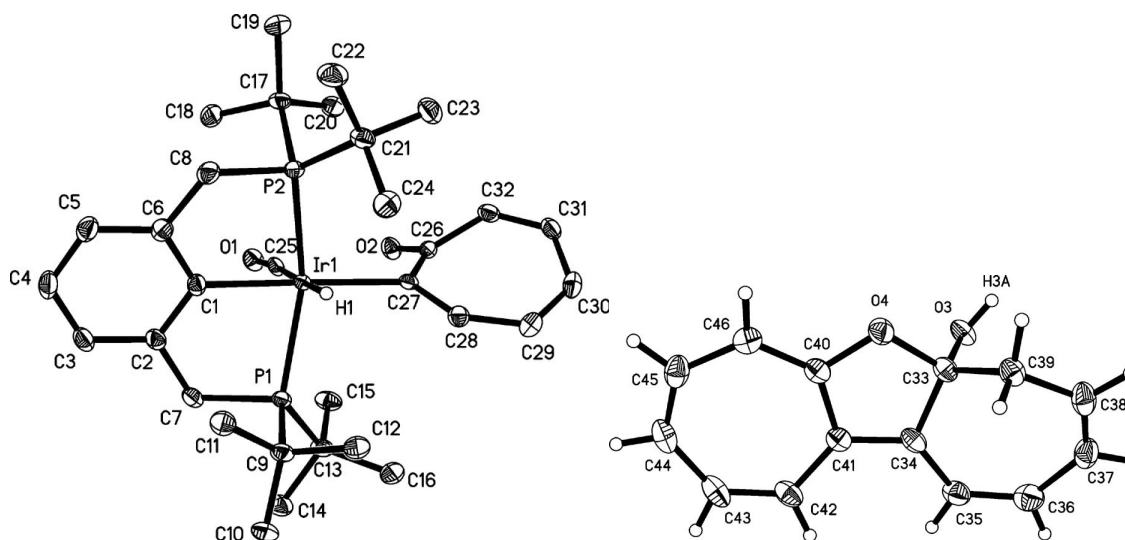
Reactions of complex **1** (17 mM) with a hydrogen acceptor (*tert*-butylethylene or norbornene) and various ketones were investigated by Xiawei Zhang.^{15,16} Use of acyclic ketone 3-pentanone resulted in the formation of metallacyclic complexes **2** and **3**, whose stability presumably prevents catalytic turnover (Scheme 7.1). Use of cyclic ketones cyclohexanone and 3-methylcyclohexanone resulted in the formation of aryloxy hydride complexes **4** and **6** through successive dehydrogenation events (Scheme 7.2). Catalytic turnover was inhibited due to the formation of the stable aryloxy hydride.

Scheme 7.1. Reaction of 3-pentanone with **1**.¹⁵



Scheme 7.2. Reaction of cyclohexanone and 3-methylcyclohexanone with **1**.¹⁵

Cycloheptanone was next investigated as a ketone substrate.^{15,16} It was hypothesized that the possible dehydrogenation products of cycloheptanone should not form alcohols, and, as a result, cycloheptanone might undergo catalytic dehydrogenation. Treatment of complex **1** (17 mM) with cycloheptanone (51 mM) and NBE (170 mM) at 120 °C for 12 hours and subsequent recrystallization yielded an orange solid. The product was identified as complex **7** through NMR spectroscopy and X-ray crystallography (Scheme 7.3). Addition of CO to the resulting solution yielded the η^1 -troponyl iridium CO complex **9**, and dark amber-colored crystals were crystallized from the solution. Surprisingly, the expected CO adduct **9** was found to have co-crystallized with organic compound **10** (Figure 7.1). Compound **10** is a previously unreported dimerization product of tropone.¹⁷ My investigations sought to characterize complexes **7** and **8** and to investigate the formation of novel tropone dimer **10**.

Scheme 7.3. Addition of cycloheptanone to **1**.**Figure 7.1.** Crystal structures of CO adduct **9** and tropone dimer **10**.¹⁵

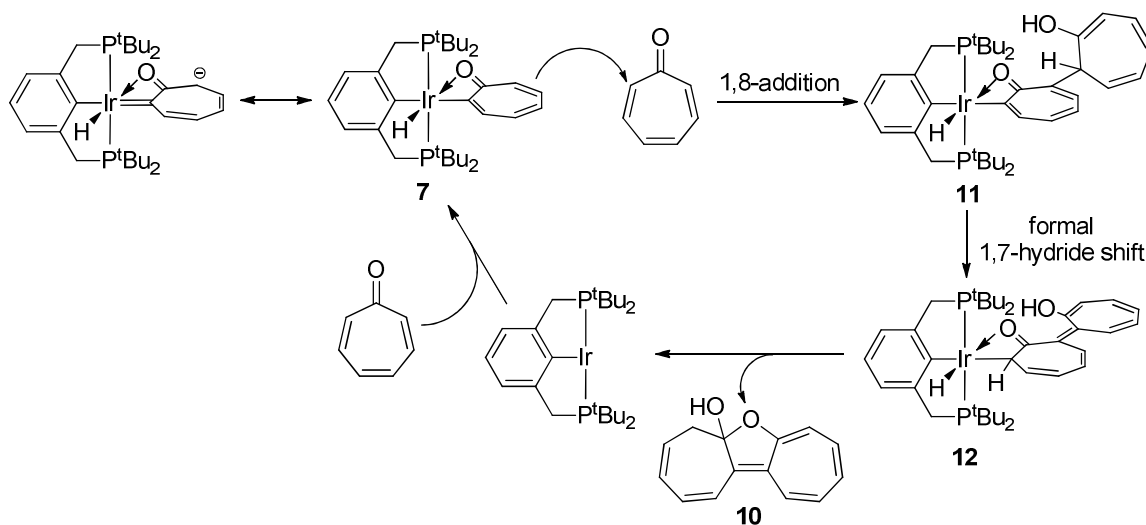
7.3 Results and Discussion

Reaction of complex **1** (26 mM) with NBE (39 mM) and a small excess of tropone (32 mM) at room temperature yielded the kinetic product **8** (Scheme 7.3), which was characterized by NMR spectroscopy. Complex **8** was found to be much less stable than the analogous kinetic C-H adduct **2**; it isomerizes to complex **7** within one hour at room temperature. This difference in stability may be attributable to the greater strain in the 4-membered metallacyclic ring as compared to the 5-membered metallacyclic unit in **2**. In analogy to the reaction of pentanone (Scheme 7.1), initial formation of **8**, despite

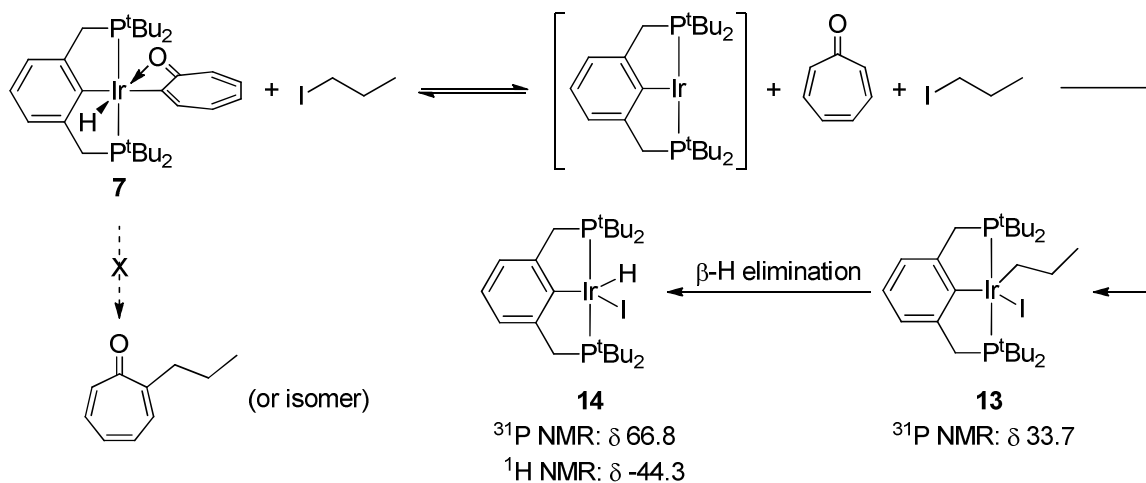
the greater thermodynamic stability of **7**, suggests that coordination of the carbonyl moiety to the iridium atom does not precede C-H bond activation.

When excess tropone was reacted with complex **1** and norbornene, a dark-colored solution was formed in contrast to the orange-colored solution that was obtained from the reaction with only one equivalent of tropone. Upon further investigation, when a large excess of tropone (26 equivalents) was reacted with complex **1** and a small excess of norbornene, tropone was consumed completely to form primarily compound **10**. Addition of tropone to a solution containing a catalytic amount of complex **7** also yielded tropone dimer **10**, indicating that the tropone adduct **7** is a probable intermediate in the dimerization mechanism. A control experiment in which tropone and norbornene was heated to 120 °C in the absence of complex **1** resulted in observation of exclusively starting materials by gas chromatography and NMR spectroscopy.

A possible mechanism for dimerization is given in Scheme 7.4. Complex **7** has a resonance form that suggests that C32 (Figure 7.1) may be nucleophilic. Nucleophilic attack by complex **7** on free tropone in a 1,8-fashion yields intermediate **11** after proton transfer. The ability of tropone to undergo nucleophilic 1,8-addition reactions is well precedented,¹⁸⁻²⁰ but to our knowledge, no examples of tropone serving as a nucleophile have been reported in the literature. A formal 1,7-hydride shift would yield iridium alkyl hydride intermediate **12**. Reductive elimination and hemiketal formation would then afford dimerization product **10**. In this reaction mechanism, reductive elimination of the alkyl hydride intermediate **12** should be facile because the metallacycle lacks resonance stabilization.

Scheme 7.4. Possible mechanism for tropone dimerization.

An attempt to observe nucleophilic behavior of complex **7** was performed by the addition of excess 1-iodopropane to a solution of complex **7**. While no reaction was observed after 3 h at room temperature, heating to 110 °C resulted in the disappearance of complex **7** by ^{31}P NMR spectroscopy and the appearance of signals consistent with propyl iodide complex **13**²¹ and hydrido iodide complex **14**.²² GC analysis of the reaction solution following the reaction revealed only the presence of tropone. No evidence of the propyl adduct of tropone was observed. A possible mechanism for the observed results is given in Scheme 7.5.

Scheme 7.5. Addition of 1-iodopropane to **7**.

7.4 Summary

The adducts of the reaction of tropone with complex **1**, complexes **7** and **8**, have been synthesized and characterized. The kinetic product, complex **8**, isomerizes to the thermodynamic product, complex **7**, at room temperature. The formation of the novel tropone dimer **10** appears to be catalyzed by complex **7**. A possible mechanism for the dimerization reaction is suggested in which tropone, normally an electrophile, acts as a nucleophile upon activation by C-H oxidative addition to the iridium(I) center. The concept of utilizing C-H addition of a molecule to a transition metal complex to induce nucleophilic character at a remote site of a substrate molecule is a possible area for further investigation.

7.5 Experimental

All reactions, recrystallizations, and routine manipulations were conducted under argon using an argon-filled glove box or by using standard Schlenk techniques. Reagent grade solvents were used and dried according to established methods, then degassed with argon. All NMR solvents were dried, vacuum-transferred, and stored in an argon-filled glove box. ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained on 300-MHz or 400-MHz Varian Spectrometers. ^1H and ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and were referenced to residual protiated (^1H) or deuterated solvent (^{13}C). $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shifts are referenced to an external standard, Me_3P in mesitylene- d_{12} solvent (δ -62.4 ppm), in a capillary tube. GC-MS analyses were carried out with a Varian GC-MS (3900 GC and 2100T MS). Complex **1** was prepared as described in the literature.¹²

(PCP)Ir(H)(κ -O,C-OC $_7$ H $_5$) isomers, (troponyl hydride complexes **7 and **8**):** 15 mg of ($^t\text{BuPCP}$)IrH $_2$ (0.026 mmol) was dissolved in 1 mL of *p*-xylene solution containing 3.7 mg of norbornene (0.039 mmol) at room temperature. To the resulting solution was added 3.1 μL of tropone (0.032 mmol); after stirring for ca. 1 min, the red solution turned orange. The reaction was monitored by NMR. Complex **8** was formed in 95% yield ($^{31}\text{P}\{^1\text{H}\}$ NMR). ^{31}P NMR (162 MHz, *p*-xylene- d_{10}): δ 62.54 (d, $J_{\text{PH}} = 12.8$ Hz). ^1H NMR (400 MHz, *p*-xylene- d_{10}): 1.34 (t, $J_{\text{PH}} = 6.4$ Hz, 18H, C(CH $_3$) $_3$), 0.90 (t, $J_{\text{PH}} = 6.2$ Hz, 18 H, C(CH $_3$) $_3$), -10.19 (t, $J_{\text{PH}} = 18.2$ Hz, 1H, Ir-*H*).

Complex **8** isomerized to **7** at room temperature in about one hour. Complex **7**: $^{31}\text{P}\{^1\text{H}\}$ NMR (121.4 MHz, benzene- d_6): δ 58.68 (d, $J_{\text{PH}} = 14.0$ Hz). ^1H NMR (300 MHz, benzene- d_6): δ 8.54 (d, $J_{\text{HH}} = 8.4$ Hz, 1H, tropone CH), 7.26 (d, $J_{\text{HH}} = 7.2$ Hz, 2H, PCP, *m*-H), 7.18 (t, $J_{\text{HH}} = 7.2$ Hz, 1H, PCP, *p*-H), 6.73–6.40 (m, 4H, tropone C_4H_4), 3.60 (d of vt, $J_{\text{PH}} = 3.0$ Hz, $J_{\text{HH}} = 16.8$ Hz, 2H, CH_2), 3.25 (d of vt, $J_{\text{PH}} = 4.2$ Hz, $J_{\text{HH}} = 16.8$ Hz, 2H, CH_2), 1.15 (t, $J_{\text{PH}} = 6.4$ Hz, 18H, $\text{C}(\text{CH}_3)_3$), 1.11 (t, $J_{\text{PH}} = 6.3$ Hz, 18H, $\text{C}(\text{CH}_3)_3$), –29.53 (t, $J_{\text{PH}} = 14.4$ Hz, 1H, Ir-H).

5,5-dihydrodicyclohepta[b,d]furan-5a-ol, (10): 15 mg of (PCP)IrH₂ (0.026 mmol), 3.1 μL of tropone (0.032 mmol), and 6.2 mg of norbornene (0.065 mmol) was dissolved in 0.8 mL of *p*-xylene- d_{10} to yield complex **7** after 3 hours at room temperature. To this reaction mixture, additional tropone (100 μL , 1.00 mmol) was added, and the reaction mixture was heated at 80 °C. After 11 hours, no further change in the tropone concentration was observed by NMR spectroscopy. Column chromatography (20:1 $\rightarrow$ 1:1 hexanes:ethyl acetate) afforded the product as a dark red oil (35.6 mg, 32 % isolated yield). Addition of excess D₂O (25 μL , 1.4 mmol) to a solution of **10** (35.6 mg, 0.168 mmol) in methylene chloride- d_2 (0.8 mL) resulted in the disappearance of the singlet at δ 9.69 ppm in the ^1H NMR spectrum. ^1H NMR (400 MHz, methylene chloride- d_2): δ 9.69 (s, 1H), 7.71 (dd, $J = 8.6$ Hz, 1.2 Hz, 1H), 7.30 (ddd, $J = 12.0$ Hz, 7.6 Hz, 1.7 Hz, 1H), 7.23–7.10 (m, 5H), 6.85 (dd, $J = 8.1$ Hz, 1.2 Hz, 1H), 6.82 (td, $J = 7.4$ Hz, 1.3 Hz, 1H), 3.89 (s, 2H). ^{13}C NMR (100 MHz, methylene chloride- d_2): δ 188.64, 155.91, 154.52, 141.06, 138.72, 138.18, 135.61, 135.00, 130.91, 128.87, 125.80, 120.54, 118.14, 37.18. GC-MS (EI) calculated for $\text{C}_{14}\text{H}_{10}\text{O}^+$ ($\text{C}_{14}\text{H}_{12}\text{O}_2 - \text{H}_2\text{O}$): 194.07, found: 194.00.

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Chapter 8

Synthesis and Characterization of (^tBuPCP)Ir(Me)(F)

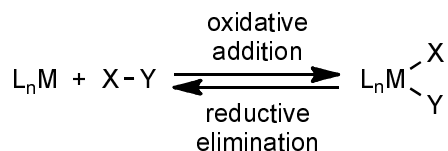
Abstract

Carbon-fluorine bonds are the strongest known single bonds to carbon and as a consequence can prove very hard to cleave. Though vinyl and aryl C-F bonds can undergo oxidative addition to transition metal complexes, this reaction has appeared inoperable with aliphatic substrates. In this chapter, I report the addition of methyl fluoride's C(sp³)-F bond to an iridium center via the initial, reversible cleavage of a C-H bond. The methyl fluoride addition product was characterized through NMR spectroscopy, LIFDI mass spectrometry, and elemental analysis.

8.1 Introduction

The oxidative addition of single-bonded substrates to transition metal centers and the microscopic reverse, reductive elimination, comprise an especially useful reaction class (Scheme 8.1). The addition and elimination of bonds to carbon are key steps in the majority of organic reactions catalyzed or promoted by metal complexes. In this context, the addition of carbon-halogen bonds, specifically C-Cl, C-Br and C-I, has been studied and exploited extensively over the past five decades.¹⁻⁶ The formation and cleavage of carbon-fluorine bonds is of great interest in medicinal and environmental chemistry;⁷⁻¹⁴ for example, approximately 20% of pharmaceuticals and 40% of agrochemicals have C-F bonds.⁸ Examples of oxidative addition and reductive elimination of C-F bonds, however, are essentially limited to those with aryl and vinyl carbon atoms.^{7,14-17} By contrast, we reported the oxidative addition of C(sp³)-F bonds to a transition metal center.¹⁸ Notably, these reactions do not proceed via direct (3-centered) C-F addition, nor by any of the several pathways that have previously been proposed for carbon-halogen oxidative addition,¹⁻⁶ but instead the C(sp³)-F additions take place via initial oxidative addition of a C(sp³)-H bond.¹⁸

Scheme 8.1. General reaction of oxidative addition and reductive elimination.

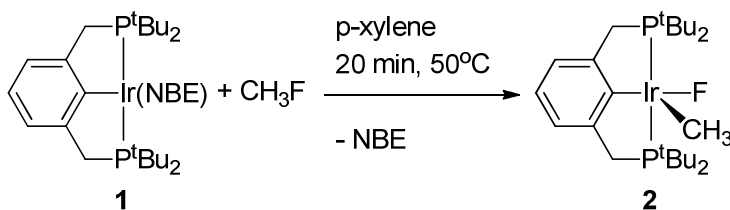


We recently reported that the pincer-ligated iridium complex (PCP)Ir (PCP = $\kappa^3\text{-C}_6\text{H}_3\text{-2,6-[CH}_2\text{P}(t\text{-Bu})_2\text{]}_2$) undergoes oxidative addition of C(sp³)-O bonds.¹⁹ Our

study was limited to aryloxy-carbon bonds (ArO-C) which have homolytic bond dissociation energies less than 65 kcal/mol (e.g. 63.8 ± 1 kcal/mol for $\text{CH}_3\text{-OPh}^{20}$). By contrast, fluorine forms the strongest known bonds to sp^3 -hybridized-carbon; for example the $\text{H}_3\text{C-F}$ bond dissociation energy is 110 ± 1 kcal/mol.²⁰ Nonetheless, because we found that more electronegative OR groups (e.g. $\text{R} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) favored C-OR addition to $(\text{PCP})\text{Ir}$,¹⁹ we considered that C-F addition to the same fragment might be possible as well. As part of the study reported in reference 18, my investigations focused on the synthesis and characterization of the methyl fluoride oxidative addition product.

8.2 Results and Discussion

$(\text{PCP})\text{Ir}(\text{NBE})$ (**1**; NBE = norbornene) acts as a precursor to the active fragment $(\text{PCP})\text{Ir}$.²¹ When fluoromethane (1 atm) was added to a *p*-xylene- d_{10} solution of **1**, ^{31}P NMR spectroscopy revealed complete conversion to a single major product (**2**; δ 50.4 ppm, doublet, $^2J_{\text{FP}} = 10.5$ Hz; yield by NMR spectroscopy > 95 %) within 20 min at 50 °C (Scheme 8.2). In benzene- d_6 solvent, product **2** is characterized by a triplet at δ – 28.20 ppm ($^2J_{\text{PC}} = 4.3$ Hz) in the ^{13}C NMR spectrum and a signal at δ 1.85 ppm (Ir-CH_3) in the ^1H NMR spectrum, which appears as a broad singlet at room temperature and as a doublet of triplets at 80 °C ($^3J_{\text{PH}} = 4.7$ Hz, $^3J_{\text{FH}} = 3.5$ Hz). When ^{31}P -decoupling is applied, this ^1H NMR signal appears as a doublet ($^3J_{\text{FH}} = 3.5$ Hz) (Figure 8.1). These ^1H and ^{13}C NMR signals are characteristic of a methyl group coordinated to iridium at the apical site of a square pyramidal structure.^{19,22} Accordingly, the ^1H NMR spectrum indicates a PCP ligand with only C_s symmetry, while 2D NOESY spectra show that the putative methyl ligand interacts with only one set of phosphino-*t*-butyl groups.¹⁸

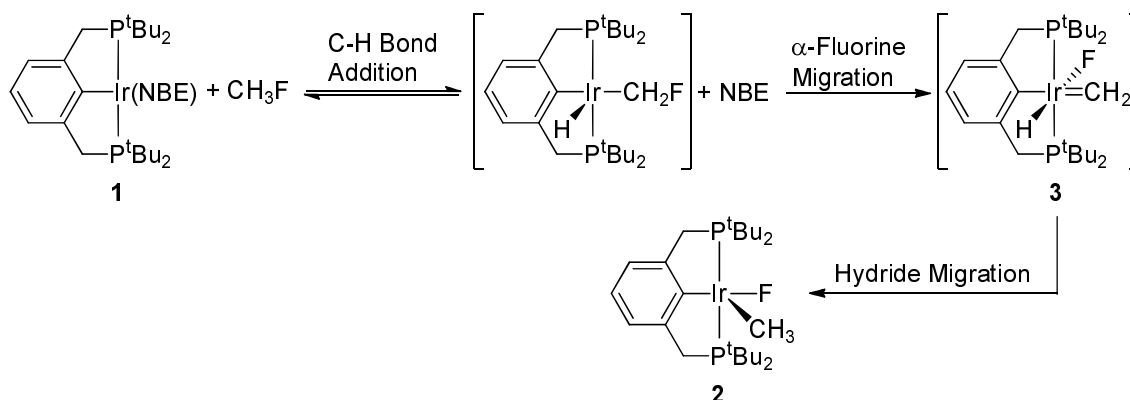
Scheme 8.2. Oxidative addition of CH_3F to complex **1**.

The ^{19}F NMR spectrum shows a broad signal at δ -252.6 ppm (peak width at half-height, $W_{1/2} = 28.6$ Hz) at 25 $^\circ\text{C}$; both the broadness and chemical shift are consistent with that of other iridium fluoride complexes, in particular coordinatively unsaturated complexes.^{23,24} While the width of the ^{19}F NMR signal precluded direct observation of the ^{31}P - ^{19}F coupling that was observed in the ^{31}P NMR spectrum ($^2J_{\text{FP}} = 10.5$ Hz), application of ^{31}P -decoupling ($^{19}\text{F}\{^{31}\text{P}\}$ NMR) resulted in a decrease in $W_{1/2}$ from 28.6 Hz to 13.9 Hz (Figure 8.2), confirming the existence of ^{31}P - ^{19}F coupling. Simulation of the ^{19}F NMR signal using Spinworks software successfully reproduced it (with and without ^{31}P -decoupling) based on coupling to two ^{31}P nuclei with $^2J_{\text{PF}} = 10.5$ Hz, coupling to three ^1H nuclei with $^3J_{\text{HF}} = 3.5$ Hz, and a linewidth of 10.0 Hz (Figures 8.3 and 8.4).

When the reaction was conducted with ^{13}C -labeled methyl fluoride, the major signal in the ^1H -decoupled ^{13}C NMR spectrum ($^{13}\text{C}\{^1\text{H}\}$) was a triplet at δ -28.20 ppm ($^2J_{\text{PC}} = 4.4$ Hz); without ^1H decoupling, this signal appeared as a quartet of triplets ($^1J_{\text{HC}} = 136$ Hz, $^2J_{\text{PC}} = 4.4$ Hz) due to coupling with three protons. The ^1H - ^{13}C coupling of 136 Hz was also manifest in the ^1H NMR signal at δ 1.85 ppm. The assignment of these signals to an iridium-bound methyl group derived from methyl fluoride is thus confirmed. The $^2J_{\text{PC}}$ coupling was also manifest in the ^{31}P NMR signal, which appeared as a partially

resolved doublet of doublets at δ 50.4 ppm that could be simulated (Spinworks) with coupling constants $^2J_{\text{FP}} = 10.5$ Hz and $^2J_{\text{PC}} = 4.4$ Hz, and a linewidth of 4.5 Hz (Figure 8.5). The results of elemental analysis and LIFDI (liquid introduction field desorption ionization) mass spectrometry²⁵ of **2** (Figure 8.6) were fully consistent with the characterization of **2** as (PCP)Ir(CH₃)F.

We have previously shown that oxidative addition of the methyl–oxygen bond of anisole derivatives (H₃C–OAr) occurs via initial addition of a methyl C–H bond to (PCP)Ir as evidenced by a significant normal CH₃/CD₃ kinetic isotope effect (KIE).¹⁹ When **1** was treated with a large excess of 3,5-bis(trifluoromethyl)benzylfluoride and its deuterated (CD₂F) analogue (at least 5 fold excess of each), a CH₂F/CD₂F kinetic isotope effect of 2.7(3) at 60 °C was determined, implying that C–H bond activation is involved in or occurs prior to the product-determining step in the oxidative addition of the C(sp³)-F bond.¹⁸ In analogy with the mechanism of C–O bond activation in anisole derivatives, we propose that initial C–H bond activation of methyl fluoride is followed by α -fluorine migration²⁶ to generate an intermediate methyldiene complex (**3**); iridium-to-methyldiene hydride migration then completes the net C–F oxidative addition (Scheme 8.3).²⁷

Scheme 8.3. Proposed mechanism for oxidative addition of CH₃F to (PCP)Ir.

8.3 Conclusion

Considering the broader implications of these and previously reported results,¹⁸ microscopic reversibility dictates that the lowest energy pathway for C–F elimination from **2** must proceed via initial α-H migration from carbon to the metal center. This unusual mechanism may offer insight applicable toward the development of methods for the formation of sp³-C–F bonds via C–F elimination from a metal center; such reactions are of substantial current interest in the context of the synthesis of pharmaceutically important compounds.

8.4 Experimental

All operations were carried out under an argon atmosphere using standard Schlenk techniques or in an argon-filled dry box. Anhydrous pentane, *p*-xylene, *p*-xylene-*d*₁₀, methyl *t*-butyl ether, and C₆D₆ were dried over Na/K and collected by vacuum transfer. Norbornene (NBE) was purified by sublimation. All NMR experiments were performed using 400-MHz or 500-MHz Varian instruments. The residual ¹H peak of the

deuterated solvent was used as a reference for ^1H chemical shifts. ^{31}P NMR and ^{19}F NMR chemical shifts were referenced to external H_3PO_4 and CFCl_3 standards, respectively. Simulations of NMR spectra were performed using the NUMMRIT simulation implementation²⁸ within the Spinworks software program, version 3.1.7.²⁹ Elemental analysis data were obtained by the CENTC Elemental Analysis Facility at the University of Rochester using a Perkin Elmer 2400 Series II combustion analyzer. Liquid introduction field desorption ionization mass spectrometry (LIFDI) data were obtained by the High Resolution Mass Spectrometry Facility and the University of California at Riverside using a Waters GCT (2008) high resolution mass spectrometer. To remove moisture, the glass surface of J-Young NMR tubes was treated as described by Hughes *et al.*³⁰ $(\text{PCP})\text{IrH}_n$ ($\text{PCP} = \kappa^3\text{-2,6-(}^t\text{Bu}_2\text{PCH}_2)_2\text{C}_6\text{H}_3$, $n = 2$ or 4) was prepared as previously described.³¹ Fluoromethane was obtained from SynQuest Laboratories and Specialty Gases of America Inc. and was used without further purification.

$(\text{PCP})\text{Ir}(\text{Me})(\text{F})$, **2:** On a high-vacuum line, gaseous CH_3F (1 atm) was added to a J-Young tube containing a *p*-xylene solution (0.7 mL) of $(\text{PCP})\text{Ir}(\text{NBE})$ (**1**) which had been generated from $(\text{PCP})\text{IrH}_n$ (15.1 mg, 0.026 mmol) and NBE (7.2 mg, 0.076 mol). After 20 min at 50 °C, ^{31}P NMR spectroscopy revealed the disappearance of **1** and appearance of one major product, **2**. After the solvent and organic volatiles were removed in vacuo, a dark red solid (**2**) (15.5 mg) was obtained in 97% yield. NMR data for **2**: $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202 MHz): δ 50.38 (d, $^2J_{\text{FP}} = 10.5$ Hz). ^1H NMR (C_6D_6 , 500 MHz): δ 7.03 (d, $J_{\text{HH}} = 7.5$ Hz, 2H, PCP), 6.87 (t, $J_{\text{HH}} = 7.5$ Hz, 1H, PCP), 2.99 (d of vt, $J_{\text{HH}} = 17.5$ Hz, 2H, CH_2P), 2.86 (d of vt, $J_{\text{PH}} = 4.1$ Hz, $J_{\text{HH}} = 17.5$ Hz, 2H, CH_2P), 1.85 (dt, $J_{\text{PH}} = 4.7$ Hz, $J_{\text{FH}} =$

3.5 Hz, 3H, Ir-CH₃), 1.23 (vt, $J_{\text{PH}} = 6.3$ Hz, 18H, PC(CH₃)₃), 1.20 (t, $J_{\text{PH}} = 6.0$ Hz, 18H, PC(CH₃)₃). ¹³C{¹H} NMR (C₆D₆, 125 MHz): δ 150.67 (t, $J_{\text{PC}} = 7.6$ Hz, PCP), 145.45 (d, $J_{\text{FC}} = 39.4$ Hz, PCP), 121.74 (t, $J_{\text{PC}} = 7.7$ Hz, PCP), 121.64 (s, PCP), 37.30 (vt, $^1J_{\text{PC}} = 10.4$ Hz, PC(CH₃)₃), 34.73 (vt, $^1J_{\text{PC}} = 8.8$ Hz, PC(CH₃)₃), 31.91 (vt, $^1J_{\text{PC}} = 12.3$ Hz, CH₂P), 30.64 (s, PC(CH₃)₃), 29.47 (vt, $^2J_{\text{PC}} = 2.3$ Hz, PC(CH₃)₃), -28.20 (t, $^2J_{\text{PC}} = 4.4$ Hz, Ir-CH₃). ¹⁹F NMR (C₆D₆, 470 MHz): δ -252.6 (app s, Ir-F). LIFDI MS m/z (%): 620 (100) [M⁺], 618 (65) [M⁺]. Elemental analysis, calcd for C₂₅H₄₆FIrP₂: C, 48.45; H, 7.48. Found: C, 48.51; 7.43.

Figure 8.1. ¹H NMR signal of **2** (Ir-CH₃) with no decoupling (red) and with ³¹P decoupling (black).

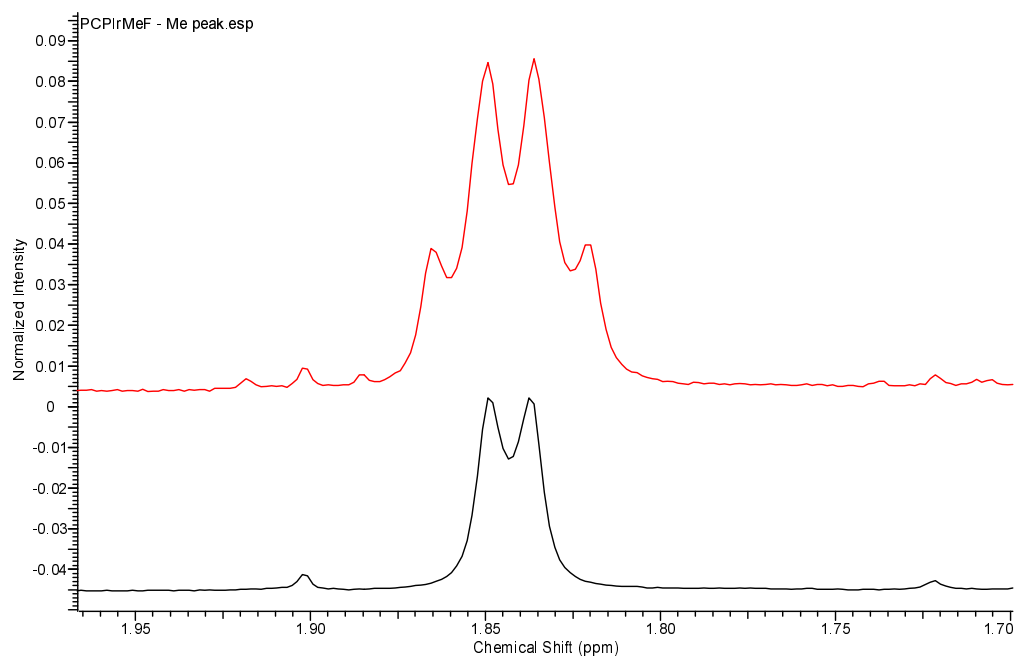


Figure 8.2. ^{19}F NMR signal of **2** without decoupling (red) and with ^{31}P decoupling (black).

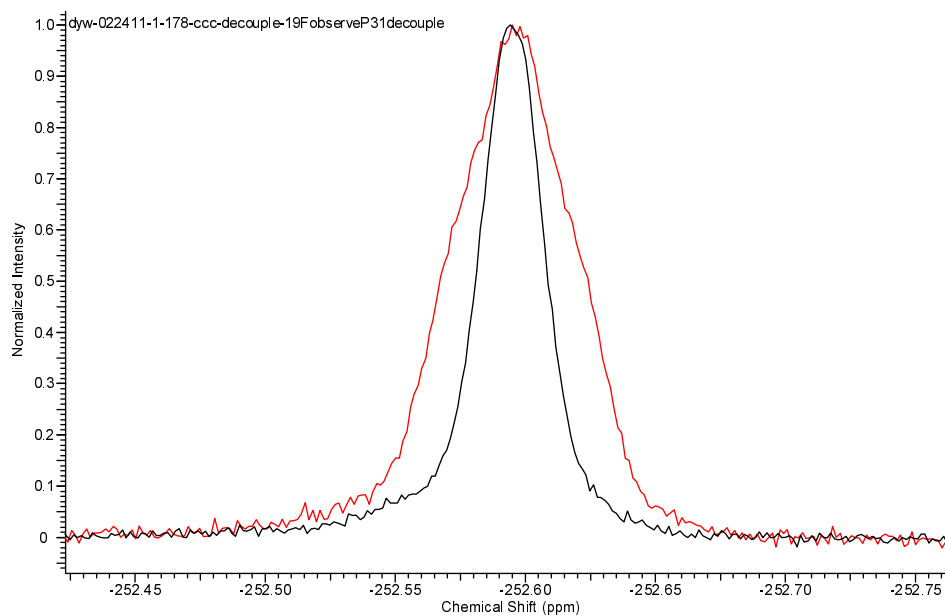


Figure 8.3. ^{19}F NMR signal of **2**: simulated with Spinworks software (top) and observed NMR data (bottom). Simulation parameters: $^2J_{\text{PF}} = 10.5$ Hz; $^3J_{\text{HF}} = 3.5$ Hz; linewidth = 10.0 Hz.

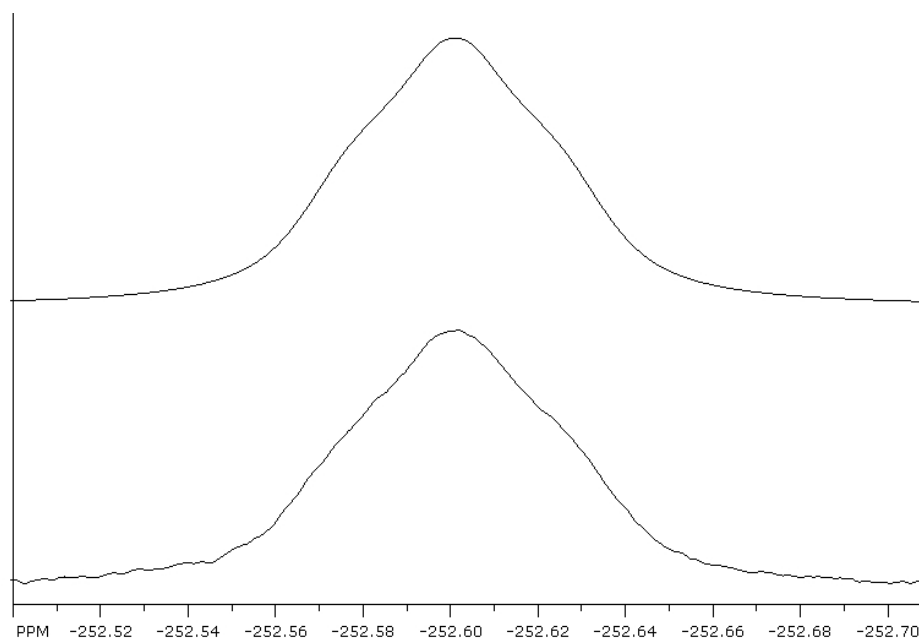


Figure 8.4. $^{19}\text{F}\{^{31}\text{P}\}$ NMR signal of **2**: simulated with Spinworks software (top) and observed NMR data (bottom). Simulation parameters: $^3J_{\text{HF}} = 3.5$ Hz; linewidth = 10.0 Hz.

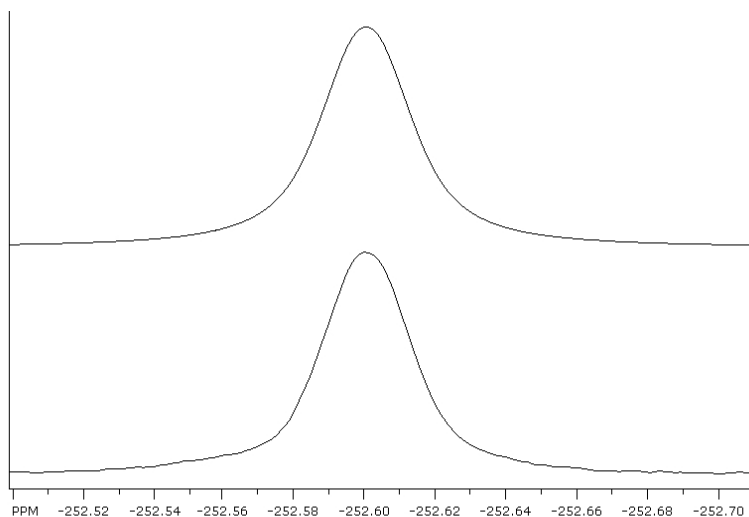


Figure 8.5. ^{31}P NMR signal of ^{13}C -labeled **2**, synthesized from the reaction with $^{13}\text{CH}_3\text{F}$, simulated with Spinworks software (top) and observed NMR data (bottom). Simulation parameters: $^2J_{\text{FP}} = 10.5$ Hz; $^2J_{\text{PC}} = 4.4$ Hz; linewidth = 4.5 Hz.

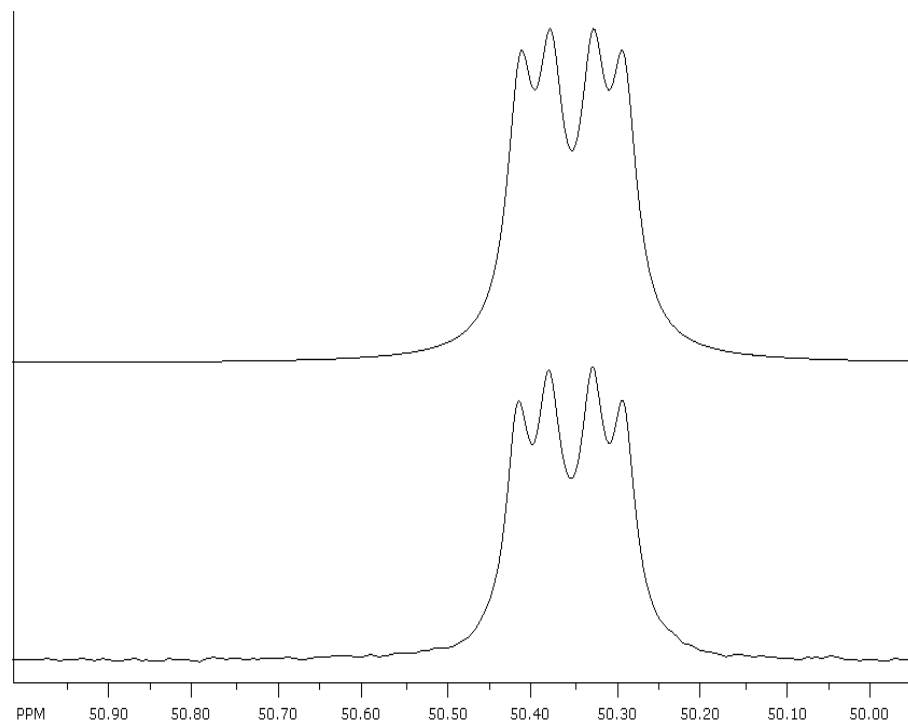
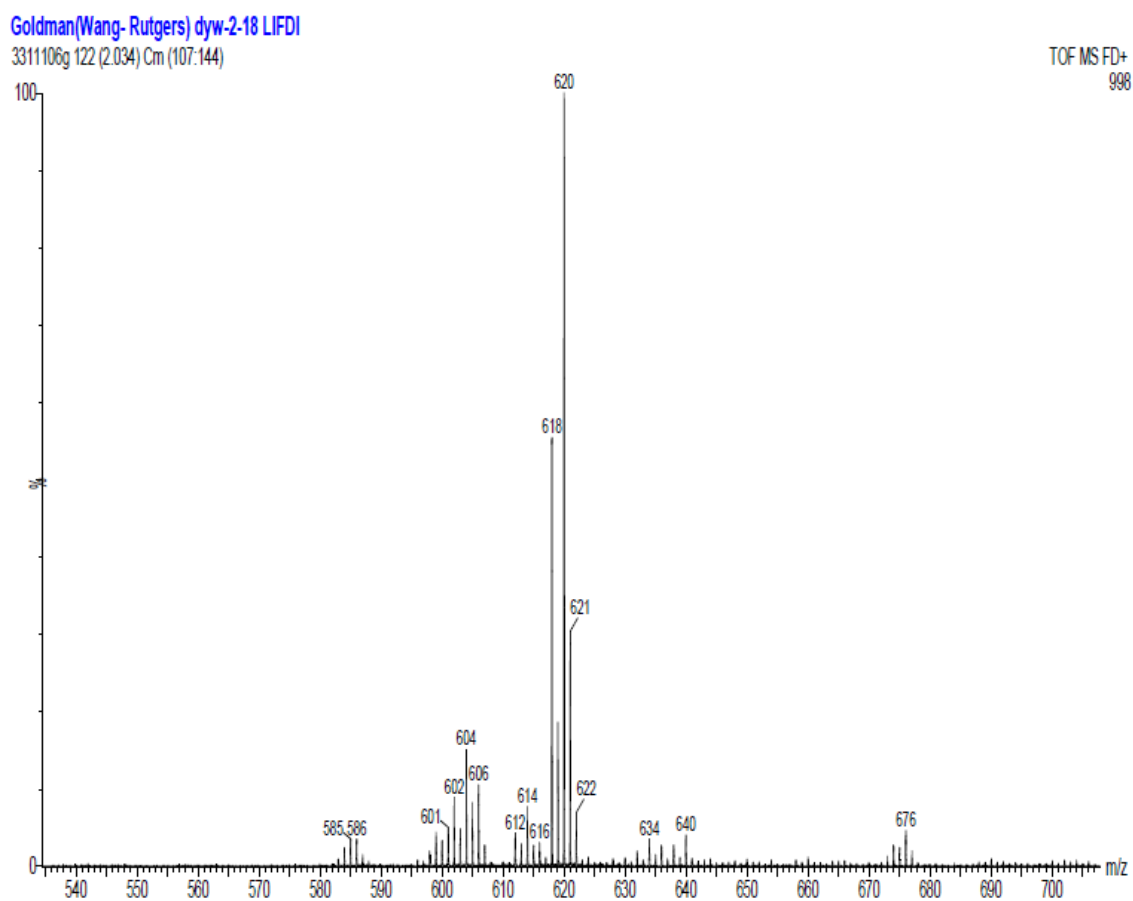


Figure 8.6. LIFDI-MS spectrum of **2**. The cluster of peaks with $M = 618$ - 622 shows the mass distribution expected for $(PCP)Ir(CH_3)F$ (**2**). The clusters with $M = 612$ - 616 and $M = 604$ - 608 are consistent with $(PCP)Ir(N_2)$ and $(PCP)Ir(H)(OH)$ impurities respectively, possibly introduced during sample handling.



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