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ACTIVATION OF ARYL C-H AND C-X BONDS BY A PINCER-LIGATED 'PCP' IRIDIUM COMPLEX

by

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ABSTRACT OF THE DISSERTATION

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Dissertation Director:

Alan S. Goldman

The activation of carbon-hydrogen (C-H) bonds mediated by transition metal complexes is a fundamental step in a vast array of chemical transformations and industrial processes. As such, research into the understanding of the factors governing both efficiency and selectivity of these reactions has been intense. The work presented in this thesis comprises results of experiments designed to evaluate the ability of a pincerligated iridium complex to activate the C-H bonds of several classes of aryl substrates.

The pincer-ligated iridium fragment (PCP)Ir (PCP = { κ^3 -2,6-bis[(di-*tert*butylphosphino)methyl]phenyl}) rapidly and reversibly adds the C-H bond of benzene, giving a kinetically labile addition product. The kinetics and thermodynamics of C-H activation of a series of halogen-, alkyl-, and trifluoromethyl-substituted arenes were studied with a particular focus on determining whether "directing" effects play a significant role. In regard to electronic effects, it was observed that electron withdrawing aryl substituents favor C-H activation. Products of C-H activation *ortho* to weakly or

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non-coordinating substituents (e.g., Cl, Br, CF₃) are kinetically more stable than those of the *meta-* and *para-*substituted analogs, due to steric crowding in the transition state for addition and elimination. However, there is no thermodynamic preference for the *ortho*-substituted complexes. In addition to C-H activation, (PCP)Ir also activates C-X bonds (X = Cl, Br) under certain conditions, yielding product mixtures through a mechanism that remains unclear.

Several series of polycyclic aromatic substrates (naphthalenes, biphenyls, bipyridines, and associated tricyclic analogs) were also studied, giving insight into the utility of aryl C-H activation and preferred binding modes of the (PCP)Ir fragment. Not surprisingly, steric effects play a significant role in the regioselectivity of polycyclic aromatic C-H bond activation by (PCP)Ir. Cyclometalation reactions resulting from single or double C-H activation processes yield particularly stable products. Additional results included an unexpected C-C activation, and several products stabilized by heteroatom (N, O) coordination to iridium. Activation of large polycycles like terpyridine yielded stable, κ^2 chelates that may be of value in research on organic light emitting diodes (OLEDs). Finally, several congested (PCP)Ir dimers were synthesized by taking advantage of the remarkable stability of the products from cyclometalation to the (PCP)Ir complex.

Dedication

To my parents

and to every young student who struggles to find his focus.

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It has been my great privilege to be affiliated with CENTC since 2007. Being a member of this National Science Foundation Center for Chemical Innovation provided me with the opportunity to meet and get to know many important chemists from across

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Chapter 1

Introduction

Even after vigorous research for more than half a century, a thorough understanding of the factors affecting selectivity and efficiency in the functionalization of hydrocarbons remains one of the major goals of modern chemistry. Despite the availability of a broad range of hydrocarbons from fossil fuels, their use as feedstocks for chemical transformations has been limited for two critical reasons. First, both carboncarbon (C-C) and carbon-hydrogen (C-H) bonds are strong, requiring creativity in the development of energetically favorable processes. Second, functionalizing a specific C-C or C-H bond generally requires a highly *selective* process that can efficiently distinguish among many substrate bonds in order to produce the intended product. Without access to selective processes, hydrocarbons are generally consigned to be used as fuels.

The abundance of C-H bonds in the small molecules used as building blocks for chemical syntheses translates into great value for reliable processes through which these bonds can be broken and/or transformed into other linkages. One highly successful approach to these reactions, known as C-H activations (and other similar strong bond activations: C-O, C-C, C-F, etc.), involves oxidative addition to transition metals (M). The process of oxidative addition entails cleavage of an X-Y bond (e.g., C-H), generation of new M-X and M-Y bonds, and a net two-electron oxidation of the metal center.¹ Over the years, as research has proven the efficacy of a vast array of metal complexes and

respective reaction conditions, the topic of oxidative addition and the reverse reaction, reductive elimination, has been extensively reviewed.²⁻¹⁵

One of the earliest accounts of small molecule activation was published in 1962, when Vaska reported the activation of the H-H bond of molecular H₂ through oxidative addition to the complex *trans*-(PPh₃)₂Ir(CO)(Cl) (Vaska's complex, eq. 1).¹⁶ Subsequently, he elaborated on this process, reporting its central role in the catalytic hydrogenation of ethylene and acetylene.¹⁷ Around the same time, Wilkinson also reported catalytic hydrogenation of olefins via oxidative addition of H₂ to a similar square planar complex, (PPh₃)₃RhCl (Wilkinson's catalyst, eq. 2).¹⁸

$$CI \longrightarrow Ir \longrightarrow CO + H_2 \longrightarrow CI \longrightarrow Ir \longrightarrow H$$

$$PPh_3 \qquad \qquad PPh_3$$

$$PPh_3 \qquad \qquad PPh_3 \qquad \qquad (1)$$

Almost concurrent with Vaska and Wilkinson's groundbreaking experiments with H_2 , the first example of C-H bond activation via oxidative addition to a transition metal complex was reported by Chatt in 1965.¹⁹ In this work, the ruthenium(0) complex $Ru(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane) activated a C-H bond of naphthalene to give a naphthyl hydride complex (eq. 3). In another study of *aryl* C-H

bond activation, Green reported the addition of benzene to a tungsten fragment, yielding the corresponding phenyl hydride complex in 1972 (eq. 4).²⁰



Despite having generally lower bond enthalpies than aryl C-H bonds, it wasn't until the early 1980's that successful *alkyl* C-H bond activation reactions were reported. Bergman isolated an iridium cyclohexyl hydride product from photolytic loss of H₂ from $Cp*Ir(PMe_3)(H)_2$ (eq. 5).²¹ Independently, Graham and coworkers reported a similar process, with the formation of an iridium neopentyl hydride complex following irradiation of $Cp*Ir(CO)_2$ and subsequent loss of CO (eq. 6).²² In 1984, Jones also reported both alkyl and aryl C-H activation reactions yielding oxidative addition products with rhodium complexes instead of iridium.²³





With newly developed facility for successful alkyl C-H activation reactions allowing for elegant, detailed mechanistic studies, several groups discovered a surprising thermodynamic preference for the *strongest* C-H bonds. Jones,²⁴ Bercaw,²⁵ and Bergman²⁶ separately observed that alkane oxidative addition to widely differing metal complexes followed the counterintuitive preference for primary C-H bonds, with secondary next, and tertiary C-H bonds last. These surprising results, along with generally mild reaction conditions across these preliminary investigations, have attracted the interest of innumerable researchers who continue to probe and report on these fundamental transformations.

One common theme among the metal complexes is the importance of 3coordinate, d⁸ metal centers. As three-coordinate species, d⁸ metals are highly electron deficient, and therefore reactive, and have been studied extensively.^{27,28} During the 1960's, around the time that C-H activation was first being reported, cyclometalation reactions of ligand aryl and alkyl groups were also discovered and reported in the literature.^{29,30} Building on this idea, Moulton and Shaw successfully performed an intermolecular C-H activation reaction with the bulky diphosphine ligand 1,2-bis[(di-*tert*butylphosphino)methyl]benzene and the metals iridium and rhodium.³¹ These cyclmetalation reactions produced stable, 18-electron complexes in which the metal center is held by a tridentate, meridionally-bound, "pincer" ligand (eq. 7). Due to the

(6)

stong binding of the tridentate pincer, these "PCP-ligated" metal complexes (PCP = ligand binding through phosphorus, carbon, and phosphorus) were discovered to have unusually high thermal stability (>180 °C).



Over the nearly forty years since the report from Moulton and Shaw, extensive attention has been given to these uniquely "tunable" and stable ligand systems. Pincer ligand complex reactivity can be modified systematically by variation of the metal center, ligand donor atoms, steric bulk, connecting "arms", etc, and many different systems have been reported.³²⁻³⁷ With such versatility of design, these complexes have found application beyond C-H bond activation, and have also been studied in the activation of other strong bonds such as C-O, C-C, and C-F.³⁸⁻⁴¹

Since olefinic feedstocks are critical to the synthetic chemical industry, catalysts that can *selectively* dehydrogenate (i.e., perform C-H activation reactions selectively) alkanes are highly desirable. In preliminary work on stoichiometric reactions, Crabtree found that endothermic dehydrogenation reactions could be driven forward by coupling them with the exothermic hydrogenation of a sacrificial alkene such as *tert*-butylethylene (TBE).⁴²⁻⁴⁴ Subsequently, Jensen and Kaska found that the iridium pincer complex (PCP)IrH₂, in conjunction with TBE, showed excellent stability and efficiency in the catalytic transfer dehydrogenation of cyclooctane (eq. 8).^{45,46} Analogous rhodium pincer catalysts were also explored, but did not display the same level of activity.⁴⁷ The ability

of the (PCP)IrH₂ catalyst to withstand high temperatures also allowed for high rates and turnover numbers even in acceptorless conditions.^{48,49} Perhaps most impressively, Goldman reported in 1999 that the (^{iPr}PCP)IrH₂ complex was able to catalytically and *selectively* dehydrogenate *n*-alkanes to α -olefins (eq. 9).⁵⁰



As mentioned above, our group has reported the C-H activation and oxidative addition of alkanes.⁵⁰ But this fundamental reaction has also been exploited in the context of more complex, multistep reaction sequences such as dehydroaromatization⁵¹ and alkane metathesis.^{52,53} We have also reported the C-H activation of alkynes⁵⁴ and especially pertinent to much of the content of this thesis, arenes.⁵⁵ Beyond C-H activation reactions, our group has reported the oxidative addition of other strong bonds such as the N-H bonds of aniline^{56,57} and ammonia, the C-O bond of an anisole derivative,⁴⁰ and the C-F bond of fluoromethane.⁴¹ In both of the latter cases, the final products were achieved through preliminary C-H activation, followed by additional reaction steps.

1.2 Research Goals of this Thesis

With the broad goal of designing effective catalysts for chemical transformations in mind, a comprehensive knowledge of the factors affecting the selectivity of organometallic complexes is critical. Therefore, the results presented in this thesis will hopefully illuminate some aspects of how Moulton and Shaw's almost forty year-old pincer-ligated iridium complex interacts with the strong bonds (almost exclusively C-H) of a wide variety of aromatic substrates.

Chapter 2 contains the results from an extensive set of kinetic and thermodynamic studies of halogen-, alkyl-, and trifluoromethyl-substituted benzene substrates. Alkyl groups are slightly electron-donating and sterically bulky, thus disfavoring oxidative addition to iridium. Halogen substituents are electron withdrawing, but have varying steric bulk which proved helpful in augmenting our understanding of so-called *ortho* "directing" groups.

Chapter 3 presents the results of C-H activation reactions with naphthalene (reflecting back on Chatt in 1965)¹⁹ and a series of naphthalene derivatives. Unlike benzene, naphthalene has two unique types of C-H bonds (α and β), and results show that only the β positions are preferentially activated by the (PCP)Ir fragment. Access to the α C-H bonds can be achieved through appropriately chosen naphthalene substituents.

Extending from the two rings of naphthalene to *three*, results of oxidative addition reactions with two tricyclic fused-ring systems are discussed in chapter 4. While anthracene yielded unremarkable results analogous to those with napthalene, phenanthrene proved altogether more interesting, undergoing a double C-H activation mechanism to yield a thermodynamically stable, bidentate, cyclometalated product.

7

Chapter 5 contains the results of C-H activation reactions with biphenyl and a series of biphenyl derivatives. The fascinating results with phenanthrene prompted many questions concerning the value and thermodynamic driving force for cyclometalation reactions that yield 5-member metalacycles. Biphenyl is very similar in structure to phenanthrene, but lacks the coplanarity of the latter's aromatic ring system. Results show that substantial steric barriers can be overcome in favor of a cyclometalated κ^2 biphenyl product.

The addition of an extra phenyl ring to biphenyl yields the tricyclic molecule terphenyl. Results of experiments with all three isomeric terphenyls (*para, meta,* and *ortho*) are presented in chapter 6, with emphasis on new observations concerning the regioselectivity of (PCP)Ir. Chapter 7 discusses the singular result that C-C activation is the preferred process with a substrate that contains acute bond strain like biphenylene.

Biphenyl substrates are structurally reminiscent of one of the most ubiquitous of all bidentate ligands in organometallic chemistry: 2,2'-bipyridine. Assuming that bipyridine would complex with the PCPIr fragment through typical N,N coordination, this substrate was analyzed to see if its standard mode of reactivity would dominate over potential C-H activation processes. Excitingly, results presented in chapter 8 show that this is *not* the case. Bipyridine and a related series of substituted bipyridines form highly stable cyclometalated products that originate from a single C-H activation process and subsequent coordination of one nitrogen to give 18-electron complexes.

Chapters 9 and 10 present results from novel reaction strategies designed to exploit the knowledge accumulated in chapters 2 - 8 concerning the fundamental patterns of reactivity for (PCP)Ir and the types of products generated through C-H activation
mechanisms. In chapter 9, interesting results from unsuccessful attempts to coerce κ^3 chelation in a meridional conformation perpendicular to the PCP ligand system are discussed. Chapter 10 contains data and observations pertaining to a series of sterically congested (PCP)Ir dimers formed by taking advantage of favorable cyclometalation reactions.

Finally, chapter 11 collects together the results of attempted C-H activation reactions with various polycyclic aromatic substrates that don't fit neatly into any of the aforementioned categories.

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Chapter 2

Activation of Aryl C-H Bonds in a Series of Substituted Benzene Substrates

Abstract

The selective and catalytic activation and functionalization of C-H bonds continues to be an important focus of research in organometallic chemistry. In the late 1990's, several research groups began to develop a strategy for achieving selectivity through "site-directed" functionalization. This method involves so-called "directing" groups" (i.e., functional groups on aromatic substrates) which coordinate to a metal center, thereby bringing an ortho C-H bond into close enough proximity for preferential activation by the transition metal in a subsequent step. While this method has been shown to be highly effective for certain metal complexes, it has been shown by our group (and others) that in some cases, the so-called "directing group" actually *hinders* the kinetics of ortho C-H bond activation reactions. Building on previous research with nitro and carbonyl functional groups, results are presented herein for the C-H activation of a series of halogen- and alkyl-substituted benzene derivatives. Mechanistic investigations of these reactions combined with DFT calculations reveal that steric crowding in the transition state significantly slows the rates of oxidative addition and the reverse reaction, reductive elimination, of ortho C-H bonds. In addition, there is little or no thermodynamic preference for the *ortho* product in these instances. These data are consistent with previous work in our group and provide evidence against a "site-directed" oxidative addition mechanism.

2.1 Introduction

The theme of this thesis concerns the quest for a thorough understanding of the factors affecting selectivity in C-H activation reactions. Among the most unreactive (i.e., strong) and ubiquitous of all atomic linkages, the simple C-H bond is the attractive target of a vast array of functionalization processes. Therefore, processes that are *selective* and *catalytic* in the activation of C-H bonds within complex molecules are of great value and potential utility. Toward this goal, oxidative addition of C-H bonds to organometallic complexes has proven to be a highly successful platform for a variety of fundamental transformations. Especially relevant to the work presented herein, activation of C-H bonds by late transition metals has been well-studied.¹⁻¹³

One strategy that has proven to be particularly useful, is the use of "directing" groups in order to promote C-H activation at the *ortho* position of an aromatic substrate.¹⁴⁻²⁶ Using the zero-valent, Group 8 transition metal ruthenium, Murai and co-workers have done extensive research on the utility of acyl and imino groups for this purpose, reporting insertion of olefins²⁷ (eq. 1) and acetylenes²⁸ into aryl C-H bonds and additional variations on this coupling scheme.^{29,30} One thing these directing groups have in common is a double bond that is fully conjugated with the aromatic π -system of the substrate. It has been shown that the oxygen or nitrogen atoms of these substitutents precoordinate to the metal, thereby directing the metal center toward the *ortho* C-H bond.



In 2000, our group reported that the pincer-ligated iridium fragment (PCP)Ir (PCP = κ^3 -C₆H₃-2,6-(CH₂P(^tBu)₂)₂) adds aryl C-H bonds to give isolable aryl hydride complexes.³¹ We refer to (PCP)Ir as a "fragment" because it is a highly reactive, unsaturated complex with multiple open coordination sites that must be generated *in situ*. The three-coordinate tridentate PCP unit is the only ligand, and provides a semi-rigid backbone that securely chelates the reactive metal center. Analogous to Ru(0), the Ir(I) metal atom in this complex has a d⁸ electron configuration. This 14-electron precursor fragment can be generated by the reaction of the "parent" complex (PCP)IrH₂ with a strained alkene acceptor such as norbornene (NBE) (eq. 2).³¹



Our experiments with the (PCP)Ir fragment and substrates similar to those studied by Murai (and others) showed quantitative selectivity for activation of the C-H bond *ortho* to coordinating groups (acetyl, nitro).³² However, results of low-temperature experiments showed that the "directing" groups do *not* pre-coordinate to the metal center. On the contrary, the functional groups were found to actually hinder the kinetics of the initial C-H activation process. At low temperatures, the dominant kinetic products resulted from C-H activation at the least sterically hindered aromatic positions (*meta* and *para*). The thermodynamic products found at higher temperatures resulted exclusively from *ortho* C-H activation and were stabilized by coordination of the functional groups to the metal center *after* oxidative addition of the C-H bond (eq. 3).



In all of the above cases, aryl C-H bonds were activated preferentially over the C-X (X = C, N) bonds connecting the aryl substituents (acetyl, acyl, imino, nitro, etc.). This is likely due to a number of factors including the inherent strength of the C-C or C-N bond, π -system conjugation as discussed above, and steric bulk. In aryl substrates such as halobenzenes where the bond to a functional group is less robust (C-Cl, C-Br, C-I), selective activation of C-H bonds is significantly more challenging, since mixtures of oxidative addition products (C-H vs. C-X) may be likely. In these reactions, the concept of "selectivity" extends beyond the basic idea of position (*ortho, meta, para*), and must also include the type(s) of bond involved (eq. 4).



The extremely high bond enthalpy for carbon-fluorine bonds sets fluorinated substrates somewhat apart from other halogenated arenes, and they have typically been studied separately.³³⁻⁴¹ But the other halobenzenes (Cl, Br, I) are widely used as building blocks in synthetic schemes due to the ease of substitution of the heavier halogen atoms for more desirable functional groups. Their use in reactions involving transition metals often entails oxidative addition to the metal center, and so it is important to know whether C-H or C-X activation will dominate for a particular metal complex.⁴² Preferential oxidative addition of C-X bonds has been reported with Group 9⁴³⁻⁴⁶ and Group 10 metals.⁴⁷⁻⁵⁰ Selective C-H activation in the presence of aryl C-X bonds has also been reported for a few late transition metals, including iridium.

Milstein and co-workers have postulated a directing effect to explain results from the reaction of a cationic (PNP)Ir system with halobenzenes in which *ortho* C-H activation products are favored both kinetically and thermodynamically. The active form of their complex is isoelectronic with (PCP)Ir, and they found no evidence for C-X activation (eq. 5).^{51,52} Ozerov and co-workers have reported very different results of halobenzene studies with a neutral (PNP)Ir complex (also isoelectronic with (PCP)Ir). In Ozerov's system, kinetic products from C-H activation dominate at lower temperatures, with the *ortho* activation product being the most thermodynamically preferred of the many isomeric products. But at very high temperatures, C-X activation dominates to give the ultimate thermodynamic product (eq. 6).^{46,53}





Our results of experiments with (PCP)Ir and halobenzenes have provided insight into both aspects of selectivity: C-H vs. C-X and preferential ortho C-H activation. C-H activation of fluorobenzene gives exclusively ortho products, and kinetic and thermodynamic effects of the fluorine substituent are self-consistent and in good agreement with previous reports in the literature.³⁵⁻³⁸ While no C-F activation is observed with fluorobenzene, iodobenzene leads *primarily* to products of C-I activation. In between these two extremes, C-H activation reactions with chlorobenzene and bromobenzene are much less straightforward and give product mixtures in which C-H activation is the kinetically favored process, but C-X activation (X = Cl, Br) dominates thermodynamically. Interestingly, among C-H activation products for these reactions, there is no thermodynamic preference for *ortho* activation over *meta* and *para*, but the kinetics for ortho C-H activation are significantly slower. Taken together, these data suggest that the chloro and bromo substituents *do not* act as directing groups, but rather, they slow the kinetics of C-H activation through steric effects in the transition state (vide *infra*). These results are in good agreement with DFT calculations performed by our group for the addition of chloro- and fluorobenzene to (PCP)Ir.⁵⁴ Compiling the results of kinetic and thermodynamic studies of halobenzene substrates with those from additional experiments with substituted benzenes bearing methyl and trifluoromethyl groups, gives a thorough and enlightening picture of the factors affecting the selectivity of aryl C-H activation reactions.

2.2 Results and Discussion

2.2.1 Synthesis of iridium phenyl complex 2-1 from the reaction of (PCP)Ir with benzene

As mentioned in the introduction to this chapter, the reaction of (PCP)IrH₂ with an alkene acceptor such as norbornene (NBE) is known to generate a precursor of the reactive fragment "(PCP)Ir".³¹ This 14-electron fragment is able to oxidatively add both alkyl and aryl C-H bonds, including those of most common organic solvents. Therefore, the choice of a solvent with inaccessible C-H bonds was critical to the success of our experiments. Fortunately, the addition of aryl C-H bonds that are *ortho* to a methyl (or other alkyl) substituent on an aryl ring is much less favorable than those in the *meta* or *para* positions.⁵⁵ In fact, as will be discussed in this thesis, aryl C-H activation *ortho* to a methyl group has not been reported for (PCP)Ir prior to this research, and requires very special conditions in order to be observed. Therefore, *para*-xylene and mesitylene (in which all aryl C-H bonds are *ortho* to methyl groups) are the only "inert" solvents employed for the reactions presented herein.

Reaction of (PCP)IrH₂ and NBE with excess benzene at ambient temperature results in disappearance of the (PCP)IrH₂ peak in the ³¹P NMR spectrum accompanied by the appearance of a new signal at δ 67.2 ppm. The ¹H NMR spectrum shows signals characteristic of a PCP ligand in a fully symmetrical environment, i.e., all *tert*butyl and methylene linker protons are equivalent. In the absence of benzene, (PCP)IrH₂ and norbornene produce a labile "NBE complex" that appears as a broad singlet in the ³¹P NMR spectrum at δ 62.9 ppm. This species is the precursor to the 14-electron (PCP)Ir fragment as discussed above. There is no Ir-H signal in the ¹H NMR spectrum for the NBE complex, even at low temperature, indicating that the NBE may be coordinated to the metal through a π -interaction or simply that the species is fluxional on the NMR timescale (or both). Essentially, NBE acts as a "place-holder", coordinating to the (PCP)Ir fragment strongly enough to prevent it from self-cannibalizing in solution, but weakly enough to be displaced by any alternate substrate added to the reaction mixture.

In the presence of an excess of benzene at temperatures lower than ~0 °C, a hydride (Ir-H) resonance is observed at -45.56 ppm (t, $J_{HP} = 14.1$ Hz). This signal – far upfield from all the remaining aryl and PCP protons – is indicative of a five-coordinate d⁶ metal complex.⁵⁶ Additionally, the remainder of the spectrum transforms from an assemblage of rather broad peaks at room temperature to significantly sharper resonances indicative of a non-symmetric environment at lower temperatures: PCP *tert*butyl and methylene linker protons are each resolved as two inequivalent sets, and signals attributable to an η^1 -phenyl ligand appear. These data are all consistent with characterization of product **2-1** as the square pyramidal complex (PCP)Ir(H)(phenyl) (eq. 7).^{32,57} Indeed, a single-crystal x-ray diffraction structure was ultimately obtained by our group that confirms the spectroscopically determined structure.⁵⁸



2-1

It is important to note that both oxidative addition of the C-H bonds of benzene and the microscopic reverse of this process – reductive elimination – occur rapidly on the NMR time scale at room temperature. Therefore, monitoring of experiments below ambient temperature by NMR is of great value. Since *p*-xylene-d₁₀ freezes at 13 °C, mesitylene-d₁₂ (m.p. = -45 °C) was used as the solvent for rapidly exchanging substrates like benzene, when low temperature experiments were required. Accordingly, -50 °C is the approximate low temperature limit for all NMR studies of C-H activation of aryl substrates presented in this thesis. As will be discussed in the next section, mildly electron-donating alkyl substituents *dis*favor addition to (PCP)Ir, and therefore add to the metal center less favorably than benzene, and also give labile C-H activation products that must be studied near the low temperature limit. Other substrates such as the halobenzenes produce considerably less labile addition products.

Addition of carbon monoxide to the five-coordinate complex **2-1** results in the appearance of a single resonance in the ³¹P NMR spectrum at 52.3 ppm (d, $J_{PH} = 16.7$ Hz). In the ¹H NMR spectrum, a new hydride signal appears at -8.79 ppm (t, $J_{HP} = 15.9$ Hz) that persists even at ambient temperature. This new 18-electron, six-coordinate complex **2-2** does *not* undergo arene exchange, and spectral analysis is consistent with the structure shown in eq. 8.⁵⁷ Throughout the studies presented in this thesis, CO has been used to "trap" labile five-coordinate complexes as their non-exchanging, six-coordinate CO adducts. Since rapid arene exchange is indicative of a less thermodynamically favorable oxidative addition product, addition of CO to labile (PCP)Ir(aryl)(H) complexes often yields the four-coordinate, 16-electron, square-planar complex **2-3** along with the desired six-coordinate adduct as shown in eq. 8. The ratio of

products is dependent upon both the concentration of CO and the thermodynamic stability of the (PCP)Ir(aryl)(H) complex, and will be discussed further below. The unreactive species **2-3** is a stoichiometric "dead-end" in these studies, and oxidative addition of arenes to this complex does not take place.



2.2.2 Synthesis and characterization of products from the reaction of (PCP)Ir with alkyl-substituted benzene substrates

Preliminary experiments with alkyl-substituted benzene substrates (toluene, *meta*-xylene) were previously conducted by our group in order to demonstrate rapid arene exchange with benzene.^{31,57} During these studies, it was observed that the C-H addition product from benzene is slightly more thermodynamically favorable than the *meta*-xylene adduct, even taking into account the ratio of available C-H bonds (benzene = 6 and *meta*-xylene = 1) (eq. 9). Apparently, the two methyl groups on *meta*-xylene have an unfavorable effect on the C-H activation reaction.



Subsequently, similar equilibrium studies were conducted with two closelyrelated substrates based on the 2-Z-1,3-dimethylbenzene motif (Z = nitro and chloro) in order to probe electronic effects.⁵⁹ Results of these experiments in conjunction with DFT calculations suggested that both π and σ electron-withdrawing substituents on the substrate benzene ring very strongly *favor* the oxidative addition process. Using the results for arene exchange between benzene and *meta*-xylene as a starting point, the C-H activation reactions of (PCP)Ir with additional alkyl-substituted benzene substrates were rigorously studied in order to measure both the equilibria vs. benzene as well as the rates of reductive elimination from the corresponding (PCP)Ir(aryl)(H) complexes. In subsequent sections of this chapter, thermodynamic and kinetic data will also be presented for a wide range of additional aryl substrates.

Reaction of (PCP)IrH₂ and norbornene (3 equiv.) with a small excess of *meta*xylene in mesitylene- d_{12} solvent gave the C-H addition product **2-4**. Analogous to the reaction with benzene, disappearance of the dihydride peak in the ³¹P NMR spectrum was accompanied by the appearance of a new peak a 67.1 ppm. At -45 °C, a hydride (Ir-H) resonance was observed at -45.59 ppm (t, $J_{HP} = 12.7$ Hz). Since the reaction was initially run with a *small* excess of *meta*-xylene substrate (10 equiv.), a broad singlet was also observed at 62.9 ppm, indicating an equilibrium between **2-4** and the fluxional NBE complex (eq. 10). Repeating the experiment between (PCP)Ir and benzene with the same small excess concentration (10 equiv.) gave similar results, indicating that both arene substrates yield labile oxidative addition products that exist in equilibrium with the NBE complex.



This turned out to be an important and valuable observation, since equilibria between such similar arenes as benzene and *meta*-xylene would have been impossible to measure via NMR, due to overlapping, almost perfectly coincident resonances. While chemical shifts for arenes with other substituents (halogens, CF₃; *vide infra*) are significantly different than those for benzene in a few cases, there is remarkably consistent overlap of both ¹H NMR and ³¹P NMR signals for C-H activation products from a wide variety of substituted arenes. However, the ³¹P NMR resonance for the NBE complex (62.5 ppm at -20 °C) does not overlap with *any* of the products discussed in this thesis. Therefore, with few exceptions (as noted), equilibrium experiments were all conducted between the target (PCP)Ir(aryl)(H) complex and the NBE complex (eq. 11), and then indirectly compared to results for unsubstituted benzene.

While the specific strategies for collecting data relevant to thermodynamics (from equilibrium studies) and kinetics (rates of reductive elimination) are provided in the experimental section later in this chapter, several important details are worth mentioning here. All values for K_{eq} and k_{RE} discussed in this thesis have been calculated at (or extrapolated to) 25 °C. Due to the rapid exchange for the norbornene complex (and indeed, for the addition products of many of the less thermodynamically favorable substrates), all equilibria were calculated at low temperature (-20 °C) where the ³¹P NMR signal for (PCP)Ir(NBE) was shown to be sharp and accurately measurable.

Kinetic data for the rates of reductive elimination were calculated by utilizing variable temperature NMR techniques and measuring the rates of line-broadening for the Ir-H hydride resonance(s) over a suitable series of temperatures. The Varian "tempcal" protocol was used with either a methanol or ethylene glycol standard (below or above 25 °C, respectively) for accurately calibrating the temperatures of individual NMR experiments. NMR spectra were modeled using the gNMR simulation software package from Cherwell Scientific. Representative experimental and simulated spectra are shown in Figures **2.29** – **2.31** at the end of this chapter.

Individual reactions of (PCP)IrH₂ and norbornene (3 equiv.) with small excess of the alkylated substrates toluene, *tert*-butylbenzene, *ortho*-xylene, or 1,3-di-*tert*-

butylbenzene in mesitylene, gave the corresponding C-H addition products **2-5a**, **2-5b**, **2-6**, and **2-7**. Monosubstituted arenes (toluene, *tert*-butylbenzene) can undergo C-H activation with (PCP)Ir to yield three aryl hydride isomers as shown in eq. 12. With 1,2-di-substituted arenes (e.g., *ortho*-xylene), two rotameric products are formed, while with 1,3-di-substituted arenes (*meta*-xylene, 1,3-di-*tert*-butylbenzene), there is only one possible product (eq. 13).



Combined results for thermodynamic and kinetic studies of alkylbenzene substrates are given in Table 2.1. In some cases, NMR signals either coincide or overlap

sufficiently that individual analysis of the isomers/rotamers was not possible. Whenever this occurred, overlapping peaks were accurately modeled (as shown at the end of the chapter) and the data presented here have been adjusted and reported on a *per rotamer* basis. As previously noted, activation of aryl C-H bonds *ortho* to methyl groups is extremely unfavorable for the (PCP)Ir system. Therefore, as shown in Table 2.1, adducts for 1,4-dimethylbenzene (*para*-xylene) and 1,3,5-trimethylbenzene (mesitylene) were not observed. The C-H addition reactions of the remaining substrates (toluene, *tert*-butylbenzene, *ortho*-xylene, *meta*-xylene, and 1,3-di-*tert*-butylbenzene) are disfavored vs. benzene, with relative values for K_{eq} < 1, even when calculated on a "per C-H bond" basis. Kinetic data show that both the rates for reductive elimination (directly measured) and oxidative addition (calculated) are marginally faster than the corresponding values for benzene. This is consistent with the less favorable thermodynamics for these substrates.

Fragment showing the configuration of the C-H addition product	$K_{eq} (vs. C_6 H_6)$	K (per C-H)	k _{RE} (sec ⁻¹)	$\begin{pmatrix} k_{RE} \\ (vs. C_6 H_6) \end{pmatrix}$	$\frac{k_{OA}}{(vs. C_6H_6)}$	k _{0A} (per C-H)
H Ir	[1]	[1]	432	[1]	[1]	[1]
	^a 0.066	0.40	$8.2 ext{ x10}^3$	19	1.3	7.6
H H H	^a 0.13	0.81	Kinetics were not measured			
	^b 0.047	0.28	$1.2 \text{ x} 10^4$	28	1.3	7.9
	0.038	0.23	$9.9 ext{ x10}^2$	2.3	0.087	0.52
H H H	0.079	0.47	$7.5 \text{ x}10^2$	1.7	0.14	0.82
	No Measurable Reaction					
	No Measurable Reaction					

Table 2.1 Thermodynamic and kinetic data for alkyl-substituted benzene substrates vs. benzene at 25 °C.

^aSubstrates have three C-H bonds accessible for addition to (PCP)Ir, resulting in three products: two *meta* rotamers and the corresponding *para* isomer. NMR signals either coincide or overlap sufficiently that individual isomers cannot be separated. Data are reported on a "per rotamer" basis.

^bSubstrates form two rotameric products and cannot be separated; data are reported on a "per rotamer" basis.

While the data are remarkably consistent, several observations are worth noting. First, C-H activation of *tert*-butylbenzene by (PCP)Ir is slightly more thermodynamically favorable than for toluene (by a factor of two). Although this is a very small difference, it is consistent with the fact that methyl groups are weakly electron-donating through hyperconjugation of their C-H bonds, and therefore *add* electron density to the aryl ring. The *tert*-butyl group has no C-H bonds on the carbon α to the arene ring, and therefore, is unable to act in this fashion. This is consistent with previous results from our group⁵⁹ and will become a recurring theme in discussions of results for various classes of substrates presented in this thesis: the addition of aryl C-H bonds to (PCP)Ir is less favored for more electron rich substrates. Conversely, more electron withdrawing aryl substituents *favor* the C-H activation process. Aside from electronic differences, there is obviously a large size difference between methyl and *tert*-butyl groups, and steric influences cannot be ignored. Although reaction kinetics were not measured for *tert*-butylbenzene, the *para* position is remote enough from the (PCP)Ir fragment that steric effects should be minimal. (As will be discussed later in the chapter, sterics play a *major* role in the case of *ortho* C-H activation.)

A very slight electronic effect can also be seen when comparing results for one methyl substituent (toluene) vs. two (*ortho-* and *meta-*xylenes). The presence of two mildly donating methyl groups results in slightly lower values for K_{eq} vs. benzene (0.047 and 0.038 for *ortho-* and *meta-*xylene, respectively) compared to toluene (0.066). For *ortho-*xylene, this is reflected in a correspondingly faster rate of reductive elimination from the C-H addition product. The story is different for *meta-*xylene however; results show *slower* rates of both oxidative addition and reductive elimination as compared to toluene. Though the effect is minor (approximately ten-fold), it is tempting to attribute these results to slight steric factors arising from having two methyl groups in *meta* positions, and therefore closer to the metal center and steric bulk of the PCP ligand during the transition state for C-H activation. This explanation is especially tempting in light of the aforementioned observations that no aryl C-H activation for *para-*xylene or mesitylene is observed. Electronically, *para-*xylene should be comparable to *meta-*

xylene, while mesitylene, with three methyl groups, should be an even less favorable substrate. Both of these inert substrates offer aryl C-H bonds that require activation *ortho* to bulky methyl groups and are therefore sterically challenging.

Addition of CO to the five-coordinate complexes **2-4**, **2-5a**, **2-5b**, **2-6**, and **2-7** yields 18-electron, six-coordinate complexes analogous to the phenyl hydride CO adduct **2-2**. NMR spectra show the disappearance of resonances for all unstaurated five-coordinate complexes, and concurrent appearance of new signals for each of the rotameric, six-coordinate CO adducts. Unfortunately, the utility of this trapping method was undermined by the thermodynamic instability of the initial C-H activation complexes. High concentrations of the four-coordinate CO complex **2-3** were present in all of the product mixtures, despite repeated attempts with different reaction conditions. The presence of **2-3** in solution with multiple isomeric six-coordinate products ruled out the possibility of x-ray crystallographic analysis for these substrates.

2.2.3 Synthesis and characterization of products from the reaction of (PCP)Ir with halobenzenes

As mentioned in the introduction to this chapter, previous research in our group has shown that so-called "directing" groups on substrate arene rings do not always function as such. Groups such as nitro and carboxyl that are fully conjugated with the aryl ring were shown coordinating to the (PCP)Ir metal center only *after* C-H activation had taken place, thereby providing enhanced thermodynamic stability to the oxidative addition products. The alkyl groups discussed in the previous section have no place in a discussion of "directing" groups, since they cannot coordinate to a metal center, and in fact, strongly disfavor *ortho* C-H addition. Halogen substituents fall somewhere between these two extremes.

Strongly electronegative atoms like fluorine and chlorine are electron rich, and their three non-bonded lone pairs of electrons could potentially coordinate to a metal center before, during, or after a C-H activation reaction nearby. In addition, when bonded to a substrate aryl ring, halogens exert a mixture of electronic effects, rendering them somewhere intermediate between electron-withdrawing and electron-donating groups. By virtue of their inherent electronegativity, they are inductively withdrawing, pulling σ electron density away from the aryl ring. Conversely, their lone-pair electrons can interact with the aromatic π system (to varying degrees, depending on the size of the halogen atom), allowing them to weakly conjugate and donate electron density to the aryl ring. Having achieved a more thorough understanding of the steric and electronic effects of alkyl substituents, additional experiments designed to explore the influence of halogenated benzene substrates were conducted. Specifically, the goal was to determine the extent of halogen "directing" effects, if any.

2.2.3.1 Synthesis and characterization of products from the reaction of (PCP)Ir with fluorobenzene

Reaction of (PCP)IrH₂ and NBE with excess fluorobenzene at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of a two new doublets in a ratio of 3.7:1 at δ 69.2 and 67.6 ppm, respectively. The ¹H NMR spectrum shows two hydride signals far upfield, indicative of two different d⁶ five-coordinate products in the same ratio as the ³¹P NMR peaks. The smaller signal at -43.1 ppm (t, $J_{HP} = 13.9 \text{ Hz}$) shows the triplet pattern characteristic of a hydride proton bonded to the Ir metal center and coupled by two equivalent phosphorus atoms. The larger signal at -46.3 ppm (d of t, $J_{HP} = 13.7 \text{ Hz}$) is a doublet of triplets, showing splitting by both phosphorus *and* fluorine ($J_{HF} = 2.5 \text{ Hz}$). Both products are exchanging slowly at ambient temperature and the ratio of products remains unchanged over time and/or after heating. While the exact coupling mechanism between the hydride proton and the substrate fluorine atom is not clearly understood, this effect was seen with several other fluorinated substrates as well (*vide infra*).

As mentioned in the discussion of alkylbenzenes, monosubstituted aryl substrates have multiple C-H bonds available for activation by (PCP)Ir. Therefore, one challenge of analyzing data from these experiments is simply determining which isomeric products are formed and how these products relate to the NMR resonances. Addition of fluorobenzene to (PCP)Ir can potentially result in five possible aryl hydride isomers that differ in both the position of the fluoro substituent on the aryl ring as well as its orientation in regard to the metal-hydride bond (Fig. 2-1). While there are three types of aryl C-H bonds relative to the fluorine substituent (ortho, meta, para), C-H activation reactions at the ortho and meta positions can each lead to two different rotamers: "cis", in which the fluorine atom is located on the same "side" of the aryl ring as the hydride, and "trans", in which the fluorine points away from the direction of the hydride. Both experiments and DFT calculations have shown that once the C-H activation product is formed, interconversion between various isomers can only occur through a full reductive elimination followed by re-addition of the substrate. In other words, the aryl ring does *not* rotate about the Ir-C bond.





Although aryl C-H activation *ortho* to alkyl groups is an extremely unfavorable process, the opposite is true when the substituent is fluorine. In fact, C-H activation *ortho* to fluorine has been vigorously studied and has been reported to occur *exclusively* over *meta* or *para* activation in many systems.³⁶⁻⁴¹ Given the literature precedents, the two (PCP)Ir(H)(fluorophenyl) products indicated by the NMR spectra in our experiments were tentatively assigned as the two rotamers resulting from *ortho* C-H activation: *ortho*-trans **2-8a** and *ortho*-cis **2-8b** (eq. 14).



X-ray crystallographic analyses were impossible, due in part to the presence of two extremely similar products (attempts to separate and isolate them failed), and also because the five-coordinate complexes are simply too labile to crystallize out of solution. Prior research in our group has shown that the four coordinate complex (PCP)Ir(N₂) is very stable, and is easily generated from thermodynamically labile, unsaturated (PCP)Ir complexes if exposed to adventitious nitrogen in the glovebox atmosphere.⁵⁷ Repeated attempts to crystallize the fluorophenyl C-H addition product(s) failed, giving the dinitrogen complex instead. Therefore, in order to more rigorously verify the identities of the addition products, a series of experiments was conducted with other fluorinated aryl substrates bearing strategically chosen, additional substituents as outlined below.

Two important questions had to be answered in order to identify the products of C-H activation for monosubstituted arenes like fluorobenzene. According to Fig. 2.1, both the *position* of the activated C-H bond(s) on the aryl ring (vs. fluorine), and the *conformation* of the product (aryl substituent cis or trans to the metal hydride) needed to be determined. In regard to the position of the activated C-H bonds, 1,4-difluorobenzene, 4-fluorotoluene, and 1,2,3,4-tetrafluorobenzene are convenient substrates that restrict oxidative addition to the *ortho* position. All three have the potential to yield two rotamers of the respective *ortho* activation products (eq. 15). The geometrical symmetries of 1,4 difluorobenzene and 1,2,3,4-tetrafluorobenzene are structurally obvious, and for 4-fluorotoluene, the two C-H bonds *ortho* to the methyl group are inaccessible to (PCP)Ir. None of these three substrates has the potential to yield *meta* or *para* products of C-H activation.



As anticipated, reactions of (PCP)Ir with 1,4-difluorobenzene or 4-fluorotoluene vielded two products for which the resonances in the ³¹P NMR and ¹H NMR spectra coincide almost exactly with those for the products of C-H activation of fluorobenzene (2-9a,b and 2-10a,b respectively). While the NMR signals for the products from 1,2,3,4tetrafluorobenzene (2-11a,b) were shifted upfield slightly (~ 0.2 ppm), the ratio of the two products is comparable and coupling constants are remarkably similar to all of the other three substrates. These results confirmed that the two products for oxidative addition of fluorobezene both result from ortho C-H activation. In order to assign the identities of the ¹H NMR signals as *ortho*-cis and *ortho*-trans, extensive series of 1-D and 2-D NOESY ¹H NMR experiments were conducted with fluorobenzene, 1,4-difluorobenzene, and 4-fluorotoluene. These experiments showed definitive evidence that the more thermodynamically favorable product (¹H NMR δ = -46.3 ppm) is the *ortho*-trans rotamer. The *ortho*-cis rotamer (¹H NMR δ = -43.1 ppm) is the minor product in all cases. These assignments also make intuitive sense based on the steric argument that fluorine is approximately 25% larger than hydrogen (van der Waals radii of 1.48 Å vs. 1.20 Å, respectively). The ortho-trans rotamer allows the fluorine substituent to "point" toward the empty coordination site on the metal center; in the *ortho*-cis case, the fluorine resides in close proximity to the metal hydride ligand. The potential for less steric crowding in the *ortho*-trans product contributes to the greater thermodynamic stability of this rotamer (recall the ratio of products: 3.7:1 – trans to cis).

Attempts to grow x-ray quality single crystals from all four of the product mixtures (2-8, 2-9, 2-10, and 2-11) failed for reasons addressed above. Therefore, CO was added in an attempt to trap the complexes as their rigid, non-labile six-coordinate

analogs. In each case, the expected mixture of two CO adducts was formed (one corresponding to each five-coordinate rotamer). However, in a surprising result, the product ratio shifted dramatically in favor of the *ortho*-trans configuration in all cases, resulting in a very low concentration (< 2%) of the *ortho*-cis CO adduct in the final solutions (eq. 16). New attempts at crystallization were successful; the CO ligand is located trans to the metal-hydride bond and proximate to the nearest aryl fluorine atom, confirming the *ortho*-trans conformation for all four products (**2-12**, **2-13**, **2-14**, and **2-15**). X-ray crystal structures and selected data are included at the end of this chapter.



While x-ray crystallographic evidence for the six-coordinate CO adducts of products from C-H activation reactions was valuable, crystallization of the unstaurated 16-electron, five-coordinate complexes remained an attractive, though elusive, goal. Additional C-H activation reactions were therefore conducted with 1,3,5-trifluorobenzene and pentafluorobenzene. Both of these substrates have only one type of C-H bond (located *ortho* to *two* fluorine atoms), and formed only a single product, thereby solving the problem of product mixtures and the need for separation/purification. In addition, it was assumed that increasing the number of flourine substituents on the substrate arene would make it more electron deficient and potentially lead to more thermodynamically stable addition products (eq. 17).



Reaction of (PCP)IrH₂ and NBE with excess 1,3,5 trifluorobenzene at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of a single new doublet at δ 67.9 ppm. The ¹H NMR spectrum shows a hydride triplet at -44.4 ppm. Both ³¹P and ¹H NMR resonances appear at chemical shifts *between* those for the products from substrates that yielded two rotamers. This is consistent with the configuration of product **2-16**, which has fluorine atoms in *both* the *ortho*-cis and *ortho*-trans positions. Similar results were found for the product of the reaction of (PCP)Ir with pentafluorobenzene (2-17). Apparently, the three fluorine substituents of 1,3,5-trifluorobenzene did not enhance the thermodynamic stability of the addition product sufficiently, and repeated attempts to crystallize complex 2-16 failed. Ultimately, addition of CO gave the six-coordinate product 2-18 which was fully characterized by NMR and x-ray crystallography. Fortunately, the result was different for the complex 2-17, and single crystals were successfully grown and characterized without the addition of CO as the sixth ligand. To date, complex 2-17 is the only 16-electron, coordinatively unsaturated, phenyl C-H activation product for which x-ray analysis has been successful among all the experiments presented in this thesis. The x-ray crystal structure and selected data are included at the end of this chapter.

2.2.3.2 Synthesis and characterization of products from the reaction of (PCP)Ir with chlorobenzene

Given the dominance of *ortho* C-H activation with all of the fluorinated benzene substrates discussed in the last section, it was impossible to speculate on their potential for acting as "directing" groups. While it was obvious from x-ray crystallographic measurements and NMR spectra that there was no fluorine-to-metal coordination in the activation products, the question of whether the fluorine atom pre-coordinates to the metal center, thus "directing" the *ortho* C-H activation, remained unclear. However, given its small size and the extensive literature precedent for strong electronic influence on *ortho* hydrogens, such an effect seems unlikely. In any case, the heavier halogens are much more widely used than fluorine as reactive substituents in key steps of synthetic processes where "directing" effects would have potential value.

Therefore, analogous experiments were conducted with chlorinated benzene substrates. Chlorine is both less electronegative and significantly larger (1.80 Å vs. 1.48 Å) than fluorine. Accordingly, the C-Cl bond is significantly less strong than the C-F bond, meaning that C-Cl bond activation can potentially compete with C-H activation by (PCP)Ir. Absolutely no evidence was seen for C-F bond activation in any of the experiments with fluorobenzenes. In regard to chloroarenes, however, Ozerov reported that kinetic products from C-H activation dominate at lower temperatures with a neutral (PNP)Ir complex (isoelectronic with (PCP)Ir). However, at high temperatures, C-Cl activation dominates to give the ultimate thermodynamic product.^{46,53} Using a similar, but cationic complex, Milstein found no evidence for C-Cl activation, while invoking "directing" effects to explain why *ortho* C-H activation gave the thermodynamically preferred product.^{51,52}

Reaction of (PCP)IrH₂ and NBE with excess chlorobenzene at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of three new signals: a broad resonance at δ 67.9 ppm a sharp doublet at δ 67.4 ppm, and a partially resolved doublet at δ 64.8 ppm (approximate ratios 12:6:1). The ¹H NMR spectrum shows three corresponding hydride signals far upfield, indicative of three different d⁶ five-coordinate products in a similar ratio to the ³¹P NMR peaks. It is clear from both spectra that two of the three signals represent products that are rapidly exchanging on the NMR time-scale at ambient temperature. These peaks, at δ -42.2 ppm and δ -45.6 ppm correspond to those at δ 64.8 and 67.9 ppm in the ³¹P NMR spectrum, according to integrated peak areas. The remaining signal is a sharp triplet at δ -41.7 ppm ($J_{HP} = 14.7$ Hz). Spectra collected at -40 °C show that both broad resonances sharpen, as the respective rates of exchange slow down. The minor peak at δ -42.2 ppm sharpens into a triplet ($J_{HP} = 13.7 \text{ Hz}$). The major peak at δ -45.6 ppm resolves into *two* side-by-side triplets ($J_{HP} = 13.7 \text{ Hz}$ for both), with an apparent third broad signal embedded and overlapping between them. Unlike fluorobenzene then, the C-H activation of chlorobenzene yielded an array of products – possibly all five rotamers analogous to those illustrated in Fig. 2-1 (above).

Having a mixture of many structurally similar isomers once again ruled out any chance of growing single crystals for x-ray analysis. Making the process of identifying the products even more complicated, was the observation that new NMR signals grew in both the ³¹P NMR and ¹H NMR spectra over time. After 24 hours at ambient temperature, a very small triplet appeared in the ¹H NMR spectrum at δ -42.7 ppm. In addition, a new singlet peak appeared in the 31 P NMR spectrum at δ 36.9 ppm. These new resonances were eventually characterized as arising from two *different* products resulting from C-Cl activation: (PCP)Ir(phenyl)(Cl) and (PCP)Ir(H)(Cl) (2-19 and 2-20, respectively). While the mechanism leading to 2-20 has not yet been elucidated, the C-H activation products from (PCP)Ir and chlorobenzene all eventually disappear, converting quantitatively to 2-19 and 2-20 (eq. 18). Without heating, the C-H activation products persist for several days in solution. Heating a solution of the products at 75 °C leads to quantitative conversion to the C-Cl activation mixture within 30 minutes. Therefore, all results presented in this thesis that derive from C-H activation reactions with chlorinated substrates (or brominated, *vide infra*) were carefully collected from reactions with freshly combined reagents (chlorinated substrate, NBE, and (PCP)Ir), and products of C-Cl

activation were rigorously excluded from all thermodynamic and kinetic calculations and data.



With the results from fluorobenzene as a guide, it seemed likely that *ortho* activation of chlorobenzene would yield separate, easily identifiable products having unique NMR signals. Additionally, it seemed obvious that the major peak at ambient temperature was representative of multiple, similar products. Its position at δ -45.6 ppm was also perfectly coincident with *all* the hydride NMR signals seen with the C-H activation products from alkylbenzenes as discussed earlier in this chapter, making *meta* and/or *para* activation products seem particularly likely.

As a first step toward probing the identities of the chlorophenyl products, experiements were conducted with (PCP)Ir and three selectively deuterated chlorobenzene analogs – all of which were commercially available. The first two, chlorobenzene-4- d_1 and chlorobenzene-3,5- d_2 were chosen in order to isolate the C-H bonds *para* and *meta* to the chloro substituent, respectively. Oxidative addition of the C-D bonds by (PCP)Ir selectively erased the corresponding proton peaks from the ¹H NMR spectrum, thereby connecting the isomers with the respective NMR signals and leaving the remaining peaks for C-H activation unchanged (eq. 19).



Reaction of (PCP)Ir with chlorobenzene-4- d_1 caused no apparent change in the ¹H NMR spectrum. At first, this was a perplexing result, since there is no obvious reason that (PCP)Ir wouldn't activate the *para* C-H bond. Reaction with chlorobenzene-3,5- d_2 at ambient temperature produced an ¹H NMR spectrum with the two most downfield resonances intact ($\delta = -41.7$ and -42.2 ppm), but missing the large, broad peak at δ -45.6 ppm. At low temperature (-40 °C), the signal at -45.6 ppm showed a small, broad hump, indicating a minor product, but the two sharp triplets formerly observed at this temperature and chemical shift were no longer present. Fully deuterated chlorobenzene- d_5 was also run as a control, and as expected, all hydride signals in the ¹H NMR spectrum disappeared, while the ³¹P NMR spectrum remained unchanged. Taken all together, the results from deuterated substrates seemed sufficient to identify the products based on *position* of the C-H bond, but the orientations (cis, trans) remained unclear (eq. 20).



Therefore, similar to the strategy for fluorobenzene, products of the C-H activation of chlorobenzene were further analyzed through systematic experiments with other chlorinated aryl substrates bearing additional substituents that block access to key C-H bonds, or otherwise serve as identifiers in the NMR spectra of their C-H activation products. In regard to the position of the activated C-H bonds, 1,4-dichlorobenzene, 4- chlorotoluene, and 1,2,3,4-tetrachlorobenzene restrict oxidative addition to the *ortho* position, as discussed with the fluoro analogs. All three have the potential to yield two rotamers of the respective *ortho* activation products (eq. 21). The geometrical symmetries of 1,4 dichlorobenzene and 1,2,3,4-tetrachlorobenzene are structurally obvious, and for 4-chlorotoluene, the two C-H bonds *ortho* to the methyl group are inaccessible to (PCP)Ir. None of these three substrates has the potential to yield *meta* or *para* products of C-H activation.



Reactions of (PCP)Ir with all three of the *ortho*-limiting substrates shown in eq. 21 yielded two products (**2-22a,b**, **2-23a,b**, and **2-24a,b** respectively) for which the resonances in the ³¹P NMR and ¹H NMR spectra coincide almost exactly with those for the suspected products of *ortho* C-H activation of chlorobenzene. Indeed, these results confirmed that the two most downfield signals in the ¹H NMR spectrum arise from *ortho*

C-H activation. In order to assign the identities of the ¹H NMR signals as *ortho*-cis and *ortho*-trans, a series of 1-D and 2-D NOESY ¹H NMR experiments was conducted with chlorobenzene, 1,4-dichlorobenzene, and 4-chlorotoluene. These experiments provided definitive evidence that the more thermodynamically favorable product (¹H NMR δ = -41.7 ppm) is the *ortho*-trans rotamer. The *ortho*-cis rotamer (¹H NMR δ = -42.2 ppm) is the minor product in all cases. These assignments are directly analogous to those for fluorobenzene. However, in the present case, the *ortho*-trans rotamer has a significantly larger thermodynamic advantage over the *ortho*-cis rotamer (6:1) compared with the products from fluorobenzene (3.7:1). The same intuitive rationale also applies here: the large chlorine substituent is considerably less crowded when in the *ortho*-trans conformation.

As was the case with solutions of products from fluorobenzene, X-ray crystallographic analyses were impossible. This was due in part to the presence of several extremely similar products (attempts to separate and isolate them failed), and also because the five-coordinate complexes are simply too labile to crystallize out of solution. Additionally, slow but steady C-Cl activation continually undermined the integrity of all product mixtures. In an effort to halt C-Cl activation and trap the C-H addition products as their rigid, non-labile six-coordinate analogs, CO was added to fresh solutions of all of the above chloro-substituted product mixtures. In each case, the expected mixture of CO adducts was formed (one corresponding to each five-coordinate rotamer). New attempts at crystallization were successful for the CO adducts of **2-22**, **2-23**, and **2-24**, but the crystals for the latter two were too disordered for accurate x-ray analysis. Only the CO adduct of the (PCP)Ir(1,4-dichlorophenyl)(H) complex (**2-25** – eq. 22) yielded crystals of
sufficient quality. As expected, the CO ligand is located trans to the metal-hydride bond and proximate to the nearest aryl chlorine atom, confirming the *ortho*-trans conformation. To date, complex **2-25** is the only chloro-substituted phenyl C-H activation product for which x-ray crystallographic analysis has been successful. The x-ray crystal structure and selected data are included at the end of this chapter.



2.2.3.3 Synthesis and characterization of products from the reaction of (PCP)Ir with bromobenzene

In an effort to evaluate even larger aryl substituents, analogous experiments were conducted with brominated benzene substrates. Continuing down the list of halogens, bromine is slightly less electronegative and slightly larger (1.90 Å vs. 1.80 Å) than chlorine. And whereas the C-Cl bond is weak enough to compete (kinetically) with C-H activation reactions to a small, but measurable extent, C-Br has an even lower bond enthalpy, dominating the products of C-H activation both kinetically and thermodynamically. Fortunately, conducting C-H activation reactions of bromobenzene (and analogous substrates) at low temperatures allowed for accurate observation of the desired products as well as thermodynamic and kinetic calculations.

Reaction of (PCP)IrH₂ and NBE with excess bromobenzene at -40 °C results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of five new signals: an overlapping pair of doublets (δ 67.62 and 67.48 ppm; $J_{\rm HP}$ = 13.0 Hz for both), a very small, broad signal at δ 64.8 ppm, a sharp doublet at δ 61.5 ppm (J_{HP} = 14.2 Hz), and a singlet at δ 33.4 ppm. The peak at δ 33.4 ppm was identified in separate experiments as the product of C-Br activation: (PCP)Ir(phenyl)(Br) **2-26** (Scheme 2.1). The ¹H NMR spectrum shows four hydride signals far upfield, indicative of four different d⁶ five-coordinate products in a similar ratio to the corresponding ³¹P NMR peaks. Aside from the immediate presence of a signal in the ³¹P NMR spectrum for the C-Br activation product, these spectral data are exactly analogous to those observed for the C-H activation of chlorobenzene in number and relative chemical shifts of the hydride signals. A separate reaction with (PCP)Ir and 4bromotoluene yielded the two ortho rotamers, and prevented meta and para C-H activation, lending evidence to the identification of products in the ¹H NMR for reactions with bromobenzene (Scheme 2.1).



Scheme 2.1. Products from the reaction of (PCP)Ir with bromobenzene

Several observations are worth noting. The ¹H NMR signal for the *ortho*-trans C-H activation product (**2-27a**) is even further downfield than that for the analogous chlorophenyl complex (δ -33.6 ppm vs. δ -41.7 ppm). As the six-coordinate CO complexes have demonstrated, hydride resonances for saturated, 18-electron (PCP)Ir complexes generally appear in the δ -7 to -20 ppm region. Therefore, it makes sense that the presence of a large bromine substituent proximal to the empty sixth coordination site in the *ortho*-trans rotamer would promote a downfield shift in the hydride resonance, vs. the less sterically demanding chlorine substituent. Both the ³¹P NMR and ¹H NMR signals corresponding to the *ortho*-cis C-H activation product (**2-27b**) are very small. As the size of the halogen substituent increases, the ratio of products, *ortho*-trans:*ortho*-cis also increases, demonstrating the unfavorable steric crowding that occurs in the *ortho*-cis product due to the proximity of the halogen substituent to the hydride ligand: fluorobenzene (3.7:1); chlorobenzene (6:1); bromobenzene (8.6:1). With respect to reactions of (PCP)Ir with bromobenzene, the *ortho*-cis product was sufficiently disfavored that accurate kinetic and thermodynamic measurements were not possible (see the next section of this chapter). Finally, it should be noted that direct observation and measurements relating to the *para* product of C-H activation (**2-27e**) were not possible for bromobenzene and related substrates. (This was also true in the chlorobenzene case.) The NMR resonances for the *para* products were embedded in the more easily identifiable signals for the *meta* rotamers (**2-27c,d**) in both cases.

As mentioned previously, C-Br activation occurs concurrently with C-H activation during reactions with (PCP)Ir. Analogous to the reaction with chlorobenzene, two products are formed: (PCP)Ir(phenyl)(Br) and (PCP)Ir(H)(Br) (**2-26** and **2-28**, respectively). Complex **2-26** is the dominant product, and the mechanism leading to complex **2-28** remains unclear. All of the C-H activation products from (PCPIr) and bromobenzene eventually convert to a mixture of **2-26** and **2-28** (eq. 23).



In an effort to halt C-Br activation and trap the C-H addition products as their rigid, non-labile six-coordinate analogs, CO was added to fresh solutions of all of the above bromo-substituted product mixtures. Complicated mixtures of CO adducts were formed. Therefore, a different strategy was employed: (PCP)Ir was reacted with 4-

bromotoluene (in order to limit C-H activation to the *ortho* position). The resulting solution was heated and converted fully to the bromotolyl analog of **2-26** (in solution with a small percentage of **2-28**). Subsequent addition of CO yielded the corresponding six-coordinate complex **2-29** (eq. 24). In a separate reaction with (PCP)Ir and 3,5-dimethyl-bromobenzene (chosen for its highly unfavorable electronic and steric attributes), vigorus heating gave product **2-28** in good yield (eq. 25). Both **2-28** and **2-29** were isolated and characterized by x-ray crystallography. X-ray crystal structures and selected data are included at the end of this chapter.



2.2.3.4 Comparison of thermodynamic and kinetic data for the reactions of (PCP)Ir with halobenzenes

Combined results for thermodynamic and kinetic studies of halobenzene substrates are given in Table 2.2. In some cases, NMR signals either coincide or overlap sufficiently that individual analysis of the isomers/rotamers was not possible. Whenever this occurred, overlapping peaks were accurately modeled (as shown at the end of the chapter) and the data presented here have been adjusted and reported on a *per rotamer* basis (e.g., *meta* and *para* products for chlorobenzene). As previously noted, reaction of (PCP)Ir with fluorobenzene gave only products of *ortho* C-H activation, therefore there are no data for *meta* and *para* products from this substrate. In addition, the *ortho*-cis product for activation of bromobenzene was too thermodynamically unfavorable for accurate measurement.

Table 2.2 Thermodynamic and kinetic data for halobenzene substrates vs. benzene at 25 °C.

Fragment showing the configuration of the C-H addition product	$\begin{array}{c} \mathbf{K}\\ (\text{vs. } \mathbf{C}_{6}^{\text{eq}}\mathbf{H}_{6}) \end{array}$	K _{eq} (per C-H)	k _{RE} (sec ⁻¹)	$\begin{array}{c} \mathbf{k}_{\mathrm{RE}} \\ (\mathrm{vs.}\ \mathbf{C}_{6}^{\mathrm{H}}\mathbf{H}_{6}) \end{array}$	$\begin{array}{c} \mathbf{k}_{_{\mathrm{OA}}}\\ (\mathrm{vs.}\ \mathbf{C}_{_{6}}\mathbf{H}_{_{6}})\end{array}$	k _{0A} (per C-H)
	[1]	[1]	432	[1]	[1]	[1]
H H	$1.7 \text{ x} 10^3$	$1.0 \text{ x} 10^4$	0.29	6.7 x10 ⁻⁴	1.2	6.9
	$5.6 ext{ x10}^2$	$3.4 ext{ x10}^3$	1.5	$3.5 \text{ x} 10^{-3}$	1.9	12
	12	73	0.012	2.8 x10 ⁻⁵	3.4 x10 ⁻⁴	2.0 x10 ⁻³
H	2.1	13	28	0.065	0.14	0.83
H CI	^a 8.9	53	88	0.20	1.8	11
H H H	11	67	2.1 x10 ⁻³	4.9 x10 ⁻⁶	5.4 x10 ⁻⁵	$3.2 \text{ x}10^{-4}$
HIR-BR	^a 12	70	62	0.14	1.7	10

^aSubstrates have three C-H bonds accessible for addition to (PCP)Ir, resulting in three products: two *meta* rotamers and the corresponding *para* isomer. NMR signals either coincide or overlap sufficiently that individual isomers cannot be separated. Data are reported on a "per rotamer" basis.

The data in Table 2.2 are remarkably self-consistent and provide a logical framework for interpreting the mechanism of C-H activation for the halobenzenes. Fluorobenzene is perhaps the least interesting substrate, since the data are perfectly in line with expectations, accurately reflecting the presence of a small, highly electronegative substitutent. The strong influence of fluorine, inductively withdrawing electron density from the aryl ring, results in C-H activation products that are thermodynamically preferred over benzene by factors of 3.4×10^3 and 1.0×10^4 for *ortho*-cis and *ortho*-trans, respectively (on a "per C-H bond" basis). Their respective rates of reductive elimination are correspondingly much slower than benzene, while calculated rates of oxidative addition are faster by a modest factor of 10. Interestingly, the *ortho*-trans rotamer is preferred by a factor of \sim 3, and accordingly, eliminates and adds slightly more slowly than the *ortho*-cis rotamer. This is consistent with the hypothesis that the *ortho*-cis rotamer requires that the fluorine reside in close proximity to the hydride, causing minor steric crowding (Fig. 2.2).





The data for chlorobenzene illuminate several important points regarding the mechanism of C-H addition. First, the *ortho*-cis rotamer is significantly less favorable vs.

ortho-trans, as discussed previously (6:1 in favor of the latter). More interestingly, there is essentially no thermodynamic preference for the *ortho*-trans rotamer vs. the *meta* and *para* products. All of these products are favored by approximately the same factor over benzene (73 and 53 for *ortho*-trans and *metas/para*, respectively), demonstrating the mild inductively withdrawing effect of the chloro substituent, and arguing *against* a "directing" effect. If the mechanism involved pre-coordination of the aryl chlorine and subsequent "directing" to the *ortho* C-H bonds, then it would be expected that the C-H activation reaction would lead to an obvious prejudice toward the *ortho* products. These data clearly demonstrate that this is not the case.

There are further surprising results in the kinetic data. The *meta* and *para* products reductively eliminate from (PCP)Ir slightly slower than benzene – perfectly in agreement with the thermodynamic data. But the *ortho*-cis rotamer, thermodynamically favored over benzene by a small factor of 13, eliminates more slowly by a factor of ~15 and also *adds* more slowly, despite the thermodynamic advantage. These trends in the data are significantly more pronounced for the *ortho*-trans rotamer. Although the *ortho*-trans product is thermodynamically favored over benzene by a factor of a factor of 73, its measured rate of reductive elimination (0.012 sec⁻¹) is slower than that for benzene by a factor of almost 4 x 10⁴! Its calculated rate of oxidative addition to (PCP)Ir is slower than benzene by a factor of 500. So, not only is it clear that "directing" effects play no role in these reactions, but the data indicate that in fact, the chloro substituent actually *hinders* the oxidative addition reaction that yields the most thermodynamically preferred product.

Expanding the discussion to include bromobenzene, the data are perfectly consistent with and analogous to those for chlorobenzene. As mentioned in the previous

section, the *ortho*-cis product is very unfavorable for this substrate. Thermodynamic values for the other products are comparable to those for the respective chlorophenyl adducts; i.e., more favorable than benzene by a factor of ~10. However, the kinetic ramifications of the bromo substituent on the addition and elimination of the *ortho*-trans product are even more pronounced than they were for chlorobenzene. The measured rate of reductive elimination (0.0021 sec^{-1}) is slower than that for benzene by a factor of more than 2×10^5 . Likewise, the rate of oxidative addition is even slower than for the *ortho*-trans product from chlorobenzene.

All of these data considered together, support the hypothesis that sterically bulky aryl substituents have a profound effect on the energy of the transition state for the oxidative addition (and the reverse reaction, reductive elimination). Addition of an aryl C-H bond to (PCP)Ir proceeds via preliminary C-H bond coordination to the metal, forming a σ -complex, and subsequent oxidative cleavage to yield the aryl hydride product.⁵² A general reaction coordinate diagram for formation of the *ortho*-trans addition product is shown in Figure 2.3.



Figure 2.3. Reaction coordinate diagram for the oxidative addition of chlorobenzene to (PCP)Ir, giving the *ortho*-trans product.

Considering the geometrical configuration of the transition state, there are two limiting cases for the orientation of the approaching aryl ring (Fig. 2.4). In the horizontal case, there would be no steric difference between the transition states leading to *ortho*-cis and *ortho*-trans products. In the equatorial plane, as far as possible from both phosphines, bulky aryl substituents would have little or no steric interaction with the PCP ligand system. Therefore, kinetic data for the *ortho* rotamers would be approximately the same as that for the *meta* and *para* products. This scenario is not in accord with the data in Table 2.2. In the vertical extreme, *ortho* substituents would have maximum steric interaction with the PCP ligand, leading to a significant decrease in the rate of oxidative addition for the *ortho* products. However, the two *ortho* rotamers would be rendered kinetically indistinguishable, since both *ortho* positions would experience the same steric interactions. This scenario is also contrary to the experimental data, since rates for the *ortho*-trans rotamers are slower than for *ortho*-cis in all cases.

Figure 2.4. Limiting geometries for the orientation of the approaching aryl ring during C-H activation by (PCP)Ir



In fact, the actual geometry must be something *between* the two extremes depicted in Figure 2.4. As shown in Figure 2.5, a diagonal or "canted" approach by the aryl ring allows for rationalization of the experimental data. In the transition state leading to the *ortho*-cis rotamer, the chlorine substituent is directed *away* from the metal center, decreasing, but not eliminating steric interactions with the PCP ligand. In the transition state leading to the *ortho*-trans rotamer, the chlorine atom is very close to the metal center, and experiences much more significant steric crowding, leading to slower rates of oxidative addition and reductive elimination.

Figure 2.5. Geometry with a canted aryl ring for the transition states leading to the *ortho*-cis and *ortho*-trans rotamers



A DFT computational study of the oxidative addition of chlorobenzene and fluorobenzene to (PCP)Ir was conducted by Goldman group member David Y. Wang and collaborator, Karsten Krogh-Jespersen. Results of this study are presented in Tables 2.3 and 2.4, below. In each case, three sets of data were generated by varying the steric bulk of the phosphine ligands (PR₂; R = H, methyl, and *tert*butyl). Overall, the calculated results are in excellent agreement with the experimental data presented above. For fluorobenzene, calculations show that the *ortho*-trans product is the most thermodynamically favorable and has the highest energetic barriers to both oxidative addition and reductive elimination. For chlorobenzene, the transition state leading to the *ortho*-trans rotamer was calculated to have the highest barrier - vs. the other rotamers consistent with the experimental kinetic data. However, despite results to the contrary with less bulky H and methyl groups on the phosphines, the calculations did not find that the *ortho*-trans product was the most thermodynamically favorable for the *tert*-butyl phosphine ligand system. This discrepency was noted by Wang in his doctoral thesis and attributed it to the calculations overstating the steric interactions between the chlorine

atom and the PCP ligand system.⁵⁴

Table 2.3. Results of DFT calculations for the oxidative addition of fluorobenzene to (PCP)Ir.

ΔG (kcal/mol)							
R = tBu	R4PCPIr + FPh	C-H ^o -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 ^o -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 ^o -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	

		0			
R = tBu	R4PCPIr + CIPh	C-H ^o -complex	TS (barrier to OA)	aryl hydride	barrier to RE
2-CIPh-Cltrans	0.0	not located	23.4	4.2	19.2
2-CIPh-Clcis	0.0	11.7	18.1	5.5	12.6
3-CIPh-Cltrans	0.0	10.3	17.1	2.9	14.2
3-CIPh-Clcis	0.0	11.1	16.9	3.3	13.6
4-CIPh	0.0	11.4	18.1	4.2	13.9
R = Me	R4PCPIr + CIPh	C-H ^o -complex	TS	aryl hydride	barrier to RE
2-CIPh-Cltrans	0.0	not located	7.5	-10.4	17.9
2-CIPh-Clcis	0.0	2.7	3.6	-6.0	9.6
3-CIPh-Cltrans	0.0	3.2	2.1	-4.5	6.6
3-CIPh-Clcis	0.0	3.4	2.3	-4.2	6.5
4-CIPh	0.0	3.5	2.7	-2.8	5.5
<u>.</u>	-				_
R = H	R4PCPIr + CIPh	C-H ^o -complex	TS	aryl hydride	barrier to RE
2-CIPh-Cltrans	0.0	not located	4.6	-7.9	12.5
2-CIPh-Clcis	0.0	1.7	3.1	-2.7	5.8
3-CIPh-Cltrans	0.0	0.3	1.4	-1.2	2.6
3-CIPh-Clcis	0.0	0.4	1.2	-1.3	2.5
4-CIPh	0.0	0.7	1.8	-0.4	2.2

Table 2.4. Results of DFT calculations for the oxidative addition of chlorobenzene to (PCP)Ir.

 ΔG

2.2.4 Synthesis and characterization of products from the reaction of (PCP)Ir with trifluoromethyl-substituted benzene substrates

The data from experiments with benzene substrates bearing alkyl groups and halogen substituents support a reasonably thorough understanding of the mechanism of oxidative addition by (PCP)Ir. Electron deficient substrates add more favorably, and sterically bulky groups on the aryl ring inhibit addition of the *ortho* C-H bond. At one extreme, methyl substituents are both mildly electron donating (a result of hyperconjugation) and sterically demanding, compared to single atom substituents like halogens. Therefore, the lack of C-H activation *ortho* to methyl substituents is consistent with the unfavorable electronic *and* steric influences these groups exhibit. At the other extreme, fluorine substituents are both strongly electron withdrawing and small in size, satisfying both criteria for favorable addition. As a result, C-H bond activation *ortho* to fluorine is faster than for bulkier groups and yields very thermodynamically stable products.

In order to probe the limits of electronic and steric requirements for this system, a series of experiments was conducted with benzene substrates bearing trifluoromethyl substituents. The CF₃ group is larger than methyl due to the larger van der Waals radius of fluorine vs. hydrogen (1.47 Å vs 1.20 Å), and should therefore have a correspondingly greater steric effect on C-H activation to (PCP)Ir. Electronically, however, the three fluorine atoms make the CF₃ group among the most powerfully electron withdrawing aryl substituents, which should *favor* the C-H activation reaction.

Reaction of (PCP)IrH₂ and NBE with a small excess of (trifluoromethyl)benzene at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of three somewhat broad, overlapping signals at δ 67.92, 68.09, and 68.27 ppm with a ratio of approximately 1:1:1. The ¹H NMR spectrum shows one broad hydride signal far upfield at δ -45.6 ppm, indicative of three products rapidly exchanging on the NMR time scale (based on the ³¹P NMR spectrum). Based on previous results for reactions with toluene which also gave three products (two *meta* rotamers and the *para* isomer), and the knowledge that C-H activation *ortho* to the trifluoromethyl group should be unfavorable, the three products were identified as the two *meta* rotamers and the *para* isomer, **2-30a**, **b**, and **c**, respectively (eq. 26).



NMR analyses at -20 °C showed sharp and separated peaks in both the ¹H NMR and ³¹P NMR spectra, indicative of slower rates of exchange (i.e., oxidative addition and reductive elimination of the substrate). The peaks in the ³¹P NMR spectrum resolved into doublets ($J_{HP} = 14.0 \text{ Hz}$) and the broad signal in the ¹H NMR spectrum resolved into three overlapping, but clearly identifiable triplets ($J_{HP} = 13.2 \text{ Hz}$) with a ratio of approximately 1:1:1. Due to the steric bulk of the trifluoromethyl group, it was not surprising that no evidence was observed for ortho C-H activation. However, there was a very profound electronic effect from the fluorine atoms. This was obvious even before thermodynamic and kinetics experiments were conducted, simply through comparison of the spectra for toluene vs. (trifluoromethyl)benzene addition. The NMR signal for products of toluene addition was too broad to be observed at ambient temperature. In contrast, while not fully resolved, the corresponding signal for (trifluoromethyl)benzene was very obvious under the same conditions. This clearly indicated that electronics were favoring the addition of (trifluoromethyl)benzene vs. toluene. Formal thermodynamic and kinetics experiments confirmed this hypothesis (see below).

Based on the electronic effects seen with (trifluoromethyl)benzene, additional experiments were conducted with 1,3-bis(trifluoromethyl)benzene, 1,4bis(trifluoromethyl)benzene, and 1,3,5-tris(trifluoromethyl)benzene. Analogous to the results seen with *meta*-xylene, reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at ambient temperature gave a single product, **2-31** (eq. 27). The comparison between spectra of the products from these two substrates is striking. Whereas the hydride triplet for *meta*-xylene is barely resolved, and still somewhat broad even at -40 °C, the hydride signal for 1,3-bis(trifluoromethyl)benzene is sharply well-defined at ambient temperature.



Successful C-H activation of 1,4-bis(trifluoromethyl)benzene by (PCP)Ir was not expected. As mentioned earlier in this thesis, *para*-xylene is used as an inert solvent for C-H activation reactions of aryl substrates precisely because the combination of steric and electronic influences of the two methyl substituents preclude reaction at any of its four C-H bonds. Very surprisingly, this was *not* the case for 1,4-bis(trifluoromethyl)benzene. Reaction of (PCP)Ir with NBE and a small excess of 1,4-bis(trifluoromethyl)benzene at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of one new signal: a doublet at δ 69.03 ppm ($J_{HP} = 13.7$ Hz). The ¹H NMR spectrum shows a sharp, well-resolved sextet at δ -43.8 ppm. Since a triplet was expected based on hyride coupling to two phosphorus atoms, the appearance of a sextet indicated additional coupling of similar magnitude (J_{HP} = J_{HF} = 13.9 Hz) to the three fluorine atoms of a trifluoromethyl substituent. In view of the results from experiments with halobenzenes, in which it was shown that bulkier *ortho* substituents disfavor the *ortho*-cis activation product, the single product from 1,4-bis(trifluoromethyl)benzene activation was assigned as the *ortho*-trans rotamer, **2-32** (eq. 28).



At elevated temperatures (> 100 °C), the ¹H NMR signal for **2-32** showed very little broadening, indicating slow kinetics for exchange of this substrate. This would be expected based on the steric bulk of the trifluoromethyl group and in view of the mechanistic discussion of the transition state presented in the last section. Despite the consistency of the NMR and line-broadening evidence, C-H activation of 1,4bis(trifluoromethyl)benzene came as a total surprise, and was the first example of (PCP)Ir activation of a C-H bond *ortho* to a methyl-type substituent of such large size.

Inspired by this result, a reaction between (PCP)Ir and 1,3,5tris(trifluoromethyl)benzene was attempted, but no C-H activation was detected. Apparently, the extremely unfavorable sterics of having two CF₃ groups *ortho* to the site of C-H activation is too much of a barrier to addition, despite the favorable electronics of having three trifluoromethyl substituents. In spite of the slow rate of exchange for 2-32 and the extremely favorable electronics for 2-31, multiple attempts to crystallize these five-coordinate products were unsuccessful. Therefore, CO was added in an attempt to trap the complexes as their rigid, non-labile six-coordinate analogs 2-33 and 2-34 (eq. 29 and 30). Attempts to crystallize the six-coordinate CO complexes were successful; the CO ligand is located trans to the metal-hydride bond in both cases and the *ortho*-trans conformation was confirmed for 2-34. X-ray crystal structures and selected data are included at the end of this chapter.



Combined results for thermodynamic and kinetic studies of trifluoromethylsubstituted substrates are given in Table 2.5. In the case of (trifluoromethyl)benzene, NMR signals overlap sufficiently that individual analysis of the isomers/rotamers was not possible. Overlapping peaks were accurately modeled (as shown at the end of the chapter) and the data presented here have been adjusted and reported on a *per rotamer* basis. While this chapter will conclude with a broad comparison of thermodynamic and kinetic data from all of the substrates discussed herein, it is helpful to look specifically at the electronic influence of trifluoromethyl substituents.

The products from C-H activation of (trifluoromethyl)benzene and 1,3bis(trifluoromethyl)benzene show the strongly favorable electronic effect of having one and two trifluoromethyl substituents, respectively, without invoking steric effects. One CF₃ group enhances the thermodynamics vs. benzene by a factor of 27, while two have a much greater impact, raising the ratio to 3.1×10^4 for 1,3-bis(trifluoromethyl)benzene. Correspondingly, the rates of elimination for these complexes are significantly slower than for benzene, and addition proceeds slightly faster – all in keeping with the powerful electronic effect of the CF₃ group(s).

The truly remarkable results, however, are shown for the *ortho*-trans product of C-H activation of 1,4-bis(trifluoromethyl)benzene. Adding severe steric constraints on the product conformation lessens the thermodynamic advantage of having two CF₃ substituents, but still results in a slight preference vs. benzene (3.1 per C-H bond). But despite only a very modest thermodynamic advantage, 1,4-bis(trifluoromethyl)benzene eliminates at a rate almost 1×10^6 times *more slowly* than benzene! Oxidative addition is similarly slow, demonstrating the profound steric impact on the transition state for C-H addition as discussed in the last section.

Fragment showing the configuration of the C-H addition product	$\begin{array}{c} \mathbf{K}\\ (\text{vs. } \mathbf{C}_{6}^{\text{eq}}\mathbf{H}_{6}) \end{array}$	K (per C-H)	k _{RE} (sec ⁻¹)	$\begin{array}{c} \mathbf{k}_{\mathrm{RE}} \\ (\mathrm{vs.}\ \mathbf{C}_{6}\mathbf{H}_{6}) \end{array}$	$\begin{array}{c} \mathbf{k}_{_{\mathrm{OA}}}\\ (\mathrm{vs.}\ \mathbf{C}_{_{6}\mathbf{H}_{_{6}}})\end{array}$	k _{0A} (per C-H)
	[1]	[1]	432	[1]	[1]	[1]
H CF3	^a 27	$1.6 \text{ x} 10^2$	39	0.090	2.5	15
	$5.1 \text{ x} 10^3$	3.1×10^4	0.62	1.4 x10 ⁻³	7.1	43
H ^{F₃C_{//} H^{CF₃}}	2.1	3.1	6.4 x10 ⁻⁴	1.5 x10 ⁻⁶	3.0 x10 ⁻⁶	4.6 x10 ⁻⁶
$\begin{bmatrix} F_{3}C_{\prime,}\\ Ir \\ F_{3}C \end{bmatrix} = CF_{3}$	No Measurable Reaction					

Table 2.5. Thermodynamic and kinetic data for trifluoromethyl-substituted substrates vs. benzene at 25 °C.

^aSubstrates have three C-H bonds accessible for addition to (PCP)Ir, resulting in three products: two *meta* rotamers and the corresponding *para* isomer. NMR signals either coincide or overlap sufficiently that individual isomers cannot be separated. Data are reported on a "per rotamer" basis.

2.2.5 Studies of combined effects of alkyl, halogen, and trifluoromethyl substituents

As one final step toward creating an accurate and complete description of the factors influencing the aryl C-H activation reactions discussed in this chapter, (PCP)Ir was reacted with a series of substituted benzene substrates bearing various strategically selected combinations of alkyl, halogen, and trifluoromethyl groups. The substrates 3-fluorotoluene, 3-methylbenzotrifluoride, and 4-methylbenzotrifluoride were chosen in order to add one methyl group to the fluoro, chloro, and trifluoromethyl groups already discussed in depth above. In order to study the effect of *two* methyl groups, 5-fluoro-1,3-dimethylbenzene and 5-chloro-1,3-dimethylbenzene were chosen. Most of the C-H activation reactions were successful, and are shown in Scheme 2.1.





Of all the products, only **2-35a** was successfully trapped as the six-coordinate CO adduct and analyzed by x-ray crystallography. The x-ray crystal structure and selected data are included at the end of this chapter. Attempts to crystallize the remaining products were not successful for reasons analogous to those discussed with similar substrates earlier in this chapter. Reactions of (PCP)Ir with 5-chloro-1,3-dimethylbenzene and 4-methylbenzotrifluoride yielded discernable C-H activation products, but in each case, they were too thermodynamically unfavorable (very small NMR signals) for accurate thermodynamic and kinetic measurements.

For clarity in the presentation and discussion of data from these C-H activation reactions, the substrates have been segregated according to three substituents: fluoro, chloro, and trifluoromethyl groups. Thermodynamic and kinetic data for fluorine-bearing substrates are given in Table 2.6. Data from the reactions with 3-fluorotoluene show the combined influences of fluoro and methyl substituents perfectly, with values intermediate between those for fluorobenzene and toluene. The unfavorable effect of a methyl substituent results in lower values of K_{eq} for the 3-fluorotoluene rotamers vs. their fluorobenzene analogs, but still significantly higher than that for toluene. These trends are also reflected in the rates of reductive elimination vs. benzene (k_{RE} toluene >> 3-fluorotoluene > fluorobenzene).

As with the discovery that C-H activation of 1,4-bis(trifluoromethyl)benzene was successful, similar results with 5-fluoro-1,3-dimethylbenzene were unexpected and very surprising given that the product must necessarily have a methyl group *ortho* to the new metal-aryl carbon bond. Attempts to crystallize this product and its six-coordinate CO adduct are still underway, but evidence from NMR spectra support the existence of *both* rotameric products. The unfavorable effect of having two methyl groups on the aryl ring is shown clearly in Table 2.6: K_{eq} values for these products are much lower than for either the fluorobenzene or 3-fluorotoluene analogs. Surprisingly, rates of reductive elimination are comparable to the fluorinated analogs, but much slower than for *meta*xylene, indicating the steric effect of having two *ortho* substituents, one of which is a methyl group. The most striking data is seen in the column for rates of oxidative addition: 5-fluoro-1,3-dimethylbenzene adds almost 3 x10³ more slowly than fluorobenzene to form the *ortho*-trans product.

K k_{RE} k_{oa} Fragment showing the K_{eq} k_{re} k_{oa} $(vs. \tilde{C_6}H_6)$ configuration of the C-H $(vs. C_6H_6)$ $(vs. C_6H_6)$ (per C-H) $(\operatorname{sec}^{-1})$ (per C-H) addition product 432 [1] [1] [1] [1] [1] Н ^a0.066 0.40 8.2×10^3 19 1.3 7.6 н 9.9×10^2 0.038 0.23 2.3 0.087 0.52 н F,,, $1.7 \text{ x} 10^3$ 6.7 x10⁻⁴ $1.0 \text{ x} 10^4$ 0.29 1.2 6.9 H 5.6×10^2 3.4×10^3 1.5 3.5×10^{-3} 1.9 12 Н $2.7 \text{ x} 10^2$ 1.6×10^3 $1.3 \text{ x} 10^{-3}$ 0.56 0.35 2.1 н $3.8 \text{ x} 10^{-3}$ 88 5.3×10^2 1.7 0.33 2.0 Н F, $8.2 \text{ x} 10^{-4}$ 0.19 0.56 1.9 $4.4 \text{ x} 10^{-3}$ $2.5 \text{ x} 10^{-3}$ H $1.4 \text{ x} 10^{-3}$ 8.4 x10⁻³ °0.061 0.37 9.7 0.023

Table 2.6. Thermodynamic and kinetic data for substrates with fluoro and alkyl substituents vs. benzene at 25 °C.

^aSubstrates have three C-H bonds accessible for addition to (PCP)Ir, resulting in three products: two *meta* rotamers and the corresponding *para* isomer. NMR signals either coincide or overlap sufficiently that individual isomers cannot be separated. Data are reported on a "per rotamer" basis.

^cThe *ortho*-cis rotamer product of C-H activation of 5-fluoro-1,3-dimethylbenzene is thermodynamically unfavorable and difficult to measure; the thermodynamic data must be considered an estimate.

Thermodynamic and kinetic data for chlorine-bearing substrates are given in Table 2.7 and reflect similar trends as seen in Table 2.6 for the fluorobenzene derivatives. Data from the reactions with 3-chlorotoluene show the combined influences of chloro and methyl substituents perfectly, with values intermediate between those for chlorobenzene and toluene. In each case, the unfavorable effect of a methyl substituent results in lower values of K_{eq} for the 3-chlorotoluene rotamers vs. their chlorobenzene analogs, but still significantly higher than that for toluene. A similar effect can be seen in the comparison of the *meta* rotamer products of 3-chlorotoluene addition with *meta*-xylene. The presence of the added chlorine atom enhances the thermodynamic favorability of the addition products ($K_{eq} = 21$ vs. 0.23 for *meta*-xylene). These trends are also reflected in the rates of reductive elimination vs. benzene (k_{RE} toluene >> 3-chlorotoluene > chlorobenzene). However, in regard to elimination rates, the steric component of having the large chlorine atom in the *ortho* position is clearly to dominant factor, resulting in very similar values (vs. benzene) for the *ortho*-trans rotamers of chlorobenzene vs. 3-chlorotoluene (2.5 x10⁻⁵ vs. 4.5 x10⁻⁵).

The presence of an added methyl group made the *ortho*-cis rotamer product from 3-chlorotoluene simply too thermodynamically unfavorable for accurate measurement of kinetic data. Likewise, NMR spectra seem to indicate that C-H activation is possible for the extremely sterically demanding substrate 5-chloro-1,3-dimethylbenzene, but this addition is too unfavorable for accurate measurement and analysis.

K Fragment showing the k_{oa} k_{RE} k_{oa} K_{eq} k_{re} $(vs. \tilde{C_6}H_6)$ configuration of the C-H $(vs. C_6H_6)$ $(vs. C_6H_6)$ (per C-H) $(\operatorname{sec}^{-1})$ (per C-H) addition product 432 [1] [1] [1] [1] [1] Н 8.2×10^3 ^a0.066 0.40 19 1.3 7.6 Н 9.9×10^2 0.038 0.23 2.3 0.087 0.52 н CI/ 2.8×10^{-5} $3.4 \text{ x} 10^{-4}$ $2.0 \text{ x} 10^{-3}$ 0.012 12 73 н 2.1 28 0.065 0.14 0.83 13 Н CI ^b8.9 0.20 53 88 1.8 11 н⁴ CL/ $1.4 \text{ x} 10^{-3}$ $1.9 \text{ x} 10^{-2}$ $4.5 \text{ x} 10^{-5}$ 2.3 x10⁻⁴ 5.2 31 H Ratio of product too small for accurate kinetic 7.0 1.2 н measurements C CI ^b3.6 1.3×10^{2} 21 0.30 6.5 1.1 CI. C-H activation was detected, but the product is too thermodynamically unfavorable for accurate determination of K_{eq} or k_{RE}

Table 2.7. Thermodynamic and kinetic data for substrates with chloro and alkyl substituents vs. benzene at 25 °C.

^aSubstrates have three C-H bonds, resulting in three products: data are reported on a "per rotamer" basis. ^bSubstrates form two rotameric products; data are reported on a "per rotamer" basis.

Finally, thermodynamic and kinetic data for trifluoromethyl-bearing substrates are given in Table 2.8. Once again, the tug-of-war between weakly electron donating methyl groups and strongly electron withdrawing trifluoromethyl groups is vividly demonstrated in the comparisons between C-H activation products and their respective rates of reaction. Since these two substituents have very similar steric bulk, the data vary strictly according to electronic effects. In the simplest case, trifluorotoluene is thermodynamically favored over toluene by a factor of 410, clearly showing the electronic benefit of the three fluorine atoms. This preference is also reflected in the rates of reductive elimination (200 times slower for trifluorotoluene) and oxidative addition (twice as fast).

Comparing *meta*-substituted products, changing one methyl group to trifluoromethyl yields a 140-fold improvement in thermodynamic favorability. Changing *both* groups from methyl to trifluoromethyl gives a product that is 1.4×10^5 more favorable than the *meta*-xylyl analog! Accordingly, these electronic effects are reflected in the rate data: 1,3-bis(trifluoromethyl)benzene adds 80 times more quickly than *meta*xylene and eliminates 1600 times more slowly.

Probably the single most fascinating result in all of these reactions is the discovery that 1,4-bis(trifluoromethyl)benzene will undergo C-H activation and oxidative addition to (PCP)Ir. Clearly, the electronic effects shown with the 1,3-bis(trifluoromethyl) analog discussed above are strong enough to overcome severe steric crowding in the transition state for addition of the 1,4-bis(trifluoromethyl) substrate. Switching only one methyl group in *para*-xylene to trifluoromethyl did not apparently give enough of an electronic boost to what is an extremely hindered addition mechanism. NMR spectra show inconclusive evidence of a possible addition product for (PCP)Ir and 4-methylbenzotrifluoride, but based on the K_{eq} for 1,4-bis(trifluoromethyl)benzene (already fairly low), further disfavoring the substrate with a methyl substituent makes the 4-methylbenzotrifluoride addition product seem unlikely.

Fragment showing the configuration of the C-H addition product	$\begin{array}{c} \mathrm{K}\\ \mathrm{(vs.}\ \mathrm{C}_{_{6}\mathrm{H}_{_{6}}}\mathrm{H}_{_{6}})\end{array}$	K _{eq} (per C-H)	k _{RE} (sec ⁻¹)	$\begin{array}{c} k\\ k_{\rm RE}\\ (\rm vs.\ C_6H_6) \end{array}$	$\begin{array}{c} \mathbf{k}_{_{\mathrm{OA}}}\\ (\mathrm{vs.}\ \mathbf{C}_{_{6}}\mathbf{H}_{_{6}})\end{array}$	k _{0A} (per C-H)		
	[1]	[1]	432	[1]	[1]	[1]		
	^a 0.066	0.40	$8.2 ext{ x10}^{3}$	19	1.3	7.6		
H	0.038	0.23	$9.9 ext{ x10}^2$	2.3	0.087	0.52		
	No Measurable Reaction							
H CF3	^a 27	$1.6 \text{ x} 10^2$	39	0.090	2.5	15		
H ^I r CF ₃ CF ₃	$5.1 ext{ x10}^3$	3.1 x10 ⁴	0.62	1.4 x10 ⁻³	7.1	43		
H ^{F₃C_{//} H^{CF₃}}	2.1	3.1	6.4 x10 ⁻⁴	1.5 x10 ⁻⁶	3.0 x10 ⁻⁶	4.6 x10 ⁻⁶		
	^b 5.5	33	$1.2 \text{ x} 10^2$	0.27	1.5	8.9		
F ₃ C _{//,} Ir	C-H activation was detected, but the product is too thermodynamically unfavorable for accurate determination of K_{eq} or k_{RE}							

Table 2.8. Thermodynamic and kinetic data for substrates with trifluoromethyl and alkyl substituents vs. benzene at 25 $^{\circ}$ C.

^aSubstrates have three C-H bonds, resulting in three products: data are reported on a "per rotamer" basis. ^bSubstrates form two rotameric products; data are reported on a "per rotamer" basis.

A complete data table containing thermodynamic and kinetic data for all reactions and substrates discussed in this chapter is included immediately following the reference section (**Table 2.9**).

2.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

General conditions for equilibrium studies: Except as noted, values for K_{eq} were calculated based on the integrated peak areas in the ³¹P NMR spectrum for the product complex vs. the NBE complex: (PCP)Ir(NBE). Since NBE binds to the 14-electron

fragment very weakly, the resulting complex is fluxional and rapidly exchanging at ambient temperature. Therefore, all spectra were recorded at -20 °C – a suitably low temperature at which the resonance for the NBE complex is well-defined and can be accurately measured. The chemical shift for (PCP)Ir(NBE) (s, δ 62.5 ppm) does not interfere with any of the substrate resonances, ensuring complete separation of all peaks measured for these studies.

Since norbornene also acts as the hydrogen acceptor during the generation of the 14-electron (PCP)Ir fragment for these reactions, one additional equivalent of NBE was added to each reaction mixture for this purpose. It is known that a small percentage of the iridium complex exists as (PCP)IrH₄ rather than (PCP)IrH₂. While this introduces a minor systematic error in the calculations, we are confident that the error is negligibly small for two reasons. First, all K_{eq} values were reported *vs. the value for benzene*. Therefore, error inherent in the concentrations of (PCP)Ir(NBE) should cancel as long as they are consistent. Second, all K_{eq} values were calculated at more than one ratio of concentrations as a check on accuracy.

In the summaries provided for each individual substrate below, excess concentrations (given as equivalents vs. the concentration of (PCP)Ir) are listed for the reaction from which the reported value for K_{eq} was calculated. The values listed in Tables 2.1, 2.2, and 2.5 – 2.9 have been extrapolated to 25 °C – the same temperature for which rates of reductive elimination (k_{RE}) are reported.

General conditions for kinetic studies: Rates of reductive elimination were monitored via ¹H NMR analysis of the resonance corresponding to the Ir-*H*. In all cases, the

reaction was cooled to a suitably low temperature at which the hydride peak(s) was sharp and exchanging as slowly as possible on the NMR time scale. Temperatures for these experiments were calibrated according to the Varian "tempcal" protocol, using a methanol standard for values below ambient temperature (25 °C) and an ethylene glycol standard for values *above* 25 °C. The temperature values reported with the Eyring plots at the end of this chapter were generated by the "tempcal" protocol, and are reported to two decimal places as recorded directly from the instrument.

Beginning at a low temperature in the slow exchange regime, exchange of the product complex was monitored at a series of increasing temperatures (in roughly five degree increments). At each temperature, a new calibration check was performed, the NMR probe was re-tuned, and the instrument was newly locked and shimmed prior to the collection of spectral data. The temperature was raised until the respective resonance was completely featureless, though generally still observable as a broad signal.

After the collection of spectra at an appropriate series of temperatures, simulations of the peak shapes were performed using the "gNMR" simulation software package from Cherwell Scientific. Coupling constants and line-widths were meticulously chosen in order to accurately reflect the experimental data, and were standardized at low temperatures where the resonances are sharp and well-defined. The values for the rate of reductive elimination (k_{RE}) generated by the simulation software were used to generate Eyring plots [ln(k/T) vs. ((1/T) x 1000)] for each substrate (included at the end of this chapter in Figures **2.6** – **2.28**). Data for the slope and intercept from the individual plots were then used to calculate the value for k_{RE} at 25 °C – the temperature at which *all* rates are compared in Table **2.9**. In the summaries provided for each individual substrate below, excess substrate concentrations (given as equivalents vs. the concentration of (PCP)Ir) were used in all cases in order to ensure negligible competition from the sacrificial acceptor norbornene. In two cases (the *ortho*-trans products from the reactions of (PCP)Ir with bromobenzene and 1,4-bis(trifluoromethyl)benzene, respectively), reductive elimination was too slow to exhibit appreciable line broadening, even at elevated temperatures (maximum 120 °C for the Varian 400 NMR). Additionally, both of these reactions showed significant product degradation as the temperature increased above 75 °C. In these cases, different methods were used in order to calculate the rates of elimination as discussed under the respective substrates below.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. After reacting with norbornene, but prior to the addition of substrate, the (PCP)Ir fragment exists as the labile NBE complex as described above in the introduction to this chapter. The exact configuration of this complex is unknown. If norbornene is added in very low concentration (2 equivalents), the low temperature NMR spectrum shows peaks indicative of an extremely labile addition product which may be the result of C-H activation of either norbornane or *p*-xylene solvent. At higher

concentrations of norbornane, there is no evidence supporting a product of C-H

activation, indicating that the dominant conformation may be a π complex of norbornene.

Norbornene in *p*-xylene (stock solution): ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 5.99 (t, $J_{HH} = 1.8$ Hz, 2H, H_A), 2.81 (m, $J_{HH} = 1.7$ Hz, 2H, H_B), 1.59 (d of m, $J_{HH} = 7.3$ Hz and others, 2H, H_C), 1.42 (d of m, $J_{HH} = 8.0$ Hz and others, 1H, H_D), 1.05 (d of m, J_{HH} = 7.9 Hz and others, 1H, H_E), 1.01 (d of m, $J_{HH} = 7.4$ Hz and others, 2H, H_F).



Norbornane in *p*-xylene (hydrogenated product from generation of the 14-electron (PCP)Ir fragment): ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 2.31 (m, 1H, H_A), 1.99 (m, 1H, H_B), 1.67 (vd, J_{HH} = 7.7 Hz, 2H, H_C), 1.49 (d of m, J_{HH} = 6.5 Hz and others, 8H, H_D).



Reaction of (PCP)IrH₂/H₄ with norbornene: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2

equivalents of norbornene were added from a stock solution in *p*-xylene. ³¹P NMR (121.4 MHz, -20 °C, mesitylene- d_{12}): δ 62.9 (br s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 7.22-7.09 (m, 3H, PCP aryl *H*), 3.23 (vs, 4H, C H_2 , π complex product?), 3.14 (vs, 4H, C H_2 , C-H activation product?), 1.25 (br s, 36H, C(C H_3)₃, π complex product?), 1.17 (d of t, 36H, C(C H_3)₃, C-H activation product?), -45.59 (br s, 1H, Ir-*H*).

Reaction of (PCP)Ir with benzene (2-1): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Benzene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 67.7 (d, $J_{PH} = 13.0$ Hz). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): δ 7.84 (d, $J_{HH} = 7.2$ Hz, 1H, phenyl *ortho*-H), 7.75 (d, $J_{HH} = 7.2$ Hz, 1H, phenyl *ortho*-H), 7.75 (d, $J_{HH} = 7.2$ Hz, 1H, phenyl *ortho*-H), 7.36 (t, $J_{HH} = 7.2$ Hz, 1H, phenyl H), 7.20-7.00 (m, 4H, PCP, phenyl), 6.94 (t, $J_{HH} = 7.2$ Hz, 1H, phenyl H), 7.20-7.00 (m, 4H, PCP, phenyl), 6.94 (t, $J_{HH} = 6.4$ Hz, 18H, C(CH₃)₃), 0.92 (t, $J_{HP} = 6.0$ Hz, 18H, C(CH₃)₃), -45.59 (t, $J_{HP} = 13.2$ Hz, 1H, Ir-*H*).

Equilibrium study: competition experiment between norbornene and benzene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 10 equivalents of norbornene were then added to the solution, along with 10 equivalents of benzene. The product ratio

(2-1 vs. (PCP)Ir(NBE)) was obtained by comparing the integrated peak areas in the 31 P NMR spectrum at -20 °C.

Kinetics studies: measuring the rate of elimination of benzene from 2-1. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of benzene were added to the reaction mixture. The resulting solution was analyzed at a series of temperatures from -40 °C to 0 °C.

Reaction of 2-1 with CO to form 2-2: A solution of **2-1** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The dark orange solution immediately turned pale yellow upon thawing. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 53.2 (d, $J_{PH} = 11.0$ Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.24 (d, $J_{HH} = 7.4$ Hz, 1H, phenyl *ortho*-H), 8.12 (d, $J_{HH} = 7.4$ Hz, 1H, phenyl *ortho*-H), remaining aryl-*H* peaks from substrate and PCP ligand are obscured by solvent peaks, 3.27 (d of vt, $J_{HP} = 4.2$ Hz, $J_{HH} = 15.7$ Hz, 4H, CH₂), 1.13 (t, $J_{HP} = 6.8$ Hz, 18H, C(CH₃)₃), 1.12 (t, $J_{HP} = 6.8$ Hz, 18H, C(CH₃)₃), -8.94 (t, $J_{HP} = 17.8$ Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with CO to form 2-3: Upon addition of CO to solutions containing (PCP)Ir and labile, rapidly exchanging substrates, some percentage of 4-coordinate
(PCP)Ir(CO) is formed. The fraction of **2-3** formed varies according to the lability of the original complex and the pressure of CO gas added to the reaction tube. The product is pale yellow and can be recrystallized to yield nearly colorless needles. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 82.9 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.95 (m, 3H, PCP aryl-*H*), 3.39 (t, $J_{HP} = 4$ Hz, 4H, C H_2), 1.29 (t, $J_{HP} = 6.2$ Hz, 36H, C(C H_3)₃).

Reaction of (PCP)Ir with *meta*-**xylene (2-4)**: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. *Meta*-xylene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. ³¹P NMR (121.4 MHz, -50 °C, mesitylene- d_{12}): δ 67.9 (br s). ¹H NMR (400 MHz, -50 °C, mesitylene- d_{12}): δ 7.51 (s, 1H, *meta*-xylyl *ortho*-H), 7.41 (s, 1H, *meta*-xylyl *ortho*-H), 7.25 (m, 3H, *meta*-xylyl *para* H, PCP), remaining PCP aryl-*H* peaks are obscured by solvent peaks, 3.28 (d of vt, J_{HP} = 3.0 Hz, J_{HH} = 16.3 Hz, 4H, C H_2), 2.50 (s, 3H, *meta*-xylyl C H_3), 2.48 (s, 3H, *meta*-xylyl C H_3), 0.97 (t, J_{HP} = 6.2 Hz, 18H, C(C H_3)₃), 0.95 (t, J_{HP} = 6.0 Hz, 18H, C(C H_3)₃), -45.54 (t, J_{HP} = 14.0 Hz, 1H, Ir-H).

Equilibrium study: competition experiment between norbornene and *meta*-xylene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 10 equivalents of norbornene were then added to the solution, along with 250 equivalents of *meta*-xylene. The product ratio (2-4 vs. (PCP)Ir(NBE)) was obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rate of elimination of *meta*-xylene from 2-4. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of *meta*-xylene were added to the reaction mixture. The resulting solution was analyzed at a series of temperatures from -40 °C to 0 °C.

Reaction of (PCP)Ir with toluene (2-5a): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Toluene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. Even at low temperature, the three product isomers (*meta*-cis, *meta*-trans, and *para*) give overlapping resonances in both the ³¹P NMR and ¹H NMR spectra. ³¹P NMR (121.4 MHz, -45 °C, mesitylene- d_{12}): δ 67.3 (br s). Due to the high concentration of toluene required to compete with NBE in solution, all ¹H NMR aryl signals (PCP and tolyl) are obscured by those for the protiated *para*-xylene used as the solvent for the stock solutions of norbornene and toluene. ¹H NMR (400 MHz, -45 °C, mesitylene- d_{12}): δ 3.27 (m, 4H, CH₂ from three product rotamers), 0.95 (m, 36H,

C(CH₃)₃ from three product rotamers), -45.42 (t, $J_{HP} = 14.3$ Hz, 1H, Ir-*H*, *meta*-rotamer), -45.45 (t, $J_{HP} = 14.3$ Hz, 1H, Ir-*H*, *meta*-rotamer), -45.52 (t, $J_{HP} = 13.5$ Hz, 1H, Ir-*H*, *para*-rotamer).

Equilibrium study: competition experiment between norbornene and toluene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 10 equivalents of norbornene were then added to the solution, along with 100 equivalents of toluene. The product ratios (2-5a *meta*-cis, *meta*-trans, and *para* vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rate of elimination of toluene from 2-5a. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of toluene were added to the reaction mixture. The resulting solution was analyzed at a series of temperatures from -35 °C to -10 °C.

Reaction of (PCP)Ir with *tert***-butylbenzene (2-5b)**: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. *Tert*-

butylbenzene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark orange. Even at low temperature, the three product isomers (*meta*-cis, *meta*-trans, and *para*) give overlapping resonances in both the ³¹P NMR and ¹H NMR spectra. ³¹P NMR (121.4 MHz, -30 °C, mesitylene- d_{12}): δ 67.8 (br s). Due to the high concentration of *tert*-butylbenzene required to compete with NBE in solution, all ¹H NMR aryl signals (PCP and *tert*-butylphenyl) are obscured by those for the protiated *para*-xylene used as the solvent for the stock solutions of norbornene and *tert*-butylbenzene. ¹H NMR (400 MHz, -30 °C, mesitylene- d_{12}):, δ 3.33 (m, 4H, CH₂ from three product rotamers), 1.56, 1.54 (overlapping multiplets, 9H, *tert*butylphenyl C(CH₃)₃), 0.98 (m, 36H, PCP C(CH₃)₃ from three product rotamers), – 45.67 (m, 1H, Ir-*H*, overlapping signals from three products).

Equilibrium study: competition experiment between norbornene and tert-

butylbenzene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 5 equivalents of norbornene were then added to the solution, along with 10 equivalents of *tert*butylbenzene. The product ratios (**2-5b** *meta*-cis, *meta*-trans, and *para* vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Reaction of (PCP)Ir with *ortho*-xylene (2-6): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2

equivalents of norbornene were added from a stock solution in *p*-xylene. *Ortho*-xylene (50 eq; 0.50 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. Even at low temperature, the two product isomers give overlapping resonances in both the ³¹P NMR and ¹H NMR spectra. ³¹P NMR (121.4 MHz, -45 °C, mesitylene- d_{12}): δ 67.0 (br s). Due to the high concentration of *ortho*-xylene required to compete with NBE in solution, all ¹H NMR aryl signals (PCP and *ortho*-xylyl) are obscured by those for the protiated *para*-xylene used as the solvent for the stock solutions of norbornene and *ortho*-xylene. ¹H NMR (400 MHz, -45 °C, mesitylene- d_{12}): δ 3.29 (m, 4H, CH₂ from two product rotamers), 0.97 (m, 36H, C(CH₃)₃ from two product rotamers), -45.50 (t, J_{HP} = 13.4 Hz, 1H, Ir-*H, meta*-rotamer), -45.62 (t, J_{HP} = 13.4 Hz, 1H, Ir-*H, meta*-rotamer).

Equilibrium study: competition experiment between norbornene and ortho-xylene.

5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 5 equivalents of norbornene were then added to the solution, along with 50 equivalents of *ortho*-xylene. The product ratio (**2-6** vs. (PCP)Ir(NBE)) was obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rate of elimination of *ortho*-xylene from 2-6. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to

generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 50 equivalents of *ortho*-xylene were added to the reaction mixture. The resulting solution was analyzed at a series of temperatures from -45 °C to -15 °C.

Reaction of (PCP)Ir with 1,3-di-*tert***butylbenzene (2-7)**: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,3-Di-*tert*butylbenzene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark orange-brown. ³¹P NMR (121.4 MHz, -50 °C, mesitylene- d_{12}): δ 67.8 (br s). Due to the high concentration of 1,3-di-*tert*butylbenzene required to compete with NBE in solution, all ¹H NMR aryl signals (PCP and di-*tert*butylphenyl) are obscured by those for the protiated *para*-xylene used as the solvent for the stock solutions of norbornene and 1,3-di-*tert*butylbenzene. ¹H NMR (400 MHz, -50 °C, mesitylene- d_{12}): δ 3.33 (d of vt, $J_{HH} = 17.1$ Hz, 4H, CH_2), 1.55, 1.54 (overlapping singlets, 18H, di-*tert*butylphenyl C(CH_3)₃), 0.97 (overlapping triplets, $J_{HP} = 5.9$ Hz, 36H, PCP C(CH_3)₃), -45.77 (t, $J_{HP} = 13.5$ Hz, 1H, Ir-H).

Equilibrium study: competition experiment between norbornene and 1,3-di-

*tert***butylbenzene.** 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 5 equivalents of norbornene were then added to the solution, along with 25

equivalents of 1,3-di-*tert* butylbenzene. The product ratio (**2-7** vs. (PCP)Ir(NBE)) was obtained by comparing the integrated peak areas in the 31 P NMR spectrum at -20 °C.

Kinetics studies: measuring the rate of elimination of 1,3-di-tertbutylbenzene from

2-7. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of 1,3-di-*tert* butylbenzene were added to the reaction mixture. The resulting solution was analyzed at a series of temperatures from -35 °C to 0 °C.

Reaction of (PCP)Ir with fluorobenzene (2-8a,b): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Fluorobenzene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. ³¹P NMR (121.4 MHz, - 20 °C, mesitylene- d_{12}): δ 68.4 (d, $J_{PH} = 13.1$ Hz, *ortho*-trans isomer), 66.8 (d, $J_{PH} = 11.2$ Hz, *ortho*-cis isomer). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 7.79 (vt, J_{HH} and $J_{HF} = 5.5$ Hz, 1H, *ortho*-trans fluorophenyl *ortho-H*), 7.75 (vt, J_{HH} and $J_{HF} = 5.5$ Hz, 1H, *ortho*-trans fluorophenyl *ortho-H*), remaining ¹H NMR aryl signals (PCP and fluorophenyl) are obscured by residual solvent, 3.37 (t of t, $J_{HP} = 3.5$ Hz, $J_{HH} = 16.4$ Hz, 2H, CH_2 , *ortho*-trans rotamer), 3.27 (t of t, $J_{HP} = 3.5$ Hz, $J_{HH} = 16.4$ Hz, 2H, CH_2 , *ortho*-trans rotamer), 1.03 (t, $J_{HP} = 6.4$ Hz, 18H, $C(CH_3)_3$, obscured by norbornene peaks), 0.97 (t, $J_{HP} = 6.0$ Hz, 18H, $C(CH_3)_3$, obscured by norbornene peaks), methylene and *tert* butyl peaks for the *ortho*-cis rotamer are obscured, -43.07 (t, J_{HP} = 13.3 Hz, 1H, Ir-*H*, *ortho*-cis rotamer), - 46.33 (t of d, J_{HP} = 13.4 Hz, J_{HF} = 2.2 Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Equilibrium study: competition experiment between norbornene and fluorobenzene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 200 equivalents of norbornene were then added to the solution, along with 20 equivalents of fluorobenzene. The product ratios (**2-8a,b** vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rates of elimination of fluorobenzene from 2-8a and 2-8b. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of fluorobenzene were added to the reaction mixture. The hydride signal corresponding to product 2-8a was analyzed at a series of temperatures from 40 °C to 85 °C. The hydride signal corresponding to product 2-8b was analyzed at a series of temperatures from 35 °C to 60 °C.

Reaction of (PCP)Ir with 1,4-difluorobenzene (2-9): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature,

and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,4-Difluorobenzene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 68.8 (d, $J_{PH} = 13.2$ Hz, *ortho*-trans isomer), 67.5 (d, $J_{PH} = 11.2$ Hz, *ortho*-cis isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.54 (vt, J_{HH} and $J_{HF} =$ 5.5 Hz, 1H, *ortho*-trans difluorophenyl *ortho-H*), 7.52 (vt, J_{HH} and $J_{HF} = 5.5$ Hz, 1H, *ortho*-cis difluorophenyl *ortho-H*), remaining ¹H NMR aryl signals (PCP and substrate are obscured by residual solvent, 3.41 (t of t, $J_{HP} = 3.7$ Hz, $J_{HH} = 16.6$ Hz, 2H, CH_2 , *ortho*-trans rotamer), 3.30 (t of t, $J_{HP} = 3.7$ Hz, $J_{HH} = 16.6$ Hz, 2H, CH_2 , *ortho*-trans rotamer), 1.05 (t, $J_{HP} = 6.4$ Hz, 18H, C(CH_3)₃), 0.99 (t, $J_{HP} = 6.0$ Hz, 18H, C(CH_3)₃), methylene and *tert*butyl peaks for the *ortho*-cis rotamer are obscured, –43.11 (t, $J_{HP} =$ 13.3 Hz, 1H, Ir-*H*, *ortho*-cis rotamer), –46.34 (t of d, $J_{HP} = 13.4$ Hz, $J_{HF} = 2.2$ Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Reaction of (PCP)Ir with 4-fluorotoluene (2-10): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,4-Difluorobenzene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 68.6 (d, J_{PH} = 12.7 Hz, *ortho*-trans isomer), 67.6 (d, J_{PH} = 9.5 Hz, *ortho*-cis isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.58 (br s, 1H, *ortho*-trans fluorotolyl *ortho-H*), 7.54 (br s, 1H, *ortho*-cis fluorotolyl *ortho-H*), remaining ¹H NMR aryl signals (PCP and substrate) are obscured by residual solvent, 3.46 (t of t, J_{HP} =

3.3 Hz, $J_{\text{HH}} = 17.7$ Hz, 2H, CH_2 , *ortho*-trans rotamer), 3.34 (t of t, $J_{\text{HP}} = 3.6$ Hz, $J_{\text{HH}} = 16.6$ Hz, 2H, CH_2 , *ortho*-trans rotamer), 3.01 (t of t, $J_{\text{HP}} = 3.9$ Hz, $J_{\text{HH}} = 16.8$ Hz, 2H, CH_2 , *ortho*-cis rotamer), 2.93 (t of t, $J_{\text{HP}} = 3.9$ Hz, $J_{\text{HH}} = 17.3$ Hz, 2H, CH_2 , *ortho*-cis rotamer), 1.34 (t, $J_{\text{HP}} = 7.1$ Hz, 18H, $C(CH_3)_3$, *ortho*-cis rotamer), 1.24 (t, $J_{\text{HP}} = 6.7$ Hz, 18H, $C(CH_3)_3$, *ortho*-cis rotamer), 1.24 (t, $J_{\text{HP}} = 6.7$ Hz, 18H, $C(CH_3)_3$, *ortho*-trans rotamer), 1.04 (t, $J_{\text{HP}} = 6.4$ Hz, 18H, $C(CH_3)_3$, *ortho*-trans rotamer), -43.11 (t, $J_{\text{HP}} = 13.3$ Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -46.33 (t of d, $J_{\text{HP}} = 13.5$ Hz, $J_{\text{HF}} = 2.7$ Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Reaction of (PCP)Ir with 1,2,3,4-tetrafluorobenzene (2-11): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,2,3,4-Tetrafluorobenzene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 68.5 (d, $J_{PH} = 12.7$ Hz, *ortho*-trans isomer), 67.2 (d, $J_{PH} = 11.2$ Hz, *ortho*-cis isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.33 (t, $J_{HF} = 9.6$ Hz, 1H, *ortho*-trans tetrafluorophenyl *H*), remaining ¹H NMR aryl signals (PCP and substrate) are obscured by residual solvent, 3.34 (t of t, $J_{HP} = 3.5$ Hz, $J_{HH} = 17.4$ Hz, 2H, CH_2 , *ortho*-trans rotamer), 3.25 (t of t, $J_{HP} = 3.5$ Hz, $J_{HH} = 16.4$ Hz, 2H, CH_2 , *ortho*-trans rotamer), 0.96 (t, $J_{HP} = 6.7$ Hz, 18H, C(CH_3)₃, *ortho*-trans rotamer), methylene and *tert*butyl peaks for the *ortho*-cis rotamer are obscured, -43.25 (t, $J_{HP} = 13.3$ Hz, 1H, Ir-H, *ortho*-trans rotamer). **Reaction of 2-8 with CO to form 2-12**: A solution of **2-8** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The bright orange solution immediately turned pale yellow upon thawing. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane; pale yellow crystals were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 57.7 (s, *ortho*-cis isomer), 54.7 (s, *ortho*trans isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.36 (t, J_{HH} and $J_{\text{HF}} = 6.3$ Hz, 1H, *ortho*-cis fluorophenyl *ortho-H*), 8.21 (t, J_{HH} and $J_{\text{HF}} = 6.2$ Hz, 1H, *ortho*-trans fluorophenyl *ortho-H*), remaining ¹H NMR aryl signals (PCP and fluorophenyl) are obscured by residual solvent, 3.30 - 3.15 (overlapping, 4H, CH_2 , *ortho*-trans and *ortho*cis rotamers), 1.27 (t, $J_{\text{HP}} = 6.6$ Hz, 36H, C(CH_3)₃, *ortho*-cis rotamer), 1.10 (t, $J_{\text{HP}} = 6.3$ Hz, 36H, C(CH_3)₃, *ortho*-trans rotamer), -8.70 (d of t, $J_{\text{HP}} = 17.9$ Hz, $J_{\text{HF}} = 9.7$ Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -9.52 (d of t, $J_{\text{HP}} = 17.1$ Hz, $J_{\text{HF}} = 2.3$ Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Reaction of 2-9 with CO to form 2-13: A solution of **2-9** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The bright orange solution immediately turned pale yellow upon thawing. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane; pale yellow crystals were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 57.3 (s, *ortho*-cis isomer), 54.4 (s, *ortho*trans isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.41 (t, J_{HH} and $J_{HF} = 6.3$ Hz, 1H, *ortho*-cis fluorophenyl *ortho*-*H*), 8.27 (t, J_{HH} and J_{HF} = 6.2 Hz, 1H, *ortho*-trans fluorophenyl *ortho*-*H*), remaining ¹H NMR aryl signals (PCP and difluorophenyl) are obscured by residual solvent, 3.30 – 3.15 (overlapping, 4H, CH₂, *ortho*-trans and *ortho*cis rotamers), 1.29 (t, J_{HP} = 6.6 Hz, 36H, C(CH₃)₃, *ortho*-cis rotamer), 1.11 (t, J_{HP} = 6.3 Hz, 36H, C(CH₃)₃, *ortho*-trans rotamer), -8.65 (d of t, J_{HP} = 17.6 Hz, J_{HF} = 9.5 Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -9.57 (d of t, J_{HP} = 17.3 Hz, J_{HF} = 2.2 Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Reaction of 2-10 with CO to form 2-14: A solution of **2-10** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The bright orange solution immediately turned pale yellow upon thawing. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane; pale yellow crystals were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 55.6 (s, *ortho*-cis isomer), 52.4 (s, *ortho*trans isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.19 (br, 1H, *ortho*-cis fluorotolyl *ortho-H*), 8.03 (br, 1H, *ortho*-trans fluorotolyl *ortho-H*), remaining ¹H NMR aryl signals (PCP and fluorotolyl) are obscured by residual solvent, 3.22 (d of vt, $J_{HP} =$ 4.0 Hz, $J_{HH} =$ 16.4 Hz, 4H, CH_2 , *ortho*-trans rotamer), 2.94 (d of vt, $J_{HP} =$ 4.1 Hz, $J_{HH} =$ 17.2 Hz, 4H, CH_2 , *ortho*-cis rotamer), 1.26 (vt, $J_{HP} =$ 6.6 Hz, 36H, C(CH₃)₃, *ortho*-cis rotamer), 1.11 (d of t, $J_{HP} =$ 5.9 Hz, 36H, C(CH₃)₃, *ortho*-trans rotamer), -8.71 (d of t, $J_{HP} =$ 17.6 Hz, $J_{HF} =$ 9.5 Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -9.55 (d of t, $J_{HP} =$ 17.3 Hz, $J_{HF} =$ 2.2 Hz, 1H, Ir-*H*, *ortho*-trans rotamer). **Reaction of 2-11 with CO to form 2-15**: A solution of **2-11** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The bright orange solution immediately turned pale yellow upon thawing. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane; pale yellow crystals were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 56.8 (d, $J_{PH} = 14.7$ Hz, *ortho*-cis isomer), 53.6 (d, $J_{PH} = 14.7$ Hz, *ortho*-trans isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.89 (m, 1H, *ortho*-cis tetrafluorophenyl *ortho-H*), 7.76 (m, 1H, *ortho*-trans tetrafluorophenyl *ortho-H*), remaining ¹H NMR aryl signals (PCP and tetrafluorophenyl) are obscured by residual solvent, 3.30 – 3.00 (overlapping, 4H, *CH*₂, *ortho*-trans and *ortho*-cis rotamers), 1.27 (vt, $J_{HP} = 6.8$ Hz, 36H, C(*CH*₃)₃, *ortho*-cis rotamer), 1.00 (d of t, $J_{HP} = 6.7$ Hz, 36H, C(*CH*₃)₃, *ortho*-trans rotamer), -8.82 (d of t, $J_{HP} = 1.8$ Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Reaction of (PCP)Ir with 1,3,5-trifluorobenzene (2-16): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,3,5-Trifluorobenzene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 68.9 (d, $J_{PH} = 12.7$ Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.18 (d, $J_{HH} = 7.3$ Hz, 2H, PCP aryl *H*), 7.05 (t, $J_{HH} = 7.6$ Hz, 1H, PCP aryl *H*), 6.63 (m, 2H, trifluorobenyl *H*), 3.39 (d of t, $J_{HP} = 3.6$ Hz, $J_{HH} = 16.7$ Hz,

2H, CH₂), 3.31 (d of t, J_{HP} = 3.6 Hz, J_{HH} = 16.4 Hz, 2H, CH₂), 1.03 (overlapping t, 36H, C(CH₃)₃), -44.39 (d of t, J_{HP} = 13.6 Hz, J_{HF} = 2.1 Hz, 1H, Ir-H).

Reaction of (PCP)Ir with pentafluorobenzene (2-17): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Pentafluorobenzene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane/octane; orange-pink crystals were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 68.5 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.12 (d, $J_{\text{HH}} = 7.5$ Hz, 2H, PCP aryl *H*), 7.00 (t, $J_{\text{HH}} = 7.8$ Hz, 1H, PCP aryl *H*), 3.33 (d of t, $J_{\text{HP}} = 3.3$ Hz, $J_{\text{HH}} = 16.8$ Hz, 2H, CH₂), 3.26 (d of t, $J_{\text{HP}} = 3.3$ Hz, $J_{\text{HH}} = 16.4$ Hz, 2H, CH₂), 0.97 (overlapping t, 36H, C(CH₃)₃), -44.37 (t, $J_{\text{HP}} = 13.3$ Hz, 1H, Ir-*H*).

Reaction of 2-16 with CO to form 2-18: A solution of **2-16** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The bright orange solution immediately turned pale yellow upon thawing. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane; pale yellow crystals were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 55.8 (d, $J_{PH} = 14.9$ Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): PCP aryl peaks obscured by residual solvent, δ 6.59 (m, 1H, trifluorophenyl *H*), 6.52 (m, 1H, trifluorophenyl *H*), 3.23 (vt, $J_{HP} = 3.5$ Hz, 4H, CH₂), 1.07 (overlapping t, 36H, C(CH₃)₃), -9.32 (d of t of d, J_{HP} = 16.5 Hz, J_{HF} (near) = 10.8 Hz, J_{HF} (far) = 2.8 Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with chlorinated substrates to form 2-19 and 2-20: In all reactions between (PCP)Ir and chloro-substituted aryl substrates, C-Cl bond activation becomes a thermodynamically competitive process (vs. C-H activation) over extended reaction times or at elevated temperatures. In addition to products of C-H activation, at least two products of C-Cl activation are formed: (PCP)Ir(Cl)(phenyl) (2-19) and (PCP)Ir(H)(Cl) (2-20). The exact mechanism for the formation of these products (particularly **2-20**) is unknown, but possibly involves C-H activation of one or more of the phosphine *tert* butyl groups, since ³¹P NMR evidence indicates the presence of a small concentration of a species having inequivalent phosphorus atoms. ¹H NMR spectra are very complicated for these reaction mixtures, due to the large number of C-H activation products (up to five rotameric isomers) in addition to the C-Cl activation products. Based on previous results from experiments conducted by our group, as well as similar products with brominated substrates (*vide infra*), the ³¹P NMR resonance for complex **2-19** is δ 36.9 ppm (s, 2*P*). Inequivalent P atoms are shown as follows: δ 50.2 (d, J_{PP} = 350 Hz) and 9.0 (d, $J_{PP} = 350$ Hz).

Reaction of (PCP)Ir with chlorinated substrates to form 2-20: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Chlorobenzene (10 eq; 0.10 mmol) was added to the resulting solution; after

stirring for one minute, the dark red-orange solution turned orange. The kinetic products of this reaction result exclusively from C-H activation. After heating at 75 °C for 15 min, a complicated mixture of products is obtained that includes **2-20**. ³¹P NMR (121.4 MHz, 25 °C, benzene-*d*₆): δ 68.0 (d, *J*_{PH} = 12.2 Hz). ¹H NMR (400 MHz, 25 °C, benzene-*d*₆): δ 7.04 (d, *J*_{HH} = 7.2 Hz, 2H, PCP *meta*-*H*), 6.96 (t, *J*_{HH} = 7.2 Hz, 1H, PCP *para*-*H*), 3.06 (d of vt, *J*_{HP} = 3.5 Hz, *J*_{HH} = 17.3 Hz, 4H, C*H*₂), 1.29 (t, *J*_{HP} = 6.6 Hz, 18H, C(C*H*₃)₃), 1.24 (t, *J*_{HP} = 6.6 Hz, 18H, C(C*H*₃)₃), -42.58 (t, *J*_{HP} = 12.6 Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with chlorobenzene (2-21a,b,c,d,e): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Chlorobenzene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. ³¹P NMR (121.4 MHz, -20 °C, mesitylene- d_{12}): δ 67.4 (m, *meta* and *para* products), 66.8 (d, $J_{PH} = 11.2$ Hz, *ortho*-trans isomer), 64.2 (d, $J_{PH} = 11.2$ Hz, *ortho*-cis isomer). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): all PCP aryl, substrate aryl, PCP methylene and *tert*butyl hydrogen resonances are obscured by residual solvent and/or the presences of multiple (5) isomeric products, -41.25 (t, $J_{HP} = 14.3$ Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -45.64 (m, $J_{HP} = 13.6$ Hz, 1H, Ir-*H*, 2 *meta* rotamers and *para* isomer).

Equilibrium study: competition experiment between norbornene and

chlorobenzene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of

mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 100 equivalents of norbornene were then added to the solution, along with 20 equivalents of chlorobenzene. The product ratios (**2-21a,b,c,d,e** vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rates of elimination of chlorobenzene from 2-21a, 2-21b, and 2-21c,d,e. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene-*d*₁₂ in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of chlorobenzene were added to the reaction mixture. The hydride signal corresponding to product 2-21a was analyzed at a series of temperatures from 65 °C to 90 °C. The hydride signal corresponding to product 2-21b was analyzed at a series of temperatures from 0 °C to 25 °C. The signal corresponding to the combined *meta* and *para* products (2-21c,d,e) was analyzed at a series of temperatures from -5 °C to 25 °C.

Reaction of (PCP)Ir with 1,4-dichlorobenzene (2-22): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,4-Dichlorobenzene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 68.2 (s, *ortho*-trans isomer), 64.6 (s, *ortho*-cis

isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.86 (m, overlapping doublets, 1H, *ortho*-trans and *ortho*-cis dichlorophenyl *ortho-H*), 7.20 (d, $J_{HH} = 7.5$ Hz, 2H, *ortho*-cis dichlorophenyl aryl *H*), 7.13 (d, $J_{HH} = 7.5$ Hz, 2H, *ortho*-trans dichlorophenyl aryl *H*), remaining ¹H NMR PCP aryl signals are obscured by residual solvent, 3.50 - 3.10 (overlapping, 4H, CH_2 , *ortho*-trans and *ortho*-cis rotamers), 1.13 (t, $J_{HP} = 6.3$ Hz, 18H, C(CH_3)₃), 1.01 (t, $J_{HP} = 6.3$ Hz, 18H, C(CH_3)₃), *tert*butyl peaks for the *ortho*-cis rotamer are obscured, -42.34 (t, $J_{HP} = 14.1$ Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -42.82 (t, $J_{HP} = 14.1$ Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Reaction of (PCP)Ir with 4-chlorotoluene (2-23): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 4-Chlorotoluene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. ³¹P NMR (121.4 MHz, 0 °C, mesitylene- d_{12}): δ 67.0 (d, $J_{PH} = 15.0$ Hz, *ortho*-trans isomer), 64.6 (d, $J_{PH} = 15.0$ Hz, *ortho*-cis isomer). ¹H NMR (400 MHz, 0 °C, mesitylene- d_{12}): δ 7.64 (s, 1H, *ortho*-trans chlorotolyl *ortho-H*), 7.54 (s, 1H, *ortho*-cis chlorotolyl *ortho-H*), 7.19 (d, $J_{HH} = 7.5$ Hz, 2H, *ortho*-trans dichlorophenyl aryl *H*), remaining ¹H NMR PCP aryl signals are obscured by residual solvent, 3.31 (d of vt, $J_{HP} = 4.1$ Hz, $J_{HH} = 16.8$ Hz, 4H, CH_2 , *ortho*-trans rotamer), 1.14 (t, $J_{HP} = 6.3$ Hz, 18H, C(CH₃)₃), 1.03 (t, $J_{HP} = 6.3$ Hz, 18H, C(CH₃)₃), methylene and *tert*butyl peaks for the *ortho*-cis rotamer are obscured, -41.60 (t, $J_{HP} = 14.8$ Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Reaction of (PCP)Ir with 1,2,3,4-tetrachlorobenzene (2-24): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in pxylene. 1,2,3,4-Tetrachlorobenzene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 67.5 (d, J_{PH} = 12.6 Hz, ortho-trans isomer), 64.8 (d, J_{PH} = 11.1 Hz, ortho-cis isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.89 (s, 1H, ortho-trans tetrachlorophenyl ortho-H), 7.19 (s, 1H, orthocis tetrachlorophenyl *ortho-H*), 7.08 (d, $J_{\rm HH}$ = 7.5 Hz, 2H, PCP aryl H), 7.00 (t, $J_{\rm HH}$ = 7.5 Hz, 1H, PCP aryl H), 3.25 (d of vt, J_{HP} = 3.4 Hz, J_{HH} = 16.0 Hz, 4H, CH₂, ortho-trans rotamer), methylene peaks for the *ortho*-cis rotamer are obscured, 1.36 (t, $J_{HP} = 7.1$ Hz, 18H, C(CH₃)₃ ortho-cis isomer), 1.29 (t, J_{HP} = 7.0 Hz, 18H, C(CH₃)₃ ortho-cis isomer), 1.03 (t, $J_{HP} = 6.3$ Hz, 18H, C(CH₃)₃ ortho-trans isomer), 0.95 (t, $J_{HP} = 6.3$ Hz, 18H, $C(CH_3)_3$ ortho-trans isomer), -41.18 (t, $J_{HP} = 15.7$ Hz, 1H, Ir-H, ortho-trans rotamer), -42.43 (t, $J_{\rm HP}$ = 12.9 Hz, 1H, Ir-*H*, ortho-cis rotamer).

Reaction of 2-22 with CO to form 2-25: A solution of **2-22** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The bright orange solution immediately turned pale yellow upon thawing. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; pale yellow crystals were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 55.6 (s, *ortho*-cis isomer),

51.5 (s, *ortho*-trans isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): 8.60 (d, $J_{HH} =$ 2.5 Hz, 1H, *ortho*-cis dichlorophenyl *ortho-H*), 8.49 (d, $J_{HH} =$ 2.6 Hz, 1H, *ortho*-trans dichlorophenyl *ortho-H*), 7.22 (d, $J_{HH} =$ 7.5 Hz, 2H, *ortho*-cis dichlorophenyl aryl *H*), 7.20 (d, $J_{HH} =$ 7.5 Hz, 2H, *ortho*-trans dichlorophenyl aryl *H*), remaining ¹H NMR PCP aryl signals are obscured by residual solvent, 3.31 (m, 4H, C H_2 , *ortho*-cis isomer), 3.22 9m, 4H, C H_2 , *ortho*-trans isomer), 1.14 (t, $J_{HP} =$ 6.5 Hz, 18H, C(C H_3)₃), *tert*butyl peaks for the *ortho*-cis rotamer are obscured, -8.07 (t, $J_{HP} =$ 16.4 Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -9.28 (t, $J_{HP} =$ 16.4 Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Reaction of (PCP)Ir with brominated substrates to form 2-26 and 2-28: In all reactions between (PCP)Ir and bromo-substituted aryl substrates, C-Br bond activation becomes a thermodynamically competitive process (vs. C-H activation) over extended reaction times or at elevated temperatures. In addition to products of C-H activation, at least two products of C-Br activation are formed: (PCP)Ir(Br)(phenyl) (2-26) and (PCP)Ir(H)(Cl) (2-28). The exact mechanism for the formation of these products (particularly 2-28) is unknown, but possibly involves C-H activation of one or more of the phosphine *tert*butyl groups, since ³¹P NMR evidence indicates the presence of a small concentration of a species having inequivalent phosphorus atoms. ¹H NMR spectra are very complicated for these reaction mixtures, due to the large number of C-H activation products. Based on previous results from experiments conducted by our group, as well as similar products with chlorinated substrates, the ³¹P NMR resonance for complex 2-26 is δ 33.8

ppm (s, 2*P*). Inequivalent P atoms are shown as follows: δ 49.6 (d, J_{PP} = 350 Hz) and 8.8 (d, J_{PP} = 370 Hz).

Reaction of (PCP)Ir with brominated substrates to form 2-28: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Bromobenzene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. The kinetic products of this reaction result exclusively from C-H activation. After heating at 75 °C for 15 min, a complicated mixture of products is obtained that includes 2-28. ³¹P NMR (121.4 MHz, 25 °C, benzene- d_6): δ 67.7 (d, $J_{PH} = 12.2$ Hz). ¹H NMR (400 MHz, 25 °C, benzene- d_6): δ 7.15 (d, $J_{HH} = 7.2$ Hz, 2H, PCP *meta-H*), 7.03 (t, $J_{HH} = 7.2$ Hz, 1H, PCP *para-H*), 3.14 (d of vt, $J_{HP} = 3.3$ Hz, $J_{HH} = 18.0$ Hz, 4H, CH_2), 1.23 (t, $J_{HP} = 6.6$ Hz, 18H, $C(CH_3)_3$), -43.87 (t, $J_{HP} = 11.7$ Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with bromobenzene (2-27a,b,c,d,e): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Bromobenzene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark orange-brown. The *ortho*-cis product (2-27b) can be seen in the NMR spectrum but is too thermodynamically disfavored for accurate characterization and is not included here. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 67.5 (m, *meta* and *para* products), 61.5 (d,

 $J_{\rm PH} = 16.9$ Hz, *ortho*-trans isomer). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): all PCP aryl, substrate aryl, PCP methylene and *tert* butyl hydrogen resonances are obscured by residual solvent and/or the presences of multiple (4) isomeric products, -33.59 (t, $J_{\rm HP} = 15.8$ Hz, 1H, Ir-*H*, *ortho*-trans rotamer), -45.56, -45.57, -45.68 (overlapping triplets, $J_{\rm HP} = 15.6$ Hz, 1H, Ir-*H*, *meta* rotamers and *para* isomer).

Equilibrium study: competition experiment between norbornene and

bromobenzene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 100 equivalents of norbornene were then added to the solution, along with 20 equivalents of bromobenzene. The product ratios (**2-27a,c,d,e** vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rates of elimination of bromobenzene from 2-27a.

The *ortho*-trans C-H activation product is the least labile of the isomeric (PCP)Ir(H)(bromophenyl) addition products. Variable temperature NMR linebroadening studies analogous to those employed in the study of the kinetics of reductive elimination of such substrates as benzene were not possible for **2-27a**. Although similar experiments were attempted, as the temperature was raised above 50 °C, C-Br activation became a competitive process, and rapidly undermined the integrity of all C-H addition products, making accurate line-broadening measurements impossible. Therefore, a different strategy was employed. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 2 equivalents of bromobenzene were added to the reaction mixture, forming the desired products of C-H addition. The NMR tube was then sealed with a J-Young teflon cap, removed from the glove box and frozen in liquid nitrogen. 20 equivalents of 1,3-

bis(trifluoromethyl)benzene were then vacuum transferred to the reaction mixture (while frozen) and the entire solution was kept frozen and only allowed to warm up inside the NMR at the temperatures selected for data collection. The substrate 1,3bis(trifluoromethyl)benzene was chosen because it forms a thermodynamically favorable C-H addition product: therefore, it was assumed that every time bromobenzene was reductively eliminated from the (PCP)Ir fragment, 1,3-bis(trifluoromethyl)benzene would quickly add and then prevent future oxidative additions of bromobenzene. ³¹P NMR spectra were recorded approximately every three minutes while the bromobenzene complexes disappeared and the peak for the 1,3-bis(trifluoromethyl)phenyl addition product grew into the spectrum. The reactions generally required approximately 30-45 minutes to go to completion. Plots of the integrated first-order rate equation (ln[bromophenyl *ortho*-trans product] vs. 1/time) were used in order to calculate rates of reductive elimination at -40, -20, and 0 °C and then extrapolated to 25 °C for comparison with data from the other substrates.

Kinetics studies: measuring the rates of elimination of bromobenzene from 2-27c, 2-27d, and 2-27e. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of bromobenzene were added to the reaction mixture. The overlapping hydride signals corresponding to the combined *meta* and *para* products (**2-27c,d,e**) were analyzed at a series of temperatures from -25 °C to 5 °C.

Reaction of (PCP)Ir and 4-bromotoluene with CO to form 2-29: A solution of (PCP)Ir and 4-bromotoluene was heated to 75 °C for 60 min in order to encourage C-Br activation. The resulting solution (generated in a J-Young NMR tube) was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The dark red-orange solution immediately turned pale yellow upon thawing. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; pale yellow crystals were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 31.9. ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): all aryl signals (PCP, tolyl) are obscured by solvent and excess, unreacted substrate, δ 3.57 (d of t, J_{HP} = 4.1 Hz, J_{HH} = 15.9 Hz, 2H, CH_2), 2.87 (d of t, J_{HP} = 3.7 Hz, J_{HH} = 15.8 Hz, 2H, CH_2), 1.32 (vt, J_{HP} = 6.7 Hz, 18H, C(CH_3)₃), 0.74 (vt, J_{HP} = 6.2 Hz, 18H, C(CH_3)₃).

Reaction of (PCP)Ir with benzotrifluoride (α,α,α -trifluorotoluene) (2-30a,b,c): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 10 equivalents of norbornene were added from a

stock solution in *p*-xylene. Benzotrifluoride (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark orange-brown. Even at low temperature, the three product isomers (*meta*-cis, *meta*-trans, and *para*) give overlapping resonances in both the ³¹P NMR and ¹H NMR spectra. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 67.4 (br s, *meta* isomer), 67.2 (br s, *meta* isomer), 67.0 (br s, *para* isomer). All ¹H NMR aryl signals (PCP and trifluorotolyl) are obscured by those for the protiated *para*-xylene used as the solvent for the stock solutions of norbornene and trifluorotoluene. ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): δ 3.25 (d of vt, 4H, C H_2 from three product rotamers), 0.88 (m, 36H, C(C H_3)₃ from three product rotamers), -45.51 (t, J_{HP} = 13.6 Hz, 1H, Ir-*H*, *meta*-rotamer).

Equilibrium study: competition experiment between norbornene and

trifluorotoluene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 10 equivalents of norbornene were then added to the solution, along with 10 equivalents of toluene. The product ratios (**2-30a,b,c** vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rate of elimination of trifluorotoluene from 2-30. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of trifluorotoluene were added to the reaction mixture. The resulting solution was analyzed at a series of temperatures from -5 °C to 30 °C.

Reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene (2-31): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,3-bis(trifluoromethyl)benzene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark orange-brown. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 68.1 (d, $J_{PH} = 11.2$ Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.34 (d, $J_{HH} = 6.4$ Hz, 2H, substrate *ortho*-H), 7.58 (s, 1H, substrate *para*-H), PCP aryl-*H* peaks are obscured by solvent peaks, 3.33 (d of vt, $J_{HP} = 3.8$ Hz, $J_{HH} = 17.0$ Hz, 4H, CH_2), 0.92 (t, $J_{HP} = 6.2$ Hz, 18H, C(CH_3)₃), 0.90 (t, $J_{HP} = 6.0$ Hz, 18H, C(CH_3)₃), -45.52 (t, $J_{HP} = 13.2$ Hz, 1H, Ir-*H*).

Equilibrium study: competition experiment between fluorobenzene and 1,3bis(trifluoromethyl)benzene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. Since 1,3bis(trifluoromethyl)benzene adds too strongly for comparison with norbornene, 10 equivalents of fluorobenzene were added to the solution, along with 10 equivalents of 1,3-bis(trifluoromethyl)benzene. The product ratio (2-31 vs. (PCP)Ir(H)(fluorophenyl)) was obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C. The equilibrium constant vs. fluorobenzene was calculated and then compared to norbornene in order to generate the final K_{eq} .

Kinetics studies: measuring the rate of elimination of 1,3-

bis(trifluoromethyl)benzene from 2-31. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of 1,3-bis(trifluoromethyl)benzene were added to the reaction mixture. The resulting solution was analyzed at a series of temperatures from 45 °C to 90 °C.

Reaction of (PCP)Ir with 1,4-bis(trifluoromethyl)benzene (2-32): 5.9 mg of PCPIrH₂

(0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,4-bis(trifluoromethyl)benzene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark orange-brown. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 69.0 (d, $J_{PH} = 13.5$ Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.33 (s, 1H, substrate *ortho*-H), 7.47 (d, $J_{HH} = 8.6, 2H$, substrate aryl-H), PCP aryl-*H* peaks are obscured by solvent peaks, 3.38 (d of vt, $J_{HP} = 2.9$ Hz, $J_{HH} = 16.0$ Hz, 2H, CH_2), 3.17 (d of vt, $J_{HP} = 3.1$ Hz, $J_{HH} = 16.2$ Hz, 2H, CH_2), 1.30 (t, $J_{HP} = 5.3$ Hz, 18H, $C(CH_3)_3$), 0.99 (t, $J_{HP} = 6.0$ Hz, 18H, $C(CH_3)_3$), -43.81 (t, $J_{HP} = 14.4$ Hz, $J_{HF} = 13.6$ Hz, 1H, Ir-*H*).

Equilibrium study: competition experiment between norbornene and 1,4bis(trifluoromethyl)benzene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 10 equivalents of norbornene were then added to the solution, along with 10 equivalents of 1,4-bis(trifluoromethyl)benzene. The product ratio (2-32 vs. (PCP)Ir(NBE)) was obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rate of elimination of 1,4-

bis(trifluoromethyl)benzene from 2-32. Variable temperature NMR line-broadening studies analogous to those employed in the study of the kinetics of reductive elimination of such substrates as benzene were not possible for **2-32** since the kinetics for reductive elimination were so slow. Even at high temperatures (>100 °C), line broadening was negligible. Therefore, a different strategy was employed; experiments analogous to those conducted for the *ortho*-trans isomer of the bromobenzene addition product (discussed above) were conducted. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene-*d*₁₂ in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 100 equivalents of 1,4-bis(trifluoromethyl)benzene were added to the reaction mixture, forming the desired C-H addition product. The NMR tube was then sealed with a J-Young teflon cap,

removed from the glove box and frozen in liquid nitrogen. 10 equivalents of 1,3bis(trifluoromethyl)benzene were then vacuum transferred to the reaction mixture (while frozen) and the entire solution was kept frozen and only allowed to warm up inside the NMR at the temperatures selected for data collection. The substrate 1,3bis(trifluoromethyl)benzene was chosen because it forms a thermodynamically favorable C-H addition product: therefore, it was assumed that every time 1,4bis(trifluoromethyl)benzene was reductively eliminated from the (PCP)Ir fragment, 1,3bis(trifluoromethyl)benzene would quickly add and then prevent future oxidative additions of 1,4-bis(trifluoromethyl)benzene. ³¹P NMR spectra were recorded approximately every three minutes while the addition product from 1,4bis(trifluoromethyl)benzene disappeared and the peak for the 1,3bis(trifluoromethyl)phenyl addition product grew into the spectrum. The reactions generally required approximately 30-45 minutes to go to completion. A plot of the integrated first-order rate equation (ln[C-H addtion product] vs. 1/time) was used in order to calculate the rate of reductive elimination at 25 °C.

Reaction of 2-31 with CO to form 2-33: A solution of **2-31** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The bright orange solution immediately turned pale yellow upon thawing. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane; pale yellow crystals were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 54.9 (d, $J_{PH} = 15.9$ Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.69 (d, $J_{HH} = 6.4$ Hz, 2H, substrate *ortho*-H), 7.83 (s, 1H, substrate *para*-H), PCP aryl-*H* peaks are obscured by solvent peaks, 3.28 (d of vt, $J_{HP} = 4.2 \text{ Hz}$, $J_{HH} = 16.3 \text{ Hz}$, 4H, CH₂), 1.08 (t, $J_{HP} = 6.2 \text{ Hz}$, 18H, C(CH₃)₃), 1.07 (t, $J_{HP} = 6.0 \text{ Hz}$, 18H, C(CH₃)₃), -8.91 (t, $J_{HP} = 18.8 \text{ Hz}$, 1H, Ir-*H*).

Reaction of 2-32 with CO to form 2-34: A solution of **2-32** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The dark orange solution immediately turned pale yellow upon thawing. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane; pale yellow needles were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 52.6 (d, $J_{PH} = 13.1$ Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 9.16 (s, 1H, substrate *ortho*-H), 7.61 (d, $J_{HH} = 8.6$, 2H, substrate aryl-H), PCP aryl-*H* peaks are obscured by solvent peaks, 3.39 (d of vt, $J_{HP} =$ 2.9 Hz, $J_{HH} = 16.0$ Hz, 2H, CH_2), 3.22 (d of vt, $J_{HP} = 3.1$ Hz, $J_{HH} = 16.2$ Hz, 2H, CH_2), 1.01 (t, $J_{HP} = 6.6$ Hz, 18H, C(CH_3)₃), 0.99 (t, $J_{HP} = 6.5$ Hz, 18H, C(CH_3)₃), -8.43 (t, $J_{HP} =$ = 17.8 Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with 3-fluorotoluene (2-35a,b): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 3-Fluorotoluene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 68.7 (d, J_{PH} = 13.4 Hz, *ortho*-trans isomer), 67.7 (d, J_{PH} = 13.0 Hz, *ortho*-cis isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.62 (vt, J_{HH} and J_{HF} =

5.2 Hz, 1H, *ortho*-trans 3-fluorotolyl *ortho-H*), 7.61 (vt, J_{HH} and $J_{HF} = 5.2$ Hz, 1H, *ortho*cis 3-fluorotolyl *ortho-H*), remaining ¹H NMR aryl signals (PCP and 3-fluorotolyl) are obscured by residual solvent, 3.46 (t of t, $J_{HP} = 3.4$ Hz, $J_{HH} = 16.6$ Hz, 2H, CH_2 , *ortho*trans rotamer), 3.34 (t of t, $J_{HP} = 3.4$ Hz, $J_{HH} = 16.6$ Hz, 2H, CH_2 , *ortho*-trans rotamer), 1.09 (t, $J_{HP} = 6.4$ Hz, 18H, C(CH₃)₃), 1.04 (t, $J_{HP} = 6.0$ Hz, 18H, C(CH₃)₃), methylene and *tert*butyl peaks for the *ortho*-cis rotamer are obscured, -43.19 (t, $J_{HP} = 13.9$ Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -46.33 (t of d, $J_{HP} = 13.6$ Hz, $J_{HF} = 2.5$ Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Equilibrium study: competition experiment between norbornene and 3-

fluorotoluene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 100 equivalents of norbornene were then added to the solution, along with 5 equivalents of 3fluorotoluene. The product ratios (**2-35a,b** vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rates of elimination of 3-fluorotoluene from 2-35a

and 2-35b. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of 3-fluorotoluene were added to the reaction mixture. The hydride signal corresponding to product 2-35a was

analyzed at a series of temperatures from 35 °C to 80 °C. The hydride signal corresponding to product **2-35b** was analyzed at a series of temperatures from 30 °C to 50 °C.

Reaction of (PCP)Ir with 1,3-dimethyl-5-fluorobenzene (2-36a,b): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,3-dimethyl-5-fluorobenzene (3 eq; 0.030 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned slightly darker orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 72.4 (d, $J_{PH} = 15.5$ Hz, *ortho*-trans isomer), 68.0 (d, $J_{PH} = 13.6$ Hz, *ortho*-cis isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): all ¹H NMR aryl signals (PCP and substrate) are obscured by residual solvent, 3.46 (t of t, $J_{HP} = 3.1$ Hz, $J_{HH} = 17.1$ Hz, 2H, CH_2 , fluorine-cis rotamer), 3.33 (t of t, $J_{HP} = 3.7$ Hz, $J_{HH} = 16.5$ Hz, 2H, CH_2 , fluorine-cis rotamer), 1.10 (t, $J_{HP} = 6.3$ Hz, 18H, C(CH_3)₃), 1.07 (t, $J_{HP} = 6.3$ Hz, 18H, C(CH_3)₃), methylene and *tert*butyl peaks for the fluorine-trans rotamer are obscured, -42.21 (t, $J_{HP} = 16.0$ Hz, 1H, Ir-*H*, fluorine-trans rotamer), -45.02 (d of t, $J_{HP} = 14.2$ Hz, $J_{HF} = 10.6$ Hz, 1H, Ir-*H*, fluorine-cis rotamer).

Equilibrium study: competition experiment between norbornene and 1,3-dimethyl-

5-fluorobenzene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 10 equivalents of norbornene were then added to the solution, along with 10

equivalents of 1,3-dimethyl-5-fluorobenzene. The product ratios (**2-36a,b** vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rates of elimination of 1,3-dimethyl-5-fluorobenzene from 2-36a and 2-36b. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene-*d*₁₂ in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 3 equivalents of 1,3-dimethyl-5-fluorobenzene were added to the reaction mixture. The hydride signal corresponding to product 2-36a was analyzed at a series of temperatures from 35 °C to 60 °C. The hydride signal corresponding to product 2-36b was analyzed at a series of temperatures from 25 °C to 55 °C.

Reaction of (PCP)Ir with 3-chlorotoluene (2-37a,b,c,d): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 5 equivalents of norbornene were added from a stock solution in *p*-xylene. 3-Chlorotoluene (5 eq; 0.050 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. ³¹P NMR (121.4 MHz, -20 °C, mesitylene- d_{12}): δ 67.4 (br d, $J_{PH} = 11.2$ Hz, *ortho*-trans isomer), 67.1 (m, *meta* and *para* products), 63.8 (d, $J_{PH} = 13.4$ Hz, *ortho*-cis isomer). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): all PCP aryl, substrate aryl, PCP methylene and *tert*butyl hydrogen resonances are obscured by residual solvent and/or the presence of multiple (4)

isomeric products, δ –41.88 (t, J_{HP} = 14.8 Hz, 1H, Ir-*H*, *ortho*-trans rotamer), –42.27 (t, J_{HP} = 13.3 Hz, 1H, Ir-*H*, *ortho*-cis rotamer), –45.63 (t, J_{HP} = 14.5 Hz, 1H, Ir-*H*, *meta* rotamer), –45.66 (t, J_{HP} = 14.5 Hz, 1H, Ir-*H*, *meta* rotamer).

Equilibrium study: competition experiment between norbornene and 3-

chlorotoluene. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 5 equivalents of norbornene were then added to the solution, along with 5 equivalents of 3chlorotoluene. The product ratios (**2-37a,b,c,d** vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rates of elimination of 3-chlorotoluene from 2-37a,

2-37b, and 2-37c,d. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene-*d*₁₂ in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of 3-chlorotoluene were added to the reaction mixture. The hydride signal corresponding to product **2-37a** was analyzed at a series of temperatures from 60 °C to 85 °C. The hydride signal corresponding to product **2-37b** was too small for accurate analysis. The signal corresponding to the combined *meta* and *para* products (**2-37c,d**) was analyzed at a series of temperatures from -20 °C to 20 °C.

Reaction of (PCP)Ir with 3-methylbenzotrifluoride (2-38): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 10 equivalents of norbornene were added from a stock solution in *p*-xylene. 3-methylbenzotrifluoride (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark orange-brown. ³¹P NMR (121.4 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 68.0 (s), 67.8 (s). ¹H NM

Equilibrium study: competition experiment between norbornene and 3methylbenzotrifluoride. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. One equivalent of norbornene was added in order to generate the 14-electron (PCP)Ir fragment. An additional 10 equivalents of norbornene were then added to the solution, along with 10 equivalents of 3-methylbenzotrifluoride. The product ratios (2-38a,b vs. (PCP)Ir(NBE)) were obtained by comparing the integrated peak areas in the ³¹P NMR spectrum at -20 °C.

Kinetics studies: measuring the rate of elimination of 3-methylbenzotrifluoride from 2-38. 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at ambient temperature. Two equivalents of norbornene were added in order to generate the 14-electron (PCP)Ir fragment. After waiting five minutes for the formation of the (PCP)Ir(NBE) complex, 10 equivalents of 3-methylbenzotrifluoride were added to the reaction mixture. The resulting solution was analyzed at a series of temperatures from -5 °C to 30 °C.

Reaction of 2-35 with CO to form 2-39: A solution of **2-35** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The dark orange solution immediately turned pale yellow upon thawing. Solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane; pale yellow prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 55.6 (s, *ortho*-cis isomer), 52.6 (s, *ortho*trans isomer). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.17 (vt, J_{HH} and J_{HF} = 6.3 Hz, 1H, *ortho*-cis 3-fluorotolyl *ortho-H*), 8.01 (vt, J_{HH} and J_{HF} = 6.5 Hz, 1H, *ortho*-trans 3-fluorotolyl *ortho-H*), remaining ¹H NMR aryl signals (PCP and 3-fluorotolyl) are obscured by residual solvent, 3.26 (m, 4H, C H_2 , *ortho*-cis rotamer), 3.32 (m, 4H, C H_2 , *ortho*-trans rotamer), 1.27 (t, J_{HP} = 7.6 Hz, 36H, C(C H_3)₃ *ortho*-cis rotamer), 1.11 (t, J_{HP} = 7.6 Hz, 36H, C(C H_3)₃ *ortho*-trans rotamer), -8.76 (d of t, J_{HP} = 16.9 Hz, J_{HF} = 9.9 Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -9.57 (t of d, J_{HP} = 17.5 Hz, J_{HF} = 2.2 Hz, 1H, Ir-*H*, *ortho*trans rotamer).
2.4 Conclusion

Results from C-H activation reactions of (PCP)Ir and a series of benzene derivatives bearing alkyl, halogen, and trifluoromethyl substituents are remarkably selfconsistent with regard to both electronic and steric effects. Alkyl groups are both bulky and slightly electron donating, and *disfavor* oxidative addition. Halogens and trifluoromethyl groups are electron withdrawing, and in this sense, favor the thermodynamics of the C-H activation reaction. As the size of the substituent increases $(H < F < Cl < Br < CF_3)$, the rates of *ortho* addition and elimination decrease drastically: k_{RE} (benzene) vs. k_{RE} (1,4-bis(trifluoromethyl)benzene) = 7 x10⁶).

Despite many literature reports of transition metal complex mediated aryl C-H activation reactions in which *ortho* 'directing' substituents precoordinate to the metal center, results of our studies demonstrate that this is *not* the case for (PCP)Ir and haloarenes. Both experimental results and DFT calculations support the argument that the sterics of the transition state for oxidative addition and reductive elimination markedly slow the kinetics of these processes when *ortho* substituents are larger than hydrogen (F, Cl, Br, CF₃). Additionally, there is no thermodynamic preference for *ortho* vs. *meta* or *para* addition products.

2.5 References

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Kinetic and Thermodynamic Data

The following pages contain supporting information corresponding to the kinetic data (k_{RE}) reported and discussed in chapter 2:

Table 2.9 includes combined thermodynamic and kinetic data for *all* substrates vs.

 benzene.

Figures 2.6 – 2.28 are the Eyring plots derived from the simulated spectral modeling program gNMR. In two cases (the *ortho*-trans rotamers of the C-H activation products from the reaction of (PCP)Ir with bromobenzene and 1,4-bis(trifluoromethyl)benzene), plots derived from the integrated first order rate law are presented rather than Eyring plots, since the disappearance of these substrates was monitored directly via NMR analysis.

Figure 2.29 shows comparisons between experimental and simulated spectra for substrates with three overlapping products.

Figure 2.30 shows comparisons between experimental and simulated spectra for substrates with two overlapping products.

Figure 2.31 shows comparisons between experimental and simulated spectra for substrates with a single product.

X-ray crystal structures and selected crystallographic data are presented immediately after this supporting information.

Fragment showing the configuration of the C-H addition product	$\begin{array}{c} K\\ eq\\ (vs. C_6H_6) \end{array}$	K (per C-H)	k _{RE} (sec ⁻¹)	$\begin{array}{c} k_{RE} \\ (vs. C_6 H_6) \end{array}$	$\begin{array}{c} k_{OA} \\ (vs. C_6H_6) \end{array}$	k _{OA} (per C-H)			
H Ir	[1]	[1]	432	[1]	[1]	[1]			
H Ir	^a 0.066	0.40	$8.2 ext{ x10}^3$	19	1.3	7.6			
H Ir - tBu	^a 0.13	0.81	ŀ	Cinetics were	not measure	d			
H Ir	^b 0.047	0.28	1.2 x10 ⁴	28	1.3	7.9			
H	0.038	0.23	9.9 x10 ²	2.3	0.087	0.52			
H ^I r tBu	0.079	0.47	$7.5 \text{ x} 10^2$	1.7	0.14	0.82			
	No Measurable Reaction								
	No Measurable Reaction								
H H	$1.7 \text{ x} 10^3$	1.0 x10 ⁴	0.29	6.7 x10 ⁻⁴	1.2	6.9			
H F	$5.6 ext{ x10}^2$	$3.4 ext{ x10}^3$	1.5	3.5 x10 ⁻³	1.9	12			
Hr Cl.,	12	73	0.012	2.8 x10 ⁻⁵	3.4 x10 ⁻⁴	2.0 x10 ⁻³			
H	2.1	13	28	0.065	0.14	0.83			
H Ir CI	^a 8.9	53	88	0.20	1.8	11			
Br.,. Ir	11	67	2.1 x10 ⁻³	4.9 x10 ⁻⁶	5.4 x10 ⁻⁵	3.2 x10 ⁻⁴			
H Br	C-H activ	vation was de unfavorable	tected, but th for accurate d	e product is t letermination	oo thermodyı of K _{eq} or k _{RF}	namically			
HIR Br	^a 12	70	62	0.14	1.7	10			
H CF3	^a 27	1.6 x10 ²	39	0.090	2.5	15			

Table 2.9. Thermodynamic and Kinetic Data for all Substrates vs. Benzene at 25 °C.

Fragment showing the configuration of the C-H addition product	$\begin{array}{c} K\\ (\text{vs. } C_6^{\text{eq}} H_6) \end{array}$	K (per C-H)	k _{RE} (sec ⁻¹)	$\begin{pmatrix} k \\ (vs. C_6H_6) \end{pmatrix}$	$\begin{pmatrix} k \\ OA \\ (vs. C_6H_6) \end{pmatrix}$	k _{OA} (per C-H)
H ^I H ^{CF3}	5.1 x10 ³	3.1 x10 ⁴	0.62	1.4 x10 ⁻³	7.1	43
H ^{F₃C_{1/2} H^{CF₃}CF₃}	2.1	3.1	6.4 x10 ⁻⁴	1.5 x10 ⁻⁶	3.0 x10 ⁻⁶	4.6 x10 ⁻⁶
$\begin{array}{c} F_{3}C_{\prime,}\\ Ir \\ H \\ F_{3}C \end{array} \\ \leftarrow CF_{3} \\ \end{array}$			No Measura	ble Reaction		
H Fr.	$2.7 \text{ x} 10^2$	1.6 x10 ³	0.56	1.3 x10 ⁻³	0.35	2.1
HF	88	$5.3 ext{ x10}^2$	1.7	3.8 x10 ⁻³	0.33	2.0
	5.2	31	1.9 x10 ⁻²	4.5 x10 ⁻⁵	2.3 x10 ⁻⁴	1.4 x10 ⁻³
H CI	1.2	7.0	Ratio of p	roduct too sn measur	nall for accur rements	ate kinetic
	^b 3.6	21	1.3 x10 ²	0.30	1.1	6.5
	^b 5.5	33	1.2 x10 ²	0.27	1.5	8.9
F ₃ C _{//.}	C-H activation was detected, but the product is too thermodynamically unfavorable for accurate determination of K_{eq} or k_{RE}					
H Ir	0.19	0.56	1.9	4.4 x10 ⁻³	8.2 x10 ⁻⁴	2.5 x10 ⁻³
H F	°0.061	0.37	9.7	0.023	1.4 x10 ⁻³	8.4 x10 ⁻³

^aSubstrates have three C-H bonds accessible for addition to (PCP)Ir, resulting in three products: two *meta* rotamers and the corresponding *para* isomer. NMR signals either coincide or overlap sufficiently that individual isomers cannot be separated. Data are reported on a "per rotamer" basis. ^bSubstrates form two rotameric products and cannot be separated; data are reported on a "per rotamer" basis. ^cThe *ortho*-cis rotamer product of C-H activation of 5-fluoro-1,3-dimethylbenzene is thermodynamically unfavorable and difficult to measure; the thermodynamic data must be considered an estimate.



Figure 2-6. Eyring plot for reductive elimination of benzene from (PCP)Ir (based on the hydride signal).

Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
-39.24	233.91	8	-3.38	0.00428	4.28
-33.53	239.62	12	-2.99	0.00417	4.17
-28.24	244.91	18	-2.61	0.00408	4.08
-22.49	250.66	27	-2.23	0.00399	3.99
-16.87	256.28	39	-1.88	0.00390	3.90
-12.63	260.52	52	-1.61	0.00384	3.84
-2.27	270.88	100	-1.00	0.00369	3.69



Figure 2-7. Eyring plot for reductive elimination of toluene from (PCP)Ir (based on the hydride signals).

Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000

-40.22	232.93	1.3	-5.19	0.00429	4.29
-30.18	242.97	6.6	-3.61	0.00412	4.12
-27.45	245.70	10	-3.20	0.00407	4.07
-22.83	250.32	21	-2.48	0.00399	3.99
-17.11	256.04	47	-1.70	0.00391	3.91
-11.28	261.87	107	-0.90	0.00382	3.82



Figure 2-8. Eyring plot for reductive elimination of *ortho*-xylene from (PCP)Ir (based on the hydride signals).

Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
-42.87	230.28	2.5	-4.52	0.00434	4.34
-35.84	237.31	7.7	-3.43	0.00421	4.21
-31.35	241.80	15	-2.78	0.00414	4.14
-23.79	249.36	43	-1.76	0.00401	4.01
-19.67	253.48	75	-1.22	0.00395	3.95



Figure 2-9. Eyring plot for reductive elimination of *meta*-xylene from (PCP)Ir (based on the hydride signal).

Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
-44.44	228.71	7	-3.49	0.00437	4.37
-38.71	234.44	12	-2.97	0.00427	4.27
-33.65	239.50	19	-2.53	0.00418	4.18
-27.67	245.48	30	-2.10	0.00407	4.07
-22.97	250.18	42	-1.78	0.00400	4.00
-18.33	254.82	63	-1.40	0.00392	3.92
-13.41	259.74	90	-1.06	0.00385	3.85
-2.28	270.87	190	-0.35	0.00369	3.69





Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
-38.71	234.44	8	-3.38	0.00427	4.27
-33.65	239.50	12	-2.99	0.00418	4.18
-27.04	246.11	21	-2.46	0.00406	4.06
-22.97	250.18	29	-2.15	0.00400	4.00
-16.28	256.87	49	-1.66	0.00389	3.89
-13.61	259.54	61	-1.45	0.00385	3.85
-1.31	271.84	150	-0.59	0.00368	3.68
-27.04 -22.97 -16.28 -13.61 -1.31	246.11 250.18 256.87 259.54 271.84	21 29 49 61 150	-2.46 -2.15 -1.66 -1.45 -0.59	$\begin{array}{c} 0.00406 \\ 0.00400 \\ 0.00389 \\ 0.00385 \\ 0.00368 \end{array}$	4 4 3 3 3

Figure 2-11. Eyring plot for reductive elimination of the *ortho*-trans rotamer of fluorobenzene from (PCP)Ir (based on the hydride signal).



-		• • • •				,
	43.11	316.26	1.7	-5.23	0.00316	3.16
	49.24	322.39	3	-4.68	0.00310	3.10
	55.51	328.66	5	-4.19	0.00304	3.04
	58.18	331.33	6.5	-3.93	0.00302	3.02
	65.41	338.56	11	-3.43	0.00295	2.95
	71.30	344.45	18	-2.95	0.00290	2.90
	74.58	347.73	23	-2.72	0.00288	2.88
	82.22	355.37	41	-2.16	0.00281	2.81
	86.77	359.92	60	-1.79	0.00278	2.78

Temperature (°C) Temperature (K) Rate (sec⁻¹) $\ln(k/T)$ (1/T) (1/T)

(1/T) x 1000

Figure 2-12. Eyring plot for reductive elimination of the *ortho*-cis rotamer of fluorobenzene from (PCP)Ir (based on the hydride signal).



Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	$\ln(k/T)$	(1/T)	(1/T) x 1000
1	1 ()				
40.15	313.30	8	-3.67	0.00319	3.19
43.11	316.26	11	-3.36	0.00316	3.16
49.24	322.39	21	-2.73	0.00310	3.10
55.51	328.66	38	-2.16	0.00304	3.04
58.18	331.33	50	-1.89	0.00302	3.02
65.41	338.56	100	-1.22	0.00295	2.95

Figure 2-13. Eyring plot for reductive elimination of the *ortho*-trans rotamer of chlorobenzene from (PCP)Ir (based on the hydride signal).



Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	$\ln(k/T)$	(1/T)	(1/T) x 1000
1	1 ()				
65.90	339.05	2.5	-4.91	0.00295	2.95
70.80	343.95	4	-4.45	0.00291	2.91
76.90	350.05	8	-3.78	0.00286	2.86
80.50	353.65	12	-3.38	0.00283	2.83
87.83	360.98	25	-2.67	0.00277	2.77
93.12	366.27	43	-2.14	0.00273	2.73

Figure 2-14. Eyring plot for reductive elimination of the *ortho*-cis rotamer of chlorobenzene from (PCP)Ir (based on the hydride signal).



Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
3.00	276.15	2.5	-4.70	0.00362	3.62
8.52	281.67	5	-4.03	0.00355	3.55
14.33	287.48	9	-3.46	0.00348	3.48
19.58	292.73	16	-2.91	0.00342	3.42
24.22	297.37	25	-2.48	0.00336	3.36
29.77	302.92	45	-1.91	0.00330	3.30

Figure 2-15. Eyring plot for reductive elimination of the *meta* and *para* rotamers of chlorobenzene from (PCP)Ir (based on the hydride signals).



Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	$\ln(k/T)$	(1/T)	(1/T) x 1000

-1.77	271.38	9	-3.41	0.00368	3.68
3.00	276.15	14	-2.98	0.00362	3.62
8.52	281.67	23	-2.51	0.00355	3.55
14.33	287.48	37	-2.05	0.00348	3.48
19.58	292.73	58	-1.62	0.00342	3.42
24.22	297.37	85	-1.25	0.00336	3.36
29.77	302.92	125	-0.89	0.00330	3.30





Initial catalyst concentration = 22.0 mM

		Ratio	Ratio	Concentration of	
Time (min)	Time (sec)	(13BTFMB vs. BRBZ)	(BRBZ vs. 13BTFMB)	BRBZ complex	ln[BRBZ]
		Taken from NMR spectra		(mM)	
0	0	5.68	0.1761	3.2934	1.1919
3	180	7.1	0.1408	2.7160	0.9992
5	300	7.96	0.1256	2.4554	0.8983
7	420	8.57	0.1167	2.2989	0.8324
9	540	9.45	0.1058	2.1053	0.7444
11	660	10.44	0.0958	1.9231	0.6539
13	780	11.45	0.0873	1.7671	0.5693
15	900	13.08	0.0765	1.5625	0.4463
17	1020	14.26	0.0701	1.4417	0.3658
19	1140	16.65	0.0601	1.2465	0.2203
21	1260	18.12	0.0552	1.1506	0.1403
23	1380	19.93	0.0502	1.0511	0.0499
25	1500	21.34	0.0469	0.9848	-0.0153
29	1740	26.6	0.0376	0.7971	-0.2268
31	1860	29.24	0.0342	0.7275	-0.3181
33	1980	31.65	0.0316	0.6738	-0.3948
37	2220	38.24	0.0262	0.5607	-0.5787
40	2400	42.5	0.0235	0.5057	-0.6817

Figure 2-17. Plot of the integrated first-order rate equation for reductive elimination of the *ortho*-trans rotamer of bromobenzene from (PCP)Ir at -10 $^{\circ}$ C (based on the ³¹P NMR spectrum).



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Initial catalyst concentration = 18.7 mM
```

		Ratio	Ratio	Concentration of	
Гime (min)	Time (sec)	(13BTFMB vs. BRBZ)	(BRBZ vs. 13BTFMB)	BRBZ complex	ln[BRBZ]
		Taken from NMR spectra		(mM)	
0	0	5.69	0.1757	2.7892	1.0258
2.5	150	6.1	0.1639	2.6282	0.9663
5	300	6.15	0.1626	2.6098	0.9593
7.5	450	6.22	0.1608	2.5845	0.9495
10	600	6.55	0.1527	2.4715	0.9048
12.5	750	6.76	0.1479	2.4046	0.8774
15	900	6.88	0.1453	2.3680	0.8621
17.5	1050	7.48	0.1337	2.2005	0.7887
20	1200	7.77	0.1287	2.1277	0.7550
22.5	1350	8.04	0.1244	2.0642	0.7247
25	1500	8.34	0.1199	1.9979	0.6921
27.5	1650	8.53	0.1172	1.9580	0.6719
30	1800	8.82	0.1134	1.9002	0.6420
32.5	1950	9.33	0.1072	1.8064	0.5913
35	2100	9.65	0.1036	1.7521	0.5608
37.5	2250	9.71	0.1030	1.7423	0.5552
40	2400	10.04	0.0996	1.6902	0.5249
42.5	2550	10.43	0.0959	1.6325	0.4901

Figure 2-18. Eyring plot for reductive elimination of the *meta* and *para* rotamers of bromobenzene from (PCP)Ir (based on the hydride signals).



Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	$\ln(k/T)$	(1/T)	(1/T) x 1000
-30.78	242.37	1	-5.49	0.00413	4.13
-24.32	248.83	2	-4.82	0.00402	4.02
-19.89	253.26	3	-4.44	0.00395	3.95
-12.66	260.49	5	-3.95	0.00384	3.84
-8.05	265.10	7.5	-3.57	0.00377	3.77
-1.26	271.89	12	-3.12	0.00368	3.68
8.13	281.28	24	-2.46	0.00356	3.56



Figure 2-19. Eyring plot for reductive elimination of trifluorotoluene from (PCP)Ir (based on the hydride signals).

mperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
-4.69	268.46	1.4	-5.26	0.00372	3.72
-0.85	272.30	2.2	-4.82	0.00367	3.67
3.34	276.49	3.8	-4.29	0.00362	3.62
8.45	281.60	6.7	-3.74	0.00355	3.55
14.04	287.19	12	-3.18	0.00348	3.48
19.81	292.96	22	-2.59	0.00341	3.41
24.57	297.72	37	-2.09	0.00336	3.36
29.32	302.47	62	-1.58	0.00331	3.31

Temperature (°C) Temperature (K) Rate (sec⁻¹)

 $\ln(k/T)$

(1/T) x 1000

Figure 2-20. Eyring plot for reductive elimination of 1,3-bis(trifluoromethyl)benzene from (PCP)Ir (based on the hydride signal).



Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
42.11	315.26	3.5	-4.50	0.00317	3.17
49.10	322.25	6.5	-3.90	0.00310	3.10
55.44	328.59	12	-3.31	0.00304	3.04
59.70	332.85	17	-2.97	0.00300	3.00
65.52	338.67	27.5	-2.51	0.00295	2.95
68.84	341.99	36	-2.25	0.00292	2.92
78.45	351.60	78	-1.51	0.00284	2.84
81.04	354.19	95	-1.32	0.00282	2.82
88.65	361.80	170	-0.76	0.00276	2.76

Figure 2-21. Plot of the integrated first-order rate equation for reductive elimination of the *ortho*-trans rotamer of 1,4-bis(trifluoromethyl)benzene from (PCP)Ir at 25 °C (based on the ^{31}P NMR spectrum).



Initial catalyst concentration = 20.6 mM

		Ratio	Ratio	Concentration of	
Time (min)	Time (sec)	(13BTFMB vs. 14BTFMB)	(14BTFMB vs. 13BTFMB)	14BTFMB complex	ln[14BTFMB]
		Taken from NMR spectra		(mM)	
31.5	1890	2.33	0.4292	6.1862	1.8223
34.5	2070	2.83	0.3534	5.3786	1.6824
36.5	2190	3.08	0.3247	5.0490	1.6192
39.5	2370	3.5	0.2857	4.5778	1.5212
41.5	2490	3.89	0.2571	4.2127	1.4381
43.5	2610	4.4	0.2273	3.8148	1.3389
46.5	2790	4.87	0.2053	3.5094	1.2554
48.5	2910	5.56	0.1799	3.1402	1.1443
50.5	3030	6	0.1667	2.9429	1.0794
53.5	3210	6.75	0.1481	2.6581	0.9776
55.5	3330	7.5	0.1333	2.4235	0.8852
58.5	3510	8.75	0.1143	2.1128	0.7480
60.5	3630	9.36	0.1068	1.9884	0.6873
63.5	3810	10.25	0.0976	1.8311	0.6049
65.5	3930	11.09	0.0902	1.7039	0.5329
68.5	4110	13.23	0.0756	1.4476	0.3699
70.5	4230	14.04	0.0712	1.3697	0.3146
73.5	4410	14.53	0.0688	1.3265	0.2825
75.5	4530	15.32	0.0653	1.2623	0.2329

Figure 2-22. Eyring plot for reductive elimination of the *ortho*-trans rotamer of 3-fluorotoluene from (PCP)Ir (based on the hydride signal).



Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
33.70	306.85	1.3	-5.46	0.00326	3.26
39.97	313.12	2.4	-4.87	0.00319	3.19
43.10	316.25	3.3	-4.56	0.00316	3.16
49.10	322.25	5.7	-4.03	0.00310	3.10
55.59	328.74	9.5	-3.54	0.00304	3.04
61.57	334.72	16.7	-3.00	0.00299	2.99
63.36	336.51	19	-2.87	0.00297	2.97
70.90	344.05	34	-2.31	0.00291	2.91
75.36	348.51	47	-2.00	0.00287	2.87
81.37	354.52	72	-1.59	0.00282	2.82

Figure 2-23. Eyring plot for reductive elimination of the *ortho*-cis rotamer of 3-fluorotoluene from (PCP)Ir (based on the hydride signal).



Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
	_				
29.28	302.43	3.5	-4.46	0.00331	3.31
33.70	306.85	7	-3.78	0.00326	3.26
39.97	313.12	19	-2.80	0.00319	3.19
43.10	316.25	31	-2.32	0.00316	3.16
49.10	322.25	78	-1.42	0.00310	3.10

Figure 2-24. Eyring plot for reductive elimination of the *ortho*-trans rotamer of 3-chlorotoluene from (PCP)Ir (based on the hydride signal).



Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
60.21	333.36	3.8	-4.47	0.00300	3.00
65.49	338.64	7.6	-3.80	0.00295	2.95
70.64	343.79	15	-3.13	0.00291	2.91
73.28	346.43	21	-2.80	0.00289	2.89
76.58	349.73	31	-2.42	0.00286	2.86
84.01	357.16	75	-1.56	0.00280	2.80

Figure 2-25. Eyring plot for reductive elimination of the *meta* rotamers of 3-chlorotoluene from (PCP)Ir (based on the hydride signals).



Femperature (°C)	Temperature (K)	Rate (sec ⁻¹)	$\ln(k/T)$	(1/T)	(1/T) x 1000
-17.89	255.26	4.2	-4.11	0.00392	3.92
-16.91	256.24	4.7	-4.00	0.00390	3.90
-9.13	264.02	9.5	-3.32	0.00379	3.79
-5.89	267.26	12	-3.10	0.00374	3.74
-1.68	271.47	17.5	-2.74	0.00368	3.68
4.54	277.69	29	-2.26	0.00360	3.60
8.54	281.69	38	-2.00	0.00355	3.55
14.78	287.93	62	-1.54	0.00347	3.47
19.68	292.83	92	-1.16	0.00341	3.41



Figure 2-26. Eyring plot for reductive elimination of 3-methylbenzotrifluoride from (PCP)Ir (based on the hydride signals).

Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
-6.66	266.49	2.1	-4.84	0.00375	3.75
-0.98	272.17	4.5	-4.10	0.00367	3.67
4.40	277.55	9.5	-3.37	0.00360	3.60
10.88	284.03	21	-2.60	0.00352	3.52
14.27	287.42	32	-2.20	0.00348	3.48
19.82	292.97	64	-1.52	0.00341	3.41
24.27	297.42	110	-0.99	0.00336	3.36
29.37	302.52	185	-0.49	0.00331	3.31



Figure 2-27. Eyring plot for reductive elimination of the ortho-trans rotamer of 5-fluoro-1,3-dimethylbenzene from (PCP)Ir (based on the hydride signal).

Temperature (K)	Rate (sec ⁻¹)	$\ln(k/T)$	(1/T)	(1/T) x 1000
• • • • •				
306.65	5	-4.12	0.00326	3.26
312.80	10	-3.44	0.00320	3.20
318.45	18	-2.87	0.00314	3.14
323.51	31	-2.35	0.00309	3.09
327.65	46	-1.96	0.00305	3.05
332.98	75	-1.49	0.00300	3.00
	Temperature (K) 306.65 312.80 318.45 323.51 327.65 332.98	Temperature (K) Rate (sec ⁻¹) 306.65 5 312.80 10 318.45 18 323.51 31 327.65 46 332.98 75	Temperature (K) Rate (sec ⁻¹) ln(k/T) 306.65 5 -4.12 312.80 10 -3.44 318.45 18 -2.87 323.51 31 -2.35 327.65 46 -1.96 332.98 75 -1.49	Temperature (K)Rate (sec $^{-1}$)ln(k/T)(1/T)306.655-4.120.00326312.8010-3.440.00320318.4518-2.870.00314323.5131-2.350.00309327.6546-1.960.00305332.9875-1.490.00300



Figure 2-28. Eyring plot for reductive elimination of the *ortho*-cis rotamer of 5-fluoro-1,3-dimethylbenzene from (PCP)Ir (based on the hydride signal).

Temperature (°C)	Temperature (K)	Rate (sec ⁻¹)	ln(k/T)	(1/T)	(1/T) x 1000
23.50	296.65	8	-3.61	0.00337	3.37
33.50	306.65	28	-2.39	0.00326	3.26
39.65	312.80	58	-1.69	0.00320	3.20
45.30	318.45	110	-1.06	0.00314	3.14
50.36	323.51	5.7	-4.04	0.00309	3.09
54.50	327.65	9.5	-3.54	0.00305	3.05

Figure 2-29a. Simulated and experimental ¹H NMR hydride resonances for the three products (**2-5a**) from the reaction of (PCP)Ir with toluene at -40 $^{\circ}$ C.

gNMR simulation for $k_{RE} = 0.5$ sec-1:



cpirhnberesidualtolu100eg_h=40
N 1
$\Lambda \Lambda \Lambda$
$\mathcal{N} \land \mathcal{N} \land $
ware and a second and a
5.05 -45.10 -45.15 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.50 -45.60 -45.65 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 -46.4

Figure 2-29b. Simulated and experimental ¹H NMR hydride resonances for the three products (**2-5a**) from the reaction of (PCP)Ir with toluene at -35 °C.

gNMR simulation for $k_{RE} = 1.3$ sec-1:

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Figure 2-29c. Simulated and experimental ¹H NMR hydride resonances for the three products (**2-5a**) from the reaction of (PCP)Ir with toluene at -30 $^{\circ}$ C.

gNMR simulation for $k_{RE} = 6.6$ sec-1:

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				\mathcal{A}	\mathcal{M}	^			
-45.050	-45.150	-45.250	-45.350	-45.450	-45.550	-45.650	-45.750	-45.850	-45.950

120716_pcpirhnberesidualtolu100eq_h-30	-4.0
	-3.5
	-3.0
	-2.5
	-2.0
	-1.5
	-1.0
	-0.5
	-0.0
	0.5
	1.0
	1.5
00 -45.05 -45.10 -45.15 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.55 -45.50 -45.55 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 11 10000	-46.00

Figure 2-29d. Simulated and experimental ¹H NMR hydride resonances for the three products (**2-5a**) from the reaction of (PCP)Ir with toluene at -25 °C.



Experimental ¹H NMR spectrum:

gNMR simulation for $k_{RE} = 10^{\text{sec-1}}$:



.00 -45.05 -45.10 -45.15 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.50 -45.55 -45.60 -45.65 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 -46.00

Figure 2-29e. Simulated and experimental ¹H NMR hydride resonances for the three products (**2-5a**) from the reaction of (PCP)Ir with toluene at -20 $^{\circ}$ C.





Figure 2-29f. Simulated and experimental ¹H NMR hydride resonances for the three products (**2-5a**) from the reaction of (PCP)Ir with toluene at -15 $^{\circ}$ C.



Experimental ¹H NMR spectrum:



.00 -45.05 -45.10 -45.15 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.55 -45.55 -45.60 -45.65 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 -11 (ppm)

Figure 2-29g. Simulated and experimental ¹H NMR hydride resonances for the three products (**2-5a**) from the reaction of (PCP)Ir with toluene at -10 $^{\circ}$ C.




Figure 2-30a. Simulated and experimental ¹H NMR hydride resonances for the two products (**2-38a,b**) from the reaction of (PCP)Ir with 3-methylbenzotrifluoride at -5 °C.



Experimental ¹H NMR spectrum:

gNMR simulation for $k_{RE} = 2.1$ sec-1:



Figure 2-30b. Simulated and experimental ¹H NMR hydride resonances for the two products (**2-38a,b**) from the reaction of (PCP)Ir with 3-methylbenzotrifluoride at 0 °C.



Experimental ¹H NMR spectrum:

gNMR simulation for $k_{RE} = 4.5$ sec-1:



Figure 2-30c. Simulated and experimental ¹H NMR hydride resonances for the two products (**2-38a,b**) from the reaction of (PCP)Ir with 3-methylbenzotrifluoride at 5 °C.



Experimental ¹H NMR spectrum:



00 -45.05 -45.10 -45.15 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.55 -45.50 -45.55 -45.60 -45.65 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 -45.95

Figure 2-30d. Simulated and experimental ¹H NMR hydride resonances for the two products (**2-38a,b**) from the reaction of (PCP)Ir with 3-methylbenzotrifluoride at 10 °C.



Experimental ¹H NMR spectrum:

gNMR simulation for $k_{RE} = 21^{\text{sec-1}}$:



.00 -45.05 -45.10 -45.15 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.55 -45.55 -45.60 -45.65 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 -11 (ppm)

Figure 2-30e. Simulated and experimental ¹H NMR hydride resonances for the two products (**2-38a,b**) from the reaction of (PCP)Ir with 3-methylbenzotrifluoride at 15 °C.





Figure 2-30f. Simulated and experimental ¹H NMR hydride resonances for the two products (**2-38a,b**) from the reaction of (PCP)Ir with 3-methylbenzotrifluoride at 20 °C.





Figure 2-30g. Simulated and experimental ¹H NMR hydride resonances for the two products (**2-38a,b**) from the reaction of (PCP)Ir with 3-methylbenzotrifluoride at 25 °C.



Experimental ¹H NMR spectrum:



00 -45.05 -45.10 -45.15 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.50 -45.55 -45.60 -45.65 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 -46.00

Figure 2-31a. Simulated and experimental ¹H NMR hydride resonances for product **2-31** from the reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at 45 °C.







Figure 2-31b. Simulated and experimental ¹H NMR hydride resonances for product **2-31** from the reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at 50 °C.

Sun Mar 17 20:25:01 2013: \\psf\ Home\ Desktop\ GNMR\ 1,3-bis(trifluoromethyl)benzene.dta W1: 1H Axis = ppm Scale = 18.16 Hz/ cm

Experimental ¹H NMR spectrum:

gNMR simulation for $k_{RE} = 6.5$ sec-1:



Figure 2-31c. Simulated and experimental ¹H NMR hydride resonances for product **2-31** from the reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at 55 °C.

gNMR simulation for $k_{RE} = 12^{\text{sec-1}}$:





Figure 2-31d. Simulated and experimental ¹H NMR hydride resonances for product **2-31** from the reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at 60 °C.

gNMR simulation for $k_{RE} = 17^{\text{sec-1}}$:



Experimental ¹H NMR spectrum:



00 -45.05 -45.10 -45.15 -45.20 -45.25 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.55 -45.55 -45.56 -45.55 -45.70 -45.75 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 -46.00

Figure 2-31e. Simulated and experimental ¹H NMR hydride resonances for product **2-31** from the reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at 65 °C.



Experimental ¹H NMR spectrum:

gNMR simulation for $k_{RE} = 27.5$ sec-1:



00 -45.05 -45.10 -45.15 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.50 -45.55 -45.50 -45.65 -45.67 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 -46.00

Figure 2-31f. Simulated and experimental ¹H NMR hydride resonances for product **2-31** from the reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at 70 °C.



Experimental ¹H NMR spectrum:

gNMR simulation for $k_{RE} = 36^{\text{sec-1}}$:



.00 -45.05 -45.10 -45.15 -45.20 -45.25 -45.30 -45.35 -45.40 -45.45 -45.50 -45.55 -45.60 -45.65 -45.70 -45.75 -45.80 -45.85 -45.90 -45.95 -46.00

Figure 2-31g. Simulated and experimental ¹H NMR hydride resonances for product **2-31** from the reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at 75 °C.



Experimental ¹H NMR spectrum:

gNMR simulation for $k_{RE} = 78^{\text{ sec-1}}$:



Figure 2-31h. Simulated and experimental ¹H NMR hydride resonances for product **2-31** from the reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at 80 °C.



Experimental ¹H NMR spectrum:

gNMR simulation for $k_{RE} = 95$ sec-1:



Figure 2-31i. Simulated and experimental ¹H NMR hydride resonances for product **2-31** from the reaction of (PCP)Ir with 1,3-bis(trifluoromethyl)benzene at 85 °C.



gNMR simulation for $k_{RE} = 170^{\text{ sec-1}}$:





Figure 2.32. X-ray crystal structure for compound 2-12.

 Table 2.10.
 Crystal data and structure refinement for 2-12.

Empirical formula	C31 H48 F Ir O P2	
Formula weight	709.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 18.1420(15) Å	a= 90°.
	b = 16.5610(13) Å	b=90°.
	c = 19.8508(16) Å	g = 90°.
Volume	5964.2(8) Å ³	
Z	8	
Density (calculated)	1.581 Mg/m ³	
Absorption coefficient	4.613 mm ⁻¹	
F(000)	2864	
Crystal size	0.44 x 0.28 x 0.09 mm ³	
Theta range for data collection	1.96 to 32.11°.	
Index ranges	-25<=h<=27, -24<=k<=24	4, -29<=l<=29
Reflections collected	63076	
Independent reflections	10346 [R(int) = 0.0277]	
Completeness to theta = 32.11°	99.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.7384 and 0.2417	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	10346 / 1 / 341	
Goodness-of-fit on F ²	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0188, wR2 = 0.042	17
R indices (all data)	R1 = 0.0249, wR2 = 0.043	38
Largest diff. peak and hole	1.482 and -0.941 e.Å ⁻³	

Ir(1)-C(31)	1.9218(16)	P(1)-C(13)	1.8892(17)
Ir(1)-C(1)	2.1068(16)	P(1)-C(9)	1.8940(17)
Ir(1)-C(25)	2.1466(16)	P(2)-C(8)	1.8442(17)
Ir(1)-P(2)	2.3356(4)	P(2)-C(17)	1.8873(17)
Ir(1)-P(1)	2.3428(4)	P(2)-C(21)	1.8914(17)
Ir(1)-H(1)	1.584(9)	F(1)-C(26)	1.3837(19)
P(1)-C(7)	1.8335(18)	O(1)-C(31)	1.147(2)
C(31)-Ir(1)-C(1)	82.78(6)	C(7)-P(1)-Ir(1)	101.76(6)
C(31)-Ir(1)-C(25)	99.21(6)	C(13)-P(1)-Ir(1)	119.82(6)
C(1)-Ir(1)-C(25)	177.64(6)	C(9)-P(1)-Ir(1)	115.44(6)
C(31)-Ir(1)-P(2)	96.21(5)	C(8)-P(2)-C(17)	104.86(8)
C(1)-Ir(1)-P(2)	81.92(5)	C(8)-P(2)-C(21)	102.80(8)
C(25)-Ir(1)-P(2)	99.07(4)	C(17)-P(2)-C(21)	110.16(8)
C(31)-Ir(1)-P(1)	96.97(5)	C(8)-P(2)-Ir(1)	101.69(6)
C(1)-Ir(1)-P(1)	82.10(5)	C(17)-P(2)-Ir(1)	119.25(6)
C(25)-Ir(1)-P(1)	96.36(4)	C(21)-P(2)-Ir(1)	115.59(5)
P(2)-Ir(1)- $P(1)$	157.800(14)	C(6)-C(1)-Ir(1)	121.27(12)
C(31)-Ir(1)-H(1)	173.5(9)	C(2)-C(1)-Ir(1)	120.71(12)
C(1)-Ir(1)-H(1)	90.8(9)	C(26)-C(25)-Ir(1)	125.04(12)
C(25)-Ir(1)-H(1)	87.2(9)	C(30)-C(25)-Ir(1)	123.04(12)
P(2)-Ir(1)-H(1)	83.7(8)	O(1)-C(31)-Ir(1)	170.24(15)
P(1)-Ir(1)-H(1)	81.2(8)	C(3)-C(2)-C(1)	120.53(16)
C(7)-P(1)-C(13)	104.69(8)	F(1)-C(26)-C(27)	114.29(15)
C(7)-P(1)-C(9)	101.93(8)	F(1)-C(26)-C(25)	119.48(14)
C(13)-P(1)-C(9)	110.42(8)		

 Table 2.11.
 Selected bond lengths [Å] and angles [°] for 2-12.



Figure 2.33. X-ray crystal structure for compound 2-13.

Empirical formula	C31 H47 F2 Ir O P2	
Formula weight	727.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 18.1440(9) Å	a= 90°.
	b = 16.8163(8) Å	b= 90°.
	c = 19.9179(10) Å	$g = 90^{\circ}$.
Volume	6077.2(5) Å ³	
Z	8	
Density (calculated)	1.591 Mg/m ³	
Absorption coefficient	4.534 mm ⁻¹	
F(000)	2928	
Crystal size	0.32 x 0.27 x 0.22 mm ³	
Theta range for data collection	1.94 to 30.53°.	
Index ranges	-25<=h<=16, -19<=k<=24	4, -27<=l<=28
Reflections collected	35490	
Independent reflections	9222 [R(int) = 0.0270]	
Completeness to theta = 30.53°	99.2 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.4354 and 0.3248	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	9222 / 1 / 350	
Goodness-of-fit on F ²	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0292, wR2 = 0.0647	
R indices (all data)	R1 = 0.0393, wR2 = 0.069	90
Largest diff. peak and hole	4.301 and -1.249 e.Å ⁻³	

 Table 2.12.
 Crystal data and structure refinement for 2-13.

Ir(1)-C(31)	1.924(3)	P(1)-C(9)	1.885(3)
Ir(1)-C(1)	2.105(3)	P(2)-C(8)	1.835(3)
Ir(1)-C(25)	2.147(3)	P(2)-C(17)	1.891(3)
Ir(1)-P(2)	2.3366(7)	P(2)-C(21)	1.891(3)
Ir(1)-P(1)	2.3429(8)	F(1)-C(26)	1.384(4)
Ir(1)-H(1)	1.578(10)	F(2)-C(29)	1.366(4)
P(1)-C(7)	1.840(3)	O(1)-C(31)	1.146(4)
P(1)-C(13)	1.883(3)		
C(31)-Ir(1)-C(1)	83.59(12)	C(7)-P(1)-Ir(1)	102.25(11)
C(31)-Ir(1)-C(25)	97.38(13)	C(13)-P(1)-Ir(1)	120.06(11)
C(1)-Ir(1)-C(25)	178.98(12)	C(9)-P(1)-Ir(1)	114.32(9)
C(31)-Ir(1)-P(2)	96.81(10)	C(8)-P(2)-C(17)	104.79(15)
C(1)-Ir(1)-P(2)	81.47(8)	C(8)-P(2)-C(21)	102.60(14)
C(25)-Ir(1)-P(2)	98.07(8)	C(17)-P(2)-C(21)	110.14(14)
C(31)-Ir(1)-P(1)	98.51(10)	C(8)-P(2)-Ir(1)	101.37(10)
C(1)-Ir(1)-P(1)	81.64(8)	C(17)-P(2)-Ir(1)	119.68(10)
C(25)-Ir(1)-P(1)	98.52(8)	C(21)-P(2)-Ir(1)	115.61(10)
P(2)-Ir(1)-P(1)	155.71(3)	C(2)-C(1)-Ir(1)	121.9(2)
C(31)-Ir(1)-H(1)	174.9(15)	C(6)-C(1)-Ir(1)	120.6(2)
C(1)-Ir(1)-H(1)	91.3(15)	C(2)-C(7)-P(1)	110.5(2)
C(25)-Ir(1)-H(1)	87.7(15)	C(30)-C(25)-Ir(1)	123.6(2)
P(2)-Ir(1)-H(1)	82.9(15)	F(1)-C(26)-C(27)	113.9(3)
P(1)-Ir(1)-H(1)	80.2(15)	F(1)-C(26)-C(25)	119.2(3)
C(7)-P(1)-C(13)	104.08(15)	F(2)-C(29)-C(28)	118.6(3)
C(7)-P(1)-C(9)	103.62(15)	F(2)-C(29)-C(30)	117.7(3)
C(13)-P(1)-C(9)	110.17(14)	O(1)-C(31)-Ir(1)	172.4(3)

Table 2.13.Selected bond lengths [Å] and angles [°] for 2-13.



Figure 2.34. X-ray crystal structure for compound 2-14.

Empirical formula	C32 H46 F Ir O P2	
Formula weight	719.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 16.3479(7) Å	a= 90°.
	b = 14.0236(6) Å	b= 108.5720(10)°.
	c = 14.6488(7) Å	$g = 90^{\circ}$.
Volume	3183.4(2) Å ³	
Ζ	4	
Density (calculated)	1.502 Mg/m ³	
Absorption coefficient	4.322 mm ⁻¹	
F(000)	1448	
Crystal size	0.20 x 0.13 x 0.04 mm ³	
Theta range for data collection	2.18 to 30.57°.	
Index ranges	-23<=h<=23, -19<=k<=20, -20<=l<=20	
Reflections collected	19006	
Independent reflections	9358 [R(int) = 0.0253]	
Completeness to theta = 30.57°	99.4 %	
Absorption correction	Semi-empirical from equ	ivalents
Max. and min. transmission	0.8461 and 0.4785	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	9358 / 1613 / 627	
Goodness-of-fit on F ²	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.09	36
R indices (all data)	R1 = 0.0494, $wR2 = 0.0983$	
Absolute structure parameter	0.00(11)	
Largest diff. peak and hole	1.046 and -0.585 e.Å ⁻³	

 Table 2.14.
 Crystal data and structure refinement for 2-14.

Ir(1A)-C(32A)	1.925(6)	P(1A)-C(9A)	1.951(11)
Ir(1A)-C(1A)	2.130(3)	P(2A)-C(8A)	1.774(13)
Ir(1A)-C(25A)	2.217(3)	P(2A)-C(21A)	1.854(11)
Ir(1A)-P(2A)	2.351(7)	P(2A)-C(17A)	1.875(10)
Ir(1A)-P(1A)	2.316(8)	C(26A)-F(1A)	1.332(5)
Ir(1A)-H(1A)	1.600(10)	C(32A)-O(1A)	1.139(6)
P(1A)-C(13A)	1.882(11)		
P(1A)-C(7A)	1.917(13)		
C(32A) Ir(1A) $C(1A)$	86 6(3)	$C(7\Lambda) \mathbf{P}(1\Lambda) C(0\Lambda)$	102 8(6)
C(32A) - II(1A) - C(1A) C(32A) Ir(1A) C(25A)	80.0(<i>3</i>)	C(13A) P(1A) Ir(1A)	102.0(0) 117.1(5)
C(32A) - II(1A) - C(25A)	37.3(3)	C(13A)- $I(1A)$ - $II(1A)C(7A) P(1A) Ir(1A)$	117.1(3) 105 3(5)
$C(1A) - \Pi(1A) - C(23A)$ C(22A) Ir(1A) D(2A)	175.4(3)	C(7A)- $I(1A)$ - $II(1A)C(0A) P(1A) Ir(1A)$	105.5(5) 120.0(5)
C(32A) - II(1A) - I(2A) C(1A) Ir(1A) P(2A)	95.1(5) 81.2(4)	C(9A) - I(1A) - II(1A) C(8A) - D(2A) - C(21A)	120.0(3)
$C(1A) - \Pi(1A) - \Gamma(2A)$ C(25A) Ir(1A) D(2A)	91.3(4)	C(8A) - F(2A) - C(21A) C(8A) - D(2A) - C(17A)	101.0(0) 110.8(6)
C(23A) - II(1A) - I'(2A) C(22A) Ir(1A) D(1A)	97.9(3)	C(0A) - F(2A) - C(17A) C(21A) P(2A) - C(17A)	110.0(0)
C(32A) - II(1A) - F(1A)	97.0(3) 81.2(4)	C(21A)-F(2A)-C(1/A)	111.0(0) 07.2(5)
C(1A)-II(1A)-P(1A)	81.2(4)	$C(\delta A)$ -P(2A)-If(1A) C(21A) P(2A) Ir(1A)	97.3(3) 121.5(5)
C(25A)-Ir(1A)-P(1A)	98.4(3)	C(21A)-P(2A)-Ir(1A)	121.5(5)
P(2A)-Ir(1A)-P(1A)	157.7(3)	C(17A)-P(2A)-Ir(1A)	112.5(4)
C(32A)- $Ir(1A)$ - $H(1A)$	175.5(4)	C(2A)-C(1A)-Ir(1A)	121.8(6)
C(1A)- $Ir(1A)$ - $H(1A)$	89.3(3)	C(6A)- $C(1A)$ - $Ir(1A)$	117.9(6)
C(25A)-Ir(1A)-H(1A)	86.2(3)	C(26A)-C(25A)-Ir(1A)	118.9(3)
P(2A)-Ir(1A)-H(1A)	82.4(4)	C(30A)-C(25A)-Ir(1A)	121.0(3)
P(1A)-Ir(1A)-H(1A)	83.6(4)	O(1A)-C(32A)-Ir(1A)	172.2(8)
C(13A)-P(1A)-C(7A)	100.2(6)		
C(13A)-P(1A)-C(9A)	108.4(5)		

 Table 2.15.
 Selected bond lengths [Å] and angles [°] for 2-14.





Empirical formula	C31 H45 F4 Ir O P2	
Formula weight	763.81	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 18.2060(14) Å	a= 90°.
	b = 16.8972(13) Å	b= 90°.
	c = 20.0222(15) Å	g = 90°.
Volume	6159.4(8) Å ³	
Ζ	8	
Density (calculated)	1.647 Mg/m ³	
Absorption coefficient	4.487 mm ⁻¹	
F(000)	3056	
Crystal size	$0.40 \ge 0.36 \ge 0.076 \text{ mm}^3$	
Theta range for data collection	1.93 to 31.50°.	
Index ranges	-26<=h<=26, -24<=k<=24	4, - 29<=l<=29
Reflections collected	74277	
Independent reflections	10258 [R(int) = 0.0291]	
Completeness to theta = 31.50°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.7150 and 0.2106	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	10258 / 1 / 367	
Goodness-of-fit on F ²	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0285, WR2 = 0.064	41
R indices (all data)	R1 = 0.0351, $wR2 = 0.067$	76
Largest diff. peak and hole	5.217 and -1.515 e.Å ⁻³	

 Table 2.16.
 Crystal data and structure refinement for 2-15.

Ir(1)-C(31)	1.927(3)	P(2)-C(8)	1.841(3)
Ir(1)-C(1)	2.106(3)	P(2)-C(17)	1.883(3)
Ir(1)-C(25)	2.146(3)	P(2)-C(21)	1.891(3)
Ir(1)-P(1)	2.3379(7)	F(1)-C(26)	1.369(4)
Ir(1)-P(2)	2.3428(7)	F(2)-C(27)	1.348(3)
Ir(1)-H(1)	1.583(10)	F(3)-C(28)	1.349(3)
P(1)-C(7)	1.835(3)	F(4)-C(29)	1.357(4)
P(1)-C(9)	1.886(3)	O(1)-C(31)	1.143(4)
P(1)-C(13)	1.888(3)		
C(31)-Ir(1)-C(1)	83.69(11)	P(2)-Ir(1)-H(1)	81.7(12)
C(31)-Ir(1)-C(25)	98.33(11)	C(7)-P(1)-C(9)	105.64(14)
C(1)-Ir(1)-C(25)	177.94(10)	C(7)-P(1)-C(13)	102.46(13)
C(31)-Ir(1)-P(1)	96.38(9)	C(9)-P(1)-C(13)	109.79(13)
C(1)-Ir(1)-P(1)	81.49(8)	C(7)-P(1)-Ir(1)	101.20(10)
C(25)-Ir(1)-P(1)	97.82(7)	C(9)-P(1)-Ir(1)	119.29(10)
C(31)-Ir(1)-P(2)	98.39(9)	C(13)-P(1)-Ir(1)	115.97(9)
C(1)-Ir(1)-P(2)	81.86(8)	C(8)-P(2)-C(17)	104.61(13)
C(25)-Ir(1)-P(2)	98.23(7)	C(8)-P(2)-C(21)	103.24(13)
P(1)-Ir(1)-P(2)	156.33(2)	C(17)-P(2)-C(21)	110.21(13)
C(31)-Ir(1)-H(1)	172.4(12)	C(8)-P(2)-Ir(1)	102.17(10)
C(1)-Ir(1)-H(1)	88.8(12)	C(17)-P(2)-Ir(1)	119.80(9)
C(25)-Ir(1)-H(1)	89.2(12)	C(21)-P(2)-Ir(1)	114.47(9)
P(1)-Ir(1)-H(1)	81.2(12)	O(1)-C(31)-Ir(1)	171.9(3)

Table 2.17. Selected bond lengths [Å] and angles [°] for 2-15.



Figure 2.36. X-ray crystal structure for compound 2-17.

Empirical formula	C31.50 H45.50 F5 Ir P2	
Formula weight	773.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.6945(8) Å	a= 65.436(1)°.
	b = 17.6452(13) Å	b=75.348(1)°.
	c = 19.1011(14) Å	$g = 80.524(1)^{\circ}$.
Volume	3164.4(4) Å ³	
Ζ	4	
Density (calculated)	1.623 Mg/m ³	
Absorption coefficient	4.370 mm ⁻¹	
F(000)	1546	
Crystal size	0.28 x 0.16 x 0.08 mm ³	
Theta range for data collection	1.97 to 31.00°.	
Index ranges	-15<=h<=15, -25<=k<=2	5, - 27<=l<=27
Reflections collected	39089	
Independent reflections	19848 [R(int) = 0.0253]	
Completeness to theta = 31.00°	98.4 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.7462 and 0.5718	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	19848 / 6 / 742	
Goodness-of-fit on F ²	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0335, WR2 = 0.077	73
R indices (all data)	R1 = 0.0436, w $R2 = 0.08$	17
Largest diff. peak and hole 2.338 and -1.0	02 e.Å ⁻³	

 Table 2.18.
 Crystal data and structure refinement for 2-17.

Ir(1)-C(1)	2.077(3)	P(2)-C(17)	1.880(3)
Ir(1)-C(25)	2.133(3)	P(2)-C(21)	1.881(4)
Ir(1)-P(1)	2.3102(8)	F(1)-C(26)	1.364(4)
Ir(1)-P(2)	2.3293(8)	F(2)-C(27)	1.355(4)
Ir(1)-H(1)	1.589(10)	F(3)-C(28)	1.343(4)
P(1)-C(7)	1.836(3)	F(4)-C(29)	1.353(4)
P(1)-C(13)	1.879(3)	F(5)-C(30)	1.364(4)
P(1)-C(9)	1.881(4)		
P(2)-C(8)	1.835(3)		
C(1)-Ir(1)-C(25)	175.14(12)	C(13)-P(1)-C(9)	112.72(16)
C(1)-Ir(1)-P(1)	81.61(9)	C(7)-P(1)-Ir(1)	102.87(11)
C(25)-Ir(1)-P(1)	98.60(8)	C(13)-P(1)-Ir(1)	121.10(11)
C(1)-Ir(1)-P(2)	81.31(9)	C(9)-P(1)-Ir(1)	110.59(12)
C(25)-Ir(1)-P(2)	98.68(8)	C(8)-P(2)-C(17)	103.34(15)
P(1)-Ir(1)-P(2)	162.64(3)	C(8)-P(2)-C(21)	104.10(16)
C(1)-Ir(1)-H(1)	93.2(5)	C(17)-P(2)-C(21)	110.74(17)
C(25)-Ir(1)-H(1)	91.6(5)	C(8)-P(2)-Ir(1)	102.51(11)
P(1)-Ir(1)-H(1)	89.7(4)	C(17)-P(2)-Ir(1)	120.40(11)
P(2)-Ir(1)-H(1)	88.2(4)	C(21)-P(2)-Ir(1)	113.42(12)
C(7)-P(1)-C(13)	103.11(16)		
C(7)-P(1)-C(9)	104.15(18)		

Table 2.19. Selected bond lengths [Å] and angles [°] for 2-17.





Empirical formula	C31 H46 F3 Ir O P2	
Formula weight	745.82	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 17.9402(12) Å	a= 90°.
	b = 16.8844(11) Å	b= 90°.
	c = 19.8634(13) Å	g = 90°.
Volume	6016.8(7) Å ³	
Z	8	
Density (calculated)	1.647 Mg/m ³	
Absorption coefficient	4.586 mm ⁻¹	
F(000)	2992	
Crystal size	0.21 x 0.11 x 0.04 mm ³	
Theta range for data collection	1.95 to 31.00°.	
Index ranges	-26<=h<=26, -24<=k<=2	3, -28<=l<=28
Reflections collected	70858	
Independent reflections	9564 [R(int) = 0.0323]	
Completeness to theta = 31.00°	99.7 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.746 and 0.553	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	9564 / 1 / 358	
Goodness-of-fit on F ²	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0232, wR2 = 0.054	46
R indices (all data)	R1 = 0.0297, wR2 = 0.057	77
Largest diff. peak and hole	4.019 and -0.936 e.Å ⁻³	

 Table 2.20.
 Crystal data and structure refinement for 2-18.

Ir(1)-C(31)	1.930(2)	P(1)-C(9)	1.890(2)
Ir(1)-C(1)	2.105(2)	P(2)-C(8)	1.833(2)
Ir(1)-C(25)	2.170(2)	P(2)-C(17)	1.891(2)
Ir(1)-P(2)	2.3514(5)	P(2)-C(21)	1.892(2)
Ir(1)-P(1)	2.3551(5)	F(1)-C(26)	1.363(3)
Ir(1)-H(1)	1.581(9)	F(2)-C(28)	1.361(3)
P(1)-C(7)	1.835(2)	F(3)-C(30)	1.375(3)
P(1)-C(13)	1.888(2)	O(1)-C(31)	1.143(3)
C(31)-Ir(1)-C(1)	83.12(8)	P(1)-Ir(1)-H(1)	81.3(9)
C(31)-Ir(1)-C(25)	97.18(9)	C(7)-P(1)-C(13)	103.57(10)
C(1)-Ir(1)-C(25)	179.65(8)	C(7)-P(1)-C(9)	102.79(10)
C(31)-Ir(1)-P(2)	95.97(7)	C(13)-P(1)-C(9)	109.83(10)
C(1)-Ir(1)-P(2)	81.07(6)	C(7)-P(1)-Ir(1)	102.30(7)
C(25)-Ir(1)-P(2)	98.72(6)	C(13)-P(1)-Ir(1)	120.58(7)
C(31)-Ir(1)-P(1)	97.46(7)	C(9)-P(1)-Ir(1)	115.05(7)
C(1)-Ir(1)-P(1)	81.46(6)	C(8)-P(2)-C(17)	101.79(10)
C(25)-Ir(1)-P(1)	98.68(5)	C(8)-P(2)-C(21)	104.29(10)
P(2)-Ir(1)- $P(1)$	156.467(19)	C(17)-P(2)-C(21)	110.32(10)
C(31)-Ir(1)-H(1)	172.6(10)	C(8)-P(2)-Ir(1)	101.09(7)
C(1)-Ir(1)-H(1)	89.5(9)	C(17)-P(2)-Ir(1)	117.00(7)
C(25)-Ir(1)-H(1)	90.2(9)	C(21)-P(2)-Ir(1)	119.25(7)
P(2)-Ir(1)-H(1)	82.9(9)	O(1)-C(31)-Ir(1)	171.8(2)

Table 2.21. Selected bond lengths [Å] and angles [°] for 2-18.



Figure 2.38. X-ray crystal structure for compound 2-25.

Empirical formula	C31 H47 Cl2 Ir O P2	
Formula weight	760.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbcn	
Unit cell dimensions	a = 31.4158(18) Å	a= 90°.
	b = 12.5241(7) Å	b= 90°.
	c = 16.3015(10) Å	g = 90°.
Volume	6413.9(6) Å ³	
Ζ	8	
Density (calculated)	1.576 Mg/m ³	
Absorption coefficient	4.452 mm ⁻¹	
F(000)	3056	
Crystal size	0.24 x 0.23 x 0.07 mm ³	
Theta range for data collection	1.75 to 32.04°.	
Index ranges	-46<=h<=46, -18<=k<=18, -24<=l<=24	
Reflections collected	82148	
Independent reflections	11178 [R(int) = 0.0550]	
Completeness to theta = 32.04°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.4146	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11178 / 1018 / 492	
Goodness-of-fit on F ²	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0525, $wR2 = 0.1146$	
R indices (all data)	R1 = 0.0715, $wR2 = 0.1230$	
Largest diff. peak and hole	2.487 and -3.135 e.Å ⁻³	

 Table 2.22.
 Crystal data and structure refinement for 2-25.
Ir(1A)-C(31)	1.918(5)	C(7A)-P(1)	1.856(10)
Ir(1A)-C(1)	2.115(5)	C(9A)-P(1)	1.883(11)
Ir(1A)-C(25)	2.163(5)	C(13A)-P(1)	1.876(11)
Ir(1A)-P(2)	2.3386(12)	C(31)-O(1)	1.150(7)
Ir(1A)-P(1)	2.3612(12)	P(2)-C(8)	1.843(6)
Ir(1A)-H(1A)	1.5933(2)	P(2)-C(17)	1.865(6)
Cl(1A)-C(26)	1.762(6)	P(2)-C(21)	1.906(6)
Cl(2A)-C(29)	1.754(7)		
C(31)-Ir(1A)-C(1)	85.7(2)	C(2)-C(7A)-P(1)	108.7(6)
C(31)-Ir(1A)-C(25)	99.7(2)	P(1)-C(7A)-H(7A1)	110.0
C(1)-Ir(1A)-C(25)	174.0(2)	P(1)-C(7A)-H(7A2)	110.0
C(31)-Ir(1A)-P(2)	96.24(17)	C(12A)-C(9A)-P(1)	109.5(8)
C(1)-Ir(1A)-P(2)	80.41(14)	C(10A)-C(9A)-P(1)	110.8(9)
C(25)-Ir(1A)-P(2)	96.30(14)	C(11A)-C(9A)-P(1)	113.3(10)
C(31)-Ir(1A)-P(1)	99.75(17)	C(15A)-C(13A)-P(1)	110.8(8)
C(1)-Ir(1A)-P(1)	81.08(14)	C(14A)-C(13A)-P(1)	112.2(14)
C(25)-Ir(1A)-P(1)	100.43(14)	C(16A)-C(13A)-P(1)	107.3(8)
P(2)-Ir(1A)- $P(1)$	154.47(4)	C(26)-C(25)-Ir(1A)	129.2(4)
C(31)-Ir(1A)-H(1A)	173.37(17)	C(30)-C(25)-Ir(1A)	118.4(4)
C(1)-Ir(1A)-H(1A)	87.93(14)	C(27)-C(26)-Cl(1A)	112.8(5)
C(25)-Ir(1A)-H(1A)	86.59(16)	C(25)-C(26)-Cl(1A)	122.7(4)
P(2)-Ir(1A)-H(1A)	80.84(4)	O(1)-C(31)-Ir(1A)	170.1(5)
P(1)-Ir(1A)-H(1A)	81.06(3)		

Table 2.23. Selected bond lengths [Å] and angles [°] for 2-25.





Empirical formula	C26.5 H50 Br Ir P2	
Formula weight	702.72	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	P6(1)22	
Unit cell dimensions	a = 16.4749(15) Å	a= 90°.
	b = 16.4749(15) Å	b= 90°.
	c = 19.3064(17) Å	g = 120°.
Volume	4538.1(7) Å ³	
Z	6	
Density (calculated)	1.543 Mg/m ³	
Absorption coefficient	5.851 mm ⁻¹	
F(000)	2106	
Crystal size	0.25 x 0.08 x 0.03 mm ³	
Theta range for data collection	2.47 to 26.37°.	
Index ranges	-20<=h<=20, -18<=k<=20, -24<=l<=17	
Reflections collected	25092	
Independent reflections	3113 [R(int) = 0.0681]	
Completeness to theta = 26.37°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8440 and 0.3225	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3113 / 10 / 156	
Goodness-of-fit on F ²	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0271, $wR2 = 0.0596$	
R indices (all data)	R1 = 0.0350, wR2 = 0.0627	
Absolute structure parameter	-0.011(11)	
Largest diff. peak and hole	1.094 and -0.649 e.Å ⁻³	

Table 2.24. Crystal data and structure refinement for 2-28.

Ir(1)-C(1)	2.032(6)	P(1)-C(5)	1.840(5)
Ir(1)-P(1)	2.3113(14)	P(1)-C(6)	1.881(5)
Ir(1)-P(1)#1	2.3113(14)	P(1)-C(10)	1.895(5)
Ir(1)-Br(1)	2.5443(7)		
Ir(1)-H(1)	1.59(2)		
C(1)-Ir(1)-P(1)	82.48(3)	P(1)#1-Ir(1)-H(1)	104.7(11)
C(1)-Ir(1)-P(1)#1	82.48(3)	Br(1)-Ir(1)-H(1)	81.5(14)
P(1)-Ir(1)-P(1)#1	164.96(6)	C(5)-P(1)-C(6)	103.5(2)
C(1)-Ir(1)-Br(1)	180.000(15)	C(5)-P(1)-C(10)	104.6(3)
P(1)-Ir(1)-Br(1)	97.52(3)	C(6)-P(1)-C(10)	111.7(2)
P(1)#1-Ir(1)-Br(1)	97.52(3)	C(5)-P(1)-Ir(1)	101.66(18)
C(1)-Ir(1)-H(1)	98.5(14)	C(6)-P(1)-Ir(1)	119.80(17)
P(1)-Ir(1)-H(1)	77.6(10)	C(10)-P(1)-Ir(1)	113.26(16)

Table 2.25. Selected bond lengths [Å] and angles [°] for 2-28.





Empirical formula	C34 H54.50 Br Ir O P2	
Formula weight	813.33	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.1155(14) Å	a= 88.759(2)°.
	b = 16.0779(14) Å	b= 66.929(2)°.
	c = 17.0100(15) Å	$g = 65.310(2)^{\circ}$
Volume	3405.3(5) Å ³	
Ζ	4	
Density (calculated)	1.586 Mg/m ³	
Absorption coefficient	5.213 mm ⁻¹	
F(000)	1634	
Crystal size	$0.56 \ge 0.09 \ge 0.02 \text{ mm}^3$	
Theta range for data collection	1.76 to 32.10°.	
Index ranges	-20<=h<=22, -23<=k<=2	3, 0<=l<=25
Reflections collected	38262	
Independent reflections	38262 [R(int) = 0.0000]	
Completeness to theta = 32.10°	98.1 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8989 and 0.2342	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	38262 / 1133 / 766	
Goodness-of-fit on F ²	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.096	66
R indices (all data)	R1 = 0.0655, WR2 = 0.102	26
Largest diff. peak and hole	2.965 and -1.714 e.Å ⁻³	

 Table 2.26.
 Crystal data and structure refinement for 2-29.

Ir(1)-C(32)	1.912(4)	P(1)-C(13)	1.893(4)
Ir(1)-C(1)	2.050(3)	P(1)-C(9)	1.899(4)
Ir(1)-C(25)	2.139(4)	P(2)-C(8)	1.839(4)
Ir(1)-P(1)	2.3892(9)	P(2)-C(17)	1.905(4)
Ir(1)-P(2)	2.4199(9)	P(2)-C(21)	1.907(4)
Ir(1)-Br(1)	2.6270(4)	O(1)-C(32)	1.140(4)
P(1)-C(7)	1.836(3)		
C(32)-Ir(1)-C(1)	89.12(14)	C(7)-P(1)-C(13)	106.96(16)
C(32)-Ir(1)-C(25)	178.49(15)	C(7)-P(1)-C(9)	102.38(16)
C(1)-Ir(1)-C(25)	92.06(13)	C(13)-P(1)-C(9)	107.68(16)
C(32)-Ir(1)-P(1)	90.83(11)	C(7)-P(1)-Ir(1)	98.82(11)
C(1)-Ir(1)-P(1)	81.16(10)	C(13)-P(1)-Ir(1)	123.28(12)
C(25)-Ir(1)-P(1)	90.28(10)	C(9)-P(1)-Ir(1)	114.88(12)
C(32)-Ir(1)-P(2)	88.44(11)	C(8)-P(2)-C(17)	105.75(16)
C(1)-Ir(1)-P(2)	81.24(10)	C(8)-P(2)-C(21)	101.79(17)
C(25)-Ir(1)-P(2)	90.81(10)	C(17)-P(2)-C(21)	108.56(17)
P(1)-Ir(1)-P(2)	162.39(3)	C(8)-P(2)-Ir(1)	95.96(12)
C(32)-Ir(1)-Br(1)	85.38(11)	C(17)-P(2)-Ir(1)	117.89(12)
C(1)-Ir(1)-Br(1)	173.40(9)	C(21)-P(2)-Ir(1)	122.89(12)
C(25)-Ir(1)-Br(1)	93.49(10)		
P(1)-Ir(1)-Br(1)	95.25(2)	Torsion angle:	
P(2)-Ir(1)-Br(1)	102.22(3)	C(1)-Ir(1)-C(25)-C(30)	-10.5(3)

Table 2.27. Selected bond lengths [Å] and angles [°] for 2-29.





Empirical formula	C33 H47 F6 Ir O P2	
Formula weight	827.85	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.3529(5) Å	a= 78.289(1)°.
	b = 16.3317(8) Å	b= 82.948(1)°.
	c = 19.2587(9) Å	$g = 78.669(1)^{\circ}$.
Volume	3415.5(3) Å ³	
Ζ	4	
Density (calculated)	1.610 Mg/m ³	
Absorption coefficient	4.060 mm ⁻¹	
F(000)	1656	
Crystal size	0.28 x 0.10 x 0.05 mm	m ³
Theta range for data collection	1.83 to 29.58°.	
Index ranges	-15<=h<=15, -22<=k<=22, -26<=l<=26	
Reflections collected	38559	
Independent reflections	18955 [R(int) = 0.030)5]
Completeness to theta = 29.58°	98.9 %	
Absorption correction	Semi-empirical from	equivalents
Max. and min. transmission	0.8228 and 0.3960	
Refinement method	Full-matrix least-squa	ares on F ²
Data / restraints / parameters	18955 / 1636 / 944	
Goodness-of-fit on F ²	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0	0.0736
R indices (all data)	R1 = 0.0446, WR2 = 0	0.0785
Largest diff. peak and hole	2.803 and -1.018 e.Å	-3

Table 2.28. Crystal data and structure refinement for 2-33.

Ir(1)-C(33)	1.914(3)	P(2)-C(21)	1.886(3)
Ir(1)-C(1)	2.110(3)	P(2)-C(17)	1.893(3)
Ir(1)-C(25)	2.141(3)	F(1)-C(31)	1.334(5)
Ir(1)-P(2)	2.3347(8)	F(2)-C(31)	1.339(5)
Ir(1)-P(1)	2.3434(8)	F(3)-C(31)	1.335(4)
Ir(1)-H(1)	1.594(10)	F(4)-C(32)	1.341(4)
P(1)-C(7)	1.836(3)	F(5)-C(32)	1.347(5)
P(1)-C(13)	1.878(3)	F(6)-C(32)	1.338(4)
P(1)-C(9)	1.889(3)	O(1)-C(33)	1.140(4)
P(2)-C(8)	1.839(3)		
C(33)-Ir(1)-C(1)	91.63(13)	C(7)-P(1)-C(9)	102.97(15)
C(33)-Ir(1)-C(25)	93.74(13)	C(13)-P(1)-C(9)	110.65(15)
C(1)-Ir(1)-C(25)	174.59(12)	C(7)-P(1)-Ir(1)	101.35(11)
C(33)-Ir(1)-P(2)	95.21(10)	C(13)-P(1)-Ir(1)	117.22(11)
C(1)-Ir(1)-P(2)	79.60(9)	C(9)-P(1)-Ir(1)	118.10(11)
C(25)-Ir(1)-P(2)	99.21(8)	C(8)-P(2)-C(21)	104.54(15)
C(33)-Ir(1)-P(1)	100.04(10)	C(8)-P(2)-C(17)	104.28(17)
C(1)-Ir(1)-P(1)	81.70(9)	C(21)-P(2)-C(17)	109.92(15)
C(25)-Ir(1)-P(1)	98.01(8)	C(8)-P(2)-Ir(1)	99.64(11)
P(2)-Ir(1)-P(1)	156.12(3)	C(21)-P(2)-Ir(1)	120.73(11)
C(33)-Ir(1)-H(1)	176.0(12)	C(17)-P(2)-Ir(1)	115.11(11)
C(1)-Ir(1)-H(1)	87.9(12)	C(2)-C(1)-C(6)	117.8(3)
C(25)-Ir(1)-H(1)	86.7(12)	C(2)-C(1)-Ir(1)	121.5(2)
P(2)-Ir(1)-H(1)	80.8(12)	C(6)-C(1)-Ir(1)	120.6(2)
P(1)-Ir(1)-H(1)	83.9(12)	O(1)-C(33)-Ir(1)	178.5(3)
C(7)-P(1)-C(13)	103.76(16)		

Table 2.29. Selected bond lengths [Å] and angles [°] for 2-33.





Empirical formula	C33 H47 F6 Ir O P2	
Formula weight	827.85	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.4309(6) Å	a= 90°.
	b = 21.5496(13) Å	b= 108.771(1)°.
	c = 15.6373(10) Å	g = 90°.
Volume	3328.0(3) Å ³	
Z	4	
Density (calculated)	1.652 Mg/m ³	
Absorption coefficient	4.167 mm ⁻¹	
F(000)	1656	
Crystal size	0.09 x 0.07 x 0.01 mm ³	
Theta range for data collection	1.89 to 31.60°.	
Index ranges	-15<=h<=15, -31<=k<=31, -22<=l<=23	
Reflections collected	42886	
Independent reflections	11125 [R(int) = 0.0215]	
Completeness to theta = 31.60°	99.6 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.9595 and 0.7055	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	11125 / 1 / 403	
Goodness-of-fit on F ²	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0168, WR2 = 0.0393	
R indices (all data)	R1 = 0.0196, $wR2 = 0.0404$	
Largest diff. peak and hole	0.950 and -0.384 e.Å ⁻³	

Table 2.30. Crystal data and structure refinement for 2-34.

Ir(1)-C(33)	1.9182(15)	P(2)-C(17)	1.8960(15)
Ir(1)-C(1)	2.1072(14)	P(2)-C(21)	1.9090(15)
Ir(1)-C(25)	2.1774(14)	F(1)-C(31)	1.3394(18)
Ir(1)-P(1)	2.3527(4)	F(2)-C(31)	1.3485(19)
Ir(1)-P(2)	2.3663(4)	F(3)-C(31)	1.3501(17)
Ir(1)-H(1)	1.584(9)	F(4)-C(32)	1.3343(19)
P(1)-C(7)	1.8411(15)	F(5)-C(32)	1.333(2)
P(1)-C(13)	1.8891(15)	F(6)-C(32)	1.338(2)
P(1)-C(9)	1.8966(15)	O(1)-C(33)	1.1410(19)
P(2)-C(8)	1.8378(15)		
C(33) Ir(1) $C(1)$	92 94(6)	C(7) P(1) C(12)	103 62(7)
C(33)-II(1)- $C(1)$	92.94(0) 102.07(6)	$C(7)$ - $\Gamma(1)$ - $C(13)$	103.02(7)
C(33)-II(1)- $C(23)$	103.07(0)	C(1) - F(1) - C(3) C(12) P(1) C(0)	102.12(7)
C(1)-If(1)- $C(25)$	162.87(5)	C(13)-P(1)-C(9)	110.28(7)
C(33)-Ir(1)-P(1)	97.74(5)	C(7)-P(1)-Ir(1)	100.30(5)
C(1)-Ir(1)-P(1)	80.05(4)	C(13)-P(1)-Ir(1)	118.97(5)
C(25)-Ir(1)-P(1)	103.42(4)	C(9)-P(1)-Ir(1)	118.14(5)
C(33)-Ir(1)-P(2)	92.36(5)	C(8)-P(2)-C(17)	104.00(7)
C(1)-Ir(1)-P(2)	78.63(4)	C(8)-P(2)-C(21)	103.36(7)
C(25)-Ir(1)-P(2)	94.46(4)	C(17)-P(2)-C(21)	109.46(7)
P(1)-Ir(1)-P(2)	156.811(13)	C(8)-P(2)-Ir(1)	98.19(5)
C(33)-Ir(1)-H(1)	174.0(6)	C(17)-P(2)-Ir(1)	121.47(5)
C(1)-Ir(1)-H(1)	83.4(7)	C(21)-P(2)-Ir(1)	116.88(5)
C(25)-Ir(1)-H(1)	81.1(7)	C(2)-C(1)-Ir(1)	120.96(10)
P(1)-Ir(1)-H(1)	77.0(7)	C(6)-C(1)-Ir(1)	120.63(11)
P(2)-Ir(1)-H(1)	91.5(7)	O(1)-C(33)-Ir(1)	173.61(14)

Table 2.31. Selected bond lengths [Å] and angles [°] for 2-34.



Figure 2.43. X-ray crystal structure for compound 2-39.

Empirical formula	C32 H50 F Ir O P2	
Formula weight	723.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 17.8663(15) Å	a= 90°.
	b = 17.1070(14) Å	b= 90°.
	c = 20.1100(17) Å	$g = 90^{\circ}$.
Volume	6146.4(9) Å ³	
Ζ	8	
Density (calculated)	1.564 Mg/m ³	
Absorption coefficient	4.478 mm ⁻¹	
F(000)	2928	
Crystal size	0.24 x 0.11 x 0.07 mm ³	
Theta range for data collection	1.93 to 30.03°.	
Index ranges	-25<=h<=24, -24<=k<=24, -28<=l<=28	
Reflections collected	65868	
Independent reflections	8986 [R(int) = 0.0502]	
Completeness to theta = 30.03°	99.9 %	
Absorption correction	Semi-empirical from equiv	valents
Max. and min. transmission	on 0.7446 and 0.4129	
Refinement method	Full-matrix least-squares of	on F^2
Data / restraints / parameters	8986 / 1 / 351	
Goodness-of-fit on F ²	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0254, WR2 = 0.0554	
R indices (all data)	R1 = 0.0412, wR2 = 0.063	31
Largest diff. peak and hole	3.122 and -0.847 e.Å ⁻³	

Table 2.32. Crystal data and structure refinement for 2-39.

Ir(1)-C(32)	1.933(3)	P(1)-C(13)	1.891(3)
Ir(1)-C(1)	2.114(3)	P(1)-C(9)	1.892(3)
Ir(1)-C(25)	2.154(3)	P(2)-C(8)	1.838(3)
Ir(1)-P(2)	2.3409(7)	P(2)-C(17)	1.888(3)
Ir(1)-P(1)	2.3458(7)	P(2)-C(21)	1.892(3)
Ir(1)-H(1)	1.593(10)	F(1)-C(26)	1.392(3)
P(1)-C(7)	1.840(3)	O(1)-C(32)	1.140(3)
C(32)-Ir(1)-C(1)	83.62(12)	C(7)-P(1)-C(9)	104.16(13)
C(32)-Ir(1)-C(25)	97.53(12)	C(13)-P(1)-C(9)	109.45(13)
C(1)-Ir(1)-C(25)	178.49(10)	C(7)-P(1)-Ir(1)	101.89(9)
C(32)-Ir(1)-P(2)	97.57(9)	C(13)-P(1)-Ir(1)	121.17(9)
C(1)-Ir(1)-P(2)	81.50(8)	C(9)-P(1)-Ir(1)	114.30(9)
C(25)-Ir(1)-P(2)	97.36(8)	C(8)-P(2)-C(17)	102.13(13)
C(32)-Ir(1)-P(1)	97.70(9)	C(8)-P(2)-C(21)	104.60(13)
C(1)-Ir(1)-P(1)	81.38(8)	C(17)-P(2)-C(21)	110.16(13)
C(25)-Ir(1)-P(1)	99.41(7)	C(8)-P(2)-Ir(1)	101.57(10)
P(2)-Ir(1)- $P(1)$	155.57(3)	C(17)-P(2)-Ir(1)	115.76(9)
C(32)-Ir(1)-H(1)	176.5(18)	C(21)-P(2)-Ir(1)	119.82(10)
C(1)-Ir(1)-H(1)	94.1(17)	C(6)-C(1)-Ir(1)	120.6(2)
C(25)-Ir(1)-H(1)	84.7(17)	C(2)-C(1)-Ir(1)	121.7(2)
P(2)-Ir(1)-H(1)	79.5(17)	C(26)-C(25)-Ir(1)	124.4(2)
P(1)-Ir(1)-H(1)	84.5(17)	C(30)-C(25)-Ir(1)	124.5(2)
C(7)-P(1)-C(13)	103.44(14)	O(1)-C(32)-Ir(1)	172.3(3)

Table 2.33. Selected bond lengths [Å] and angles [°] for 2-39.

Chapter 3

Reaction of (PCP)Ir with Naphthalene and a series of Naphthalene derivatives

Abstract

Whereas chapter 2 focused on results with benzene and benzene derivatives, results are presented in this chapter for C-H activation experiments with (PCP)Ir and naphthalene. Unlike benzene, naphthalene has two unique types of C-H bonds, and results show that (PCP)Ir will only oxidatively add *one* of them. Experiments with dimethyl derivatives of naphthalene were conducted in order to identify which C-H bonds are activated, and variable temperature NMR studies produced compelling evidence for a hypothesis concerning a mechanism involving η^2 -aryl π coordination. For each C-H activation reaction, there are two possible products, and observations concerning the thermodynamics and kinetics leading to these are also presented.

Several naphthalene derivatives were studied in order to further probe the reactivity of this substrate. 1-Fluoronaphthalene reacts with (PCP)Ir giving results analogous to those with fluorobenzene: *ortho* C-H activation is the dominant process. Two methoxynaphthalene derivatives yielded illuminating results concerning the mechanism and thermodynamic advantage of cyclometalation reactions.

3.1 Introduction

Benzene is among the simplest, most ubiquitous, and useful of the aromatic hydrocarbons. The special stability gained by having a de-localized π -electron system arranged in a cyclic geometry allows this small molecule to serve as a robust framework for a huge array of functional groups and their associated electronic influences. As such, benzene is a fundamental component of innumerable organic compounds and synthetic transformations. Naphthalene, one size larger in the aromatic family of compounds (10 π -electrons), has similar reactivity and electronic properties to benzene, but also exhibits several key structural differences.

In contrast with unsubstituted benzene, in which all six carbon-hydrogen bonds are equivalent, naphthalene contains two geometrically unique types of C-H bonds (Fig. 3.1). In addition, the C-C bonds are *not* all the same length.

Figure 3.1. Structural features of naphthalene



These structural features contribute to interesting patterns of reactivity that have been studied in various contexts with organometallic complexes since Chatt's groundbreaking experiments with ruthenium in the 1960's.¹ Perhaps the single most important aspect of the interaction between naphthalene and metal complexes, is the distinctly favorable π -coordination (η^2) mode that naphthalene can adopt in a variety of systems.¹⁻⁷ The prevalence of this ligand binding mode has been thoroughly studied and for many transition metal complexes, there is an equilibrium between η^1 and η^2 conformations (eq. 1).^{3,5}

C-H activation reactions of naphthalene have been studied far less thoroughly than for benzene, and have tended to focus, understandably, on the fundamental differences in reactivity between the α and β positions and the potential ramifications for regioselectivity in activation processes.⁸⁻¹² Calculated bond dissociation energies have yielded comparable values for the two types of C-H bonds (111 ± 0.3 kcal/mol).¹³

Various functionalization reactions have been studied with naphthalene, including the addition of alkyl or aryl substituents,^{14,15} and there have been many much more specialized applications studied under both stoichiometric and catalytic conditions.¹⁶⁻²¹ There has even been at least one pincer-type ligand system synthesized with naphthalene as the fulcrum of the backbone.²²

While there are far fewer commercially available naphthalene derivatives as compared with benzene, most of them have substituents at carbon (1), probably owing to the preference for electrophilic aromatic substitution reactions at that position. Results from our experiments show that (PCP)Ir activates naphthalene β C-H bonds *exclusively* (*vide infra*), therefore making this a potentially valuable approach to selectively functionalized naphthalene derivatives. In addition, cyclometalation reactions with naphthalene have not been well-studied,²³ and can be strategically exploited with the (PCP)Ir complex according to results reported later in this chapter.

3.2 Results and Discussion

3.2.1 Synthesis and characterization of iridium naphthyl complex 3-1 from the reaction of (PCP)Ir with naphthalene

Initially, reactions with (PCP)Ir and napthalene were studied in order to determine whether the metal center would preferentially activate either the α or β C-H bonds. There are two factors that contribute to α C-H bonds being potentially less attractive to (PCP)Ir. First, the α carbon is the preferred target in electrophilic substitution reactions involving naphthalene, due to the more favorable resonance structures available for the intermediate in this reaction (7 total resonance forms, with 4 that preserve the aromaticity; electrophilic attack at the β position requires an intermediate with 6 resonance forms, only 2 of which are aromatic). Given the results discussed in chapter 2, (PCP)Ir acts more as a nucleophile than an electrophile (i.e., (PCP)Ir preferentially activates C-H bonds in *less* electron rich substrates), and so it would be likely to prefer β C-H bonds. Second, C-H activation at the α position would result in having an sp² C-C bond *ortho* to the Ir-C bond in the oxidative addition product. While the resulting configuration should be less sterically hindered than for activation *ortho* to a methyl substituent (Fig. 3.2), similar C-H activation reactions have not been previously detected in past experiments conducted by our research group.



The reaction of (PCP)IrH₂ with an alkene acceptor such as norbornene (NBE) is known to generate a precursor of the reactive fragment "(PCP)Ir".²⁴ Reaction of (PCP)IrH₂ and NBE with excess naphthalene at ambient temperature results in disappearance of the peak corresponding to the parent complex in the ³¹P NMR spectrum accompanied by the appearance of a single peak at δ 68.0 ppm. The ¹H NMR spectrum shows signals characteristic of a PCP ligand in a fully symmetrical environment, i.e., all *tert*-butyl and methylene linker protons are equivalent. A broad hydride (Ir-H) resonance is observed at -45.52 ppm – precisely the same chemical shift as seen for the (PCP)Ir(phenyl)(H) complex. This signal – far upfield from all the remaining aryl and PCP protons – is indicative of a five-coordinate d⁶ metal complex.²⁵ In the absence of naphthalene, (PCP)IrH₂ and norbornene produce a labile "NBE complex" that appears as a broad singlet in the ³¹P NMR spectrum at 62.9 ppm. There is no Ir-H signal in the ¹H NMR spectrum for the NBE complex, even at low temperature, for reasons discussed previously.

In the presence of a small excess of naphthalene at temperatures lower than ~0 °C, the hydride (Ir-H) signal begins to sharpen and separate into two separate resonances, indicative of the presence of two closely related C-H activation products. Additionally,

the remainder of the spectrum transforms from an assemblage of rather broad peaks at room temperature to significantly sharper resonances indicative of a non-symmetric environment at lower temperatures: PCP tertbutyl and methylene linker protons are each resolved as two inequivalent sets, and signals attributable to an η^1 -naphthyl ligand appear. At -40 °C, the far-upfield signal in the ¹H NMR spectrum resolves into two overlapping triplets at δ -45.38 and -45.44 ppm (J_{HP} = 13.7 Hz) – very similar to the pairs of products seen previously in cases of *meta* aryl C-H activation. Based on analogous results with benzene, these data are all consistent with characterization of products **3-1a**,**b** as two rotamers of the square pyramidal complex (PCP)Ir(H)(naphthyl).^{26,27} However, there are additional signals that appear at low temperature that were not detectable at ambient temperature. The ¹H NMR spectrum has a new broad signal at δ 1.20 ppm corresponding to apparently equivalent PCP *tert*-butyl hydrogens. Integration of this peak vs. the *tert*-butyl signal for the naphthyl addition products (seen as broad at ambient temperature at δ 0.92 ppm, but significantly sharper at -40 °C) gives an approximate 1:2 ratio. A new resonance also appears in the 31 P NMR spectrum: a broad peak at δ 66.7 ppm in a ratio of approximately 1:3.5 vs. the peak for the products of C-H activation as discussed above. Given the lack of a hydride resonance that corresponds to the additional peak in the ³¹P NMR spectrum, and based on literature precedents,²⁻⁵ the additional NMR data, only seen in low temperature experiments, are consistent with characterization of product **3-2** as the π -coordination complex of (PCP)Ir and naphthalene (eq. 2).



It is clear from the low temperature NMR experiments that the η^2 -naphthalene complex is extremely labile and in equilibrium with the formal C-H oxidative addition products. In reactions with an excess of norbornene, the (PCP)IrNBE complex also competes with both naphthalene products, leading to a dynamic equilibrium in solution involving all three complexes. Rigorous equilibrium measurements were not conducted. The formation of product **3-2** is a novel process in the context of the aryl C-H activation reactions presented in this thesis; an analogous product for the reaction of (PCP)Ir and benzene was not detected.

With two types of C-H bonds available in naphthalene for oxidative addition by (PCP)Ir, there are four possible products, since each addition can potentially yield two rotamers (Figure 3.3).



Figure 3.3. Four possible products for C-H activation of naphthalene.

Since only two of a possible four C-H activation products are apparent in the NMR spectra, identifying them was an important goal in the context of understanding the selectivity of (PCP)Ir and the mechanism of oxidative addition. As a first step, CO was added to the solution of **3-1a,b** and **3-2** in an effort to trap the products as their six-coordinate CO adducts. Similar to previous reactions in which CO was added to labile, rapidly exchanging complexes, a substantial amount (~35%) of the four-coordinate (PCP)Ir(CO) **3-3** was detected in the product mixture (eq. 3).



Upon CO addition, all NMR resonances pertaining to the (PCP)IrNBE complex and **3-2** disappeared. The ³¹P NMR spectrum showed two new signals at ambient temperature, **3-4a,b**. These peaks, at δ 53.6 and 53.0 ppm are present in a 1:1 ratio and

correlate with similarly sharp hydride triplets in the ¹H NMR spectrum at δ -8.79 and -8.89 ppm (J_{HP} = 17.3 Hz for both). This data is analogous to similar CO addition reactions with substituted benzene substrates, as previously discussed. Unfortunately, with a mixture of very similar products (attempts to separate them were unsuccessful) crystallization and confirmation of product identities by x-ray analysis was not possible.

3.2.2 Identification of naphthalene addition products 3-1a and 3-1b through reaction of (PCP)Ir with a series of dimethylnaphthalene substrates

In order to attempt a different strategy, (PCP)Ir was reacted with four dimethyl naphthalene derivatives in order to exploit the inability of the metal complex to activate aryl C-H bonds *ortho* to alkyl substituents. These substrates are shown in Figure 3.4, and the accessible C-H bonds are identified by type: α or β .

Figure 3.4. Four dimethylnaphthalene isomers





1,4-dimethylnaphthalene

1,5-dimethylnaphthalene



2,7-dimethylnaphthalene



2,6-dimethylnaphthalene

1,4-Dimethylnaphthalene was chosen in order to restrict C-H activation to only one of the fused rings, acting as an analog of *ortho*-xylene (see chapter 2). The β positions (C6 and C7) are accessible, but the α positions (C5 and C8) are significantly more hindered than in unsubstituted naphthalene. 1,5-Dimethylnaphthalene effectively restricts C-H activation to the β C-H bonds as well (C3 or C7) with the possible exception of a very hindered α position (C4 or C8) due to its proximity to the alkyl substituent on the neighboring ring. 2,7-Dimethylnaphthalene allows access only to α positions (C4 and C5), while 2,6-dimethylnaphthalene acts similarly, restricting potential C-H activation to α positions C4 and C8.

Results from this series of reactions demonstrated that *all* C-H activation reactions occur at β positions. The only product detected in the reactions with 2,6- and 2,7-dimethylnapthalenes was the η^2 -naphthalene π -coordination complex. In these substrates, (PCP)Ir was blocked from approaching the β C-H bonds and no C-H activation products were detected. Both 1,4- and 1,5-dimethylnaphthalenes yielded ¹H and ³¹P NMR spectra strikingly similar to those from the reaction with unsubstituted naphthalene: two C-H activation products (**3-5a,b** and **3-6a,b**, respectively), very labile at ambient temperature, but sharpening at -40 °C, indicating slower exchange. Thus, the two products are simply the two rotamers of the β C-H activation (eq. 4).



With the products identified, it is clear that (PCP)Ir will not perform C-H activation at the α positions in unsubstituted naphthalene. The presence of two rotamer products in a 1:1 ratio is consistent with the symmetry of the naphthalene molecule, and the oxidative addition process seems simple and straightforward. However, upon analyzing the NMR spectra for these reactions at various temperatures, one inconsistency with the current scheme became obvious. NMR resonances at -40 °C are sharp, indicating slow exchange on the the NMR time scale for the addition and elimination of naphthalene at this temperature. As the temperature is raised, the hydride signal for *one* of the two products starts to broaden (indicating faster exchange) significantly sooner than for the other product, although the ratio of products does not change. That is, the rate of reductive elimination for one of the rotamers is apparently faster than for the other, allowing it to exchange more rapidly and show broadening in the NMR spectra at lower temperatures. This was an extremely perplexing result, since there is very little difference in the geometries of the two rotamers. In the context of the mechanistic results with benzene, it would be difficult to imagine any kind of steric effect in the transition state having an influence and causing a difference between two such similar complexes. The same phenomenon was observed with the addition products from 1,4dimethylnaphthalene, but *not* for those from 1,5-dimethylnaphthalene.

While further experiments are warranted to illuminate the cause(s) for this kinetic difference, it seems likely that the key is the formation of the η^2 -naphthalene complex. Given the literature precedents, one proposed explanation is that the mechanism for C-H activation begins with the formation of the $\eta^2 \pi$ -complex (Figure 3.5).

Figure 3.5. Proposed reaction coordinate diagram for C-H activation of naphthalene



Assuming preliminary π coordination by naphthalene, each of the two rotamer products of C-H activation derives from a *different* η^2 precursor as shown in Scheme 3.1. There are four equivalent "A" positions for π -coordination in naphthalene, and all four proceed to a C-H activation reaction that yields product **3-1a** as defined in eq. 4 (above).

Once coordinated as an η^2 complex to an "A" position, there is only *one* C-H bond available for activation (the one at the β carbon), since it has been proven that α C-H bonds are not accessible under these conditions. There are only *two* equivalent "B" positions for π -coordination in naphthalene, and both of these proceed to a C-H activation reaction that yields the *opposite* rotamer (product **3-1b**). Once coordinated as an η^2 complex to a "B" position, there are *two* C-H bonds available for activation (both at β carbons).





The NMR data show that the combinations of four "A" positions (each with only one available C-H bond) and two "B" positions (each with two available C-H bonds) must produce a 1:1 mixture of rotamers. But looking at the process of reductive elimination, in which the C-H bond eliminates and an η^2 complex is re-formed, it is possible that the transition state to either the "A" or "B" position η^2 complex is slightly lower in energy vs. the other one. Various hypotheses can be formulated for which pathway is the lower energy route, but each rotamer *must return* to the $\eta^2 \pi$ -complex from which it started.

It is interesting to note that this slight difference in rates of reductive elimination for the two rotamers is not observed for 1,5-dimethylnaphthalene. This seems to indicate that there is, in fact, a possible steric effect originating with the η^2 complex or the transition state for elimination. In 1,5-dimethylnaphthalene, there are only two equivalent β C-H bonds (by symmetry) available for activation by (PCP)Ir (Figure 3.6). But there are *two* possible η^2 complexes that can lead to C-H activation at the accessible β carbon. Because of the presence of the methyl substituent at C1, the η^2 complex at the "B" position now only has one choice of C-H bond in order to proceed with oxidative addition (in unsubstituted naphthalene, there are two). Therefore, the η^2 complex at position "B" has equalized with the η^2 complex at position "A" in two ways. First, they both have only one accessible C-H bond for acitvation, and second, they are sterically similar as shown in Figure 3.6, which is not true for either unsubstituted napthalene or 1,4-dimethylnaphthalene. Both of the latter substrates exhibit the small difference in kinetics, while 1,5-dimethylnaphthalene does not. Additional experiments and/or DFT calculations are required in order to elucidate the exact rationale for these observations.



Figure 3.6. (PCP)Ir coordination and C-H activation of 1,5-dimethylnaphthalene

3.2.3 Synthesis and characterization of products from the reaction of (PCP)Ir with 1-fluoronaphthalene

As was discussed in the last section, (PCP)Ir does not activate the α C-H bonds of naphthalene. In an effort to see if substituent effects might encourage oxidative addition at one of the less favored α positions, experiments were conducted with (PCP)Ir and 1-fluoronaphthalene. In chapter 2, it was shown that fluoro substituents have a strong electronic effect on C-H activation reactions by (PCP)Ir, yielding exclusively *ortho*-activated products. There is also plenty of literature precedent for this phenomenon.²⁸⁻³³ Therefore, using 1-fluoronaphthalene as a substrate, an expected product would be generated by (PCP)Ir activation of the bond at C2 (a preferred β position). However,

since there is no available C-H bond on the other carbon *ortho* to the fluoro substituent, it was thought that C-H activation at C8 might be possible (eq. 5).



Reaction of (PCP)IrH₂ and NBE with a slight excess of 1-fluoronaphthalene at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of two doublets in a ratio of 3.3:1 at δ 69.04 and 67.98 ppm. The ¹H NMR spectrum shows two hydride signals far upfield, indicative of two different d^6 five-coordinate products in the same ratio as the ³¹P NMR peaks. Both signals -42.97 ppm (t, $J_{HP} = 13.9 \text{ Hz}$) and -46.26 ppm (t, $J_{HP} = 13.7 \text{ Hz}$) show the triplet pattern characteristic of a hydride proton bonded to the Ir metal center and coupled by two equivalent phosphorus atoms. Interestingly, the H-F coupling seen with fluorobenzene is not seen in this napthalene addition product. Both products are exchanging slowly with free substrate at ambient temperature, and the ratio of products remains unchanged over time and/or after heating. There is no NMR evidence for the η^2 complexes seen in equilibrium with the naphthalene and dimethylnaphthalene complexes discussed in the previous section. The electronic influence of the fluoro substituent is apparently strong enough that the C-H activation products are not eliminating back to their respective $n^2 \pi$ -complexes on the NMR time scale at ambient temperature. Based

on previous results with fluorobenzene, the two products are assigned as the *ortho*-cis and *ortho*-trans rotamer products of C-H activation at C2 of naphthalene **3-7a,b** (eq. 6).



Assuming that C-H activation at C8 would require precoordination as the η^2 complex at an "A" position (between C7 and C8), the presence of a fluoro substituent at C1 apparently has too little (if any) electronic influence to enable this reaction. Alternatively, C-H activation at C8 may occur, but be thermodynamically unfavorable compared with standard *ortho* C-H activation at the relatively favorable β position C2. Addition of CO in order to trap the products as their six-coordinate CO adducts yielded results similar to those with the fluorophenyl rotamers. Once again, the product ratio shifted dramatically in favor of the *ortho*-trans configuration, resulting in a negligible concentration of the *ortho*-cis CO adduct in the final solution (eq. 7). Crystallization of the single product was successful; the CO ligand is located trans to the metal-hydride bond and proximal to the aryl fluorine atom, confirming the *ortho*-trans conformation (**3**-**8**). The x-ray crystal structure and selected data are included at the end of this chapter.



3.2.4 Synthesis and characterization of products from the reaction of (PCP)Ir with 1-methoxy- and 2-methoxynaphthalene

Building on previous results in our group involving the C-H activation of anisole, reactions of (PCP)Ir with methoxy-substituted naphthalenes were used to probe the selectivity of C-H bond activation. In reactions with anisole, (PCP)Ir was observed to preferentially activate the C-H bond *ortho* to the methoxy substituent, yielding the kinetic product. Upon heating, a second C-H activation process yielded a cyclometalated complex as the thermodynamic product (eq. 8).^{34,35} Expanding on this work, former group member Sabuj Kundu reported preliminary results from the reaction of (PCP)Ir with 1-methoxynaphthalene, but full characterization of the products was not completed.³⁶



Methoxy-substituted naphthalene substrates were chosen specifically for their propensity for cyclometalation with aryl substrates, since electronic influences alone did

not encourage C-H activation at the less favorable α position (see 1-fluoronaphthalene, above). Reaction of (PCP)IrH₂ and NBE with a slight excess of 2-methoxynaphthalene at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of a single resonance at δ 68.36 ppm. Correspondingly, the ¹H NMR spectrum shows a single hydride signal far upfield, indicative of a d⁶ five-coordinate product; δ -44.44 ppm (t, *J*_{HP} = 13.9 Hz). These data are consistent with those collected during the reaction with anisole and indicate the formation of the *ortho* C-H activation product **3-9** (eq. 9). This product of C-H activation at the *ortho* β position is formed exclusively, with no evidence seen for formation of the product from C-H activation at the C1 α position. This is consistent with preliminary π coordination of the substrate at the 'A' position as shown in eq. 9.



Heating a solution of product **3-9** with >2 equivalents of NBE at 75 °C overnight yielded the cyclometalated product of double C-H activation, **3-10** (>95% ³¹P NMR; eq. 10). The ¹H NMR spectrum shows complete disappearance of the hydride resonance, and a new signal appears in the ³¹P NMR spectrum at δ 46.0 ppm. Experiments showed that double C-H activation cannot take place without enough NBE acceptor in solution to accommodate the transfer of four hydrogen atoms (two from preliminary formation of the (PCP)Ir fragment and two additional from the aryl (sp²) C-H and alkyl (sp³) C-H
activation reactions). With loss of all hydrides from the metal center, the cyclometalated ligand cannot reductively eliminate, and the complex is stable to decomposition at ambient temperature. Crystallization of **3-10** was successful; the x-ray crystal structure and selected data are included at the end of this chapter.



Reaction of (PCP)IrH₂ and NBE with a slight excess of 1-methoxynaphthalene at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of two new major peaks at δ 68.0 and δ 53.5 ppm. Neither of these peaks is sharp at this temperature. In addition, there is a broad signal at δ 66.0 that probably corresponds to one or several labile $\eta^2 \pi$ -complexes. At -40 °C, the signals are significantly more well-defined, and a substantial signal is also present for the (PCP)Ir(NBE) complex, indicating that one or more of the C-H activation products is labile and in equilibrium with NBE. In the ¹H NMR spectrum, there is one sharp hydride signal at δ -8.35 ppm (t, $J_{HP} = 16.5$ Hz) and at least six additional overlapping signals centered around δ -45.6 ppm. These data are consistent with the formation of products **3-11** and **3-12** (eq. 11). The hydride signal at δ -8.35 ppm indicates a six-coordinate complex and based on previous work in our group with similar complexes, is diagnostic of an Ir-H bond *trans* to the naphthyl carbon atom and *cis* to the methoxy oxygen atom.²⁶ Thus, for this substrate, C-H activation at the α position is feasible, presumably due to stabilizing oxygen coordination *after* the oxidative addition is complete. The multiple signals at δ -45.6 ppm are indicative of several 5-coordinate products of C-H activation at other positions in the substrate that are not subject to additional oxygen atom coordination due to geometry. Interestingly, *ortho* C-H activation at C2 was not detected.



Multiple C-H activation products

Heating a solution of products **3-11** and **3-12** with >2 equivalents of NBE at 75 °C overnight yielded two new signals in the ³¹P NMR spectrum: δ 49.21 (75%) and δ 44.88 ppm (25%). The ¹H NMR spectrum shows complete disappearance of the hydride signals for **3-11** and **3-12**, and a single new resonance appears at δ -28.5 ppm (t, J_{HP} = 18.1 Hz). The hydride signal at δ -28.5 ppm indicates a six-coordinate complex and based on previous work in our group with similar complexes, is diagnostic of an Ir-H bond *cis* to the naphthyl carbon atom and *trans* to the methoxy oxygen atom.²⁶ Since both ³¹P NMR signals were diagnostic of either six-coordinate or cyclometalated complexes, and there was no hydride signal associated with the minor ³¹P NMR signal, the products were tentatively assigned as **3-13** and **3-14** (eq. 12).



In his preliminary work, Sabuj Kundu observed similar results.³⁶ X-ray analysis of the major product in those experiments confirmed the structure of **3-13**, but only NMR evidence was offered to support the stucture of **3-14**. Despite the apparent thermodynamic stability of **3-13** (major product after 24 hrs of heating at 75 °C), it seemed likely that the minor product (**3-14**) would actually be the more thermodynamically stable of the two. Since **3-13** retains a hydride ligand and therefore – despite the unfavorable conformation with oxygen coordinated *between* the aryl carbon and hydride ligand – should perhaps have the potential for reductive elimination at high enough temperatures. Product **3-14** on the other hand, results from a double C-H activation process and retains no hydrides on the metal, thereby preventing any possibility of reductive elimination. This turned out to be true. Heating the product mixture (75% **3-13** and 25% **3-14**) for 15 days at 100 °C yielded net conversion (100%) of product **3-13** into **3-14**. The solution was monitored by NMR frequently during the heating process: the ratio of ³¹P NMR signals slowly changed in favor of the signal at δ 44.88 ppm until all of the signal at δ 49.21 ppm had disappeared. The relatively modest temperature of 100 °C was chosen in order to prevent the possibility of product decomposition. Product **3-14** was characterized by x-ray crystallography, confirming the structure as shown in eq. 12. The x-ray crystal structure and selected data are included at the end of this chapter.

3.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in

solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. A full discussion of the NBE complex, including NMR characterization, is included in the Experimental section of Chapter 2 (section 2.3).

Reaction of (PCP)Ir with naphthalene (3-1a,b): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Naphthalene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned lighter red-orange. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 67.2 (d, $J_{PH} = 15.8$ Hz). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): δ 67.2 (d, $J_{PH} = 15.8$ Hz). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): δ 8.25 (s, 1H, naphthyl *ortho*-H rotamer A), 8.20 (s, 1H, naphthyl *ortho*-H rotamer B), all remaining aryl H signals for both rotamers of the C-H addition product are cleanly represented: 8.10, 7.99, 7.81, 7.77, 7.72, 7.62 (all d, $J_{HH} = 8.4$ Hz, 8H, naphthyl *H*), 7.36, 7.11 (both m, $J_{HH} = 8.4$ Hz, 4H, naphthyl *H*), PCP aryl peaks are obscured by residual solvent, 3.30 (d of vt, $J_{HH} = 15.8$ Hz, 4H, CH_2), 0.92 (br t, 36H, C(CH_3)₃), -45.38 (t, $J_{HP} = 13.0$ Hz, 1H, Ir-*H*, rotamer A), -45.44 (t, $J_{HP} = 13.0$ Hz, 1H, Ir-*H*, rotamer B).

Evidence for a (PCP)Ir(η^2 -naphthalene) π complex (3-2): The ³¹P NMR and ¹H NMR spectra both contain broad resonances at low temperature that may be indicative of a labile π -complex with naphthalene coordinated to the iridium through a C-C bond. Further experiments are necessary in order to fully examine this possibility. The

following resonances do not pertain to the C-H addition products as detailed above.

Additionally, they are broad – even at low temperature (-40 °C) and broaden sufficiently to become undetectable at ambient temperature. Although the following data pertain to the unsubstituted naphthalene substrate, similar peaks can be seen in the low temperature spectra for the reaction of (PCP)Ir with both 1,4-dimethylnaphthalene and 1,5dimethylnaphthalene. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 66.7 (br s). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): δ 3.43 (br s, 4H, CH₂). The ¹H NMR resonance is also very close to where the PCP CH₂ signal appears for the four-coordinate CO complex.

Reaction of 3-1a,b with CO to form 3-4a,b: A solution of **3-1** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The orange solution immediately turned pale yellow upon thawing. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 53.6 (s, rotamer A), 53.0 (s, rotamer B). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.65 (s, 1H, naphthyl *ortho*-H rotamer A), 8.53 (s, 1H, naphthyl *ortho*-H rotamer B), all remaining aryl H signals for both rotamers of the C-H addition product are cleanly represented: 8.42, 8.33, 7.68, 7.64, 7.45, 7.40 (all d, J_{HH} = 8.4 Hz, 8H, naphthyl *H*), 7.23, 7.17 (both m, J_{HH} = 8.4 Hz, 4H, naphthyl *H*), PCP aryl peaks are obscured by residual solvent, 3.24 (d of vt, J_{HH} = 16.7 Hz, 4H, *CH*₂), 1.06 (br t, 36H, C(*CH*₃)₃), -8.79 (t, J_{HP} = 17.7 Hz, 1H, Ir-*H*, rotamer A), -8.89 (t, J_{HP} = 17.7 Hz, 1H, Ir-*H*, rotamer B).

Reaction of (PCP)Ir with 1,4-dimethylnaphthalene (3-5a,b): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*xylene. 1,4-Dimethylnaphthalene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned lighter redorange. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 67.8 (s, rotamer A), 67.6 (s, rotamer B). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): δ 8.44 (s, 1H, naphthyl *ortho*-H rotamer A), 8.38 (s, 1H, naphthyl *ortho*-H rotamer B), all remaining aryl H signals for both rotamers of the C-H addition product appear: 8.14 – 7.14 (all d, J_{HH} = 9.3 Hz, 8H, naphthyl *H*), PCP aryl peaks are obscured by residual solvent, 3.30 (d of vt, J_{HH} = 17.1 Hz, 4H, CH₂), 2.44 (s, 6H, dimethylnaphthyl CH₃), 0.92 (br t, 36H, C(CH₃)₃), –45.38 (t, J_{HP} = 13.5 Hz, 1H, Ir-*H*, rotamer A), -45.51 (t, J_{HP} = 13.5 Hz, 1H, Ir-*H*, rotamer B).

Reaction of (PCP)Ir with 1,5-dimethylnaphthalene (3-6a,b): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*xylene. 1,5-Dimethylnaphthalene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned lighter redorange. ³¹P NMR (121.4 MHz, -15 °C, mesitylene- d_{12}): δ 68.4 (s, rotamer A), 68.2 (d, $J_{PH} = 16.0$ Hz, rotamer B). ¹H NMR (400 MHz, -35 °C, mesitylene- d_{12}): δ 8.26 (s, 1H, naphthyl *ortho*-cis H rotamer A), 8.20 (s, 1H, naphthyl *ortho*-cis H rotamer B), 7.94 (s, 1H, naphthyl *ortho*-trans H rotamer A), 7.81 (s, 1H, naphthyl *ortho*-trans H rotamer B), all remaining aryl H signals for both rotamers of the C-H addition product as well as the PCP aryl peaks are obscured by residual solvent and/or excess substrate, 3.26 (d of vt, $J_{\text{HH}} = 16.4 \text{ Hz}, 4\text{H}, CH_2$), dimethylnaphthyl CH₃ obscured by free substrate, 0.86 (br, 36H, C(CH₃)₃), -45.53 (t, $J_{\text{HP}} = 13.2 \text{ Hz}$, 1H, Ir-*H*, rotamer A), -45.55 (t, $J_{\text{HP}} = 13.2 \text{ Hz}$, 1H, Ir-*H*, rotamer B).

Reaction of (PCP)Ir with 2,6-dimethylnaphthalene and 2,7-dimethylnaphthalene:

5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. When either 2,6-dimethylnaphthalene (10 eq; 0.10 mmol) or 2,7-dimethylnaphthalene (10 eq; 0.10 mmol) was added to the resulting solution, no C-H addition products were observed. Both of these substrates are similar to *para*-xylene: all aryl C-H bonds are *ortho* to C-C bonds (either sp²-sp³ or sp²-sp²). It is known that C-H addition at these positions is very unfavorable, and results from attempted reactions with these substrates are consistent with previous findings.

Reaction of (PCP)Ir with 1-fluoronaphthalene (3-7a,b): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1-Fluoronaphthalene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 68.8 (d, J_{PH} = 13.3 Hz, *ortho*-trans rotamer), 66.9 (d, J_{PH} = 12.2 Hz, *ortho*-cis rotamer). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): δ 8.24 (d, J_{HH} = 8.0 Hz, 1H, fluoronaphthyl *ortho*-H *ortho*-cis rotamer), 8.16 (d, J_{HH} = 8.0

Hz, 1H, fluoronaphthyl *ortho*-H *ortho*-trans rotamer), all remaining aryl H signals for both rotamers of the C-H addition product as well as the PCP aryl peaks are obscured by residual solvent and/or excess substrate, 3.27 (d of vt, J_{HH} = 16.4 Hz, 4H, CH_2), *ortho*-cis CH_2 obscured by *ortho*-trans signals, 0.97 (br t, J_{HH} = 6.4 Hz, 18H, C(CH_3)₃), 0.89 (br t, J_{HH} = 6.4 Hz, 18H, C(CH_3)₃), -42.79 (t, J_{HP} = 13.2 Hz, 1H, Ir-*H*, *ortho*-cis rotamer), -46.34 (t, J_{HP} = 14.0 Hz, 1H, Ir-*H*, *ortho*-trans rotamer).

Reaction of 3-7a,b with CO to form 3-8: A solution of **3-7a,b** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The orange solution immediately turned pale yellow upon thawing. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; pale yellow needles were obtained. There is only one dominant product of CO addition from the two original C-H activation rotamers. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 53.6 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.36 (d of d, J_{HH} = 8.6 Hz, J_{HF} = 4.5 Hz, 1H, fluoronaphthyl *ortho*-H), 8.18 (d, J_{HH} = 8.5 Hz, 1H, fluoronaphthyl *meta*-H), 8.02 (m, 2H, fluoronaphthyl *H*), 7.65 (d, J_{HH} = 8.5 Hz, 2H, fluoronaphthyl *H*), PCP aryl peaks are obscured by residual solvent and/or excess substrate, 3.24 (br t, 4H, CH₂), 1.10 (t, J_{HH} = 6.4 Hz, 18H, C(CH₃)₃), 1.06 (t, J_{HH} = 6.4 Hz, 18H, C(CH₃)₃), -9.50 (t of d, J_{HP} = 17.3 Hz, J_{HF} = 2.2 Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with 2-methoxynaphthalene to give kinetic C-H activation product (3-9): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene-

*d*₁₂ in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 2-Methoxynaphthalene (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright red. ³¹P NMR (121.4 MHz, 25 °C, mesitylene-*d*₁₂): δ 68.4 (s). ¹H NMR (400 MHz, 25 °C, mesitylene-*d*₁₂): δ 8.16 (s, 1H, substrate *ortho-H*), 7.70 (d of t, overlapping *J*_{HH} = 6.1 Hz, 2H, substrate aryl *H*), 7.56 (d, *J*_{HH} = 8.4 Hz, 2H, substrate aryl *H*), 7.47 (d, *J*_{HH} = 9.3 Hz, 1H, substrate aryl *H*), PCP aryl peaks are obscured by residual solvent and/or excess substrate, 3.46 (d of vt, *J*_{HH} = 16.3 Hz, *J*_{HP} = 3.9 Hz, 2H, *CH*₂), 3.40 (s, substrate OC*H*₃), 3.31 (d of vt, *J*_{HH} = 16.3 Hz, *J*_{HP} = 3.9 Hz, 2H, *CH*₂), 1.04 (t, *J*_{HH} = 6.1 Hz, 18H, C(*CH*₃)₃), 1.00 (t, *J*_{HH} = 6.1 Hz, 18H, C(*CH*₃)₃), -44.44 (t, *J*_{HP} = 14.4 Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with 2-methoxynaphthalene to give thermodynamic C-H

activation product (3-10): A solution of 3-9 in a J-Young NMR tube was allowed sit sit for 24 hr in an argon-filled glove box at ambient temperature. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; red-orange prisms were obtained. The cyclometalated product results from double C-H activation. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 46.3 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.24 (s, 1H, substrate *ortho-H*), remaining substrate *H* signals appear at 7.76, 7.66, 7.56, 7.47, PCP aryl peaks are obscured by residual solvent and/or excess substrate, 5.03 (t, J_{HP} = 8.4, 2H, CH₂), 3.33 (d of vt, J_{HH} = 4.0 Hz, J_{HP} = 3.5 Hz, 4H, CH₂), 0.97 (t, J_{HH} = 6.6 Hz, 18H, C(CH₃)₃), 0.92 (t, J_{HH} = 6.6 Hz, 18H, C(CH₃)₃). Reaction of (PCP)Ir with 1-methoxynaphthalene to give kinetic C-H activation products (3-11 and 3-12): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1-Methoxynaphthalene (2 eq; 0.020 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark orange-brown. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 67.9 (br s, C-H activation products **3-11**), 53.8 (s, C-H activation product **3-12** with O *cis* to Ir-H). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): All aryl peaks overlapping from many products and/or obscured by residual solvent and unreacted substrate, δ 3.39 (s, substrate OCH₃), PCP methylene peaks overlapping, 0.91 (br t, 36H, C(CH₃)₃ **3-11**), 0.51 (t, *J*_{HH} = 6.1 Hz, 36H, C(CH₃)₃ **3-12**), -8.36 (t, *J*_{HP} = 18.2 Hz, 1H, Ir-*H* **3-12**), -45.35, -45.40, -45.45, -45.51, -45.65 (multiple products: t, *J*_{HP} = 9.2 Hz, 1H, Ir-*H* **3-11**).

Reaction of (PCP)Ir with 1-methoxynaphthalene to give C-H activation product (3-13): A solution of 3-11 and 3-12 in a J-Young NMR tube was allowed sit sit for 6 days in an argon-filled glove box at ambient temperature. NMR analysis showed the complete disappearance of 3-11 and 3-12 and the formation of two new products 3-13 (> 90%) and 3-14 (< 10%). Product 3-13 was previously crystallized by Sabuj Kundu, and that process was not repeated here. Data for 3-13: ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 49.2 (d, J_{PH} = 13.4 Hz, C-H activation product with O *trans* to Ir-H). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): All aryl peaks overlapping from many products and/or obscured by residual solvent and unreacted substrate, δ 3.39 (s, substrate OC*H*₃), PCP methylene peaks overlapping, 0.87 (t, *J*_{HH} = 6.1 Hz, 18H, C(*CH*₃)₃), 0.81 (t, *J*_{HH} = 6.1 Hz, 18H, C(*CH*₃)₃), -28.47 (t, *J*_{HP} = 16.7 Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with 1-methoxynaphthalene to give thermodynamic C-H activation product (3-14): A solution of 3-11 and 3-12 in a J-Young NMR tube was allowed sit sit for 6 days in an argon-filled glove box at ambient temperature. NMR analysis showed the complete disappearance of 3-11 and 3-12 and the formation of two new products 3-13 (> 90%) and 3-14 (< 10%). This product mixture was heated at 100 °C for 45 days. NMR analysis confirmed slow conversion from 3-13 into the product from double C-H activation, 3-14. After nearly complete conversion, the solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; red-orange prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 45.9 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.24, 8.01, 7.78, 7.56 (d, 6H, substrate aryl *H*) PCP signals are obscured by residual solvent, 5.16 (t, J_{HP} = 9.2, 2H, CH₂), 3.34 (d of vt, J_{HH} = 4.0 Hz, J_{HP} = 3.5 Hz, 4H, CH₂), 0.97 (t, J_{HH} = 6.4 Hz, 18H, C(CH₃)₃).

3.4 Conclusion

Despite the structural similarity to benzene, naphthalene substrates show several different and illuminating patterns of reactivity with (PCP)Ir. Perhaps the most mechanistically important difference is the ability of naphthalene to form $\eta^2 \pi$ -complexes en route to C-H activation. Since there are subtle electronic differences between 'A' and 'B' positions in the molecular structure of naphthalene, the orientation of preliminary π coordination can have significant ramifications on the conformation of final products.

Consistent with previous results, steric congestion discourages C-H activation reactions. While reaction of (PCP)Ir with unsubstituted naphthalene apparently yields two products, they both result from exclusive activation of β C-H bonds. Experiments with a series of dimethyl-substituted naphthalenes yielded strong evidence in support of both preliminary π coordination and regioselectivity by (PCP)Ir for β C-H bonds.

Experiments with 1-fluoronaphthalene show that electronic influences on the C-H activation mechanism are similar to those seen with fluorobenzene. Experiments with two methoxynaphthalene substrates yielded two very important results. First, oxidative addition to (PCP)Ir of the less favored α C-H bonds is possible when there is a strategically placed substituent that can stabilize either the transition state or the product (or both). Second, cyclometalation is a very favorable process for (PCP)Ir when the formation of a 5- or 6-coordinate complex containing a 5-member metalacycle is conformationally feasible.

3.5 References

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 Table 3.1. Crystal data and structure refinement for 3-8.

Empirical formula	C35 H50 F Ir O P2	
Formula weight	759.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 19.8132(12) Å	a= 90°.
	b = 20.0538(12) Å	b=105.083(1)°.
	c = 17.2931(10) Å	g = 90°.
Volume	6634.4(7) Å ³	
Z	8	
Density (calculated)	1.522 Mg/m ³	
Absorption coefficient	4.153 mm ⁻¹	
F(000)	3072	
Crystal size	0.66 x 0.07 x 0.06 mm ³	
Theta range for data collection	1.47 to 29.13°.	
Index ranges	-27<=h<=26, -27<=k<=27, -23<=l<=23	
Reflections collected	71797	
Independent reflections	17851 [R(int) = 0.0854]	
Completeness to theta = 29.13°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7887 and 0.1703	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	17851 / 2 / 755	
Goodness-of-fit on F ²	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0508, $wR2 = 0.0932$	
R indices (all data)	R1 = 0.0786, wR2 = 0.0999	
Largest diff. peak and hole	2.721 and -1.490 e.Å ⁻³	

Ir(1)-C(35)	1.924(6)	P(1)-C(9)	1.895(6)
Ir(1)-C(1)	2.107(5)	P(1)-C(13)	1.900(5)
Ir(1)-C(26)	2.150(5)	P(2)-C(8)	1.843(5)
Ir(1)-P(2)	2.3294(13)	P(2)-C(21)	1.886(5)
Ir(1)-P(1)	2.3450(14)	P(2)-C(17)	1.890(5)
Ir(1)-H(1)	1.590(10)	F(1)-C(25)	1.387(6)
P(1)-C(7)	1.842(5)	O(1)-C(35)	1.143(6)
C(35)-Ir(1)-C(1)	86.1(2)	C(9)-P(1)-C(13)	110.2(3)
C(35)-Ir(1)-C(26)	96.0(2)	C(7)-P(1)-Ir(1)	101.67(17)
C(1)-Ir(1)-C(26)	176.59(19)	C(9)-P(1)-Ir(1)	118.20(19)
C(35)-Ir(1)-P(2)	94.85(16)	C(13)-P(1)-Ir(1)	117.22(18)
C(1)-Ir(1)-P(2)	79.79(14)	C(8)-P(2)-C(21)	103.5(2)
C(26)-Ir(1)-P(2)	97.38(14)	C(8)-P(2)-C(17)	104.0(2)
C(35)-Ir(1)-P(1)	100.53(15)	C(21)-P(2)-C(17)	110.7(2)
C(1)-Ir(1)-P(1)	81.99(15)	C(8)-P(2)-Ir(1)	100.62(16)
C(26)-Ir(1)-P(1)	100.16(14)	C(21)-P(2)-Ir(1)	120.28(16)
P(2)-Ir(1)-P(1)	155.23(5)	C(17)-P(2)-Ir(1)	114.93(18)
C(35)-Ir(1)-H(1)	175.4(19)	C(2)-C(1)-Ir(1)	121.9(4)
C(1)-Ir(1)-H(1)	89.3(19)	C(6)-C(1)-Ir(1)	120.4(4)
C(26)-Ir(1)-H(1)	88.5(19)	C(25)-C(26)-Ir(1)	126.0(4)
P(2)-Ir(1)-H(1)	83.6(19)	C(27)-C(26)-Ir(1)	121.9(4)
P(1)-Ir(1)-H(1)	79.6(19)	O(1)-C(35)-Ir(1)	172.1(5)
C(7)-P(1)-C(9)	103.1(3)		
C(7)-P(1)-C(13)	103.8(3)		

Table 3.2. Selected bond lengths [Å] and angles [°] for **3-8**.



Figure 3.8. X-ray crystal structure for compound 3-10.

 Table 3.3.
 Crystal data and structure refinement for 3-10.

Empirical formula	C35 H51 Ir O P2	
Formula weight	741.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.8900(7) Å	a= 90°.
	b = 20.3380(12) Å	b= 106.651(1)°.
	c = 13.8317(8) Å	$g = 90^{\circ}$.
Volume	3204.5(3) Å ³	
Ζ	4	
Density (calculated)	1.538 Mg/m ³	
Absorption coefficient	4.292 mm ⁻¹	
F(000)	1504	
Crystal size	0.27 x 0.14 x 0.06 mm ³	
Theta range for data collection	1.83 to 31.53°.	
Index ranges	-17<=h<=17, -29<=k<=29, -19<=l<=20	
Reflections collected	39865	
Independent reflections	10658 [R(int) = 0.0407]	
Completeness to theta = 31.53°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7828 and 0.3903	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10658 / 0 / 370	
Goodness-of-fit on F ²	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0418, $wR2 = 0.0924$	
R indices (all data)	R1 = 0.0526, $wR2 = 0.0970$	
Largest diff. peak and hole	4.695 and -2.062 e.Å ⁻³	

Ir(1)-C(35)	2.034(4)	P(1)-C(9)	1.900(4)
Ir(1)-C(25)	2.083(4)	P(2)-C(8)	1.854(4)
Ir(1)-C(1)	2.095(4)	P(2)-C(21)	1.885(4)
Ir(1)-P(2)	2.3048(10)	P(2)-C(17)	1.894(4)
Ir(1)-P(1)	2.3639(10)	O(1)-C(26)	1.373(5)
P(1)-C(7)	1.843(4)	O(1)-C(35)	1.445(5)
P(1)-C(13)	1.880(4)	C(25)-C(26)	1.437(5)
C(35)-Ir(1)-C(25)	80.88(16)	C(7)-P(1)-Ir(1)	100.83(13)
C(35)-Ir(1)-C(1)	92.41(16)	C(13)-P(1)-Ir(1)	121.34(14)
C(25)-Ir(1)-C(1)	173.26(15)	C(9)-P(1)-Ir(1)	115.64(14)
C(35)-Ir(1)-P(2)	93.27(12)	C(8)-P(2)-C(21)	103.96(19)
C(25)-Ir(1)-P(2)	99.69(11)	C(8)-P(2)-C(17)	106.66(19)
C(1)-Ir(1)-P(2)	81.18(11)	C(21)-P(2)-C(17)	110.13(19)
C(35)-Ir(1)-P(1)	97.39(12)	C(8)-P(2)-Ir(1)	102.40(14)
C(25)-Ir(1)-P(1)	98.22(11)	C(21)-P(2)-Ir(1)	127.47(13)
C(1)-Ir(1)-P(1)	81.98(11)	C(17)-P(2)-Ir(1)	104.48(15)
P(2)-Ir(1)- $P(1)$	160.40(4)	C(26)-O(1)-C(35)	115.4(3)
C(7)-P(1)-C(13)	103.4(2)	C(26)-C(25)-Ir(1)	111.4(3)
C(7)-P(1)-C(9)	103.71(19)	O(1)-C(26)-C(25)	117.8(3)
C(13)-P(1)-C(9)	109.11(19)	O(1)-C(35)-Ir(1)	113.6(3)

Table 3.4. Selected bond lengths [Å] and angles [°] for 3-10.





Empirical formula	C35 H51 Ir O P2	
Formula weight	741.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 20.2650(14) Å	a= 90°.
	b = 15.0561(10) Å	b= 90°.
	c = 20.7571(14) Å	g = 90°.
Volume	6333.2(7) Å ³	
Z	8	
Density (calculated)	1.556 Mg/m ³	
Absorption coefficient	4.344 mm ⁻¹	
F(000)	3008	
Crystal size	0.35 x 0.12 x 0.03 mm ³	
Theta range for data collection	1.95 to 30.03°.	
Index ranges	-28<=h<=28, -20<=k<=21, -29<=l<=27	
Reflections collected	59469	
Independent reflections	9255 [R(int) = 0.0880]	
Completeness to theta = 30.03°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8807 and 0.3117	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9255 / 0 / 364	
Goodness-of-fit on F ²	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.0949	
R indices (all data)	R1 = 0.0813, $wR2 = 0.1059$	
Largest diff. peak and hole	3.211 and -2.502 e.Å ⁻³	

Table 3.5. Crystal data and structure refinement for 3-14.

Ir(1)-C(35)	2.031(5)	P(1)-C(13)	1.893(6)
Ir(1)-C(26)	2.087(5)	P(2)-C(8)	1.851(5)
Ir(1)-C(1)	2.088(5)	P(2)-C(17)	1.879(5)
Ir(1)-P(1)	2.2996(13)	P(2)-C(21)	1.892(5)
Ir(1)-P(2)	2.3621(13)	O(1)-C(25)	1.378(6)
P(1)-C(7)	1.847(5)	O(1)-C(35)	1.442(6)
P(1)-C(9)	1.893(5)	C(25)-C(26)	1.379(7)
C(35)-Ir(1)-C(26)	80.6(2)	C(8)-P(2)-C(21)	103.2(2)
C(35)-Ir(1)-C(1)	93.1(2)	C(17)-P(2)-C(21)	109.5(2)
C(26)-Ir(1)-C(1)	173.7(2)	C(8)-P(2)-Ir(1)	100.38(17)
C(35)-Ir(1)-P(1)	93.49(16)	C(17)-P(2)-Ir(1)	115.75(18)
C(26)-Ir(1)-P(1)	99.33(14)	C(21)-P(2)-Ir(1)	121.43(18)
C(1)-Ir(1)-P(1)	81.31(14)	C(25)-O(1)-C(35)	114.8(4)
C(35)-Ir(1)-P(2)	96.13(16)	C(6)-C(1)-Ir(1)	121.9(4)
C(26)-Ir(1)-P(2)	98.23(14)	C(2)-C(1)-Ir(1)	121.1(4)
C(1)-Ir(1)-P(2)	81.99(14)	C(25)-C(26)-Ir(1)	111.7(4)
P(1)-Ir(1)-P(2)	161.14(5)	C(27)-C(26)-Ir(1)	133.6(4)
C(7)-P(1)-C(9)	106.2(2)	O(1)-C(35)-Ir(1)	113.4(3)
C(7)-P(1)-C(13)	104.3(2)	O(1)-C(25)-C(26)	119.3(5)
C(9)-P(1)-C(13)	110.6(2)	O(1)-C(25)-C(34)	115.8(5)
C(7)-P(1)-Ir(1)	102.25(16)	O(1)-C(35)-H(35A)	108.9
C(9)-P(1)-Ir(1)	104.60(17)	Ir(1)-C(35)-H(35A)	108.9
C(13)-P(1)-Ir(1)	127.02(19)	O(1)-C(35)-H(35B)	108.9
C(8)-P(2)-C(17)	103.5(2)	Ir(1)-C(35)-H(35B)	108.9

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Table 3.6. Selected bond lengths [Å] and angles [°] for 3-14.

Chapter 4

Reaction of (PCP)Ir with Anthracene and Phenanthrene

Abstract

Results are presented in this chapter for C-H activation experiments with (PCP)Ir and two 14 π -electron, tricyclic fused ring substrates: anthracene and phenanthrene. Both of these substrates have one additional aromatic ring fused to naphthalene, yielding larger, slightly more electronically complex molecules with three unique types of C-H bonds. The reactivity of anthracene directly mirrors that of naphthalene, including coordinating to the (PCP)Ir fragment to form an $\eta^2 \pi$ -complex detectable by NMR analysis. Also similar to naphthalene, (PCP)Ir will only oxidatively add *one* class of anthracene C-H bonds: those on the end-most carbons (C2, C3, C6, and C7). This is an interesting result since the most reactive C-H bonds in anthracene are generally regarded to be those at C9 and C10.

In reactions of (PCP)Ir with phenanthrene, results are quite different. At least four different kinetic products are formed from preliminary C-H activation. Upon heating, a double C-H activation process yields a single thermodynamic product. This cyclometalated product with a five-member metalloaromatic ring has bonds connecting iridium with phenanthrene carbons C4 and C5. Addition of CO to this complex is kinetically very slow due to crowding around the metal center, despite a 5-coordinate, square pyramidal geometry with an "open" coordination site.

4.1 Introduction

Anthracene and phenanthrene are comprised of three fused benzene rings and are therefore one size larger in the aromatic family of compounds (14 π -electrons) than naphthalene. Both molecules exhibit similar reactivity and electronic properties to benzene and naphthalene, but also have several key structural differences that have notable ramifications on C-H activation reactions with (PCP)Ir.

Whereas naphthalene contains two types of C-H bonds – discussed in detail, in chapter 3 – both anthracene and phenanthrene have *three* geometrically unique classes of C-H bonds (Fig. 4.1). In addition, like naphthalene, the C-C bonds are *not* all the same length.





These structural features contribute to interesting patterns of reactivity that have been studied in various contexts (often, alongside napthlanene) with organometallic complexes since Chatt's ground-breaking experiments with ruthenium in the 1960's.^{1,2} Analogous to the behavior of naphthalene, both anthracene and phenanthrene show a distinctly favorable π -coordination (η^2) mode in a variety of metal complexes.^{1,3-6} The prevalence of this ligand binding mode has been thoroughly studied and for many complexes, there is an equilibrium between η^1 and η^2 conformations (eq. 1).^{4,7}



Coordination from the π system has also been exploited in the *synthesis* of phenanthrene, with several reports from the Jones group concerning the use of nickel and rhodium complexes to promote coupling reactions between various alkynes and biphenylene.⁸⁻¹¹

C-H activation reactions of these tricyclic aryl systems have been studied far less thoroughly than for benzene, and have tended to focus, understandably, on the fundamental differences in reactivity between the α , β , and γ positions and the potential ramifications for regioselectivity in activation processes.^{2,12-15} Calculated bond dissociation energies have yielded comparable values for the three types of C-H bonds (111 ± 0.3 kcal/mol).¹⁶

While there are far fewer commercially available derivatives of anthracene and phenanthrene as compared with benzene, most of them have substituents at γ carbons C9 and C10. Results from our experiments show that (PCP)Ir activates anthracene β C-H bonds *exclusively* (*vide infra*), therefore making this a potentially valuable approach to selectively functionalized anthracene derivatives. (PCP)Ir acts in a similar fashion with

phenanthrene in yielding several kinetic C-H activation products. However, the favored thermodynamic product is a cyclometalated, double C-H activation complex in which iridium bonds to C4 and C5 of phenanthrene. Surprisingly, this seems to be the first report of a κ^2 binding mode for phenanthrene in transition metal systems.

4.2 Results and Discussion

4.2.1 Synthesis and characterization of iridium anthracenyl complex 4-1 from the reaction of (PCP)Ir with anthracene

Having achieved a good understanding of the regioselectivity of (PCP)Ir C-H activation reactions with naphthalene (as discussed in chapter 3), reactions of (PCP)Ir were conducted with anthracene in order to monitor for similar selectivity (i.e., activation at the β carbon C-H bonds). In anthracene, the γ carbon is the preferred target in electrophilic substitution reactions, due to the more favorable resonance structures available for the intermediate in this process. Given the results discussed in chapter 2, (PCP)Ir acts more as a nucleophile than an electrophile (i.e., (PCP)Ir preferentially activates C-H bonds in *less* electron rich substrates), and so it would be likely to prefer the β C-H bonds in anthracene, similar to the case with naphthalene. In addition, C-H activation at the α or γ positions in anthracene would result in having an sp²-sp² C-C bond ortho to the Ir-C bond in the oxidative addition product (two such bonds in the case of γ activation – Fig. 4.2).

Figure 4.2. Steric interactions *ortho* to sp^2 carbon substituents





vs.

to an sp² C

ortho to two bonds to an sp² C

The reaction of (PCP)IrH₂ with an alkene acceptor such as norbornene (NBE) is known to generate a precursor of the reactive fragment "(PCP)Ir".¹⁷ Reaction of (PCP)IrH₂ and NBE with a slight excess of anthracene at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of a single peak at δ 68.2 ppm. The ¹H NMR spectrum shows signals characteristic of a PCP ligand in a fully symmetrical environment, i.e., all *tert*butyl and methylene linker protons are equivalent. A broad hydride (Ir-H) resonance is observed at -45.5 ppm – precisely the same chemical shift as seen for the (PCP)Ir(phenyl)(H) and (PCP)Ir(naphthyl)(H) complexes. This signal – far upfield from all the remaining aryl and PCP protons – is indicative of a five-coordinate d⁶ metal complex.¹⁸ In the absence of anthracene, (PCP)IrH₂ and norbornene produce a labile "NBE complex" that appears as a broad singlet in the ³¹P NMR spectrum at 62.9 ppm.

In the presence of an excess of anthracene at temperatures lower than 10 °C, the hydride (Ir-H) signal begins to sharpen and separate into two distinct resonances, indicative of the presence of two closely related C-H activation products. Additionally, the remainder of the spectrum transforms from an assemblage of rather broad peaks at room temperature to significantly sharper resonances indicative of a non-symmetric environment at lower temperatures: PCP *tert*butyl and methylene linker protons are each resolved as two inequivalent sets, and signals attributable to an η^1 -anthracenyl ligand appear. At -40 °C, the far-upfield signal in the ¹H NMR spectrum resolves into two separate triplets at δ -45.15 and -45.44 ppm ($J_{HP} = 14.1 \text{ Hz}$) in a 1:1 ratio. As the temperature is raised, the hydride signal for *one* of the two products starts to broaden (indicating faster exchange) significantly sooner than that for the other product, although

the ratios of products does not change. At -10 °C, the more downfield signal is completely featureless, and can no longer be identified as a triplet, while the more upfield signal remains completely sharp. That is, the rate of reductive elimination for one of the rotamers is apparently faster than for the other, allowing it to exchange more rapidly with free substrate and show broadening in the NMR spectra at lower temperatures. Based on analogous results with naphthalene, and exhaustive studies to determine the conformations of the naphthyl activation products, data for anthracene are consistent with characterization of products **4-1a,b** as two rotamers of the square pyramidal complex (PCP)Ir(anthracenyl)(H) as shown in eq. 2.^{19,20}



Analogous to reactions with naphthalene, there are additional signals that appear at low temperature that were not detectable at ambient temperature. The ³¹P NMR spectrum has a new broad signal at δ 67.5 ppm in a ratio of approximately 1:7.5 vs. the peak for the products of C-H activation as discussed above. Based on similar data for C-H activation of naphthalene, and on literature precedents,^{3,4,7,21} the additional NMR data, only seen in low temperature experiments, are consistent with characterization of product **4-2** as the π -coordination complex of (PCP)Ir and anthracene (eq. 3).



Low temperature NMR experiments show that the η^2 -anthracene complex is extremely fluxional and in equilibrium with the formal C-H oxidative addition products. Rigorous equilibrium measurements were not conducted, but it is clear from the ¹H NMR and ³¹P NMR spectra, that η^2 coordination is significantly less favorable for anthracene than for naphthalene, at least in comparison with η^1 C-H activation products. As mentioned in the introduction to this chapter, exclusive C-H activation at the β position in anthracene is an important result, since reports in the literature focus on functionalizing at γ positions C9 and C10. Therefore, oxidative addition by (PCP)Ir could possibly be the basis for novel processes for functionalizing anthracene (and related substrates) at the β positions (C2, C3, C6, and C7). Attempts to crystallize the C-H activation products from anthracene were not successful.

4.2.2 Synthesis and characterization of products from the reaction of (PCP)Ir with phenanthrene

Like anthracene, the γ carbon of phenanthrene is the preferred target in electrophilic substitution reactions, due to the more favorable resonance structures available for the intermediate in this process. However, for all of the same reasons that were discussed above in the context of C-H activation of anthracene, reaction between (PCP)Ir and phenanthrene was predicted to occur exclusively at the β carbons. While experiments showed this to be the case for the kinetic products, the geometry of phenanthrene is different than that of anthracene, and this results in *four* possible product rotamers from β C-H activation (vs. two in the analogous reactions with anthracene and naphthalene - Fig. 4.3).

Figure 4.3 Four rotamers for β activation of phenanthrene



Reaction of (PCP)IrH₂ and NBE (3 equiv.) with a slight excess of phenanthrene at ambient temperature results in disappearance of the dihydride peak in the 31 P NMR

spectrum accompanied by the appearance of a two peaks at δ 68.3 ppm (95%) and 43.1 ppm (5%). The ¹H NMR spectrum shows signals characteristic of a PCP ligand in a fully symmetrical environment, i.e., all *tert*butyl and methylene linker protons are equivalent. A broad hydride (Ir-H) resonance is observed at -45.4 ppm – very similar to the chemical shift seen for the (PCP)Ir(aryl)(H) (aryl = phenyl, naphthyl, anthracenyl) complexes. This signal – far upfield from all the remaining aryl and PCP protons – is indicative of a five-coordinate d⁶ metal complex.¹⁸ In the absence of phenanthrene, (PCP)IrH₂ and norbornene produce a labile "NBE complex" that appears as a broad singlet in the ³¹P NMR spectrum at 62.9 ppm.

In the presence of an excess of phenanthrene at temperatures lower than 10 °C, the hydride (Ir-H) signal begins to separate into two distinct resonances, indicative of the presence of closely related C-H activation products. Additionally, the remainder of the spectrum transforms from an assemblage of rather broad peaks at room temperature to significantly sharper resonances indicative of a non-symmetric environment at lower temperatures: PCP *tert*butyl and methylene linker protons are each resolved as multiple inequivalent sets, and signals attributable to η^1 -phenanthrenyl ligands appear. At -40 °C, the far-upfield signal in the ¹H NMR spectrum resolves into two overlapping triplets at δ -45.39 and -45.48 ppm ($J_{HP} = 13$ Hz). In the ³¹P NMR spectrum, the resonance at δ 68.3 ppm is partially resolved into two products, while the peak at δ 43.1 ppm remains a sharp singlet.

Based on many spectra for C-H activation products (see chapters 2 and 3), the ³¹P NMR signals overlapping at δ 68.3 ppm corresponded to the two hydrides seen in the ¹H NMR spectrum far upfield at δ -45.39 and -45.48 ppm. The ³¹P NMR resonance at δ

43.1 ppm had *no corresponding hydride* resonance in the ¹H NMR spectrum.

Cyclometalated thermodynamic products from the C-H activation of methoxynaphthalenes produced ³¹P NMR resonances with chemical shifts close to this region (see chapter 3). In particular, the cyclometalated products of double C-H activation processes (**3-10** and **3-14**) had very similar chemical shifts in the ³¹P NMR spectrum. When the product mixture was checked by NMR after sitting at ambient temperature for 24 hours, the ³¹P NMR resonance at δ 43.1 ppm had grown to represent 80% of the products in solution, indicating a thermodynamic preference for this product. Since a double C-H activation process was suspected, additional NBE acceptor (2 equiv.) was added, and the solution was stored at ambient temperature for an additional 24 hrs. After this time, ³¹P NMR and ¹H NMR analysis confirmed net conversion to product **4-4**. Therefore, for experiments with phenanthrene as the substrate for C-H activation by (PCP)Ir, oxidative addition of the β C-H bonds yields the kinetic products, but the strongly favored thermodynamic product results from a slow double C-H activation process that yields a cyclometalated, 5-coordinate, 16-electron complex (eq. 4).


One notable feature of the ¹H NMR spectrum for the cyclometalated product **4-4** is worth emphasizing, since it became a diagnostic tool for the identification of similar conformations in products of other reactions. In this 5-coordinate, double C-H activation product, the PCP *tert*butyl groups reside in very different electronic environments due to the presence of an aryl ring in the apical position of the complex's square-pyramidal geometry. Therefore, they resonate as two unique triplets with a large chemical shift difference between them. For **4-4**, the triplets are at δ 1.20 and 0.75 ppm respectively. This difference of 0.45 ppm is very large compared with typical aryl C-H activation products (generally <0.1 ppm difference).

Product 4-4 was generated in excellent yield, and crystallization was successful, confirming the geometry of the product as discussed above. Since the κ^2 phenanthrene ligand is unusually bulky, CO was added to a fresh product mixture in order to determine if the 6-coordinate CO adduct could be generated. Addition of the sixth ligand was successful, yielding product 4-5 (eq. 5). Although CO addition to 16-electron, 5-

coordinate iridium complexes is generally very fast, the diagnostic color change (deep red-orange changing to bright yellow upon addition) for the conversion of **4-4** to **4-5**, was very slow, requiring several hours to go to completion. Product **4-5** was also successfully crystallized. X-ray structures and selected data for both **4-4** and **4-5** are included at the end of this chapter.



4.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in

solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. A full discussion of the NBE complex, including NMR characterization, is included in the Experimental section of Chapter 2 (section 2.3).

Reaction of (PCP)Ir with anthracene (4-1a,b): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Anthracene (10 eq; 0.10 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned lighter red-orange. ³¹P NMR (121.4 MHz, -10 °C, mesitylene- d_{12}): δ 68.2 (d, $J_{PH} = 13.4$ Hz). ¹H NMR (400 MHz, -10 °C, mesitylene- d_{12}): δ 68.2 (d, $J_{PH} = 13.4$ Hz). ¹H NMR (400 MHz, -10 °C, mesitylene- d_{12}): δ 8.40 (br s, 1H, substrate *ortho*-H rotamer A), 8.37 (s, 1H, substrate *ortho*-H rotamer B), all remaining aryl H signals for both rotamers of the C-H addition product and for PCP are obscured by residual solvent and excess, unreacted substrate peaks, 3.37 (d of vt, $J_{HH} = 18.0$ Hz, 4H, C H_2), 0.98 (br t, 36H, C(C H_3)₃), -45.21 (br, 1H, Ir-H, rotamer A), -45.44 (t, $J_{HP} = 13.1$ Hz, 1H, Ir-H, rotamer B).

Evidence for a (PCP)Ir(η^2 -anthracene) π complex (4-2): The ³¹P NMR and ¹H NMR spectra both contain broad resonances at low temperature that may be indicative of a labile π -complex with naphthalene coordinated to the iridium through a C-C bond. Further experiments are necessary in order to fully examine this possibility. The following resonances do not pertain to the C-H addition products as detailed above.

Additionally, they are broad – even at low temperature (-40 °C) and broaden sufficiently to become undetectable at ambient temperature. Although the following data pertain to the unsubstituted naphthalene substrate, similar peaks can be seen in the low temperature spectra for the reaction of (PCP)Ir with both 1,4-dimethylnaphthalene and 1,5dimethylnaphthalene. ³¹P NMR (121.4 MHz, -10 °C, mesitylene- d_{12}): δ 67.5 (br s). ¹H NMR (400 MHz, -10 °C, mesitylene- d_{12}): δ 3.56 (br s, 4H, CH₂). The ¹H NMR resonance is also very close to where the PCP CH₂ signal appears for the four-coordinate CO complex.

Reaction of (PCP)Ir with phenanthrene (4-3a,b,c,d): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Phenanthrene (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. Along with several C-H addition products, an additional signal was immediately present in the ³¹P NMR spectrum. This signal indicated the presence of product **4-4** the details for which are given in the next paragraph below. Data for the C-H addition products are given here: ³¹P NMR (121.4 MHz, -20 °C, mesitylene- d_{12}): δ 67.8 (m, C-H activation products **4-3**). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): All aryl peaks (substrate and PCP) overlapping from many products and/or obscured by residual solvent and unreacted substrate, δ 3.36 (d of vt, J_{HH} = 17.1 Hz, 4H, CH_2), 0.96 (br, 36H, C(CH_3)₃ multiple products), -45.39 (t, J_{HP} = 13.4 Hz, 1H, Ir-*H*, rotamer A), -45.49 (t, J_{HP} = 13.5 Hz, 1H, Ir-*H*, rotamer B). Reaction of (PCP)Ir with phenanthrene to give thermodynamic C-H activation product (4-4): A solution of 4-3 in a J-Young NMR tube was allowed sit sit for 24 hr in an argon-filled glove box at ambient temperature. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; redorange prisms were obtained. The cyclometalated product results from double C-H activation. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 46.3 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): All signals are broad and poorly defined at ambient temperature, despite a single, pure resonance in the ³¹P NMR spectrum.

Reaction of 4-4 with CO to form 4-5: A solution of **4-4** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. Unlike all previous CO addition reactions, the color of the orange solution remained unchanged for several hours. After 12 hr, the solution was yellow – typical for six-coordinate complexes of (PCP)Ir with CO. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; pale yellow plates were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 36.4 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.55 (d, $J_{HH} =$ 8.1 Hz, 1H, substrate *ortho-H*), 8.39 (d, $J_{HH} =$ 7.8 Hz, 1H, substrate *ortho-H*), 7.65 – 7.32 (m, substrate aryl *H*), PCP aryl peaks are obscured by residual solvent, 3.84 (d of t, $J_{HH} =$ 15.6 Hz, $J_{HP} =$ 4.3 Hz, 2H, CH₂), 3.18 (d of t, $J_{HH} =$ 15.8 Hz, $J_{HP} =$ 4.1 Hz, 2H, CH₂), 1.05 (t, $J_{HH} =$ 6.2 Hz, 18H, C(CH₃)₃), 0.18 (t, $J_{HH} =$ 6.0 Hz, 18H, C(CH₃)₃.

4.4 Conclusion

Reactions with the tricyclic fused-ring substrates anthracene and phenanthrene yielded products that expanded our understanding of how (PCP)Ir interacts with aryl substrates. Anthracene is very similar to naphthalene in its susceptibility to C-H activation by (PCP)Ir. Once again, the pincer complex oxidatively added C-H bonds in the β position preferentially to the others. This selectivity is opposite from that shown by the electrophilic aromatic substitution reactions typically employed for functionalizing these substrates. Anthracene seems to show more stability as an $\eta^2 \pi$ -complex than naphthalene.

Reactions of (PCP)Ir with phenanthrene produced four unique isomers from C-H activation, in keeping with the geometry of the substrate. However, these kinetic products covert to a single thermodynamic product reasonably quickly (< 24 hrs. at ambient temperature). The preferred product results from a double C-H activation mechanism leading to cyclometalation and the formation of a 5-member metalloaromatic ring. Despite having only 16 electrons and an open coordination site, the cyclometalated product is very stable and persists even after extended heating. Addition of CO as a sixth ligand to this product is kinetically much slower than for typical 5-coordinate, non-cyclometalated complexes, indicating significant steric crowding around the open coordination site.

4.5 References

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Figure 4.4. X-ray crystal structure for compound 4-4.

 Table 4.1. Crystal data and structure refinement for 4-4.

Empirical formula	C38 H51 Ir P2	
Formula weight	761.93	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2/n	
Unit cell dimensions	a = 18.090(3) Å	a= 90°.
	b = 10.6814(16) Å	b=103.782(3)°.
	c = 35.951(5) Å	g = 90°.
Volume	6746.5(17) Å ³	
Z	8	
Density (calculated)	1.500 Mg/m ³	
Absorption coefficient	4.078 mm ⁻¹	
F(000)	3088	
Crystal size	0.44 x 0.18 x 0.08 mm ³	
Theta range for data collection	1.85 to 30.03°.	
Index ranges	-24<=h<=25, -14<=k<=15, -50<=l<=50	
Reflections collected	75934	
Independent reflections	19716 [R(int) = 0.0562]	
Completeness to theta = 30.03°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7362 and 0.2670	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	19716 / 0 / 763	
Goodness-of-fit on F ²	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0506, $wR2 = 0.1129$	
R indices (all data)	R1 = 0.0627, wR2 = 0.1183	
Largest diff. peak and hole	5.258 and -2.833 e.Å ⁻³	

Ir(1)-C(36)	2.015(5)	P(1)-C(9)	1.906(6)
Ir(1)-C(1)	2.099(5)	P(2)-C(8)	1.849(6)
Ir(1)-C(25)	2.126(5)	P(2)-C(21)	1.866(6)
Ir(1)-P(2)	2.3243(14)	P(2)-C(17)	1.881(7)
Ir(1)-P(1)	2.3379(14)	C(36)-C(37)	1.428(7)
P(1)-C(7)	1.836(5)	C(37)-C(38)	1.426(7)
P(1)-C(13)	1.885(5)	C(25)-C(38)	1.436(7)
C(36)-Ir(1)-C(1)	92.25(19)	C(8)-P(2)-C(21)	104.5(3)
C(36)-Ir(1)-C(25)	82.0(2)	C(8)-P(2)-C(17)	103.1(3)
C(1)-Ir(1)-C(25)	174.08(19)	C(21)-P(2)-C(17)	111.4(3)
C(36)-Ir(1)-P(2)	94.97(14)	C(8)-P(2)-Ir(1)	104.4(2)
C(1)-Ir(1)-P(2)	82.14(15)	C(21)-P(2)-Ir(1)	126.62(18)
C(25)-Ir(1)-P(2)	99.49(14)	C(17)-P(2)-Ir(1)	104.2(2)
C(36)-Ir(1)-P(1)	96.24(15)	C(37)-C(36)-Ir(1)	113.7(4)
C(1)-Ir(1)-P(1)	81.66(15)	C(38)-C(37)-C(36)	117.5(5)
C(25)-Ir(1)-P(1)	97.71(14)	C(37)-C(38)-C(25)	116.0(4)
P(2)-Ir(1)- $P(1)$	160.61(5)	C(38)-C(25)-Ir(1)	110.7(3)
C(7)-P(1)-C(13)	102.5(2)		
C(7)-P(1)-C(9)	103.9(3)	Torsion angles:	
C(13)-P(1)-C(9)	109.9(3)	C(36)-C(37)-C(38)-C(2	25) -1.7(7)
C(7)-P(1)-Ir(1)	102.45(17)	C(32)-C(37)-C(38)-C(2	-0.7(8)
C(13)-P(1)-Ir(1)	124.44(19)		
C(9)-P(1)-Ir(1)	110.92(18)		

 Table 4.2.
 Selected bond lengths [Å] and angles [°] for 4-4.





Table 4.3. Crystal data and structure refinement for 4-5.

Empirical formula	C39 H51 Ir O P2	
Formula weight	789.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 11.5438(17) Å	a= 90°.
	b = 18.322(3) Å	b=102.274(3)°.
	c = 16.267(2) Å	$g = 90^{\circ}$.
Volume	3362.0(9) Å ³	
Z	4	
Density (calculated)	1.561 Mg/m ³	
Absorption coefficient	4.097 mm ⁻¹	
F(000)	1600	
Crystal size	0.26 x 0.22 x 0.06 mm ³	
Theta range for data collection	1.98 to 31.00°.	
Index ranges	-16<=h<=16, -26<=k<=26, -22<=l<=23	
Reflections collected	40659	
Independent reflections	10701 [R(int) = 0.0378]	
Completeness to theta = 31.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7911 and 0.4156	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10701 / 0 / 400	
Goodness-of-fit on F ²	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0339, $wR2 = 0.0778$	
R indices (all data)	R1 = 0.0424, $wR2 = 0.0815$	
Largest diff. peak and hole	3.027 and -1.243 e.Å ⁻³	

Ir(1)-C(39)	1.887(3)	P(2)-C(8)	1.836(3)
Ir(1)-C(1)	2.107(3)	P(2)-C(21)	1.896(3)
Ir(1)-C(28)	2.116(3)	P(2)-C(17)	1.916(3)
Ir(1)-C(25)	2.127(3)	O(1)-C(39)	1.153(4)
Ir(1)-P(2)	2.3790(8)	C(26)-C(27)	1.433(4)
Ir(1)-P(1)	2.4008(9)	C(27)-C(28)	1.432(4)
P(1)-C(7)	1.844(3)	C(25)-C(26)	1.422(4)
P(1)-C(9)	1.902(3)		
P(1)-C(13)	1.903(3)		
C(39)-Ir(1)-C(1)	99.76(13)	C(7)-P(1)-Ir(1)	97.60(11)
C(39)-Ir(1)-C(28)	167.47(13)	C(9)-P(1)-Ir(1)	119.04(11)
C(1)-Ir(1)-C(28)	92.56(12)	C(13)-P(1)-Ir(1)	121.59(11)
C(39)-Ir(1)-C(25)	88.30(13)	C(8)-P(2)-C(21)	108.21(16)
C(1)-Ir(1)-C(25)	171.82(12)	C(8)-P(2)-C(17)	101.06(15)
C(28)-Ir(1)-C(25)	79.46(12)	C(21)-P(2)-C(17)	108.89(15)
C(39)-Ir(1)-P(2)	89.53(10)	C(8)-P(2)-Ir(1)	99.50(10)
C(1)-Ir(1)-P(2)	77.20(9)	C(21)-P(2)-Ir(1)	120.19(11)
C(28)-Ir(1)-P(2)	90.96(8)	C(17)-P(2)-Ir(1)	116.34(10)
C(25)-Ir(1)-P(2)	104.52(9)	C(26)-C(25)-Ir(1)	113.6(2)
C(39)-Ir(1)-P(1)	92.52(10)	C(25)-C(26)-C(27)	116.4(3)
C(1)-Ir(1)-P(1)	79.19(9)	C(28)-C(27)-C(26)	116.9(3)
C(28)-Ir(1)-P(1)	92.06(9)	C(27)-C(28)-Ir(1)	113.3(2)
C(25)-Ir(1)-P(1)	99.14(9)	O(1)-C(39)-Ir(1)	171.6(3)
P(2)-Ir(1)-P(1)	156.31(3)		
C(7)-P(1)-C(9)	104.88(15)	Torsion angles:	
C(7)-P(1)-C(13)	103.01(15)	C(25)-C(26)-C(27)-C(28) -0.8(4)	
C(9)-P(1)-C(13)	107.33(15)	C(35)-C(26)-C(27)-C(32) -0.5(5)	

Table 4.4. Selected bond lengths [Å] and angles [°] for 4-5.

Chapter 5

Reaction of (PCP)Ir with Biphenyl and a series of Biphenyl derivatives

Abstract

In experiments with (PCP)Ir and the tricyclic, fused-ring substrate phenanthrene, an unexpected thermodynamically favored product was formed through a mechanism involving *two* C-H activation reactions. The cyclometalated product was stable, even at high temperature, despite being a coordinatively unsaturated 16-electron complex. The beneficial "metalloaromaticity" gained through the κ^2 binding mode apparently outweighed the usual reluctance of (PCP)Ir to activate C-H bonds *ortho* to alkyl (or aryl) substituents.

Phenanthene is a planar molecule, and therefore, access to the C-H bonds of C4 and C5 (leading to the cyclometalated product) is expected to be relatively facile. In contrast, the two phenyl rings of the similar substrate, biphenyl, are *not* planar; in the lowest energy conformation, the torsional angle between them is approximately 45°. Results of experiments with biphenyl show that double C-H activation leads to thermodynamically favorable products despite the requirement that the substrate's phenyl rings rotate around the aryl-aryl bond into a nearly planar conformation (at a cost of ~6 kcal/mol in unsubstituted biphenyl). Analogous results are seen even with biphenyl derivatives chosen to undermine the cyclometalation process through electronic or steric influences.

5.1 Introduction

As its name implies, the structure of biphenyl is comprised of two benzene rings connected by a single C-C (sp^2-sp^2) bond. It is similar to phenanthrene, but lacks the ethylene linker that completes penanthrene's central aromatic ring, without which, biphenyl is *not* contrained to planar geometry. In the lowest energy conformation, the two phenyl rings deviate from co-planarity by a torisional angle of 44.5° (Fig. 5.1).

Figure 5.1. Structural features of biphenyl





torsional angle

Biphenyl and its derivatives have a number of desirable properties and have been widely used as flame retardants, antifungal agents, and as additives in coolants and insulating fluids. Unfortunately, the polychlorinated derivatives are highly toxic to the environment, particularly when burned, and are classified as suspected carcinogens. Production of polychlorinated biphenyls (PCBs) was banned in the United States in 1979 and worldwide in 2001.¹⁻³ Remediation of PCB-contaminated sites is extremely costly, and entails either encapsulation (typically followed by burial in an appropriately designed and certified landfill) or destruction via physical or chemical means. To date, all chemical methods for the degradation of PCBs require extremely harsh conditions, so an effective route to catalytic dehalogenation, mediated by a transition metal complex would potentially be a valuable development.

Biphenyls can be synthesized through a variety of coupling processes, including direct arylation of benzene, and development of these methods utilizing transition metal systems has been widely reported.⁴⁻²⁶ Additionally, Jones, et al. have published numerous reports on using group 9 and 10 metals including cobalt, rhodium, nickel, palladium, and platinum to facilitate C-C activation of biphenylene to yield biphenyl products.²⁷⁻³⁷ The reaction of (PCP)Ir with biphenylene will be discussed in chapter 7.

C-H activation and functionalization reactions between transition metal complexes and biphenyls have not generated much interest, with few reports in the literature, suggesting that functionalizing benzene *prior* to coupling reactions to make biphenyls has been the preferred synthetic strategy.³⁸⁻⁴³ The unique geometry of the biphenyl molecule has, however, been exploited in various multidentate and/or chiral ligand systems.⁴⁴⁻⁵²

Not surprisingly, unsubstituted biphenyl shows reactivity similar to benzene, and as such, is a useful synthon for substituted derivatives and in the context of more elaborate syntheses. Recently, simple polyaromatic molecules based on biphenyl and bipyridyl motifs have found widespread application as chelating ligands in metal complexes designed for use in organic light-emitting diodes (OLEDs). Research and development of these complexes has grown exponentially over the last five years, with dozens of papers and patent applications being filed annually, especially in Japan and Germany.⁵³⁻⁶³

Results are presented in this chapter for reactions of (PCP)Ir and several biphenyl substrates. The inspiration for these studies was the discovery of the thermodynamically favorable cyclometalation reaction with phenanthrene. In fact, the analogous process

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does occur with biphenyls, even in derivatives with sterically demanding substituents. Most importantly, the cylcometalation also proceeds with derivatives bearing powerfully *ortho-* influencing fluoro substituents. With further development, this could be a valuable result since iridium, biphenyl, and fluoro substituents are all commonly exploited in recent OLED technological advances.

5.2.1 Synthesis and characterization of products from the reaction of (PCP)Ir with biphenyl

In the context of results from the studies of C-H activation of substituted benzenes, predicting selectivity among the C-H bonds in biphenyl would seem to be trivial, since it is in fact, a mono-substituted benzene! Therefore, the C-H bonds at carbons 3, 4, and 5 should be accessible to (PCP)Ir, yielding two *meta* rotamers and a *para* product, directly analogous to similar reactions with mono-alkylated or halogenated benzenes (eq. 1).



In accordance with results presented in chapter 2 of this thesis, activation of biphenyl at C2 or C6 should be prevented by the steric bulk of the phenyl substituent in the case of biphenyl. However, as was seen with phenanthrene, activation of the more sterically crowded (and therefore, less kinetically favored) C-H bonds leads to the *preferred* thermodynamic product.

Reaction of (PCP)IrH₂ and NBE (3 equiv.) with a slight excess of biphenyl (1.1 equiv.) at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of a two new peaks at δ 68.1 ppm (95%) and δ 42.5 ppm (5%) within 30 min. These results are directly analogous to those seen

for the reaction of (PCP)Ir with phenanthrene. The ¹H NMR spectrum shows signals characteristic of a PCP ligand in a fully symmetrical environment, i.e., all *tert*butyl and methylene linker protons are equivalent. A broad hydride (Ir-H) resonance is observed at -45.6 ppm; once again, this is very similar to the chemical shift seen for the (PCP)Ir(aryl)(H) (aryl = phenyl, naphthyl, anthracenyl, phenanthryl) complexes. This signal – far upfield from all the remaining aryl and PCP protons – is indicative of a fivecoordinate d⁶ metal complex.⁶⁴ In the absence of phenanthrene, (PCP)IrH₂ and norbornene produce a labile "NBE complex" that appears as a broad singlet in the ³¹P NMR spectrum at 62.9 ppm.

At -20 °C, the far-upfield signal in the ¹H NMR spectrum resolves into two overlapping triplets at δ -45.39 and -45.48 ppm ($J_{HP} = 13.5$ Hz). In the ³¹P NMR spectrum, the downfield resonance is resolved into two signals at δ 67.7 and δ 67.4 ppm, corresponding to the two hydride signals and in the same ratio (aprroximately 1:1). The signal at δ 42.5 ppm remains sharp at low temperature. Additionally, a small signal for the NBE complex can be observed at δ 62.6 ppm (2%). The remainder of the spectrum transforms from an assemblage of rather broad peaks at room temperature to significantly sharper resonances indicative of a non-symmetric environment at lower temperatures: PCP *tert*butyl and methylene linker protons are each resolved as multiple inequivalent sets.

Based on similar results with the closely related substrate phenanthrene, the upfield hydride signals in the ¹H NMR spectrum were assigned to the kinetic C-H addition products as shown in eq. 1. The ³¹P NMR resonance at δ 42.5 ppm had *no corresponding hydride* resonance in the ¹H NMR spectrum, and was assigned to the

cyclometalated thermodynamic product **5-1.** When the product mixture was checked by NMR after sitting at ambient temperature for 24 hours, the ³¹P NMR resonance at δ 42.5 ppm had grown to represent 65% of the products in solution. Additional NBE acceptor (2 equiv.) was added, and the solution was stored at ambient temperature for an additional 24 hrs. After this time, the ¹H NMR spectrum showed two inequivalent, widely separated signals for the PCP *tert*butyl groups at δ 1.19 and δ 0.75 ppm, and confirmed total disappearance of all hydride resonances. These results are consistent with net conversion to product **5-1**. Therefore, for experiments with biphenyl and (PCP)Ir, kinetic products are formed from C-H activation at the least hindered carbons, but the strongly favored thermodynamic product results from a slow double C-H activation process that yields a cyclometalated, 5-coordinate, 16-electron complex (eq. 2).



Product **5-1** was generated in excellent yield, and crystallization was successful, confirming the geometry of the product as discussed above. Despite the torsional angle of 45° in free biphenyl, and the associated energetic cost of rotating around the C-C single bond, the cyclometalated product shows nearly planar geometry for the biphenyl moiety. Similar to the cyclometalated product from addition of phenanthrene to (PCP)Ir, **5-1** has a slightly distorted square-pyramidal geometry with one of the substrate aryl groups *trans* to the PCP carbon atom, and the other in the apical position, *cis* to the PCP phenyl ring. This arrangement requires the PCP *tert*butyl groups above and below the plane occupied by the biphenyl ligand to move apart in order to accommodate the aryl ring coordinating between them (Fig. 5.2).





This distortion creates significantly greater steric congestion around the remaining empty coordination site on iridium. Addition of CO as sixth ligand to yield product **5-2** was successful, but slow, requiring several hours to go to completion (eq. 3). Product **5-2** was also successfully crystallized. X-ray crystal structures and selected data for both **5-1** and **5-2** are included at the end of this chapter.



5.2.2 Synthesis and characterization of products from the reaction of (PCP)Ir with alkylated biphenyl derivatives

Results from the reaction of (PCP)Ir and phenanthrene (see chapter 4) showed that cyclometalation via a double C-H activation process leads to a very thermodynamically stable, 16-electron product. Given its non-planar geometry, successful cyclometalation with biphenyl was somewhat more surprising; this result implies that the (PCP)Ir fragment can overcome a significant kinetic barrier when there is enough net thermodynamic benefit. In order to test the limits of the mechanism for cyclometalation, (PCP)Ir was reacted with a series of alkylated biphenyls. Three such substrates – 4-methylbiphenyl, 4,4'-dimethylbiphenyl, and 4,4'-di-*tert*butylbiphenyl – blocked access to the *meta* and *para* C-H bonds (i.e., C3, C4, and C5) with increasingly large alkyl groups. For cyclometalation to occur with the 4,4'-disubstituted substrates, C-H activation would need to occur at a carbon *ortho* to the biphenyl C-C bond *without prior activation* at any of the less hindered positions. In addition, the alkyl substituents themselves add steric bulk to the product(s), with at least one of them situated very close to the PCP phenyl ring (*vide infra*). A fourth substrate, 3,3'-dimethylbiphenyl adds to the torsional strain in the biphenyl substrate, increasing the barrier to rotation, and therefore, to the process of oxidative addition to iridium.

Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of 4methylbiphenyl (1.1 equiv.) at ambient temperature yields products analogous to those seen with biphenyl from the C-H activation of the unsubstituted phenyl ring (eq. 4). Likewise, after 24 hrs at ambient temperature, NMR spectra show exclusive formation of the cyclometalated products **5-3a,b**. Since the substrate in this case is unsymmetrically substituted, *two* products are made in a 1:1 ratio. This result is interesting, because it demonstrates that the (PCP)Ir fragment can accommodate the methyl group in either position as shown in eq. 4, despite the greater proximity to the PCP phenyl ring in product **5-3a**.



Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of either 4,4'dimethylbiphenyl or 4,4'-di-*tert*butylbiphenyl (1.1 equiv.) at ambient temperature frustrates the ability of the (PCP)Ir fragment to proceed with C-H activation since there are no unhindered C-H bonds in either of these substrates. Encouragingly, however, NMR spectra showed evidence of a minor amount (<3%) of the double C-H addition product along with a major signal for the (PCP)Ir(NBE) complex after 60 min. After 24 hrs. at ambient temperature, NMR spectra showed an increase in the solution concentration of the cyclometalated product to ~15 %. Although it was confirmed that C-H activation at the hindered C2 position followed by cyclometalation was possible for these substrates, the rate for this process was severely curtailed, apparently due to the 4,4' substituents and increased steric hindrance of the addition process. Both product solutions were therefore heated at 75 °C for an additional 24 hrs; subsequent NMR analyses confirmed 100% conversion to products **5-4** and **5-5** (Fig. 5.3). Figure 5.3. Products 5-4 and 5-5



Having determined that steric hindrance at C4 markedly slows down the rate, but ultimately does not block the mechanism of cyclometalation, a different strategy was explored with the substrate 3,3'-dimethylbiphenyl. In order for (PCP)Ir to form a cyclometalated product with this substrate, not only do the two phenyl rings of biphenyl have to rotate to a nearly co-planar geometry, but the methyl substituents must be *both* rotated away from the metal center, in order to avoid an *ortho* methyl group in the final product (Fig. 5.4).



Figure 5.4. Possible configurations of the product from 3,3'-dimethylbiphenyl

Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of 3,3'dimethylbiphenyl (1.1 equiv.) at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of a single new peak at δ 67.9 ppm. A broad hydride (Ir-H) resonance is observed at -45.6 ppm in the ¹H NMR spectrum; this is diagnostic of *meta* or *para* substituted aryl C-H activation. Indeed, 3,3'-dimethylbiphenyl has one unhindered site for oxidative addition by (PCP)Ir (C5). It is interesting to note that the NMR spectra show *no evidence* for the product of double C-H activation within the first two hrs. of reaction time. At -40 °C, the farupfield signal in the ¹H NMR spectrum resolves into two overlapping triplets at δ -45.48 and -45.69 ppm ($J_{HP} = 13.5$ Hz) in a 1:1 ratio, confirming the two expected *meta*-type products. Heating the solution at 75 °C for 24 hrs. yielded 100% conversion to the cyclometalated product **5-6**, with both methyl substituents rotated to point away from the metal center (eq. 5).

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} P^{t}Bu_{2} \\ P^{t}Bu_{2} \end{array} \\ P^{t}Bu_{2} \end{array} + \begin{array}{c} \begin{array}{c} 24 \text{ hr.} \\ NBE \end{array} \\ NBE \end{array} \\ \begin{array}{c} P^{t}Bu_{2} \end{array} \\ P^{t}Bu_{2} \end{array} \end{array}$$
(5)

Both products **5-5** and **5-6** were successfully crystallized. X-ray crystal structures and selected data for both are included at the end of this chapter.

5.2.3 Synthesis and characterization of products from the reaction of (PCP)Ir with fluorinated biphenyl derivatives

Several valuable insights were gained concerning the (PCP)Ir cyclometalation mechanism by studying the alkylated substrates discussed in the previous section. First, there is no requirement for preliminary activation of an unhindered C-H bond prior to addition at the less kinetically favorable C2 (or C6) position that leads to double C-H activation. Second, the presence of bulky substituents on the biphenyl substrate (methyl, *tert*butyl) does not prevent 100% conversion to the ultimate product, despite the steric requirements of the PCP ligand system.

Considering electronic effects, results in chapter 2 included the observation that aryl fluoro substituents have a strong electronic influence on promoting *ortho* C-H activation. Therefore, experiments with (PCP)Ir and two fluorinated biphenyl substrates were conducted in order to determine whether the electronic influence from fluorine would prevent or significantly slow down the rate of cyclometalation.

Reaction of (PCP)Ir with 4,4'-difluorobiphenyl at ambient temperature yielded products exclusively from *ortho* C-H activation. Analogous to reactions with fluorobenzene, the products gave sharp, slowly exchanging NMR resonances at ambient temperature and after two hours, there was no spectral evidence for cyclometalation. Therefore, the solution was heated at 75 °C for 72 hrs. NMR analysis post-heating showed 100% conversion to the cyclometalated product **5-7**, indicating that the double C-H activation process still leads to the most favorable thermodynamic product, despite the inductive electronic effect from fluorine substituents (eq. 6).



A similar experiment was conducted with (PCP)Ir and 2,2'-difluorobiphenyl. This second fluorinated substrate combines electronic and steric effects, since the lowest energy conformation of the free substrate has the two fluoro substituents *trans* to each other, at a dihedral angle of 58°. For this substrate, not only is there a strong electronic influence from fluorine promoting C-H activation at C3, but in order for cyclometalation to take place, the two phenyl rings of biphenyl have to rotate and force the fluoro substituents into very close proximity in a *cis* conformation (Fig. 5.5). This process is calculated to require ~12.5 kcal/mol.^{65,66}





Analogous to the results with 4,4'-difluorobiphenyl, reaction of (PCP)Ir with 2,2'difluorobiphenyl at ambient temperature yielded products exclusively from *ortho* C-H activation. Once again, the products gave sharp, slowly exchanging NMR resonances at ambient temperature and after two hours, there was no spectral evidence for cyclometalation. Therefore, the solution was heated at 75 °C for 24 hrs. NMR analysis post-heating showed only 5% conversion to the cyclometalated product **5-8**, indicating that the energetic barrier to double C-H activation for this substrate is much higher than for any of the previously studied biphenyls. After raising the temperature to 125 °C and heating for an additional 24 hrs., NMR analysis showed 75% conversion to **5-8**. Full conversion to the cyclometalated product was finally observed only after an additional 24 hours at 125 °C (eq. 7).



Products **5-7** and **5-8** were successfully crystallized; x-ray structures and selected data for both are included at the end of this chapter.

5.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in

solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. A full discussion of the NBE complex, including NMR characterization, is included in the Experimental section of Chapter 2 (section 2.3).

General remarks concerning the reactions of (PCP)Ir with biphenyl substrates:

Substrates in this chapter were studied in the context of exploring cyclometalation reactions involving single or double C-H activation processes. Typical results for a variety of kinetic C-H activation products are seen in all cases and are not documented here, with a few exceptions as noted below. The NMR data presented are for the cyclometalated, thermodynamically favored products.

Reaction of (PCP)Ir with biphenyl (5-1): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. Biphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned lighter red-orange. After 24 hr at ambient temperature, the solution turned very dark red-brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; dark orange-red prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.4 (s). Despite the purity of this product, the ¹H NMR spectrum shows broad peaks (as did that for the cyclometalated product from phenanthrene in the previous chapter). This could indicate

the presence of many slightly different conformations of the product – all with slightly different positions for the *tert* butyl groups, PCP backbone, etc. Correspondingly, there is significant disorder shown in the crystal structures for these complexes. ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): Aryl H signals for substrate and PCP are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.44 (br t, J_{HP} = 3.9 Hz, 4H, CH₂), 0.75 (br t, J_{HH} = 6.0 Hz, 36H, C(CH₃)₃).

Reaction of 5-1 with CO to form 5-2: A solution of **5-1** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The color of the orange solution remained unchanged for several hours. After 12 hr, the solution was yellow – typical for sixcoordinate complexes of (PCP)Ir with CO. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; pale yellow needles were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 35.4 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.42 (m, 1H, substrate *ortho-H*), 7.70 (m, 1H, substrate *ortho-H*), 7.60 – 7.10 (m, substrate aryl *H*), PCP aryl peaks are obscured by residual solvent, 3.77 (d of t, $J_{HH} = 16.5$ Hz, $J_{HP} = 3.9$ Hz, 2H, CH_2), 3.14 (d of t, $J_{HH} =$ 15.5 Hz, $J_{HP} = 3.2$ Hz, 2H, CH_2), 1.08 (t, $J_{HH} = 6.2$ Hz, 18H, $C(CH_3)_3$), 0.49 (t, $J_{HH} = 6.6$ Hz, 18H, $C(CH_3)_3$.

Reaction of (PCP)Ir with 4-methylbiphenyl (5-3): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 4-

Methylbiphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned lighter red-orange. After 24 hr at 75 °C, the solution turned very dark red-brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; dark orange-red prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.5 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.43 (d, $J_{HH} = 8.1$ Hz, 2H, substrate *H*), 7.34 (d, $J_{HH} = 7.6$ Hz, 2H, substrate *H*), 7.24 (t, $J_{HH} = 7.9$ Hz, 1H, substrate *H*), 7.15 (t, $J_{HH} =$ 6.9 Hz, 1H, substrate *H*), 7.12 (d, $J_{HH} = 6.7$ Hz, 1H, substrate *H*), aryl H signals for PCP are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.45 (br t, 4H, *CH*₂), 0.77 (br t, $J_{HH} = 5.8$ Hz, 36H, C(*CH*₃)₃ rotamer A), 0.74 (br t, $J_{HH} = 5.8$ Hz, 36H, C(*CH*₃)₃ rotamer B).

Reaction of (PCP)Ir with 4,4'-dimethylbiphenyl (5-4): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 4,4'-Dimethylbiphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned lighter red-orange. After 24 hr at 75 °C, the solution turned very dark red-brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; dark orange-red rods were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.4 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.39 (d, $J_{\text{HH}} = 7.7$ Hz, 2H, substrate *H*), 7.34 (d, $J_{\text{HH}} = 7.5$ Hz, 2H, substrate *H*), 7.16 (d, $J_{\text{HH}} = 7.9$ Hz, 2H, substrate *H*), aryl H signals for PCP are complicated and overlapping, and in some cases, obscured

by the residual solvent peaks, 3.47 (br t, J_{HP} = 3.8 Hz, 4H, C H_2), 0.77 (br t, J_{HH} = 6.0 Hz, 36H, C(C H_3)₃).

Reaction of (PCP)Ir with 4,4'-di-*tert***butylbiphenyl (5-5)**: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 4,4'-Di-*tert*butylbiphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned lighter red-orange. After 72 hr at 75 °C, the solution turned very dark red-brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; dark red prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 44.1 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.47 (d, $J_{HH} = 7.7$ Hz, 2H, substrate *H*), 7.37 (d, $J_{HH} = 7.5$ Hz, 2H, substrate *H*), 7.37 (d, $J_{HH} = 7.5$ Hz, 2H, substrate *H*), 7.37 (d, $J_{HH} = 7.6$ Hz, 360 (br t, 4H, C H_2), 1.37 (br s, 18H, substrate C(C H_3)₃), 0.77 (br t, $J_{HH} = 6.0$ Hz, 36H, C(C H_3)₃).

Reaction of (PCP)Ir with 3,3'-dimethylbiphenyl (5-6): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 3,3'-Dimethylbiphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned lighter red-orange. After 24 hr at 75 °C, the solution turned very dark red-brown. The solvent was evacuated

and the resulting solid was redissolved in and recrystallized from pentane and benzene; dark orange-red prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.4 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.45 (s, 2H, substrate *H*), 7.34 (d, $J_{\rm HH} = 8.1$ Hz, 2H, substrate *H*), 7.28 (d, $J_{\rm HH} = 9.3$ Hz, 2H, substrate *H*), aryl H signals for PCP are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.44 (br t, 4H, C H_2), 2.25 (s, 6H, substrate C H_3), 0.75 (br t, 36H, C(C H_3)₃).

Reaction of (PCP)Ir with 4,4'-difluorobiphenyl (5-7): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 4,4'-Difluorobiphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark brown-orange. After 72 hr at 75 °C, the solution turned very dark red-brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; an absolutely gigantic dark red-brown trapezoid was obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.3 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.29 (d, $J_{\text{HH}} = 7.0$ Hz, 2H, substrate *H*), 7.22 (s, 1H, substrate *H*), 7.13 (t, $J_{\text{HH}} = 7.2$ Hz, 2H, substrate *H*), aryl H signals for PCP are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.34 (t, $J_{\text{HP}} = 4.0$ Hz, 4H, CH_2), 0.68 (br t, 36H, C(CH_3)₃).
Reaction of (PCP)Ir with 2,2'-difluorobiphenyl to yield C-H activation products: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 2,2'-Difluorobiphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark brown-orange. After 24 hr at ambient temperature, C-H activation products persisted in the ³¹P NMR spectrum, with little or no evidence of cyclometallation. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 69.3 (d, $J_{PH} = 14.5$ Hz), 68.9 (d, $J_{PH} = 12.8$ Hz), 67.8 (d, $J_{PH} = 12.8$ Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): aryl H signals for substrate and PCP are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.38 (t, $J_{HH} = 15.6$ Hz, 4H, CH₂), 1.06 (t, $J_{HH} = 6.4$ Hz, 36H, C(CH₃)₃).

Reaction of (PCP)Ir with 2,2'-difluorobiphenyl to thermodynamic product (5-8):

After heating a solution of C-H activation products from (PCP)Ir and 2,2'difluorobiphenyl for 72 hr at 125 °C, the solution turned very dark red-brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; dark brown-orange prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.1 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.33 (d, $J_{\text{HH}} = 4.5$ Hz, 1H, substrate *ortho-H*), 7.32 (d, $J_{\text{HH}} = 4.5$ Hz, 1H, substrate *ortho-H*), 7.15 (t, $J_{\text{HH}} = 7.2$ Hz, 2H, substrate *H*), 7.12 (t, $J_{\text{HH}} = 7.2$ Hz, 2H, substrate *H*), aryl H signals for PCP are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.40 (br t, 4H, C H_2), 0.68 (br t, 36H, C(C H_3)₃).

5.4 Conclusion

A series of experiments with biphenyl derivatives yielded additional insight concerning the reactivity and selectivity of (PCP)Ir for C-H activation reactions of aryl substrates. Biphenyls were chosen based on results with phenanthrene that showed that thermodynamically stable products result from a cyclometalation process involving *two* successive C-H activation reactions. There are many reasons for the remarkable stability of cyclometalated products, including the fact that all hydrides are scavenged by the sacrificial acceptor norbornene, so the reverse reaction - reductive elimination – is impossible.

Successful oxidative addition reactions resulting in cyclometalated products were observed for *all* of the biphenyl susbtrates. Electron withdrawing fluoro substituents stabilized the initial C-H activation products, but did not prevent the progression to the ultimate cyclometalated product. Even with steric crowding slowing down either initial C-H activation (e.g., 4,4'-di-*tert*butylbiphenyl) or cyclometalation (e.g., 2,2'difluorobiphenyl), yields were 100% in all cases. In summary, for (PCP)Ir, double C-H activation with concommitant loss of the hydrides, followed by cyclometalation to yield a 16 electron, Ir(III) complex, is an extremely advantageous process that yields products of unprecedented stability in the context of results presented in this thesis.

5.5 References

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 Table 5.1. Crystal data and structure refinement for 5-1.

Empirical formula	C36 H51 Ir P2	
Formula weight	737.91	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pn2(1)a	
Unit cell dimensions	a = 17.3352(9) Å	a= 90°.
	b = 17.1066(8) Å	b= 90°.
	c = 10.9090(5) Å	g = 90°.
Volume	3235.0(3) Å ³	
Z	4	
Density (calculated)	1.515 Mg/m ³	
Absorption coefficient	4.249 mm ⁻¹	
F(000)	1496	
Crystal size	0.25 x 0.10 x 0.03 mm ³	
Theta range for data collection	2.21 to 32.04°.	
Index ranges	-25<=h<=25, -25<=k<=25, -16<=l<=16	
Reflections collected	40181	
Independent reflections	11172 [R(int) = 0.0397]	
Completeness to theta = 32.04°	99.9 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.8831 and 0.4164	
Refinement method	Full-matrix least-squares of	on F ²
Data / restraints / parameters	11172 / 1 / 364	
Goodness-of-fit on F ²	0.986	
Final R indices [I>2sigma(I)]	R1 = 0.0252, wR2 = 0.050)9
R indices (all data)	R1 = 0.0302, $wR2 = 0.0524$	
Absolute structure parameter	0.004(4)	
Largest diff. peak and hole	1.802 and -0.787 e.Å ⁻³	

Ir(1)-C(32)	2.012(3)	P(2)-C(8)	1.841(3)
Ir(1)-C(1)	2.097(3)	P(2)-C(21)	1.873(3)
Ir(1)-C(25)	2.103(3)	P(2)-C(17)	1.890(3)
Ir(1)-P(2)	2.3161(7)	C(30)-C(31)	1.459(4)
Ir(1)-P(1)	2.3372(7)	C(31)-C(32)	1.411(4)
P(1)-C(7)	1.844(3)	C(25)-C(30)	1.423(4)
P(1)-C(13)	1.884(3)		
P(1)-C(9)	1.903(3)		
C(32)-Ir(1)-C(1)	94.55(10)	C(8)-P(2)-C(21)	104.60(14)
C(32)-Ir(1)-C(25)	80.76(11)	C(8)-P(2)-C(17)	104.17(14)
C(1)-Ir(1)-C(25)	175.30(10)	C(21)-P(2)-C(17)	111.82(15)
C(32)-Ir(1)-P(2)	94.02(8)	C(8)-P(2)-Ir(1)	104.78(9)
C(1)-Ir(1)-P(2)	82.14(8)	C(21)-P(2)-Ir(1)	126.49(10)
C(25)-Ir(1)-P(2)	98.28(8)	C(17)-P(2)-Ir(1)	102.88(10)
C(32)-Ir(1)-P(1)	97.06(8)	C(31)-C(32)-Ir(1)	115.32(19)
C(1)-Ir(1)-P(1)	82.01(8)	C(32)-C(31)-C(30)	116.2(2)
C(25)-Ir(1)-P(1)	98.32(7)	C(25)-C(30)-C(31)	114.2(2)
P(2)-Ir(1)- $P(1)$	161.31(3)	C(30)-C(25)-Ir(1)	113.08(19)
C(7)-P(1)-C(13)	103.79(13)		
C(7)-P(1)-C(9)	104.32(13)	Torsion angles:	
C(13)-P(1)-C(9)	108.70(12)	C(25)-C(30)-C(31)-C(32) 2.2(3)
C(7)-P(1)-Ir(1)	101.40(9)	C(29)-C(30)-C(31)-C(36) -0.2(4)
C(13)-P(1)-Ir(1)	124.27(9)		
C(9)-P(1)-Ir(1)	111.88(9)		

 Table 5.2.
 Selected bond lengths [Å] and angles [°] for 5-1.





 Table 5.3.
 Crystal data and structure refinement for 5-2.

Empirical formula	C39 H52.67 Ir O P2	
Formula weight	791.62	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 11.1879(10) Å	a= 90°.
	b = 37.899(3) Å	b=94.196(2)°.
	c = 24.536(2) Å	g = 90°.
Volume	10375.6(16) Å ³	
Z	12	
Density (calculated)	1.520 Mg/m ³	
Absorption coefficient	3.982 mm ⁻¹	
F(000)	4820	
Crystal size	0.20 x 0.08 x 0.05 mm ³	
Theta range for data collection	1.75 to 30.63°.	
Index ranges	-15<=h<=15, -53<=k<=53, -34<=l<=35	
Reflections collected	124114	
Independent reflections	62612 [R(int) = 0.0560]	
Completeness to theta = 30.63°	99.4 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.8257 and 0.5031	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	62612 / 1 / 2394	
Goodness-of-fit on F ²	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0501, $wR2 = 0.096$	59
R indices (all data)	R1 = 0.0622, $wR2 = 0.1011$	
Absolute structure parameter	0.000(3)	
Largest diff. peak and hole	3.695 and -1.496 e.Å ⁻³	

Ir(1)-C(37)	1.898(7)	P(1)-C(9)	1.908(7)
Ir(1)-C(1)	2.114(7)	P(2)-C(8)	1.846(7)
Ir(1)-C(32)	2.114(6)	P(2)-C(17)	1.897(7)
Ir(1)-C(26)	2.130(6)	P(2)-C(21)	1.907(7)
Ir(1)-P(1)	2.3934(17)	O(1)-C(37)	1.130(8)
Ir(1)-P(2)	2.4055(17)	C(25)-C(31)	1.475(9)
P(1)-C(7)	1.851(6)	C(31)-C(32)	1.420(9)
P(1)-C(13)	1.890(7)	C(25)-C(26)	1.419(9)
C(37)-Ir(1)-C(1)	96.0(3)	C(7)-P(1)-Ir(1)	100.8(2)
C(37)-Ir(1)-C(32)	169.4(3)	C(13)-P(1)-Ir(1)	121.1(2)
C(1)-Ir(1)-C(32)	94.5(2)	C(9)-P(1)-Ir(1)	114.1(2)
C(37)-Ir(1)-C(26)	90.7(3)	C(8)-P(2)-C(17)	103.9(3)
C(1)-Ir(1)-C(26)	173.3(3)	C(8)-P(2)-C(21)	103.5(3)
C(32)-Ir(1)-C(26)	78.8(2)	C(17)-P(2)-C(21)	107.8(3)
C(37)-Ir(1)-P(1)	92.4(2)	C(8)-P(2)-Ir(1)	97.7(2)
C(1)-Ir(1)-P(1)	78.29(18)	C(17)-P(2)-Ir(1)	119.4(2)
C(32)-Ir(1)-P(1)	88.51(17)	C(21)-P(2)-Ir(1)	121.0(2)
C(26)-Ir(1)-P(1)	102.36(19)	C(31)-C(32)-Ir(1)	115.2(5)
C(37)-Ir(1)-P(2)	91.2(2)	C(32)-C(31)-C(25)	115.7(6)
C(1)-Ir(1)-P(2)	79.38(18)	C(26)-C(25)-C(31)	115.2(6)
C(32)-Ir(1)-P(2)	91.95(17)	C(25)-C(26)-Ir(1)	114.9(5)
C(26)-Ir(1)-P(2)	99.66(19)		
P(1)-Ir(1)-P(2)	157.63(6)	Torsion angles:	
C(7)-P(1)-C(13)	106.6(3)	C(26)-C(25)-C(31)-C(32) 1.8(8)
C(7)-P(1)-C(9)	102.1(3)	C(30)-C(25)-C(31)-C(36) -0.7(10)
C(13)-P(1)-C(9)	109.5(3)		

Table 5.4. Selected bond lengths [Å] and angles [°] for 5-2.





Table 5.5. Crystal data and structure refinement for 5-5.

Empirical formula	C56.5 H86 Ir P2		
Formula weight	1019.39		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P1		
Unit cell dimensions	a = 11.9507(8) Å	a= 65.607(1)°.	
	b = 15.3988(10) Å	b= 71.118(1)°.	
	c = 16.0786(11) Å	$g = 79.892(1)^{\circ}$	
Volume	2546.7(3) Å ³		
Z	2		
Density (calculated)	1.329 Mg/m ³		
Absorption coefficient	2.719 mm ⁻¹		
F(000)	1064		
Crystal size	0.32 x 0.30 x 0.11 m	0.32 x 0.30 x 0.11 mm ³	
Theta range for data collection	1.80 to 30.03°.		
Index ranges	-16<=h<=16, -21<=k<=20, -22<=l<=22		
Reflections collected	29561		
Independent reflections	26128 [R(int) = 0.014]	42]	
Completeness to theta = 30.03°	98.7 %		
Absorption correction	Semi-empirical from	equivalents	
Max. and min. transmission	0.7541 and 0.4766		
Refinement method	Full-matrix least-squa	ares on F ²	
Data / restraints / parameters	26128 / 1856 / 1159		
Goodness-of-fit on F ²	1.001		
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 =	0.0788	
R indices (all data)	R1 = 0.0368, wR2 =	R1 = 0.0368, w $R2 = 0.0807$	
Absolute structure parameter	0.036(4)	0.036(4)	
Largest diff. peak and hole	2.077 and -0.871 e.Å	2.077 and -0.871 e.Å ⁻³	

2.014(7)	P(2)-C(8)	1.827(7)
2.088(7)	P(2)-C(17)	1.886(7)
2.125(6)	P(2)-C(21)	1.891(7)
2.3012(18)	C(25)-C(26)	1.384(9)
2.3646(19)	C(26)-C(32)	1.465(9)
1.845(7)	C(31)-C(32)	1.418(9)
1.876(8)		
1.890(7)		
101.8(3)	C(8)-P(2)-C(17)	104.0(3)
79.1(3)	C(8)-P(2)-C(21)	106.7(3)
179.1(3)	C(17)-P(2)-C(21)	110.5(3)
90.23(19)	C(8)-P(2)-Ir(1)	102.5(3)
81.1(2)	C(17)-P(2)-Ir(1)	128.6(2)
99.25(18)	C(21)-P(2)-Ir(1)	102.8(2)
100.24(19)	C(32)-C(31)-Ir(1)	116.2(5)
81.4(2)	C(31)-C(32)-C(26)	115.9(6)
98.14(18)	C(26)-C(25)-Ir(1)	115.2(5)
161.12(6)	C(25)-C(26)-C(32)	113.4(6)
102.3(4)		
102.9(3)	Torsion angles:	
108.8(3)	C(25)-C(26)-C(32)-C(3	1) 3.6(9)
102.8(3)	C(27)-C(26)-C(32)-C(3	3) 1.8(11)
117.6(2)		
119.5(3)		
	$\begin{array}{c} 2.014(7)\\ 2.088(7)\\ 2.125(6)\\ 2.3012(18)\\ 2.3646(19)\\ 1.845(7)\\ 1.876(8)\\ 1.890(7)\\ \end{array}$ $\begin{array}{c} 101.8(3)\\ 79.1(3)\\ 179.1(3)\\ 90.23(19)\\ 81.1(2)\\ 99.25(18)\\ 100.24(19)\\ 81.4(2)\\ 98.14(18)\\ 161.12(6)\\ 102.3(4)\\ 102.9(3)\\ 108.8(3)\\ 102.8(3)\\ 117.6(2)\\ 119.5(3)\\ \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table 5.6. Selected bond lengths [Å] and angles [°] for 5-5.





 Table 5.7.
 Crystal data and structure refinement for 5-6.

Empirical formula	C38 H55 Ir P2	
Formula weight	765.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.8991(7) Å	a= 82.787(1)°.
	b = 10.3810(8) Å	b= 89.066(1)°.
	c = 19.0641(14) Å	$g = 76.620(1)^{\circ}$.
Volume	1699.7(2) Å ³	
Z	2	
Density (calculated)	1.497 Mg/m ³	
Absorption coefficient	4.047 mm ⁻¹	
F(000)	780	
Crystal size	0.38 x 0.12 x 0.06 mm ³	
Theta range for data collection	2.03 to 30.03°.	
Index ranges	-12<=h<=12, -14<=k<=14, -26<=l<=26	
Reflections collected	19717	
Independent reflections	9815 [R(int) = 0.0314]	
Completeness to theta = 30.03°	98.7 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.7933 and 0.3085	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	9815 / 0 / 384	
Goodness-of-fit on F ²	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0730	
R indices (all data)	R1 = 0.0399, $wR2 = 0.0752$	
Largest diff. peak and hole	2.359 and -1.370 e.Å ⁻³	

Ir(1)-C(36)	2.002(3)		
Ir(1)-C(1)	2.106(3)		
Ir(1)-C(30)	2.108(3)		
Ir(1)-P(1)	2.2947(9)		
Ir(1)-P(2)	2.3573(9)		
P(1)-C(7)	1.841(3)		
P(1)-C(13)	1.883(3)		
P(1)-C(9)	1.892(4)		
P(2)-C(8)	1.843(3)		
P(2)-C(21)	1.880(4)		
P(2)-C(17)	1.896(3)		
C(25)-C(30)	1.415(4)		
C(25)-C(31)	1.466(4)		
C(31)-C(36)	1.416(5)		
C(36)-Ir(1)-C(1)	99.78(13)	C(7)-P(1)-Ir(1)	103.0
C(36)-Ir(1)-C(30)	79.46(13)	C(13)-P(1)-Ir(1)	128.:
C(1)-Ir(1)-C(30)	179.07(12)	C(9)-P(1)-Ir(1)	102.1
C(36)-Ir(1)-P(1)	92.13(9)	C(8)-P(2)-C(21)	102.6
C(1)-Ir(1)-P(1)	80.87(9)	C(8)-P(2)-C(17)	102.3
C(30)-Ir(1)-P(1)	99.66(9)	C(21)-P(2)-C(17)	110.1
C(36)-Ir(1)-P(2)	99.20(9)	C(8)-P(2)-Ir(1)	101.2
C(1)-Ir(1)-P(2)	81.20(9)	C(21)-P(2)-Ir(1)	121.1
C(30)-Ir(1)-P(2)	98.38(9)	C(17)-P(2)-Ir(1)	115.9
P(1)-Ir(1)-P(2)	160.17(3)	C(30)-C(25)-C(31)	113.5
C(7)-P(1)-C(13)	103.32(16)	C(25)-C(30)-Ir(1)	114.:
C(7)-P(1)-C(9)	107.30(17)	C(36)-C(31)-C(25)	114.9
C(13)-P(1)-C(9)	110.87(16)	C(31)-C(36)-Ir(1)	117.4

Table 5.8. Selected bond lengths [Å] and angles $[\circ]$ for 5-6.

Torsion angle:

C(26)-C(25)-C(31)-C(32) 4.1(5)



Figure 5.10. X-ray crystal structure for compound 5-7.

 Table 5.9.
 Crystal data and structure refinement for 5-7.

Empirical formula	C36 H49 F2 Ir P2	
Formula weight	773.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2378(7) Å	a= 87.761(1)°.
	b = 11.6618(8) Å	b= 78.883(1)°.
	c = 14.8577(10) Å	$g = 70.070(1)^{\circ}$.
Volume	1635.67(19) Å ³	
Z	2	
Density (calculated)	1.571 Mg/m ³	
Absorption coefficient	4.215 mm ⁻¹	
F(000)	780	
Crystal size	0.32 x 0.14 x 0.04 mm ³	
Theta range for data collection	1.86 to 30.03°.	
Index ranges	-14<=h<=14, -16<=k<=16, -20<=l<=20	
Reflections collected	18944	
Independent reflections	9446 [R(int) = 0.0261]	
Completeness to theta = 30.03°	98.8 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.8495 and 0.3457	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	9446 / 0 / 382	
Goodness-of-fit on F ²	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0291, $wR2 = 0.0660$	
R indices (all data)	R1 = 0.0335, $wR2 = 0.0677$	
Largest diff. peak and hole	2.293 and -0.790 e.Å ⁻³	

Ir(1)-C(32)	1.995(3)	P(2)-C(21)	1.89	90(3)
Ir(1)-C(1)	2.092(3)	P(2)-C(17)	1.89	93(3)
Ir(1)-C(26)	2.100(3)	F(1)-C(28)	1.37	72(4)
Ir(1)-P(1)	2.3203(8)	F(2)-C(34)	1.37	73(4)
Ir(1)-P(2)	2.3503(8)	C(25)-C(26)	1.42	23(4)
P(1)-C(7)	1.847(3)	C(25)-C(31)	1.46	67(4)
P(1)-C(13)	1.884(3)	C(31)-C(32)	1.41	18(4)
P(1)-C(9)	1.886(3)			
P(2)-C(8)	1.836(3)			
C(32)-Ir(1)-C(1)	94.89(12)	C(8)-P(2)-C(21)	104.29	9(14)
C(32)-Ir(1)-C(26)	80.87(12)	C(8)-P(2)-C(17)	103.66	5(14)
C(1)-Ir(1)-C(26)	174.86(11)	C(21)-P(2)-C(17)	108.95	5(14)
C(32)-Ir(1)-P(1)	93.61(9)	C(8)-P(2)-Ir(1)	101.47	7(10)
C(1)-Ir(1)-P(1)	82.57(8)	C(21)-P(2)-Ir(1)	124.16	6(10)
C(26)-Ir(1)-P(1)	100.51(8)	C(17)-P(2)-Ir(1)	111.74	4(10)
C(32)-Ir(1)-P(2)	97.42(8)	C(25)-C(26)-Ir(1)	113.2((2)
C(1)-Ir(1)-P(2)	81.45(8)	C(26)-C(25)-C(31)	114.2((3)
C(26)-Ir(1)-P(2)	96.17(8)	C(32)-C(31)-C(25)	115.2((3)
P(1)-Ir(1)-P(2)	161.27(3)	C(31)-C(32)-Ir(1)	116.1((2)
C(7)-P(1)-C(13)	104.09(14)			
C(7)-P(1)-C(9)	105.08(14)	Torsion angles:		
C(13)-P(1)-C(9)	111.62(13)	C(26)-C(25)-C(31)-C(32)	5.5(4)
C(7)-P(1)-Ir(1)	103.89(10)	C(30)-C(25)-C(31)-C(36)	8.4(5)
C(13)-P(1)-Ir(1)	127.72(10)			
C(9)-P(1)-Ir(1)	102.36(10)			

Table 5.10. Selected bond lengths [Å] and angles [°] for 5-7.





 Table 5.11.
 Crystal data and structure refinement for 5-8.

Empirical formula	C37 H51.33 F2 Ir P2	
Formula weight	788.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R-3	
Unit cell dimensions	a = 40.4356(18) Å	a= 90°.
	b = 40.4356(18) Å	b= 90°.
	c = 10.8664(5) Å	g = 120°.
Volume	15386.6(12) Å ³	
Ζ	18	
Density (calculated)	1.531 Mg/m ³	
Absorption coefficient	4.034 mm ⁻¹	
F(000)	7170	
Crystal size	0.31 x 0.16 x 0.11 mm ³	
Theta range for data collection	1.96 to 32.04°.	
Index ranges	-60<=h<=60, -59<=k<=59, -16<=l<=15	
Reflections collected	62709	
Independent reflections	11873 [$R(int) = 0.0503$]	
Completeness to theta = 32.04°	99.6 %	
Absorption correction	Semi-empirical from equi	valents
Max. and min. transmission	0.6653 and 0.3678	
Refinement method	Full-matrix least-squares	on F ²
Data / restraints / parameters	11873 / 38 / 403	
Goodness-of-fit on F ²	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0344, WR2 = 0.0779	
R indices (all data)	R1 = 0.0459, wR2 = 0.082	23
Largest diff. peak and hole	2.775 and -0.942 e.Å ⁻³	

Ir(1)-C(36)	1.995(3)	P(1)-C(13)	1.890(3)
Ir(1)-C(25)	2.092(3)	P(2)-C(8)	1.840(3)
Ir(1)-C(1)	2.111(3)	P(2)-C(21)	1.887(3)
Ir(1)-P(1)	2.3062(8)	P(2)-C(17)	1.893(3)
Ir(1)-P(2)	2.3685(8)	C(25)-C(30)	1.426(4)
P(1)-C(7)	1.835(3)	C(30)-C(31)	1.477(4)
P(1)-C(9)	1.877(3)	C(31)-C(36)	1.428(4)
C(36)-Ir(1)-C(25)	80.23(12)	C(8)-P(2)-C(21)	102.81(14)
C(36)-Ir(1)-C(1)	98.23(11)	C(8)-P(2)-C(17)	103.24(15)
C(25)-Ir(1)-C(1)	177.93(11)	C(21)-P(2)-C(17)	110.02(15)
C(36)-Ir(1)-P(1)	91.92(8)	C(8)-P(2)-Ir(1)	101.51(10)
C(25)-Ir(1)-P(1)	100.19(8)	C(21)-P(2)-Ir(1)	115.13(10)
C(1)-Ir(1)-P(1)	81.20(8)	C(17)-P(2)-Ir(1)	121.13(10)
C(36)-Ir(1)-P(2)	98.05(8)	C(30)-C(25)-Ir(1)	114.3(2)
C(25)-Ir(1)-P(2)	97.57(8)	C(25)-C(30)-C(31)	112.8(2)
C(1)-Ir(1)-P(2)	81.24(8)	C(36)-C(31)-C(30)	114.4(3)
P(1)-Ir(1)-P(2)	160.87(3)	C(31)-C(36)-Ir(1)	116.9(2)
C(7)-P(1)-C(9)	104.36(14)		
C(7)-P(1)-C(13)	105.98(14)	Torsion angle:	
C(9)-P(1)-C(13)	111.28(14)	C(29)-C(30)-C(31)-C(32) -19.4(5)
C(7)-P(1)-Ir(1)	102.71(10)		
C(9)-P(1)-Ir(1)	126.84(10)		
C(13)-P(1)-Ir(1)	103.81(10)		

 Table 5.12.
 Selected bond lengths [Å] and angles [°] for 5-8.

Chapter 6

Reaction of (PCP)Ir with Terphenyls

Abstract

Experiments with biphenyl derivatives demonstrated that a double aryl C-H activation mechanism with (PCP)Ir will proceed to yield an extremely thermodynamically favorable cyclometalated product despite steric and electronic barriers that substantially slow the kinetics. Terphenyls have one additional phenyl ring and exhibit similar reactivity to biphenyls. Experiments were conducted with the three isomeric, unsubstituted terphenyls (*ortho*, *meta*, and *para*-terphenyl), in order to determine the regioselectivity of (PCP)Ir when there is a *choice* of positions for cyclometalation. Due to the symmetry of biphenyl substrates, there was only one choice.

For all of the terphenyl substrates, cyclometalation can potentially yield multiple isomers. Interestingly, all three yield nearly pure products (one conformation) and were able to be characterized by x-ray crystallography. When given a choice (e.g., with *meta*terphenyl), (PCP)Ir cyclometalates exclusively at the more sterically accessible "exterior" positions. In each case, product conformations have the third, unactivated phenyl ring situated as far from the PCP ligand system as possible. They also display distorted geometry that reflects the torsional strain that arises between the phenyl rings of the substrate when they are constained to a nearly co-planar arrangement.

6.1 Introduction

Unsubstituted terphenyls (also known as diphenyl benzenes) result from adding a third phenyl ring to biphenyl, yielding three possible isomers: *ortho, meta*, and *para* (Figure 6.1). They are larger and significantly less soluble than biphenyls (*para*-terphenyl in particular, has very low solubility in *para*-xylene and mesitylene), but otherwise share similar reactivity. Like biphenyl, these substrates are *not* co-planar, deviating by torsional angles of approximately 50° between the phenyl rings in the lowest energy conformation.

Figure 6.1. Three isomers of terphenyl









para-terphenyl

meta-terphenyl

ortho-terphenyl

Terphenyls can be synthesized through a variety of coupling processes, including direct arylation of biphenyl, and there have been several reports of the exploitation of these methods utilizing transition metal systems.¹⁻³ Perhaps not surprisingly, these richly aromatic systems have been studied mostly in the context of use as transition metal ligands, often for their steric bulk. They are also readily functionalized, making them attractive scaffolds for customization, leading to highly specific electronic and/or steric influences on metal complexes and the reactions they catalyze.⁴⁻¹³

Similar to biphenyl and bipyridyl motifs, terphenyls have found widespread application as chelating ligands in metal complexes designed for use in organic lightemitting diodes (OLEDs). Research and development of these complexes has grown exponentially over the last five years, with dozens of papers and patent applications being filed annually, especially in Japan and Germany.¹⁴⁻²¹

Results are presented in this chapter for reactions of (PCP)Ir and the three terphenyl isomers. Analogous to the results with biphenyls, C-H activation and subsequent cyclometalation by (PCP)Ir leads to the thermodynamically favored product. But beyond the basic mechanism of double C-H activation, terphenyl substrates offer the opportunity to study the issue of regioselectivity. While all three isomers can potentially yield multiple addition products, each of them yields a single dominant species from reaction with (PCP)Ir. Generally, cyclometalation will take place at the least sterically hindered position – hardly a surprising result, given the bulky nature of the PCP ligand system. Additionally, the products all show the third, unactivated phenyl ring situated as far from the metal center as possible. Keeping the third ring outside the crowded cleft created by the PCP *tert*butyl groups allows it to twist away from the nearly co-planar arrangement required for the two cyclometalated rings.

6.2 Results and Discussion

6.2.1 Synthesis and characterization of products from the reaction of (PCP)Ir with *para-, meta-, and ortho-terphenyl*

Kinetic products from the reaction of (PCP)Ir with terphenyl substrates are directly analogous to those seen with biphenyls. That is, (PCP)Ir quickly adds the least sterically hindered C-H bonds to form mixtures of labile, 5-coordinate aryl hydride products. While the kinetic products were thoroughly characterized by NMR, terphenyl substrates were studied exclusively for the purpose of analyzing the thermodynamically favored products of cyclometalation. Therefore, in each case, NMR spectra of the preliminary products were recorded, and then all reaction mixtures were heated for 24 hrs. at 75 °C.

The reaction of (PCP)IrH₂ with an alkene acceptor such as norbornene (NBE) is known to generate a precursor of the reactive fragment "(PCP)Ir".²² Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of *para*-terphenyl (1.1 equiv.) at -45 °C results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of several overlapping peaks at δ 67.1, δ 66.9, and δ 66.7 ppm (combined 79%) and two additional signals at δ 41.0 ppm (7%) and δ 40.0 (14%) within 30 min. The two upfield signals are diagnostic of cyclometalated products. The ¹H NMR spectrum shows three overlapping triplets at δ -45.45, δ -45.53, and δ -45.59 ppm (*J*_{HP} = 13.9 Hz). These data are consistent with a mixture of products from preliminary C-H activation (only three unique C-H bonds are available in *para*-terphenyl for this reaction), and correspond to the three downfield resonances in the ³¹P NMR spectrum. After heating at 75 °C for 24 hrs., no hydride signals remained in the ¹H NMR spectrum at ambient temperature. The ³¹P NMR spectrum showed a single resonance (100%) at δ 42.8 ppm and disappearance of all other peaks, including the second cyclometalated product, indicating that only one double C-H activation product is the lowest energy species **6-1** (eq. 1).



The substrate *para*-terphenyl has only one unique site for cyclometalation by (PCP)Ir. There are four total pairs of C-H bonds for which activation can lead to a cyclometalated product, but they are indistinguishable due to symmetry. Therefore, double C-H activation leads to two possible isomeric products (Fig. 6.2), and these are seen in the ³¹P NMR spectrum prior to heating. The thermodynamically favored isomer **6-1** has the third, unactivated phenyl ring situated as far as possible from the PCP ligand system. While the cyclometalated rings are nearly coplanar (dihedral angle = 5°) as dictated by the electronics and sterics of the PCPIr complex, the third, unactivated ring of *para*-terphenyl is free to rotate out of plane. The torsional angle of this ring, vs. the equatorial plane of the cyclometalated (PCP)Ir complex is ~36°.



Figure 6.2 Isomeric products of cyclometalation of *para*-terphenyl

The final product **6-1** was crystallized and analyzed by x-ray diffraction. The x-ray crystal structure and selected data are included at the end of this chapter.

Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of *meta*-terphenyl (1.1 equiv.) at -20 °C results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of overlapping peaks at δ 67.7 and δ 67.5 ppm (combined 90%) and two additional signals at δ 41.7 ppm (8%) and δ 32.6 (2%) within 30 min. The two upfield signals are diagnostic of cyclometalated products. The ¹H NMR spectrum shows several overlapping triplets centered at δ -45.57 ppm (*J*_{HP} = 13.9 Hz). These data are consistent with a mixture of products from preliminary C-H activation (there are four unique C-H bonds are available in *meta*-terphenyl for this reaction; Fig. 6.3).



Figure 6.3. Four unique C-H bonds and two distinct locations for cyclometalation of *meta*-terphenyl

After heating at 75 °C for 24 hrs., no hydride signals remained in the ¹H NMR spectrum at ambient temperature. The ³¹P NMR spectrum showed two resonances at δ 42.8 ppm (99%) and and δ 33.7 ppm (1%), and disappearance of all signals indicative of preliminary C-H activation products. Despite signals for two apparent cyclometalated products, one is dominant (99%) and therefore, represents the lowest energy species **6-2**.



Due to the geometry of *meta*-terphenyl, there are two distinct sites for cyclometalation by (PCP)Ir, 'A' and 'B', as shown in Fig. 6.3. Cyclometalation at either of the 'B' sites would lead to a significantly more sterically crowded product conformation, with the third, unactivated phenyl ring situated proximal to the open coordination site on the metal center. This arrangement is highly unfavorable for two reasons. First, the PCP *tert* butyl groups are tilted toward the empty coordination site from above and below, in order to accommodate the activated phenyl ring on the opposite side of the metal center (Fig. 6.4). Second, the unactivated phenyl ring of the metaterphenyl substrate is canted well away from the equatorial plane of the (PCP)Ir complex in its lowest energy conformation. Since 31 P NMR signals upfield of δ 40 ppm are typically disgnostic of "6-coordinate-like" complexes, it seems likely that the minor signal at δ 33.7 ppm in the ³¹P NMR spectrum corresponds to the much less favored product of cyclometalation at a 'B' site. The thermodynamically favored isomer 6-2 has the third, unactivated phenyl ring situated as far as possible from the PCP ligand system, similar to results with *para*-terphenyl. The final product 6-2 was crystallized and analyzed by x-ray diffraction. The x-ray crystal structure and selected data are included at the end of this chapter.



Sterically crowded More "open" to due to *tert*-butyls accommodate bending back away arvl ring from the other side

The final terphenyl substrate – the *ortho* isomer – is perhaps the most interesting of the three. As a free molecule, the *ortho* arrangement of the terminal phenyl rings brings them into close proximity. As a result, the dihedral angles between the mean plane of the central ring and the two terminal rings are 42.5° and 62.1°, respectively.²³ This contrasts with the *para-* and *meta-*terphenyls in which the dihedral angles are *all* approximately the same and less than 50°. The difference in dihedral angles in *ortho-*terphenyl results in two distinct positions for potential cyclometalation. Since oxidative addition by (PCP)Ir results in a nearly co-planar arrangement for two of the three phenyl rings in the substrate, the smaller dihedral angle will require less torsional strain, and therefore dictate the position that leads to the thermodynamic product. Evidence for these mechanistic hypotheses could possibly be observed through additional experiments with substituted *ortho-*terphenyls.

Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of *ortho*-terphenyl (1.1 equiv.) at -45 °C results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of several overlapping peaks at δ 68.0 ppm, δ 67.9 ppm and δ 67.5 ppm (combined 91%) and a single resonance at δ 41.8 ppm (9%) *after* 24 hrs. Formation of the cyclometalated product was significantly slower than for the other two isomers of terphenyl. The ¹H NMR spectrum shows several overlapping triplets centered at δ -45.57 ppm ($J_{HP} = 13.9$ Hz). These data are consistent with a mixture of products from preliminary C-H activation (there are four unique C-H bonds available in *ortho*-terphenyl for this reaction; Fig. 6.5).



Figure 6.5. Four unique C-H bonds and two distinct locations for cyclometalation of *ortho*-terphenyl

After heating at 75 °C for 24 hrs., no hydride signals remained in the ¹H NMR spectrum at ambient temperature. The ³¹P NMR spectrum showed a single resonance at δ 42.9 ppm (100%), and disappearance of all signals indicative of preliminary C-H activation products (eq. 3). Product **6-3** was crystallized and analyzed by x-ray diffraction.



The crystal structure of **6-3** confirms both the torsional strain in the terphenyl moiety and the distortion from ideal square-pyramidal geometry that results in the final cyclometalated complex. The two phenyl rings bound to the metal center show a dihedral angle of 10.4° which is a significant distortion from the ideal, co-planar (0°) arrangement. The phenyl ring that occupies the apical position actually tilts down toward the phospine ligand in order to accommodate the third substrate phenyl ring. And the overall dihedral angle between the two terminal phenyl rings is nearly 70°! As with the other two terphenyl isomers, the third, unactivated phenyl ring is situated as far from the PCP ligand system as possible. The x-ray crystal structure and selected data for **6-3** are included at the end of this chapter.

6.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in

solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. A full discussion of the NBE complex, including NMR characterization, is included in the Experimental section of Chapter 2 (section 2.3).

General remarks concerning the reactions of (PCP)Ir with terphenyl substrates: Substrates in this chapter were studied in the context of exploring cyclometalation reactions involving single or double C-H activation processes. Typical results for a variety of kinetic C-H activation products are seen in all cases and are not documented here, with a few exceptions as noted below. The NMR data presented are for the cyclometalated, thermodynamically favored products.

Reaction of (PCP)Ir with *para*-terphenyl (6-1): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. *Para*-terphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark red. After 30 min at 75 °C, the solution turned very dark red-brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; dark orange-red prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.7 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.68 (d, $J_{HH} = 8.7$ Hz, 1H, substrate *ortho-H*), 7.59 (d, $J_{HH} = 9.2$ Hz, 1H, substrate *ortho-H*), remaining aryl H signals for PCP and substrate are complicated
and overlapping, and in some cases, obscured by the residual solvent peaks, 3.43 (d of vt, 4H, CH_2), 0.80 (br t, 18H, $C(CH_3)_3$), 0.70 (br t, 18H, $C(CH_3)_3$).

Reaction of (PCP)Ir with *meta*-terphenyl (6-2): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. *Meta*-terphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark red. After 96 hr at ambient temperature, the solution turned very dark red-brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; dark orange-red prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.8 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.90 – 7.15 multiple peaks for the substrate H, remaining aryl H signals for PCP and substrate are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.46 (d of vt, 4H, CH₂), 0.80 (br t, 18H, C(CH₃)₃), 0.74 (br t, 18H, C(CH₃)₃).

Reaction of (PCP)Ir with *ortho*-terphenyl (6-3): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. *Ortho*-terphenyl (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark red. After 2 hr at 75 °C, the solution turned very dark red-brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; dark orange-red prisms were

obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.9 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.90 – 7.15 multiple peaks for the substrate H, remaining aryl H signals for PCP and substrate are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.48 (d of vt, 4H, C H_2), 0.86 (t, J_{HH} = 6.2 Hz, 18H, C(C H_3)₃), 0.77 (t, J_{HH} = 6.2 Hz, 18H, C(C H_3)₃).

6.4 Conclusion

Since terphenyls are 50% larger than biphenyl, C-H activation reactions with (PCP)Ir proceed somewhat more slowly; ¹H NMR signals for the hydrides in the products of oxidative addition are exchanging less rapidly than those observed for the addition of biphenyl. However, analogous to results with biphenyl, mild heating leads to a double C-H activation and cyclometalation mechanism that yields thermodynamically stable products.

Important observations were noted for results from each of the three different terphenyl isomers. *Para*-terphenyl has only one unique site for cyclometalation (by symmetry), but can form two isomeric products, of which, one dominates. As is the consistent trend with (PCP)Ir, the preferred pathway is the one leading to the least sterically hindered product. In the product from *para*-terphenyl, the third phenyl ring is located as far from the PCP ligand system as possible. *Meta*-terphenyl has two distinct pairs of C-H bonds that could potentially lead to cyclometalated products. Only the exterior 'A'-type location leads to the ultimate thermodynamic product.

Finally, in its free state, *ortho*-terphenyl displays more severe torsional strain than the other two terphenyl isomers. As such, in the final cyclometalated product, the dihedral angle between the two bound phenyl rings and the third, approaches 90 °C. All of the products from these reactions show significant distortion from ideal geometry for the PCP ligand system: the *tert*butyl groups are twisted away from the C-H activated substrate phenyl rings, and cause significant steric crowding of the open coordination site on iridium.

6.5 References

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 Table 6.1. Crystal data and structure refinement for 6-1.

Empirical formula	C42 H55 Ir P2		
Formula weight	814.00		
Temperature	293(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 10.4104(6) Å	a= 73.637(1)°.	
	b = 10.9466(7) Å	b= 75.868(1)°.	
	c = 16.9406(10) Å	$g = 81.215(1)^{\circ}$	
Volume	1788.95(19) Å ³		
Z	2		
Density (calculated)	1.511 Mg/m ³		
Absorption coefficient	3.850 mm ⁻¹		
F(000)	828		
Crystal size	0.18 x 0.09 x 0.04 mr	m ³	
Theta range for data collection	1.95 to 30.03°.		
Index ranges	-14<=h<=14, -15<=k	-14<=h<=14, -15<=k<=15, -23<=l<=23	
Reflections collected	20631		
Independent reflections	10316 [R(int) = 0.025	10316 [R(int) = 0.0255]	
Completeness to theta = 30.03°	98.4 %	98.4 %	
Absorption correction	Semi-empirical from	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5625	0.7461 and 0.5625	
Refinement method	Full-matrix least-squa	Full-matrix least-squares on F ²	
Data / restraints / parameters	10316 / 0 / 418	10316 / 0 / 418	
Goodness-of-fit on F ²	1.002	1.002	
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0315	R1 = 0.0315, $wR2 = 0.0712$	
R indices (all data)	R1 = 0.0365, wR2 = 0.03655, wR2 = 0.036555, wR2 = 0.036555, wR2 = 0.036555, wR2 = 0.0365555, wR2 = 0.0365555, wR2 = 0.03655555555555555555555555555555555555	R1 = 0.0365, wR2 = 0.0731	
Largest diff. peak and hole	2.807 and -1.122 e.Å	2.807 and -1.122 e.Å ⁻³	

Ir(1)-C(38)	2.008(3)	P(2)-C(8)	1.846(3)
Ir(1)-C(1)	2.097(3)	P(2)-C(17)	1.880(3)
Ir(1)-C(25)	2.098(3)	P(2)-C(21)	1.886(3)
Ir(1)-P(1)	2.2941(8)	C(37)-C(38)	1.415(4)
Ir(1)-P(2)	2.3600(8)	C(30)-C(37)	1.466(4)
P(1)-C(7)	1.841(3)	C(25)-C(30)	1.415(4)
P(1)-C(9)	1.876(3)		
P(1)-C(13)	1.888(3)		
C(38)-Ir(1)-C(1)	101.78(12)	C(8)-P(2)-C(21)	103.47(15)
C(38)-Ir(1)-C(25)	79.83(12)	C(17)-P(2)-C(21)	110.80(14)
C(1)-Ir(1)-C(25)	178.24(12)	C(8)-P(2)-Ir(1)	101.08(10)
C(38)-Ir(1)-P(1)	91.41(9)	C(17)-P(2)-Ir(1)	120.40(10)
C(1)-Ir(1)-P(1)	81.13(9)	C(21)-P(2)-Ir(1)	115.25(10)
C(25)-Ir(1)-P(1)	98.17(8)	C(30)-C(25)-Ir(1)	114.4(2)
C(38)-Ir(1)-P(2)	99.26(9)	C(25)-C(30)-C(37)	113.6(3)
C(1)-Ir(1)-P(2)	81.42(9)	C(38)-C(37)-C(30)	115.1(3)
C(25)-Ir(1)-P(2)	99.07(8)	C(37)-C(38)-Ir(1)	116.7(2)
P(1)-Ir(1)-P(2)	161.08(3)		
C(7)-P(1)-C(9)	104.32(15)	Torsion angles:	
C(7)-P(1)-C(13)	106.13(15)	C(25)-C(30)-C(37)-C(3	38) -5.0(4)
C(9)-P(1)-C(13)	110.39(15)	C(29)-C(30)-C(37)-C(4	42) -4.4(5)
C(7)-P(1)-Ir(1)	101.86(10)		
C(9)-P(1)-Ir(1)	128.58(11)	C(28)-C(27)-C(31)-C(3
C(13)-P(1)-Ir(1)	103.53(10)	C(26)-C(27)-C(31)-C(3	-36.4(4)
C(8)-P(2)-C(17)	102.82(15)		

 Table 6.2.
 Selected bond lengths [Å] and angles [°] for 6-1.





 Table 6.3. Crystal data and structure refinement for 6-2.

Empirical formula	C42 H55 Ir P2	
Formula weight	814.00	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.8218(5) Å	a= 77.268(1)°.
	b = 10.4543(6) Å	b= 83.420(1)°.
	c = 18.8352(10) Å	$g = 74.226(1)^{\circ}$.
Volume	1812.32(17) Å ³	
Z	2	
Density (calculated)	1.492 Mg/m ³	
Absorption coefficient	3.800 mm ⁻¹	
F(000)	828	
Crystal size	0.20 x 0.10 x 0.08 mm ³	
Theta range for data collection	2.07 to 31.57°.	
Index ranges	-14<=h<=14, -15<=k<=15, -27<=l<=27	
Reflections collected	21009	
Independent reflections	11547 [R(int) = 0.0186]	
Completeness to theta = 31.57°	95.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.580	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11547 / 0 / 418	
Goodness-of-fit on F ²	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0220, $wR2 = 0.0541$	
R indices (all data)	R1 = 0.0237, wR2 = 0.0549	
Largest diff. peak and hole	1.795 and -0.638 e.Å ⁻³	

Ir(1)-C(32)	2.0052(19)	P(2)-C(8)	1.844(2)
Ir(1)-C(1)	2.0884(19)	P(2)-C(21)	1.884(2)
Ir(1)-C(25)	2.1021(19)	P(2)-C(17)	1.894(2)
Ir(1)-P(1)	2.3105(5)	C(30)-C(31)	1.476(3)
Ir(1)-P(2)	2.3340(5)	C(31)-C(32)	1.416(3)
P(1)-C(7)	1.844(2)	C(25)-C(30)	1.415(3)
P(1)-C(13)	1.871(2)		
P(1)-C(9)	1.883(2)		
C(32)-Ir(1)-C(1)	93.40(8)	C(8)-P(2)-C(17)	103.57(11)
C(32)-Ir(1)-C(25)	80.68(7)	C(21)-P(2)-C(17)	108.91(10)
C(1)-Ir(1)-C(25)	173.99(7)	C(8)-P(2)-Ir(1)	101.57(7)
C(32)-Ir(1)-P(1)	93.33(6)	C(21)-P(2)-Ir(1)	123.39(7)
C(1)-Ir(1)-P(1)	82.57(6)	C(17)-P(2)-Ir(1)	112.41(7)
C(25)-Ir(1)-P(1)	98.71(5)	C(30)-C(25)-Ir(1)	113.54(13)
C(32)-Ir(1)-P(2)	97.85(6)	C(25)-C(30)-C(31)	114.26(16)
C(1)-Ir(1)-P(2)	81.78(6)	C(32)-C(31)-C(30)	115.11(17)
C(25)-Ir(1)-P(2)	97.92(5)	C(31)-C(32)-Ir(1)	116.11(13)
P(1)-Ir(1)-P(2)	161.254(19)		
C(7)-P(1)-C(13)	104.48(10)	Torsion angles:	
C(7)-P(1)-C(9)	104.91(11)	C(25)-C(30)-C(31)-C(32)) 3.6(3)
C(13)-P(1)-C(9)	111.34(10)	C(29)-C(30)-C(31)-C(36)) 2.5(3)
C(7)-P(1)-Ir(1)	103.96(7)		
C(13)-P(1)-Ir(1)	127.96(7)	C(36)-C(35)-C(37)-C(38)) -37.4(3)
C(9)-P(1)-Ir(1)	102.05(7)	C(34)-C(35)-C(37)-C(42)) -37.9(3)
C(8)-P(2)-C(21)	104.48(9)		

Table 6.4. Selected bond lengths [Å] and angles [°] for 6-2.





Table 6.5. Crystal data and structure refinement for 6-3.

Empirical formula	C42 H55 Ir P2	
Formula weight	814.00	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7055(10) Å	a= 106.058(2)°.
	b = 10.8988(10) Å	b=95.888(2)°.
	c = 16.3806(15) Å	$g = 90.028(2)^{\circ}$.
Volume	1826.1(3) Å ³	
Ζ	2	
Density (calculated)	1.480 Mg/m ³	
Absorption coefficient	3.772 mm ⁻¹	
F(000)	828	
Crystal size	0.24 x 0.12 x 0.05 mm ³	
Theta range for data collection	1.95 to 30.03°.	
Index ranges	-15<=h<=15, -15<=k<=15, -23<=l<=23	
Reflections collected	20803	
Independent reflections	10486 [R(int) = 0.0399]	
Completeness to theta = 30.03°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5645	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10486 / 0 / 418	
Goodness-of-fit on F ²	1.000	
Final R indices [I>2sigma(I)]	R1 = 0.0423, $wR2 = 0.0849$	
R indices (all data)	R1 = 0.0533, $wR2 = 0.0887$	
Largest diff. peak and hole	3.338 and -2.514 e.Å ⁻³	

Ir(1)-C(28)	1.986(4)	P(1)-C(9)	1.881(4)
Ir(1)-C(25)	2.093(4)	P(2)-C(8)	1.837(4)
Ir(1)-C(1)	2.111(4)	P(2)-C(17)	1.885(4)
Ir(1)-P(2)	2.3002(11)	P(2)-C(21)	1.892(5)
Ir(1)-P(1)	2.3624(11)	C(26)-C(27)	1.476(6)
P(1)-C(7)	1.839(4)	C(27)-C(28)	1.417(5)
P(1)-C(13)	1.880(5)	C(25)-C(26)	1.415(6)
C(28)-Ir(1)-C(25)	79.20(16)	C(8)-P(2)-C(21)	106.4(2)
C(28)-Ir(1)-C(1)	100.29(15)	C(17)-P(2)-C(21)	110.6(2)
C(25)-Ir(1)-C(1)	178.97(17)	C(8)-P(2)-Ir(1)	103.31(14)
C(28)-Ir(1)-P(2)	91.19(11)	C(17)-P(2)-Ir(1)	127.13(14)
C(25)-Ir(1)-P(2)	100.30(11)	C(21)-P(2)-Ir(1)	103.30(14)
C(1)-Ir(1)-P(2)	80.60(12)	C(26)-C(25)-Ir(1)	115.4(3)
C(28)-Ir(1)-P(1)	100.04(11)	C(25)-C(26)-C(27)	112.0(3)
C(25)-Ir(1)-P(1)	97.42(11)	C(28)-C(27)-C(26)	114.4(3)
C(1)-Ir(1)-P(1)	81.77(12)	C(27)-C(28)-Ir(1)	118.0(3)
P(2)-Ir(1)-P(1)	160.53(4)		
C(7)-P(1)-C(13)	103.5(2)	Torsion angles:	
C(7)-P(1)-C(9)	102.1(2)	C(25)-C(26)-C(27)-C(28	3) -10.4(5)
C(13)-P(1)-C(9)	110.07(19)	C(33)-C(26)-C(27)-C(32	2) -13.2(7)
C(7)-P(1)-Ir(1)	101.30(14)		
C(13)-P(1)-Ir(1)	120.79(14)	C(26)-C(33)-C(42)-C(37	7) -53.5(6)
C(9)-P(1)-Ir(1)	115.87(14)	C(34)-C(33)-C(42)-C(41)	-53.4(6)
C(8)-P(2)-C(17)	104.36(19)		

 Table 6.6.
 Selected bond lengths [Å] and angles [°] for 6-3.

Chapter 7

C-C (sp²-sp²) Bond Activation: Reaction of (PCP)Ir with Biphenylene

Abstract

Experiments with biphenyls, terphenyls, and substituted naphthalenes have shown that C-H activation reactions with (PCP)Ir can result in thermodynamically stable cyclometalated products under the right conditions. Substituents on biphenyl substrates were used to probe the electronics and sterics of the mechanism of double C-H activation. Experiments with terphenyl isomers showed that the conformation of the favored product results from C-H activation at the least hindered positions in the substrate, and that substantial torsional strain can be overcome en route to the ultimate, cyclometalated product.

All products of the above reactions feature five member, metalloaromatic rings that show varying degrees of distortion, depending on the steric bulk and torsional strain of the substrate. (PCP)Ir was reacted with biphenylene – a very strained biaryl substrate – in order to examine the possibility for cyclometalation. The reaction was successful, but resulted *not* from two successive C-H bond activation reactions, but rather from preliminary C-H activation followed by net C-C (sp^2-sp^2) bond activation. The final product is (PCP)Ir(κ^2 -biphenyl), the same cyclometalated product generated by double C-H activation of unsubstituted biphenyl.

7.1 Introduction

Biphenylene has a very similar structure to biphenyl with two phenyl rings bonded through a C-C (sp^2-sp^2) bond, but unlike the latter, biphenylene has a *second* C-C (sp^2-sp^2) bond, resulting in a four-member cyclobutadiene-type ring. There are several important ramifications of this structure. First, the molecule is constrained to a co-planar geometry, resulting in significantly strained C-C bonds between the the phenyl rings. Second, due to the requirements that the bridging carbons accommodate bond angles of 90°, they partially rehybridize in order to contribute additional p-orbital character to the inter-phenyl bonding orbitals. This process leaves the carbon atoms slightly electron deficient in terms of interactions with their respective aromatic rings as shown in Fig. 7.1.

Figure 7.1. Different C-H bonds in biphenylene



Bridging carbons are electron withdrawing, leaving H_{α} electron deficient, compared to H_{β}

Due to the electron-withdrawing nature of the bridging carbons, the α position is *less* electron rich than the β position, making the former a more attractive target for (PCP)Ir C-H activation as discussed in previous chapters of this thesis. This order of preference (α vs. β) is the reverse of what was observed with naphthalene.

Much of the literature concerning early work on C-C activation focused on the reactivity inherent in strained, cyclic molecules.¹ Biphenylene has been reasonably well-studied, with published reports from the Jones group and others.²⁻¹² In addition to the

study of conditions under which C-C activation takes place, biphenylene has also been exploited in coupling reactions.^{13,14}

The initial goal of experiments with (PCP)Ir and biphenylene was to ascertain whether the metal complex shows selectivity in C-H bond activation for specific carbon positions in the substrate. In view of the many literature reports on cyclometalation by transition metal complexes, the possibility that (PCP)Ir could effect a similar transformation was also a question of interest. In the context of our results with biphenyls and terphenyls, and the associated conformational challenges of several of those substrates, the question also remained as to what form a cyclometalated product would take. At first, it was thought that there might be two possibilities (Fig. 7.2). Ultimately, results confirmed kinetic selectivity for α C-H bonds followed by cyclometalation to give the product corresponding to the well-precedented C-C activation process.





7.2.1 Synthesis and characterization of products from the reaction of (PCP)Ir with biphenvlene

The reaction of $(PCP)IrH_2$ with an alkene acceptor such as norbornene (NBE) is known to generate a precursor of the reactive fragment "(PCP)Ir".¹⁵ Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of biphenylene (1.1 equiv.) at -20 °C results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of two new signals at δ 67.6 ppm and δ 65.0 ppm (ratio = 1:3) within 30 min. Unlike reactions with biphenyls, preliminary NMR analyses yielded no evidence of cyclometalation. Correspondingly, the ¹H NMR spectrum shows two distinct triplets in a 3:1 ratio at δ -44.68 ppm (J_{HP} = 13.5 Hz) and δ -45.70 ppm (J_{HP} = 12.1 Hz). These data are consistent with two products of preliminary C-H activation. Interestingly, ¹H NMR spectra taken at ambient temperature confirmed both hydride signals as triplets (slightly broadened compared with the low temperature spectra, due to faster exchange). For all previously tested (unsubstituted) polyaromatic substrates, spectra at ambient temperature showed only very broad signals for rapidly exchanging hydrides in the products of C-H activation. This indicates that the products from the oxidative addition of biphenylene are exchanging significantly more slowly and therefore have a higher kinetic barrier to elimination. Based on previous data with similar substrates (fluorobenzene, in particular, with its strong electronic effect) and the general trend that hydride resonances for ortho C-H activation products appear downfield from δ -45.6 ppm, these two products are assigned as 7-1a,b and are the rotamers that result from C-H activation at the α position of biphenylene (eq. 1).



After heating at 125 °C for 24 hrs., no hydride signals remained in the ¹H NMR spectrum at ambient temperature. The ³¹P NMR spectrum showed a single resonance (100%) at δ 42.8 ppm and disappearance of both resonances for the preliminary products of C-H activation. Since both ³¹P NMR and ¹H NMR spectra confirm the resonances seen for the product of the cyclometalation of biphenyl, it was concluded that net C-C bond activation of biphenylene had taken place (eq. 2). Product **7-2** was isolated pure as a dark orange-red powder, but was not analyzed by x-ray crystallography since it would have simply duplicated the results seen with biphenyl.



7.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in

solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. A full discussion of the NBE complex, including NMR characterization, is included in the Experimental section of Chapter 2 (section 2.3).

Reaction of (PCP)Ir with biphenylene (7-1a,b): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. Biphenylene (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark red. ³¹P NMR (121.4 MHz, -20 °C, mesitylene- d_{12}): δ 67.7 (s, rotamer A), 65.0 (s, rotamer B). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 7.30 – 7.00 multiple peaks for the substrate H and aryl H signals for PCP are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.31 (d of vt, 4H, *CH*₂, rotamer B), methylene signals for rotamer A are overlapped by those for rotamer B, 1.02 (br t, $J_{HH} = 6.3$ Hz, 18H, C(*CH*₃)₃, rotamer B), *tert*butyl signals for rotamer A are embedded in those for rotamer B, -44.63 (t, $J_{HP} = 13.5$ Hz, 1H, Ir-*H*, rotamer B), -45.63 (t, $J_{HP} = 12.2$ Hz, 1H, Ir-*H*, rotamer A).

Conversion of 7-1a,b to the thermodynamic product 7-2: A solution of **7-1a,b** was heated at 125 °C for 24 hr. The solution turned very dark brown-black. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.3 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ

7.60 - 7.10 multiple peaks for the substrate H, remaining aryl H signals for PCP and substrate are complicated and overlapping, and in some cases, obscured by the residual solvent peaks, 3.43 (br t, 4H, CH₂), 0.71 (br t, 36H, C(CH₃)₃).

7.4 Conclusion

Reaction of (PCP)Ir with the highly strained substrate biphenylene yielded two very interesting results. Following a mechanism well precedented in the literature, one of the two bridging C-C (sp^2-sp^2) bonds of the substrate was activated to yield the same cyclometalated product that was found during the reaction of (PCP)Ir with biphenyl. This is the first and only example of C-C bond activation by (PCP)Ir reported in this thesis.

Perhaps more interestingly, oxidative addition of biphenylene yielded both rotamers from C-H activation at the α position on one of the phenyl rings. In all other substrates dicussed in this thesis, the α C-H bond is the *less* preferred location for oxidative addition to (PCP)Ir. This reactivity is very different for biphenylene due to its strongly electron withdrawing bridging carbon atoms. The products of single C-H activation showed far more kinetic stability than those for biphenyl. In fact, trapping of one or both of these products with CO may be feasible.

7.5 References

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Chapter 8

Reaction of (PCP)Ir with 2,2'-Bipyridine and a series of Bipyridine derivatives

Abstract

Experiments have shown that (PCP)Ir is able to activate the C-H bonds of a variety of aryl substrates. Reactions with benzenes, naphthalenes, biphenyls, and terphenyls have each demonstrated different aspects of the selectivity of this robust, pincer-ligated transition metal complex. In order to further understand the factors affecting its reactivity with polycyclic aromatic substrates, experiments were conducted with (PCP)Ir and the ubiquitous organometallic ligand 2,2'-bipyridine. Contrary to expectations, bipyridine does not bind to (PCP)Ir through κ^2 N-N coordination, but undergoes C-H activation instead. A single bipyridine nitrogen atom coordinates to the metal center only *after* oxidative addition of the C-H bond, yielding a cyclometalated, 6-coordinate product.

The closely related substrate 2-phenylpyridine was also studied and yields analogous results. Products from these reactions were characterized by NMR and x-ray crystallography, and the mechanism was studied through experiments with two strategically substituted bipyridine derivatives. Understanding how (PCP)Ir interacts with these substrates could have great potential value: these ligands – in this uncommon binding mode – are currently being vigorously researched for use in applications involving organic light emitting diodes (OLEDs).

8.1 Introduction

(PCP)Ir has proven to be a surprisingly efficient and versatile agent for both single and double C-H activation (i.e., cyclometalation) reactions with a diverse array of substrates, including benzenes, naphthalenes, biphenyls, and terphenyls. In most cases of single C-H activation, the 5-coordinate products are relatively labile, with oxidative addition and reductive elimination occurring on an observable time scale (NMR). With double C-H activation reactions, however, the products show remarkable thermodynamic stability. One reason for this is certainly that the hydrogen atoms from the original C-H bonds are eventually scavenged by the sacrificial hydrogen acceptor, norbornene. In cyclometalated products that have no hydrides on the metal, the addition process cannot be reversed, meaning there is no plausible mechanism for reductive elimination. Therefore, many of the double C-H activation reactions discussed above are purely stoichiometric and cannot be made catalytic for purposes of aromatic functionalization or similar transformations.

With this in mind, (PCP)Ir was reacted with the ubiquitous organometallic ligand 2,2'-bipyridine, assuming that κ^2 N-N coordination would provide hemi-labile linkages with a 5-member cyclometalated structure. Surprisingly, bipyridine does not bind to (PCP)Ir in the conventional way, but rather undergoes C-H activation *followed by* N coordination (eq. 1).



At first, this seems like a surprising result, since there are hundreds of literature reports of bipyridine coordinating to transition metals in a κ^2 N-N fashion. However, for free, unchelated bipyridine, the two nitrogen atoms are *trans* in the lowest energy conformation (Fig. 8.1). Since (PCP)Ir is very adept at C-H activation, and as we have shown, cyclometalation is very favorable, it makes sense that reaction with the bipyridine substrate leads to a single C-H activation, and the product has both a 5-member ring *and* a hydride ligand on the metal center.

Figure 8.1. Trans conformation and carbon numbering of 2,2'-bipyridine



There have been isolated reports in the literature of this "*trans*" chelating mode for bipyridine – most of which treat the conformation as a novelty.¹ And at least one group has experimented with κ^2 N-C bipyridine on iridium in complexes designed as anti-cancer agents.² But the κ^2 N-N chelation mode dominates the literature to the point where bipyridine may be the most well-known and researched of all bidentate ligands with transition metal complexes.³ Concerning the alternate binding mode preferred by (PCP)Ir, the very similar ligand phenyl pyridine gives an analogous κ^2 N-C chelate, and there are many literature reports on its use in complexes designed to function in organic light emitting diodes (OLEDs).^{2,4-13}

Among transition metals, the efficacy of iridium in complexes demonstrating desirable luminescent properties has been reported.¹⁴⁻¹⁷ Over the last ten years, interest in

the development of highly efficient OLEDs has grown steadily; iridium and platinum complexes are now central to the research on these applications and dozens of patents are being filed yearly.¹⁸⁻²⁸ A thorough understanding of the mechanism of C-H activation by (PCP)Ir with bipyridine-type substrates may prove valuable for future development in this context.

8.2.1 Synthesis and characterization of products from the reaction of (PCP)Ir with bipyridine

The reaction of (PCP)IrH₂ with an alkene acceptor such as norbornene (NBE) is known to generate a precursor of the reactive fragment "(PCP)Ir".²⁹ Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of bipyridine (1.1 equiv.) at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of several small, somewhat broad peaks at δ 69.4, δ 67.4, δ 67.0, and δ 66.0 ppm (combined 27%) and a large signal at δ 47.1 ppm (73%) within 30 min. The small downfield signals are diagnostic of C-H activation at various positions on the aryl rings. The resonance at δ 47.1 ppm indicates the presence of a large concentration of cyclometalated product. The ¹H NMR spectrum corresponds perfectly with the ³¹P NMR spectrum, showing several very small upfield triplets from δ -44 to -45.5 ppm, and one large hydride signal at δ -9.60 ppm. Based on previous data as discussed throughout this thesis, the upfield signals indicate labile products of C-H activation reactions by (PCP)Ir. In regard to the hydride at δ -9.60 ppm, a resonance in this region is generally diagnostic of a 6-coordinate complex.

After heating at 75 °C for 12 hrs., the reaction yielded a single, pure product corresponding to the major peaks in both the ³¹P NMR (δ 47.1 ppm) and ¹H NMR (t, δ - 9.60 ppm; $J_{\rm HP}$ = 19.5 Hz) spectra. X-ray crystallographic analysis confirmed the structure as the product of a *single* C-H bond activation process, followed by coordination of nitrogen, **8-1** (eq. 2).



Previous cyclometalation reactions of (PCP)Ir with biphenyls and similar substrates gave 5-coordinate products *without* hydride ligands on the metal center. Since **8-1** retains a hydride ligand (despite excess NBE in solution), its stucture is more analogous to the products seen from the reaction of (PCP)Ir with 1-methoxynaphthalene, as discussed in chapter 3. A hydride chemical shift at δ -9.60 ppm is diagnostic of a metal-H bond *trans* to the bipyridyl carbon atom and *cis* to the coordinated bipyridyl nitrogen atom.³⁰ The x-ray crystal structure and selected data for **8-1** are included at the end of this chapter.

As mentioned in the introduction to this chapter, the κ^2 N-C chelating conformation was unexpected for this substrate. But thinking about the electronic characteristics of the (PCP)Ir fragment, this result makes sense. In order for κ^2 N-N coordination to take place, the product would be a 5-coordinate, Ir(I), 18-electron complex (Fig. 8.2). While the (PCP)Ir 14-electron fragment is obviously electrondeficient, iridium(I) apparently has a strong drive to act as a nucleophile and donate two electrons through the process of oxidative addition. Given the ability of iridium to 'switch' between +1 and +3 oxidation states and the fact that the PCP ligand system has a net formal charge of (-1), it is difficult to think of a scheme in which two neutral ligands (e.g., the N atoms of bipyridine) would successfully add to the 14-electron fragment (PCP)Ir. Without two formal (-1) charged ligands (such as those resulting from C-H activation), the metal center cannot oxidize and achieve what is apparently its preferred, low energy configuration: an Ir(III), 5- or 6-coordinate, 18-electron complex.

Figure 8.2. Comparison of N,N and N,C (PCP)Ir(bipyridyl) complexes



Iridium (I) d⁸ Net charge from ligands: -1 Electron count: 18



Iridium (III) d⁶ Net charge from ligands: -3 Electron count: 18

8.2.2 Synthesis and characterization of products from the reaction of (PCP)Ir with 2-phenylpyridine

Since results of the reation of (PCP)Ir with bipyridine demonstrated that κ^2 N-N coordination was less favorable than C-H activation in conjunction with subsequent N atom coordination, the reaction mechanism should be directly analogous to that for the reaction with 2-phenylpyridine. That is, the heteroatom in the second aryl ring is superfluous to the mechanism of oxidative addition. In order to test this hypothesis, experiments were conducted with 2-phenylpyridine for direct comparison with the results from bipyridine.

Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of 2phenylpyridine (1.1 equiv.) at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of three peaks in the 'C-H activation region': one large resonance at δ 69.2 (63% of the product mixture) and two small, somewhat broad peaks δ 68.7 and δ 67.2 ppm (combined 24%). An additional fourth peak was detected upfield at δ 46.8 ppm (13%) within 30 min. While the signals are analogous to those seen for the reaction of (PCP)Ir with bipyridine, the ratio of C-H activation products to cyclometalated products is very different. The ¹H NMR spectrum for 2-phenylpyridine corresponds perfectly with the ³¹P NMR spectrum, showing a large upfield triplet at δ -43.98 ppm and additional small signals at δ -45.34, -45.44, and -45.54 ppm. There is also a very small hydride signal at δ -9.60 ppm that overlaps with other even smaller signals, indicating different isomeric products at the outset of the reaction. The large triplet at δ -43.98 ppm is almost certainly diagnostic of the product of C-H activation *ortho* to the pyridyl nitrogen atom.

Comparing these results with those from bipyridine seems to indicate that the cyclometalation process is kinetically much faster for the latter substrate. This makes sense since bipyridine has *two* sites for cyclometalation per substrate molecule, while 2-phenylpyridine has only one (Fig. 8.3). This should increase the rate at which cyclometalation occurs for bipyridine, and conversely, the preliminary, non-cyclometalated products of C-H addition of 2-phenylpyridine should have greater kinetic stability (i.e., they apparently exchange more slowly).





After heating at 75 °C for 12 hrs., the reaction yielded a single product with sharp resonances in the ³¹P NMR (δ 47.0 ppm) and ¹H NMR (t, δ -9.62 ppm; $J_{HP} = 19.5$ Hz) spectra. X-ray crystallographic analysis confirmed the structure as the product of a *single* C-H bond activation process, followed by coordination of nitrogen, **8-2** (eq. 3) – directly analogous to the structure of **8-1**. The x-ray crystal structure and selected data for **8-2** are included at the end of this chapter.



8-2

8.2.3 Mechanistic study of the cyclometalation of bipyridines: Synthesis and characterization of products from the reaction of (PCP)Ir with 6,6'dimethylbipyridine and 4,4'-dimethylbipyridine

The conformation of the product generated by the C-H activation and cyclometalation of bipyridine (and 2-phenylpyridine) is stable to extended heating. This seems to support the logical hypothesis that the (PCP)Ir fragment approaches the substrate from the less sterically hindered direction (i.e., the *opposite* side of the C-H bond from the cleft between aryl rings where the N atom is located). After oxidative addition of the C-H bond, the N atom then coordinates to the metal center, orienting it *trans* to the PCP carbon atom and *between* the newly formed Ir-C (bipyridyl carbon) and Ir-H bonds (Fig 8.4).

Figure 8.4. Trajectory of iridium approach and C-H activation of bipyridine



This same approach was proposed in chapter 3 for the preliminary C-H activation at the α position (C8) in 1-methoxynaphthalene. However, upon heating, the naphthyl adduct isomerized to a lower energy conformation with the Ir-C and Ir-H bonds *cis* and the oxygen atom coordinated *trans* to the hydride rather than the PCP carbon atom. This contrasts with the present example, in which the bipyridyl adduct does *not* isomerize with additional heating.

In order to probe the mechanism of C-H activation, two dimethyl-substituted bipyridine substrates were chosen in order to strategically add steric hindrance to the possible angles of approach for the (PCP)Ir fragment: 6,6'-dimethylbipyridine and 4,4'-dimethylbipyridine (Scheme 8.1). In the first of these, access to the C-H bond required for cyclometalation is hindered by the methyl substituent if (PCP)Ir approaches from an angle proximal to the N atom (or, similarly, if the N atom is acting as a 'directing' group). In the second case, the opposite is true: access to the desired C-H bond is hindered by a methyl substituent if (PCP)Ir approaches from the N atom (as was proposed above).

Scheme 8.1. Product conformations from 6,6'- and 4,4'-dimethylbipyridine



4,4'-dimethylbypyridine

N trans to the Ir-H bond

Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of 6,6'dimethylbipyridine (1.1 equiv.) at ambient temperature results in ³¹P NMR and ¹H NMR spectral data that coincide almost exactly with those observed from the reaction with unsubstituted bipyridine. While there is a small fraction of products that arise from generic aryl C-H activation, the major peaks in both spectra arise from the cyclometalated product **8-3**. After heating at 75 °C for 12 hrs., the reaction yielded a single product corresponding to peaks in the ³¹P NMR (δ 46.3 ppm) and ¹H NMR (t, δ -9.80 ppm; *J*_{HP} = 20.3 Hz) spectra. X-ray crystallographic analysis confirmed the structure as the product of a *single* C-H bond activation process at C3, followed by coordination of a bipyridyl nitrogen atom *between* the new Ir-C and Ir-H bonds (eq. 4).



Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of 4,4'dimethylbipyridine (1.1 equiv.) at ambient temperature results in ³¹P NMR and ¹H NMR spectral data that show *no evidence* of cyclometalated products. On the contrary, the preliminary product of this reaction arises exclusively from C-H activation. The ³¹P NMR spectrum shows a single resonance at δ 69.2 ppm, and there is a single hydride peak in the ¹H NMR spectrum at δ -43.90 ppm ($J_{HP} = 13.5$ Hz). These data are consistent with C-H activation at C6, *ortho* to the substrate nitrogen atom, giving the 5-coordinate product **8-4** (eq. 5). This result is consistent with greatly increased steric hindrance for approach of the (PCP)Ir fragment to the C-H bond at C3. With this approach blocked, oxidative addition at C3 is disfavored due to a high kinetic barrier, and therefore, the rate of the subsequent cyclometalation mechanism is significantly decreased.

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After heating at 75 °C for 12 hrs., the reaction yielded a single product (8-5) corresponding to peaks in the ³¹P NMR (δ 46.0 ppm) and ¹H NMR (t, δ -18.98 ppm; J_{HP} = 19.1 Hz) spectra. The chemical shift for the hydride triplet is approximately 10 ppm further upfield than those for the products of reactions between (PCP)Ir and other bipyridines, and is diagnostic of a hydride *cis* to an aryl carbon and *trans* to the more electronegative bipyridyl nitrogen atom. X-ray crystallographic analysis confirmed the structure as the product of a *single* C-H bond activation process at C3, followed by coordination of the bipyridyl nitrogen atom *trans* to the Ir-H bond (eq. 6).


As the x-ray structure shows, heating the solution enabled the reactants to overcome the kinetic barrier and proceed to the preferred thermodynamic, cyclometalated product, despite the severe steric hindrance caused by having a methyl substituent on C4. Under these constraints, the (PCP)Ir had to access the C-H bond at C3 from the less preferred side (proximal to the cleft between the two aryl rings of the substrate). As shown in eq. 6, this angle of approach leads to subsequent coordination of the nitrogen atom *trans* to the Ir-H bond, instead of the *cis* orientation seen with the other bipyridine substrates. The conformation of this product also ensures that the methyl substituent at C4 resides on the same side of the (PCP)Ir complex as the hydride ligand. In the alternate conformation, the methyl would be in a very crowded environment close to the PCP phenyl ring (Fig. 8.5). Product **8-5** is one of the very few examples in which (PCP)Ir has oxidatively added an aryl C-H bond *ortho* to an alkyl substituent. X-ray crystal structures and selected data for **8-3** and **8-5** are included at the end of this chapter.

Figure 8.5. Steric crowding in the *cis* product from C-H activation of 4,4'-dimethylbipyridine (not observed)



8.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in

solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. A full discussion of the NBE complex, including NMR characterization, is included in the Experimental section of Chapter 2 (section 2.3).

General remarks concerning the reactions of (PCP)Ir with bipyridine substrates: Substrates in this chapter were studied in the context of exploring cyclometalation reactions involving single or double C-H activation processes. Typical results for a variety of kinetic C-H activation products are seen in all cases and are not documented here, with a few exceptions as noted below. The NMR data presented are for the cyclometalated, thermodynamically favored products.

Reaction of (PCP)Ir with 2,2'-bipyridine (8-1): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. Bipyridine (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. After heating at 75 °C for 12 hr, the solution turned very bright yellow-orange. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; yellow-orange prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 47.1 (d, J_{PH} = 4.8 Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 9.23 (d, J_{HH} = 5.1 Hz, substrate *H*), 8.55, 8.53 (overlapping t, J_{HH} = 9.1 Hz, substrate *H*), 8.49 (d, J_{HH} = 5.1 Hz, substrate *H*), 8.30 (d,

 $J_{\rm HH}$ = 5.1 Hz, substrate *H*), 7.56 (d, $J_{\rm HH}$ = 7.5 Hz, substrate *H*), 7.28 (d of t, $J_{\rm HH}$ = 6.9 Hz, substrate *H*), aryl H signals for PCP are obscured by the residual solvent peaks, 3.04 (d of vt, 4H, CH₂), 1.26 (t, $J_{\rm HH}$ = 6.2 Hz, 18H, C(CH₃)₃), 0.51 (t, $J_{\rm HH}$ = 6.2 Hz, 18H, C(CH₃)₃), -9.60 (t, $J_{\rm HP}$ = 18.5 Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with 2-phenylpyridine (8-2): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 2-Phenylpyridine (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. After heating at 75 °C for 72 hr, the solution turned very bright yellow-orange. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; yellow-orange prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 47.0 (d, $J_{PH} = 5.7$ Hz). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 9.04 (d, $J_{HH} = 5.1$ Hz, substrate *H*), 8.55, 8.53, 8.04, 7.53 (overlapping d, substrate *H*), 7.46 (t, $J_{HH} = 7.2$ Hz, substrate *H*), aryl H signals for PCP are obscured by the residual solvent peaks, 3.17 (d of vt, $J_{HP} = 3.2$ Hz, $J_{HH} = 15.9$ Hz, 2H, CH_2), 3.02 (d of vt, $J_{HP} = 3.8$ Hz, $J_{HH} = 15.5$ Hz, 2H, CH_2), 1.28 (t, $J_{HH} = 5.7$ Hz, 18H, $C(CH_3)_3$), 0.55 (t, $J_{HH} = 6.2$ Hz, 18H, $C(CH_3)_3$), -9.62 (t, $J_{HP} = 18.7$ Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with 6,6'-dimethylbipyridine (8-3): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-

xylene. 6,6'-Dimethylpyridine (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. After heating at 75 °C for 12 hr, the solution turned very bright yellow-orange. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; yellow-orange prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 46.3 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.63 (d, $J_{HH} = 9.1$ Hz, substrate *H*), 8.46 (d, $J_{HH} = 7.1$ Hz, substrate *H*), remaining substrate and PCP aryl H signals are obscured by the residual solvent peaks, 3.17 (s, 3H, substrate CH₃), 3.03 (d of vt, $J_{HP} = 4.3$ Hz, $J_{HH} = 15.6$ Hz, 4H, CH_2), 2.53 (s, 3H, substrate CH_3), 1.22 (t, $J_{HH} = 5.4$ Hz, 18H, C(CH₃)₃), 0.52 (t, $J_{HH} = 5.9$ Hz, 18H, C(CH₃)₃), -9.80 (t, $J_{HP} = 20.4$ Hz, 1H, Ir-H).

Reaction of (PCP)Ir with 4,4'-dimethylbipyridine to give kinetic C-H activation

products (8-4): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene*d*₁₂ in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 4,4'-Dimethylpyridine (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene-*d*₁₂): δ 69.2 (s). ¹H NMR (400 MHz, 25 °C, mesitylene-*d*₁₂): δ 8.52 (s, substrate *H*), 8.45 (d, *J*_{HH} = 5.1 Hz, substrate *H*), remaining substrate and PCP aryl H signals are obscured by the residual solvent peaks, 3.48 (d of vt, *J*_{HP} = 4.0 Hz, *J*_{HH} = 16.5 Hz, 4H, *CH*₂), 2.27 (s, 3H, substrate *CH*₃), 2.23 (s, 3H, substrate *CH*₃), 1.08 (t, *J*_{HH} = 6.5 Hz, 18H, C(*CH*₃)₃), 1.06 (t, *J*_{HH} = 6.5 Hz, 18H, C(*CH*₃)₃), -43.90 (t, *J*_{HP} = 13.8 Hz, 1H, Ir-*H*). **Conversion of 8-4 to the thermodynamic product 8-5**: After heating a solution of the C-H activation products (**8-4**) at 75 °C for 12 hr, the solution turned very bright yelloworange. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; yellow-orange prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 46.3 (s). ¹H NMR (400 MHz, 25 °C, mesitylene d_{12}): δ 8.55 (s, substrate *H*), 8.52 (s, substrate *H*), 8.45 (d, $J_{HH} = 4.8$ Hz, substrate *H*), 8.37 (d, $J_{HH} = 4.8$ Hz, substrate *H*), remaining substrate and PCP aryl H signals are obscured by the residual solvent peaks, 3.31 (d of vt, $J_{HP} = 4.1$ Hz, $J_{HH} = 16.7$ Hz, 2H, CH_2), 3.11 (d of vt, $J_{HH} = 16.4$ Hz, 2H, CH_2), 2.90 (s, 3H, substrate CH_3), 2.78 (s, 3H, substrate CH_3), 1.23 (t, $J_{HH} = 6.1$ Hz, 18H, $C(CH_3)_3$), 0.51 (t, $J_{HH} = 6.1$ Hz, 18H, $C(CH_3)_3$), -18.98 (t, $J_{HP} = 19.4$ Hz, 1H, Ir-*H*).

8.4 Conclusion

Results for C-H activation of bipyridines were initially surprising, since N,N coordination was expected. Instead, reaction of these substrates with (PCP)Ir leads to a *single* oxidative addition of a C-H bond, followed by coordination of one of the bipyridyl nitrogen atoms to give a six-coordinate, 18 electron complex. Thus, while the cyclometalated products are somewhat reminiscent of those obtained from reactions with phenanthrene, biphenyls, and terphenyls, the mechanism through which they are generated is distinctly different.

The substrate 2-phenylpyridine gave analogous products, but the reaction was significantly slower, due both to electronic factors (one less nitrogen atom) as well as the simple fact that it has one half the number of reactive sites vs. bipyridine. All C-H activation products from bipyridine substrates are stable to extended heating.

Experiments were conducted with two dimethyl-substituted bipyridines in order to probe the mechanistic details of how the metal center approaches the substrate for preliminary C-H activation. Results showed that (PCP)Ir approaches the bipyridyl C-H bond at C6 from the *opposite* direction vs. the nearby nitrogen atom, leading to a cyclometalated product with N *cis* to the Ir-H bond. Blocking this approach with a methyl substituent significantly slows the kinetics of cyclometalation and causes a change in the product conformation so that N is *trans* to the Ir-H bond.

8.5 References

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 Table 8.1. Crystal data and structure refinement for 8-1.

Empirical formula	C34 H51 Ir N2 P2		
Formula weight	741.91		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/n		
Unit cell dimensions	a = 9.063(2) Å	a= 90°.	
	b = 30.573(7) Å	b= 102.026(3)°.	
	c = 11.887(3) Å	$g = 90^{\circ}$.	
Volume	3221.5(12) Å ³		
Ζ	4		
Density (calculated)	1.530 Mg/m ³		
Absorption coefficient	4.269 mm ⁻¹		
F(000)	1504		
Crystal size	0.20 x 0.16 x 0.07 mm ³		
Theta range for data collection	2.20 to 30.60°.		
Index ranges	-12<=h<=12, -43<=k<=43, -16<=l<=16		
Reflections collected	38097		
Independent reflections	9827 [R(int) = 0.0351]		
Completeness to theta = 30.60°	99.3 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7461 and 0.5769		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	9827 / 1 / 367		
Goodness-of-fit on F ²	1.001		
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0707		
R indices (all data)	R1 = 0.0380, wR2 = 0.0739		
Largest diff. peak and hole	1.998 and -1.918 e.Å ⁻³		

Ir(1)-C(1)	2.044(3)	P(2)-C(8)	1.837(3)
Ir(1)-C(26)	2.095(3)	P(2)-C(17)	1.893(3)
Ir(1)-N(2)	2.148(3)	P(2)-C(21)	1.894(3)
Ir(1)-P(1)	2.3207(9)	C(25)-C(26)	1.414(4)
Ir(1)-P(2)	2.3330(9)	C(25)-C(30)	1.471(4)
Ir(1)-H(1)	1.591(10)	N(2)-C(30)	1.358(4)
P(1)-C(7)	1.841(3)		
P(1)-C(13)	1.900(3)		
P(1)-C(9)	1.903(3)		
C(1)-Ir(1)-C(26)	98.59(12)	C(13)-P(1)-Ir(1)	124.09(10)
C(1)-Ir(1)-N(2)	176.27(11)	C(9)-P(1)-Ir(1)	112.21(10)
C(26)-Ir(1)-N(2)	77.94(11)	C(8)-P(2)-C(17)	103.60(15)
C(1)-Ir(1)-P(1)	81.09(9)	C(8)-P(2)-C(21)	102.65(15)
C(26)-Ir(1)-P(1)	95.13(8)	C(17)-P(2)-C(21)	108.21(15)
N(2)-Ir(1)-P(1)	97.77(7)	C(8)-P(2)-Ir(1)	100.54(10)
C(1)-Ir(1)-P(2)	82.12(9)	C(17)-P(2)-Ir(1)	118.32(11)
C(26)-Ir(1)-P(2)	99.42(8)	C(21)-P(2)-Ir(1)	120.36(10)
N(2)-Ir(1)-P(2)	99.72(7)	C(30)-N(2)-Ir(1)	116.1(2)
P(1)-Ir(1)-P(2)	159.21(3)	N(2)-C(30)-C(25)	114.6(3)
C(1)-Ir(1)-H(1)	85.7(13)	C(25)-C(26)-Ir(1)	114.6(2)
C(26)-Ir(1)-H(1)	175.7(13)	C(26)-C(25)-C(30)	116.5(3)
N(2)-Ir(1)-H(1)	97.8(13)		
P(1)-Ir(1)-H(1)	84.8(13)	Torsion angles:	
P(2)-Ir(1)-H(1)	81.8(13)	C(26)-C(25)-C(30)-N(2)	-2.0(4)
C(7)-P(1)-C(13)	102.07(14)	N(1)-C(25)-C(30)-C(31)	-1.1(4)
C(7)-P(1)-C(9)	106.53(15)		
C(13)-P(1)-C(9)	108.65(14)		
C(7)-P(1)-Ir(1)	101.09(10)		

 Table 8.2.
 Selected bond lengths [Å] and angles [°] for 8-1.





 Table 8.3.
 Crystal data and structure refinement for 8-2.

Empirical formula	C40.50 H56.50 Ir N1	C40.50 H56.50 Ir N1.50 P2	
Formula weight	818.51	818.51	
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/n		
Unit cell dimensions	a = 12.0908(6) Å	a= 90°.	
	b = 19.3314(9) Å	b=100.536(1)°.	
	c = 15.6844(7) Å	g = 90°.	
Volume	3604.1(3) Å ³		
Z	4		
Density (calculated)	1.508 Mg/m ³		
Absorption coefficient	3.823 mm ⁻¹		
F(000)	1668		
Crystal size	0.59 x 0.24 x 0.11 mr	m ³	
Theta range for data collection	1.69 to 31.50°.		
Index ranges	-17<=h<=17, -27<=k	-17<=h<=17, -27<=k<=28, -23<=l<=22	
Reflections collected	45060		
Independent reflections	11910 [R(int) = 0.026	11910 [R(int) = 0.0267]	
Completeness to theta = 31.50°	99.2 %	99.2 %	
Absorption correction	Semi-empirical from	Semi-empirical from equivalents	
Max. and min. transmission	0.6784 and 0.2113	0.6784 and 0.2113	
Refinement method	Full-matrix least-squa	Full-matrix least-squares on F ²	
Data / restraints / parameters	11910 / 1 / 422		
Goodness-of-fit on F ²	1.003		
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0242, w	R1 = 0.0242, wR2 = 0.0574	
R indices (all data)	R1 = 0.0288, wR2 = 0	R1 = 0.0288, wR2 = 0.0597	
Largest diff. peak and hole	2.451 and -0.770 e.Å ⁻	2.451 and -0.770 e.Å ⁻³	

Ir(1)-C(1)	2.0413(18)	P(2)-C(8)	1.837(2)
Ir(1)-C(31)	2.1057(19)	P(2)-C(17)	1.897(2)
Ir(1)-N(1)	2.1263(16)	P(2)-C(21)	1.900(2)
Ir(1)-P(1)	2.3103(5)	N(1)-C(29)	1.352(2)
Ir(1)-P(2)	2.3353(5)	N(1)-C(25)	1.365(2)
Ir(1)-H(1)	1.595(10)	C(25)-C(30)	1.473(3)
P(1)-C(7)	1.8395(19)	C(1)-C(2)	1.412(3)
P(1)-C(9)	1.901(2)	C(30)-C(31)	1.417(3)
P(1)-C(13)	1.902(2)		
C(1)-Ir(1)-C(31)	98.56(7)	C(13)-P(1)-Ir(1)	114.78(7)
C(1)-Ir(1)-N(1)	176.29(7)	C(8)-P(2)-C(17)	102.48(9)
C(31)-Ir(1)-N(1)	77.73(7)	C(8)-P(2)-C(21)	103.84(9)
C(1)-Ir(1)-P(1)	80.72(5)	C(17)-P(2)-C(21)	108.14(9)
C(31)-Ir(1)-P(1)	97.26(5)	C(8)-P(2)-Ir(1)	100.24(7)
N(1)-Ir(1)-P(1)	99.87(4)	C(17)-P(2)-Ir(1)	121.14(6)
C(1)-Ir(1)-P(2)	82.05(5)	C(21)-P(2)-Ir(1)	117.78(6)
C(31)-Ir(1)-P(2)	97.41(5)	C(29)-N(1)-C(25)	119.12(17)
N(1)-Ir(1)-P(2)	98.12(4)	C(29)-N(1)-Ir(1)	124.44(13)
P(1)-Ir(1)-P(2)	158.822(18)	C(25)-N(1)-Ir(1)	116.40(12)
C(1)-Ir(1)-H(1)	89.4(12)	N(1)-C(25)-C(26)	119.89(18)
C(31)-Ir(1)-H(1)	171.7(12)	N(1)-C(25)-C(30)	114.47(16)
N(1)-Ir(1)-H(1)	94.3(12)	C(2)-C(1)-Ir(1)	121.09(14)
P(1)-Ir(1)-H(1)	86.4(12)	C(6)-C(1)-Ir(1)	121.88(14)
P(2)-Ir(1)-H(1)	81.2(12)	C(32)-C(31)-Ir(1)	129.81(14)
C(7)-P(1)-C(9)	103.45(9)	C(30)-C(31)-Ir(1)	114.46(13)
C(7)-P(1)-C(13)	104.70(9)	N(1)-C(29)-C(28)	123.08(19)
C(9)-P(1)-C(13)	107.66(9)	N(1)-C(29)-H(29)	118.5
C(7)-P(1)-Ir(1)	99.91(6)	C(31)-C(30)-C(25)	115.82(17)
C(9)-P(1)-Ir(1)	123.62(7)		

Table 8.4. Selected bond lengths [Å] and angles $[\circ]$ for 8-2.





 Table 8.5.
 Crystal data and structure refinement for 8-3.

Empirical formula	C36 H55 Ir N2 P2	
Formula weight	769.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.1024(8) Å	a= 90°.
	b = 17.6046(12) Å	b=92.951(1)°.
	c = 15.8339(11) Å	g = 90°.
Volume	3369.1(4) Å ³	
Z	4	
Density (calculated)	1.518 Mg/m ³	
Absorption coefficient	4.085 mm ⁻¹	
F(000)	1568	
Crystal size	0.34 x 0.14 x 0.03 mm ³	
Theta range for data collection	1.73 to 31.55°.	
Index ranges	-17<=h<=17, -25<=k<=25, -23<=l<=23	
Reflections collected	42171	
Independent reflections	11229 [R(int) = 0.0538]	
Completeness to theta = 31.55°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8873 and 0.3372	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11229 / 1 / 387	
Goodness-of-fit on F ²	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0781	
R indices (all data)	R1 = 0.0551, $wR2 = 0.0835$	
Largest diff. peak and hole	2.675 and -1.136 e.Å ⁻³	

Ir(1)-C(1)	2.046(3)	P(1)-C(9)	1.903(4)
Ir(1)-C(31)	2.109(3)	P(2)-C(8)	1.832(3)
Ir(1)-N(1)	2.222(3)	P(2)-C(21)	1.900(4)
Ir(1)-P(1)	2.3193(9)	P(2)-C(17)	1.912(3)
Ir(1)-P(2)	2.3477(9)	C(25)-C(30)	1.482(5)
Ir(1)-H(1)	1.581(10)	C(30)-C(31)	1.402(5)
P(1)-C(7)	1.840(4)	C(25)-N(1)	1.375(4)
P(1)-C(13)	1.901(3)		
C(1)-Ir(1)-C(31)	88.92(13)	C(7)-P(1)-Ir(1)	100.10(11)
C(1)-Ir(1)-N(1)	166.96(12)	C(13)-P(1)-Ir(1)	123.80(12)
C(31)-Ir(1)-N(1)	78.04(12)	C(9)-P(1)-Ir(1)	114.87(12)
C(1)-Ir(1)-P(1)	80.83(9)	C(8)-P(2)-C(21)	103.65(16)
C(31)-Ir(1)-P(1)	97.01(9)	C(8)-P(2)-C(17)	101.03(16)
N(1)-Ir(1)-P(1)	100.99(8)	C(21)-P(2)-C(17)	107.39(16)
C(1)-Ir(1)-P(2)	82.31(9)	C(8)-P(2)-Ir(1)	102.23(11)
C(31)-Ir(1)-P(2)	100.14(9)	C(21)-P(2)-Ir(1)	119.62(11)
N(1)-Ir(1)-P(2)	99.40(8)	C(17)-P(2)-Ir(1)	119.63(12)
P(1)-Ir(1)-P(2)	155.63(3)	C(25)-N(1)-Ir(1)	113.3(2)
C(1)-Ir(1)-H(1)	92.4(14)	N(1)-C(25)-C(30)	115.6(3)
C(31)-Ir(1)-H(1)	178.1(14)	C(31)-C(30)-C(25)	117.7(3)
N(1)-Ir(1)-H(1)	100.6(14)	C(30)-C(31)-Ir(1)	114.7(2)
P(1)-Ir(1)-H(1)	81.9(14)		
P(2)-Ir(1)-H(1)	81.3(14)	Torsion angles:	
C(7)-P(1)-C(13)	102.77(16)	N(1)-C(25)-C(30)-C(31)	-3.8(4)
C(7)-P(1)-C(9)	103.99(17)	C(26)-C(25)-C(30)-N(2)	-6.4(5)
C(13)-P(1)-C(9)	108.18(16)		

 Table 8.6.
 Selected bond lengths [Å] and angles [°] for 8-3.





 Table 8.7.
 Crystal data and structure refinement for 8-5.

Empirical formula	C36 H55 Ir N2 P2		
Formula weight	769.96		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 10.5998(6) Å	a= 61.5200(10)°.	
	b = 19.3047(11) Å	b= 78.7840(10)°.	
	c = 19.6029(11) Å	$g = 77.5700(10)^{\circ}$.	
Volume	3423.4(3) Å ³		
Z	4		
Density (calculated)	1.494 Mg/m ³		
Absorption coefficient	4.020 mm ⁻¹		
F(000)	1568		
Crystal size	0.23 x 0.19 x 0.11 mm	l ³	
Theta range for data collection	1.98 to 30.03°.	1.98 to 30.03°.	
Index ranges	-14<=h<=14, -26<=k<	-14<=h<=14, -26<=k<=27, -27<=l<=27	
Reflections collected	39648	39648	
Independent reflections	19753 [R(int) = 0.042	19753 [R(int) = 0.0421]	
Completeness to theta = 30.03°	98.7 %	98.7 %	
Absorption correction	Semi-empirical from e	Semi-empirical from equivalents	
Max. and min. transmission	0.6661 and 0.4582	0.6661 and 0.4582	
Refinement method	Full-matrix least-squar	Full-matrix least-squares on F ²	
Data / restraints / parameters	19753 / 1186 / 773	19753 / 1186 / 773	
Goodness-of-fit on F ²	1.004		
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0	R1 = 0.0535, $wR2 = 0.1175$	
R indices (all data)	R1 = 0.0696, wR2 = 0	R1 = 0.0696, $wR2 = 0.1248$	
Largest diff. peak and hole	4.407 and -3.399 e.Å-	4.407 and -3.399 e.Å ⁻³	

Ir(1)-C(1)	2.087(5)	P(1)-C(9)	1.899(6)
Ir(1)-C(25)	2.113(6)	P(2)-C(8)	1.848(6)
Ir(1)-N(2)	2.171(5)	P(2)-C(17)	1.892(6)
Ir(1)-P(1)	2.3141(13)	P(2)-C(21)	1.892(6)
Ir(1)-P(2)	2.3383(14)	N(2)-C(30)	1.356(6)
Ir(1)-H(1)	1.593(10)	C(25)-C(29)	1.430(8)
P(1)-C(7)	1.839(6)	C(29)-C(30)	1.463(8)
P(1)-C(13)	1.892(6)		
C(1)-Ir(1)-C(25)	170.9(2)	C(7)-P(1)-C(9)	102.7(3)
C(1)-Ir(1)-N(2)	92.88(18)	C(13)-P(1)-C(9)	109.5(2)
C(25)-Ir(1)-N(2)	78.15(19)	C(7)-P(1)-Ir(1)	101.21(17)
C(1)-Ir(1)-P(1)	79.21(14)	C(13)-P(1)-Ir(1)	122.52(17)
C(25)-Ir(1)-P(1)	103.08(14)	C(9)-P(1)-Ir(1)	114.22(18)
N(2)-Ir(1)-P(1)	95.21(12)	C(8)-P(2)-C(17)	102.6(3)
C(1)-Ir(1)-P(2)	81.40(14)	C(8)-P(2)-C(21)	102.2(3)
C(25)-Ir(1)-P(2)	98.50(14)	C(17)-P(2)-C(21)	109.5(3)
N(2)-Ir(1)-P(2)	100.96(12)	C(8)-P(2)-Ir(1)	101.62(18)
P(1)-Ir(1)-P(2)	155.27(5)	C(17)-P(2)-Ir(1)	118.37(19)
C(1)-Ir(1)-H(1)	95(2)	C(21)-P(2)-Ir(1)	119.19(19)
C(25)-Ir(1)-H(1)	94(2)	C(30)-N(2)-Ir(1)	115.4(4)
N(2)-Ir(1)-H(1)	172(2)	C(29)-C(25)-Ir(1)	113.2(4)
P(1)-Ir(1)-H(1)	87(2)	C(25)-C(29)-C(30)	117.3(5)
P(2)-Ir(1)-H(1)	80(2)	N(2)-C(30)-C(29)	115.3(5)
C(7)-P(1)-C(13)	103.7(2)		

 Table 8.8.
 Selected bond lengths [Å] and angles [°] for 8-5.

Torsion angle:

N(1)-C(29)-C(30)-C(31) 5.6(8)

Chapter 9

Exploiting Cyclometalation: Synthetic strategies for adding a second κ^3 ligand to (PCP)Ir

Abstract

Experiments with many different polycyclic aromatic substrates have been presented in this thesis, and the combined results have enhanced our understanding of the factors affecting C-H activation reactions by (PCP)Ir. Chapters 9 and 10 contain results from experiments designed to exploit the knowledge gained in the first eight chapters. Building on the discovery that cyclometalation reactions with (PCP)Ir often lead to very stable products, four polyaromatic substrates were chosen as potential candidates for reaction mechanisms that could lead to tridentate (κ^3) chelation around the metal center. Since the PCP pincer ligand is already in a κ^3 meridional conformation, a new tridentate ligand would be required to coordinate similarly, but in a perpendicular arrangement vs. PCP (i.e., in the equatorial plane around iridium).

While all of the planned *cyclometalation* reactions were successful, giving κ^2 products, none of the four substrates (*meta*-terpyridine, 2,6-diphenylpyridine, biphenyl-3-carboxaldehyde, and 3-phenylbenzylamine) was successfully ligated at the third position. Nevertheless, interesting results were observed in all cases.

9.1 Introduction

In chapter 6 of this thesis, results were presented for the reaction between (PCP)Ir and *meta*-terphenyl. One of the reasons that particular substrate was chosen was to have the opportunity to observe whether (PCP)Ir would demonstrate any particular regioselectivity in C-H activation reactions and concommitant cyclometalation. Results showed that the metal complex cyclometalated exclusively at the exterior 'A', less sterically crowded positions (Fig. 9.1).

Figure 9.1. Two positions for cyclometalation in *meta*-terphenyl and *meta*-terpyridine exterior 'A' site



Two unique locations for cyclometalation

The crystal structure of the product indicated that the third, uncoordinated phenyl ring was significantly torsionally canted, and also that the open coordination site on the metal center was very compressed and crowded due to distortion of the PCP *tert*butyl groups in order to accommodate the coordinated phenyl ring on the opposite side of the complex. These two observations make a tridentate arrangement of a triaryl substrate seem very difficult to achieve.

However, subsequent experiments showed that cyclometalation with bipyridine substrates also leads to very stable products. Therefore, it seemed worthwhile to test the reaction of (PCP)Ir with *meta*-terpyridine (terpy). In a series of enlightening experiments twenty years ago, Crabtree, et al. studied agostic interactions in a remarkably similar complex. Their iridium system had two PPh₃ ligands that were *not* tethered to a pincer arrangement, so they had significantly more comformational flexibility than the (PCP)Ir system. Even with the added freedom, they were only able to observe an agostic interaction arising from the third phenyl ring of their substrate 2,6-diphenylpyridine, not formal ligation.¹ Nevertheless, this still seemed like a good basis for additional experiments.

Terpy ligands are widely used (though perhaps less so than the two-ring analog: bipyridine), and an understanding of the interaction between (PCP)Ir and terpy is valuable in at least two contexts. First, there are a very large number of published reports regarding use of terpy as a ligand in metal complexes.²⁻²³ A search for citations concerning binding modes other than κ^3 N-N-N yielded no results; κ^2 N-C and κ^3 C-N-C chelates of terpy seem to be rare. Given our results with bipyridine substrates, it seemed likely that terpy would behave analogously and display one or more of the less common binding modes while avoiding N-N-N coordination.

Second, terpy molecules have been extensively employed as ligands in the context of luminescent materials, especially organic light emitting diodes (OLEDs).²⁴⁻³⁰ So any knowledge gained from our reactions with (PCP)Ir could have potential value, depending on the stability and conformation of the products.

Beyond the triaryl substrates terpy and 2,6-diphenylpyridine, experiments were conducted with two additional *biaryl* substrates: biphenyl-3-carboxaldehyde and 3phenylbenzylamine. Tridentate arrangements were not detected for any of these substrates, but the experiments yielded additional information about the reactivity of the (PCP)Ir system.

9.2.1 Synthesis and characterization of products from the reaction of (PCP)Ir with *meta*-terpyridine

The substrate *meta*-terpyridine has the stucture shown in Figure 9.1 (above) and therefore, there are several variables with respect to possible C-H activation and cyclometalation by (PCP)Ir. First, like *meta*-terphenyl, there is the question of regioselectivity: 'interior' vs. 'exterior' positions. Second, as was observed with bipyridine substrates, steric influences can direct the configuration of the final product, resulting in N atom coordination either *cis* or *trans* to the metal hydride bond. The goal of this experiment was to see if the stabilization gained by N coordination combined with a *double* C-H activation process would generate a κ^3 C-N-C binding mode (Fig. 9.2)

Figure 9.2. Hypothetical C-N-C binding mode for (PCP)Ir and *meta*-terpyridine



The reaction of (PCP)IrH₂ with an alkene acceptor such as norbornene (NBE) is known to generate a precursor of the reactive fragment "(PCP)Ir".³¹ Reaction of (PCP)IrH₂ and NBE (5 equiv.) with a slight excess of *meta*-terpyridine (1.1 equiv.) at ambient temperature results in disappearance of the dihydride peak in the ³¹P NMR spectrum accompanied by the appearance of several small, somewhat broad peaks diagnostic of C-H activation products, and two substantial peaks at δ 48.2 and δ 47.9 ppm (combined, 70% of the products) within 30 min. The ¹H NMR spectrum corresponds perfectly with the ³¹P NMR spectrum, and shows results very similar to those obtained with bipyridine. Several small upfield triplets correspond to preliminary C-H activation products and two larger triplets at δ -9.55 and δ -9.69 ppm indicating cyclometalated products with N *cis* to the Ir-H bond.³² After heating at 75 °C for 12 hrs., the reaction yielded a single, pure product: ³¹P NMR (δ 48.2 ppm) and ¹H NMR (t, δ -9.55 ppm; *J*_{HP} = 18.9 Hz). X-ray crystallographic analysis confirmed the structure as the product of a *single* C-H bond activation process, followed by coordination of nitrogen, **9-1** (eq. 1).



There are two points worth noting about the conformation of **9-1**. First, analogous to the results with *meta*-terphenyl, the thermodynamically preferred product results from cyclometalation at the less hindered 'exterior' positions. Second, there are two possible rotameric conformations for the product. This most likely accounts for the additional peak δ 47.9 ppm in the ³¹P NMR spectrum. The crystal structure and selected data for **9-1** are included at the end of this chapter.

9.2.2 Synthesis and characterization of products from the reaction of (PCP)Ir with **2,6-diphenylpyridine**

The substrate 2,6-diphenylpyridine has a very similar conformation to *meta*terpyridine, except there is only one nitrogen atom – situated in the cleft on the 'interior' of the bent molecule. This arrangement means that C-H activation by (PCP)Ir at an 'exterior' position on the substrate will lead to *double* C-H activation and cyclometalation analogous to the mechanism seen with biphenyl substrates. On the 'interior' side of the molecule, cyclometalation would proceed according to the bipyridine mechanism. Since nitrogen coordination was strongly stabilizing for the cyclometalated products from bipyridine substrates (no reductive elimination was detected, even at high temperatures, despite the presence of a hydride ligand on the metal center), it was hoped that the potential thermodynamic stability of nitrogen coordination would outweigh the kinetic barrier arising from the steric hindrance of the 'interior' sites of 2,6-diphenylpyridine.

Preliminary results confirmed the hypothesis! While the ³¹P NMR and ¹H NMR spectra show typical aryl C-H activation products (>90%) within 15 minutes, there is also a small hydride triplet in the ¹H NMR spectrum at δ -9.60 ppm (t, $J_{HP} = 17.9$ Hz), indicative of a cyclometalated product with N *cis* to the Ir-H bond. Encouraged by this result, the solution was briefly heated to 75 °C for 5 min. and then rechecked by NMR. Amazingly, all peaks corresponding to aryl C-H activation were gone, along with total disappearance of the ¹H NMR signal at δ -9.60 ppm. A new hydride resonance appeared at δ - 22.2 ppm (t, $J_{HP} = 17.9$ Hz) in the ¹H NMR spectrum along with two new signals in the ³¹P NMR spectrum at δ 42.2 and δ 40.1 ppm (ratio = 1:1). These data are consistent with the formation of two cyclometalated products: **9-2** from C-H activation at an 'interior' position followed by N coordination *trans* to the Ir-H bond and **9-3** from double C-H activation at an 'exterior' position (no corresponding hydride) (eq. 2). The formation of product **9-2** was extremely surprising, since this conformation requires very close proximity of a substrate phenyl ring with the pincer PCP phenyl backbone. This unprecedented result remains the only observable instance of cyclometalation by (PCP)Ir at a sterically hindered 'interior' position of a *meta*-triaryl substrate in all the results presented in this thesis.



Additional heating at 75 °C for 18 hrs., resulted in partial conversion of **9-2** to **9-3** (ratio 1:6), demonstrating, not surprisingly, that product **9-3** is thermodynamically favored. Additional heating at 75 °C for 48 hours yielded a single product: ³¹P NMR (δ 42.2 ppm) with no corresponding hydride resonance, as expected for the product of double C-H activation (eq. 3). Product **9-3** was crystallized as dark orange needles and

characterized by x-ray crystallography. The crystal structure and selected data for **9-3** are included at the end of this chapter.



9.2.3 Results of experiments with (PCP)Ir and two biaryl substrates: biphenyl-3carboxaldehyde and 3-phenylbenzylamine

Since attempts to generate κ^3 chelation failed with triaryl substrates primarily due to a combination of steric factors, additional experiments were conducted with two *bi*aryl substrates. Since the ability of (PCP)Ir to successfully cyclometalate several biaryl substrates had already been demonstrated, a new strategy was developed based on substituted biphenyl derivatives. Both biphenyl-3-carboxaldehyde and 3phenylbenzylamine have substituents that have been shown to coordinate to metal centers through their lone pair electrons (Fig. 9.3). It was hoped that (PCP)Ir would cyclometalate the biphenyl moieties through a double C-H activation process, and the substituent heteroatom would subsequently coordinate to the metal center at the vacant coordination site. This scheme would provide for the oxidation of Ir(I) to Ir(III), and create a fully saturated, 18-electron, six-coordinate complex. **Figure 9.3**. Hypothetical κ^3 coordination



NMR data collected very soon after adding the substrates to the reaction solutions showed successful preliminary C-H activation in both cases. For biphenyl-3carboxaldehyde, it appears that initial C-H activation *ortho* to the aldehyde substituent was quickly followed by decarbonylation to give two rotamers of the complex (PCP)Ir(H)(biphenyl)(CO). NMR data show a 1:1 mixture of products and spectral signals for both ³¹P NMR (δ 56.7 and δ 56.4 ppm) and ¹H NMR (overlapping triplets at δ -12.10 and δ -12.13 ppm; J_{HP} = 15.1 Hz) are consistent with the stuctures shown in eq. 4.



For 3-phenylbenzylamine, it appears that initial C-H activation *ortho* to the benzylamine substituent, yielding the product shown in eq. 5. Subsequent cyclometalation *may have* occurred. The solution turned deep violet quickly upon mixing – a very unusual color for (PCP)Ir complexes. Upon heating, all NMR evidence of metal-hydride bonds *and* cyclometalated products disappeared. The final thermodynamic product has no hydrides and yields a single peak in the ³¹P NMR

spectrum at δ 70.0 ppm. Attempts to crystallize this product have not yet been successful.



9.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in

solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. A full discussion of the NBE complex, including NMR characterization, is included in the Experimental section of Chapter 2 (section 2.3).

General remarks concerning these attempts to add a second tridentate ligand to (PCP)Ir: Substrates in this chapter were studied in the context of exploring cyclometalation reactions involving single or double C-H activation processes. Typical results for a variety of kinetic C-H activation products are seen in all cases and are not documented here, with a few exceptions as noted below. The NMR data presented are for the cyclometalated, thermodynamically favored products.

Reaction of (PCP)Ir with *meta*-terpyridine (9-1): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. *Meta*-terpyridine (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. After heating at 75 °C for 72 hr, the solution turned very bright yellow-orange. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; yellow-orange prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 47.9 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 9.35 – 7.00 (many peaks attributed to

substrate *H*), 3.04 (d of vt, $J_{HH} = 15.4 \text{ Hz}$, $J_{HP} = 4.3 \text{ Hz}$, 4H, CH₂), 1.27 (t, $J_{HH} = 6.2 \text{ Hz}$, 18H, C(CH₃)₃), 0.49 (t, $J_{HH} = 6.2 \text{ Hz}$, 18H, C(CH₃)₃), -9.55 (t, $J_{HP} = 19.0 \text{ Hz}$, 1H, Ir-*H*).

Reaction of (PCP)Ir with 2,6-diphenylpyridine to give kinetic C-H activation

products: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 2,6-Diphenylpyridine (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 68.8 (s), 68.4 (s), 67.8 (s), 42.5 (br m). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): the spectrum is highly convoluted due to multiple products, including both single *and* double C-H activation cyclometalated products, 1.01 and 0.99 (overlapping t, 36H, C(CH₃)₃, C-H activation products), 0.83 (t, 36H, C(CH₃)₃, single activation product), -9.55 (t, $J_{HP} = 19.8$ Hz, 1H, Ir-*H*, single activation product with N *cis* to Ir-H).

Reaction of (PCP)Ir with 2,6-diphenylpyridine: conversion to preliminary

thermodynamic products: A solution of the kinetic products was heated at 75 °C for 5 min. The solution turned very dark. ³¹P NMR (121.4 MHz, -20 °C, mesitylene- d_{12}): δ 42.2 (s), 40.1 (d, $J_{PH} = 16.7$ Hz). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): the spectrum is highly convoluted due to multiple products, including both single *and* double C-H activation cyclometalated products, 0.84 (br, 18H, C(CH₃)₃, single activation product), 0.67 (t, $J_{HH} = 6.2$ Hz, 36H, C(CH₃)₃, double activation product), 0.46 (br, 18H,

 $C(CH_3)_3$, single activation product), -22.20 (t, $J_{HP} = 17.1$ Hz, 1H, Ir-*H*, single activation product with N *trans* to Ir-H).

Conversion cyclometalated product (9-2) to the final thermodynamic product (9-3): After heating a solution of 9-2 at 75 °C for 96 hr, the solution turned very dark redbrown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; dark orange-brown prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 43.3 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.42 (d, $J_{HH} = 5.1$ Hz, substrate H), 8.32 (d, $J_{HH} = 5.1$ Hz, substrate H), 8.12 (d, $J_{HH} = 5.1$ Hz, substrate H), remaining substrate aryl H signals and those for PCP are obscured by the residual solvent peaks, 3.43 (d of vt, $J_{HP} = 3.2$ Hz, $J_{HH} = 16.8$ Hz, 4H, CH_2), 0.83 (br, 18H, C(CH_3)_3), 0.63 (br, 18H, C(CH_3)_3).

Reaction of (PCP)Ir with biphenyl-3-carboxaldehyde: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. Biphenyl-3-carboxaldehyde (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned orange. After heating at 75 °C for 24 hr, the solution turned very bright yellow-pink. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 56.7 (s), 56.4 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 9.62 (s, substrate *ortho-H*), 8.65 (s, substrate *ortho-H*), 8.30 – 7.00 (remaining substrate *H* in an array of doublets and multiplets), PCP aryl H signals are obscured by the residual solvent peaks, 3.36 (d of vt, 4H, CH₂, product A), 3.08 (d of vt,
4H, CH_2 , product b), 1.18 (t, $J_{HH} = 7.0$ Hz, 36H, $C(CH_3)_3$), 0.96, 0.94 (overlapping t, $J_{HH} = 5.4$ Hz, 36H, $C(CH_3)_3$), -12.10, -12.13 (overlapping t, $J_{HP} = 15.6$ Hz, 1H, Ir-*H* two products).

Reaction of (PCP)Ir with 3-phenylbenzylamine: 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 3-Phenylbenzylamine (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned deep violet. After heating at 75 °C for 24 hr, the solution remained deep violet in color. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 70.0 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 7.80 – 7.00 (substrate *H* in an array of doublets and multiplets), PCP aryl H signals are obscured by the residual solvent peaks, 3.20 (t, J_{HP} = 3.6 Hz, 4H, CH_2), 1.44 (t, J_{HH} = 6.0 Hz, 36H, $C(CH_3)_3$).

9.4 Conclusion

Four different substrates were tested to see if κ^3 chelating ligands could be synthesized *in addition to* the pre-existing PCP ligand system on the iridium metal center. The strategy involved trying to exploit the ability of (PCP)Ir to conduct single or double C-H activation reactions en route to thermodynamically stable cyclometalated products.

Two substrates with aryl rings proximal to the open coordination site on the metal were tested, despite the knowledge that steric crowding around the site is significant. *Meta*-terpyridine yielded κ^2 chelates similar to products from reactions of (PCP)Ir with bipyridine. NMR spectra of a reaction with the closely related substrate 2,6-diphenylpyridine did indeed show what appeared to be at least N-coordination (probably cyclometalation at the sterically hindered interior 'B' position), but C-N-C coordination was not detected.

Changing the strategy to include other Lewis basic groups for coordination in the sixth position, biphenyl-3-carboxaldehyde yielded products from decarbonylation. Unfortunately, the product mixture included two rotamers (1:1 ratio), so crystallization was not feasible. The last substrate – 3-phenylbenzylamine – may have yielded products of preliminary C-H activation, but NMR spectra of the strongly colored dark violet reaction mixture did not indicate cyclometalated products.

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 Table 9.1. Crystal data and structure refinement for 9-1.

Empirical formula	C39 H54 Ir N3 P2		
Formula weight	818.99		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 10.1147(5) Å	a= 91.649(1)°.	
	b = 12.7838(6) Å	b=97.611(1)°.	
	c = 14.2271(6) Å	$g = 92.926(1)^{\circ}$	
Volume	1819.87(15) Å ³		
Z	2		
Density (calculated)	1.495 Mg/m ³		
Absorption coefficient	3.787 mm ⁻¹		
F(000)	832		
Crystal size	0.49 x 0.24 x 0.15 m	m ³	
Theta range for data collection	2.03 to 30.52°.		
Index ranges	-14<=h<=14, -18<=k	-14<=h<=14, -18<=k<=18, -20<=l<=20	
Reflections collected	21664		
Independent reflections	10949 [R(int) = 0.01]	10949 [R(int) = 0.0192]	
Completeness to theta = 30.52°	98.3 %		
Absorption correction	Semi-empirical from	Semi-empirical from equivalents	
Max. and min. transmission	0.6004 and 0.2584	0.6004 and 0.2584	
Refinement method	Full-matrix least-squ	Full-matrix least-squares on F ²	
Data / restraints / parameters	10949 / 1 / 622	10949 / 1 / 622	
Goodness-of-fit on F ²	1.003		
Final R indices [I>2sigma(I)]	R1 = 0.0208, wR2 =	R1 = 0.0208, $wR2 = 0.0513$	
R indices (all data)	R1 = 0.0223, wR2 =	0.0519	
Largest diff. peak and hole	2.157 and -0.574 e.Å	-3	

angles [°] for 9-1 .	
P(1)-C(13)	1.898(2)
P(2)-C(8)	1.835(2)
P(2)-C(17)	1.8953(19)
P(2)-C(21)	1.899(2)
N(2)-C(30)	1.367(2)
C(26)-C(30)	1.476(3)
C(25)-C(26)	1.416(3)
C(8)-P(2)-C(17)	104.19(9)
C(8)-P(2)-C(21)	103.16(10)

Table 9.2. Selected bond lengths [Å] and

2.0465(19)

2.0845(18)

2.1381(16)

2.3189(5)

Ir(1)-C(1)

Ir(1)-C(25)

Ir(1)-N(2)

Ir(1)-P(1)

Ir(1)-P(2)	2.3275(5)	N(2)-C(30)	1.367(2)
Ir(1)-H(1)	1.580(10)	C(26)-C(30)	1.476(3)
P(1)-C(7)	1.839(2)	C(25)-C(26)	1.416(3)
P(1)-C(9)	1.893(2)		
C(1)-Ir(1)-C(25)	88.97(7)	C(8)-P(2)-C(17)	104.19(9)
C(1)-Ir(1)-N(2)	167.56(7)	C(8)-P(2)-C(21)	103.16(10)
C(25)-Ir(1)-N(2)	78.60(7)	C(17)-P(2)-C(21)	108.14(9)
C(1)-Ir(1)-P(1)	82.36(5)	C(8)-P(2)-Ir(1)	101.76(7)
C(25)-Ir(1)-P(1)	100.56(5)	C(17)-P(2)-Ir(1)	122.69(6)
N(2)-Ir(1)-P(1)	99.55(4)	C(21)-P(2)-Ir(1)	114.27(7)
C(1)-Ir(1)-P(2)	82.17(5)	C(30)-N(2)-Ir(1)	115.58(13)
C(25)-Ir(1)-P(2)	98.67(5)	N(2)-C(30)-C(26)	114.84(16)
N(2)-Ir(1)-P(2)	99.78(5)	C(25)-C(26)-C(30)	116.16(16)
P(1)-Ir(1)-P(2)	155.003(18)	C(26)-C(25)-Ir(1)	114.78(13)
C(1)-Ir(1)-H(1)	100.3(12)		
C(25)-Ir(1)-H(1)	170.7(12)	Torsion angles:	
N(2)-Ir(1)-H(1)	92.2(12)	C(25)-C(26)-C(30)-N(2)	1.4(2)
P(1)-Ir(1)-H(1)	81.6(12)	N(1)-C(26)-C(30)-C(31)	0.6(3)
P(2)-Ir(1)-H(1)	82.0(12)		
C(7)-P(1)-C(9)	103.31(9)	C(28)-C(27)-C(35)-N(3)	-19.9(3)
C(7)-P(1)-C(13)	103.94(9)	N(1)-C(27)-C(35)-C(36)	-19.9(3)
C(9)-P(1)-C(13)	108.05(9)		
C(7)-P(1)-Ir(1)	101.76(6)		
C(9)-P(1)-Ir(1)	122.62(7)		
C(13)-P(1)-Ir(1)	114.56(7)		





 Table 9.3.
 Crystal data and structure refinement for 9-3.

Empirical formula	C41 H54 Ir N P2		
Formula weight	814.99		
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/c		
Unit cell dimensions	a = 16.2493(9) Å	a= 90°.	
	b = 38.975(2) Å	b=91.380(1)°.	
	c = 11.4375(6) Å	g = 90°.	
Volume	7241.4(7) Å ³		
Z	8		
Density (calculated)	1.495 Mg/m ³		
Absorption coefficient	3.805 mm ⁻¹		
F(000)	3312		
Crystal size	0.40 x 0.30 x 0.20 mm	m ³	
Theta range for data collection	1.63 to 32.04°.		
Index ranges	-24<=h<=24, -58<=k	<=58, -17<=l<=17	
Reflections collected	94622		
Independent reflections	25072 [R(int) = 0.055	53]	
Completeness to theta = 32.04°	99.5 %		
Absorption correction	Semi-empirical from	Semi-empirical from equivalents	
Max. and min. transmission	0.5166 and 0.3113	0.5166 and 0.3113	
Refinement method	Full-matrix least-squa	ares on F ²	
Data / restraints / parameters	25072 / 14 / 836		
Goodness-of-fit on F ²	1.006		
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.0437, w	0.0873	
R indices (all data)	R1 = 0.0638, wR2 = 0	0.0932	
Largest diff. peak and hole	2.937 and -2.161 e.Å-	-3	

Ir(1)-C(31)	2.011(3)	P(2)-C(8)	1.839(4)
Ir(1)-C(1)	2.095(3)	P(2)-C(17)	1.880(4)
Ir(1)-C(26)	2.117(3)	P(2)-C(21)	1.889(4)
Ir(1)-P(1)	2.3068(9)	C(25)-C(26)	1.417(5)
Ir(1)-P(2)	2.3548(9)	C(25)-C(30)	1.448(5)
P(1)-C(7)	1.842(4)	C(30)-C(31)	1.422(5)
P(1)-C(9)	1.882(3)		
P(1)-C(13)	1.898(4)		
C(31)-Ir(1)-C(1)	94.71(13)	C(8)-P(2)-C(21)	103.35(16)
C(31)-Ir(1)-C(26)	81.03(13)	C(17)-P(2)-C(21)	110.46(16)
C(1)-Ir(1)-C(26)	175.60(12)	C(8)-P(2)-Ir(1)	101.67(12)
C(31)-Ir(1)-P(1)	92.01(10)	C(17)-P(2)-Ir(1)	122.04(12)
C(1)-Ir(1)-P(1)	80.66(9)	C(21)-P(2)-Ir(1)	112.74(12)
C(26)-Ir(1)-P(1)	98.29(9)	C(31)-C(30)-C(25)	116.2(3)
C(31)-Ir(1)-P(2)	99.08(10)	C(30)-C(31)-Ir(1)	115.1(2)
C(1)-Ir(1)-P(2)	81.43(9)	C(26)-C(25)-C(30)	115.4(3)
C(26)-Ir(1)-P(2)	100.28(9)	C(25)-C(26)-Ir(1)	112.2(2)
P(1)-Ir(1)-P(2)	159.62(3)		
C(7)-P(1)-C(9)	104.59(16)	Torsion angles:	
C(7)-P(1)-C(13)	105.66(16)	C(26)-C(25)-C(30)-C(3	0.0(4)
C(9)-P(1)-C(13)	109.99(16)	N(1)-C(25)-C(30)-C(35)	5) -6.1(5)
C(7)-P(1)-Ir(1)	101.71(11)		
C(9)-P(1)-Ir(1)	126.90(12)	N(1)-C(29)-C(36)-C(37)	7) -22.3(5)
C(13)-P(1)-Ir(1)	105.96(11)	C(28)-C(29)-C(36)-C(4	1) -25.3(6)
C(8)-P(2)-C(17)	103.93(17)		

 Table 9.4.
 Selected bond lengths [Å] and angles [°] for 9-3.

Chapter 10

Exploiting Cyclometalation: Synthesis of (PCP)Ir Dimers

Abstract

Cyclometalation reactions involving (PCP)Ir often lead to very stable products (see chapters 3-8). Results from experiments with substrates chosen for their potential to cyclometalate and chelate in a tridentate fashion were presented in chapter 9; none of them reacted as planned. The triaryl substrates proved particularly frustrating in this context, due to severe steric crowding at the open coordination site on the metal center. In this chapter, steric effects are studied from an entirely different perspective. Four substrates from earlier experiments were chosen in order to examine the potential for forming highly congested (PCP)Ir dimer complexes.

Bipyridine, 4,4'-difluorobiphenyl, *meta*-terpyridine, and 2,6-diphenylpyridine were chosen for their different conformational properties, and each was reacted with two equivalents of (PCP)Ir. The resulting (PCP)Ir dimers are very large, sterically crowded complexes that demonstrate different binding modes for the (PCP)Ir fragment, depending on the steric environment.

10.1 Introduction

During the experiments with bipyridine substrates, the results for which are presented in chapter 8, it was observed that cyclometalation by (PCP)Ir proceeds much more quickly during reactions with bipyridine vs. 2-phenylpyridine. The only difference between these substrates is the absence of a single nitrogen atom in the latter.

The logical reason for this difference in rates is that 'biphenyl-type' cyclometalations involve *two* successive C-H activation reactions, while 'bipyridinetype' cyclometalations involve only a single oxidative addition of a C-H bond by (PCP)Ir. While additional experiments are required in order to measure the rates and make informed evaluations of mechanistic details, one thing is clear: all of these polycyclic aromatic substrates have more than one site available for potential cyclometalation. This fact has been addressed in previous chapters in the context of regioselectivity of the (PCP)Ir system. Therefore, experiments have been designed to exploit the possibility of creating bridging ligands from certain substrates by adding enough (PCP)Ir to cyclometalate individual substrate molecules *more than once*.

This type of bimetallic complex is not new, and there are a few reports in the literature concerning this phenomenon.^{1,2} But the results presented in this chapter are from experiments based on curiosity and a desire to push the steric limits of (PCP)Ir reactivity, rather than on literature precedent. It should also be added that recent developments in organic light emitting diode (OLED) technology have utilized iridium complexes with both biphenyl and bipyridine ligands, often with fluoro substituents (see chapters 5, 6, and 8 respectively, for references).

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Each of the substrates chosen for these dimerization studies addresses different conformational variables as shown in scheme 10.1. Products of dimerization reactions with bipyridine and 4,4'-difluorobiphenyl require that the (PCP)Ir units 'face' each other, bringing the phosphine *tert*butyl groups into very close proximity. In addition, variation in individual (PCP)Ir conformations can lead to multiple isomeric products (*vide infra*). Reactions with 2,6-diphenylpyridine assess the preference of (PCP)Ir for double vs. single C-H activation *and also* for 'interior' vs. 'exterior' cyclometalation. Finally, dimerization with *meta*-terpyridine addresses whether two (PCP)Ir fragments can both cyclometalate in very close proximity on the same side of the molecule, and how they conformationally cope with the resulting steric crowding.



Scheme 10.1. Four substrates used in dimerization reactions and variables they address

10.2.1 Synthesis and characterization of products from the dimerization reaction of (PCP)Ir with bipyridine, 4,4'-difluorobiphenyl, *meta*-terpyridine, and 2,6-diphenylpyridine

The NMR data that support the results discussed below are provided in the experimental section of this chapter and have also been discussed previously in this thesis in the context of the individual reactions of (PCP)Ir with these substrates. Therefore, the discussion here will focus on the trends in the results as well as various interesting or important structural details.

All four reactions were successful, generating the intended dimers (or mixtures of isomeric dimerized products). For reasons addressed above, and illustrated in scheme 10.1, all of the dimerization reactions had the potential to generate product mixtures, depending on the conformations of the (PCP)Ir unit. As an example, the reaction of (PCP)Ir with one half an equivalent of bipyridine yielded a mixture of three products in a 1:2:1 ratio (**10-1a,b,c**). At first, it seemed that this result reflected a statistical distribution of binding conformations for the two (PCP)Ir units. However, as was shown in chapter 8, the lower kinetic barrier to C-H oxidative addition involves approach of (PCP)Ir from the direction *opposite* to the location of the bipyridyl nitrogen atom. The resulting cyclometalated product has the N atom *cis* to the Ir-H bond. However, under the current reaction conditions, steric crowding around each bipyridine molecule is severe, with two (PCP)Ir fragments attempting to find the most favored orientation for coordination and C-H bond activation. Therefore, the (PCP)Ir complex yields both cyclometalated conformations (N *trans* and N *cis* to the Ir-H bond) leading to three

possible combinations: *trans/trans*, *trans/cis* (same as *cis/trans*) and *cis/cis*. The actual distribution of products from the dimerization reaction reflects both the lower kinetic barrier to N *cis* conformation as well as the steric contraints that encourage the N *trans* arrangement (Scheme 10.2). Fortunately, the major product **10-1a** was isolated through fractional crystallization and analyzed by x-ray diffraction. The x-ray crystal structure and selected data are included at the end of this chapter.



Scheme 10.2. Dimer from bipyridine: three conformational isomers

The dimerization reaction with 4,4'-difluorobiphenyl yielded slightly different results. Due to the slower kinetics involved in the double C-H activation mechanism, preliminary products from the reaction of (PCP)Ir with one half an equivalent of the substrate were dimerized products of single C-H activation *ortho* to the fluoro substituents (Scheme 10.3)! After heating at 75 °C for 24 hrs., the expected dimer from dual cyclometalation reactions was generated as a single product, **10-2**. Unlike results with μ -bipyridine, dimerization with biphenyl yields only one combination of (PCP)Ir conformations, as illustrated below. Crystallization of product **10-2** has not yet been successful.





Single C-H activation

Double C-H activation

Dimerization reactions with *meta*-terpyridine and 2,6-diphenylpyridine both result in products that have (PCP)Ir units cyclometalated at 'exterior' locations. Apparently, not even the steric crowding that results from the coordination of these two extremely bulky ligand systems is sufficient to encourage cyclometalation at an 'interior' position by one of the metal centers. Interestingly, reaction of (PCP)Ir with one half an equivalent of *meta*-terpyridine yields a single product, **10-3**, that features *both* conformational arrangements of the metal-ligand system (N *cis* and N *trans*). It seems likely that the first (PCP)Ir fragment cyclometalates to give the preferred N *cis* arrangement, and when the second (PCP)Ir fragment attempts to approach, the lower kinetic barrier involves approach from the opposite direction, yielding a hetero-conformational product (Scheme 10.4). Product **10-3** was isolated as yellow-green prisms and characterized via x-ray crystallography. The x-ray crystal structure and selected data are included at the end of this chapter.





Finally, dimerization of (PCP)Ir with one half an equivalent of 2,6-

diphenylpyridine was also successful, yielding a single product, **10-4**, in which all of the (PCP)Ir units are cyclometalated to 'exterior' positions through a double C-H activation mechanism. This product is interesting in comparison with the similar product from reaction with *meta*-terpyridine for two reasons. First, NMR data seem to indicate that all (PCP)Ir units are coordinated to the substrate with the same conformation (analogous to results with 4,4'-difluorobiphenyl). In addition, the metal centers in this dimer are unsaturated; they each have an open coordination site. This could allow for functionalization to yield additional dimers with different properties. Crystallization of product **10-4** has not yet been successful.

10.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in

solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. A full discussion of the NBE complex, including NMR characterization, is included in the Experimental section of Chapter 2 (section 2.3).

General remarks concerning these attempts to synthesize (PCP)Ir dimers:

Substrates in this chapter were studied in the context of exploring cyclometalation reactions involving single or double C-H activation processes. Reactions of (PCP)Ir with all of the substrates included in this chapter were fully characterized in previous chapters of this thesis. The NMR data presented are for the cyclometalated, thermodynamically favored products. In addition, the spectra are extremely complicated due to the presence of multiple isomers resulting in a very large number of proton signals. Therefore, the data reported here include the ³¹P NMR signals only, except where specific ¹H NMR signals are uniquely relevant.

Reaction of (PCP)Ir with one half an equivalent of bipyridine (10-1a,b,c): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. Bipyridine (0.5 eq; 0.005 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. After heating at 75 °C for 18 hr, the solution turned very bright yellow-orange. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from

pentane and octane; yellow-orange prisms were obtained, despite having a 2:1:1 mixture of products. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): Three products: δ 48.1 (br d, 25%), 47.2 (br d, 50%), 45.8 (br d, 25%). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ -9.58 (t, J_{HP} = 19.0 Hz, 1H, Ir-H, 50%), -11.81 (t, J_{HP} = 20.4 Hz, 1H, Ir-H, 25%), -18.80 (t, J_{HP} = 18.6 Hz, 1H, Ir-H, 25%).

Reaction of (PCP)Ir with one half an equivalent of 4,4'-difluorobiphenyl (10-2): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 4,4'-Difluorobiphenyl (0.5 eq; 0.005 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned bright orange. After heating at 75 °C for 24 hr, the solution turned dark orange-red. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; dark orange prisms were obtained, however, crystallographic analysis determined that a substantial concentration of the monomeric species was generated. Additional attempts to crystallize the dimer are in progress. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 42.3 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 3.35 (br t, 4H, CH₂), 0.68 (br t, 36H, C(CH₃)₃).

Reaction of (PCP)Ir with one half an equivalent of *meta*-terpyridine (10-3): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. *Meta*-terpyridine (0.5 eq; 0.005 mmol) was added to the resulting

solution; after stirring for one minute, the dark red-orange solution turned bright orange. After heating at 75 °C for 24 hr, the solution turned bright orange-yellow. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; bright yellow-green prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 47.1 (s, 50%), 44.7 (s, 50%). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ -9.77 (t, $J_{HP} = 20.7$ Hz, 1H, Ir-H, 50%), -19.00 (t, $J_{HP} = 18.3$ Hz, 1H, Ir-H, 50%).

Reaction of (PCP)Ir with one half an equivalent of 2,6-diphenylpyridine (10-4): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 4 equivalents of norbornene were added from a stock solution in *p*-xylene. 2,6-Diphenylpyridine (0.5 eq; 0.005 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned darker red. After heating at 75 °C for 24 hr, the solution turned very dark brown. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and octane; dark brown prisms were obtained, however, crystallographic analysis has not yet been completed. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 43.1 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 3.43 (d of vt, J_{HP} = 3.2 Hz, J_{HH} = 16.8 Hz, 4H, CH_2), 0.83 (br, 18H, $C(CH_3)_3$), 0.63 (br, 18H, $C(CH_3)_3$).

10.4 Conclusion

Four polycyclic aromatic substrates were successfully converted into bridging ligands in the formation of (PCP)Ir dimers. The products of these reactions confirmed trends in reactivity for (PCP)Ir that were explored in depth in earlier chapters of this thesis. C-H activation and cyclometalation of bipyridine-type substrates appears to be more facile than the more cumbersome double C-H activation mechanism for the cyclometalation of biphenyl-type substrates.

All of these reactions are driven by the thermodynamic stability of the ultimate cyclometalated product. The conformations of the products (*cis* vs. *trans*) are determined by steric demands rather than electronic factors.

10.5 References

- Beley, M. C., Jean Paul; Sauvage, Jean Pierre *Inorg. Chem.* **1993**, *32*, 4539. Hartshorn, C. M.; Steel, P. J. *Organometallics* **1998**, *17*, 3487. (1)
- (2)





 Table 10.1.
 Crystal data and structure refinement for 10-1a.

Empirical formula	C58 H94 Ir2 N2 P4	
Formula weight	1327.63	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.0044(6) Å	a= 104.488(1)°.
	b = 11.0873(8) Å	b=98.265(1)°.
	c = 14.7723(11) Å	$g = 99.204(1)^{\circ}$.
Volume	1383.20(17) Å ³	
Z	1	
Density (calculated)	1.594 Mg/m ³	
Absorption coefficient	4.960 mm ⁻¹	
F(000)	670	
Crystal size	0.25 x 0.20 x 0.08 mm ³	
Theta range for data collection	2.07 to 30.03°.	
Index ranges	-12<=h<=12, -15<=k<=15, -20<=l<=20	
Reflections collected	15944	
Independent reflections	7964 [R(int) = 0.0206]	
Completeness to theta = 30.03°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6924 and 0.3703	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7964 / 1 / 313	
Goodness-of-fit on F ²	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0274, $wR2 = 0.0676$	
R indices (all data)	R1 = 0.0293, $wR2 = 0.0686$	
Largest diff. peak and hole	4.331 and -1.871 e.Å ⁻³	

Ir(1)-C(1)	2.076(3)	P(2)-C(8)	1.829(3)
Ir(1)-C(29)#1	2.142(3)	P(2)-C(21)	1.902(3)
Ir(1)-N(1)	2.200(2)	P(2)-C(17)	1.906(3)
Ir(1)-P(1)	2.3224(7)	N(1)-C(25)	1.366(3)
Ir(1)-P(2)	2.3455(7)	C(25)-C(29)	1.423(4)
Ir(1)-H(1)	1.595(10)	C(25)-C(25)#1	1.449(5)
P(1)-C(7)	1.842(3)		
P(1)-C(9)	1.880(3)		
P(1)-C(13)	1.902(3)		
C(1)-Ir(1)-C(29)#1	102.55(10)	C(7)-P(1)-Ir(1)	100.82(10)
C(1)-Ir(1)-N(1)	177.38(9)	C(9)-P(1)-Ir(1)	125.44(9)
C(29)#1-Ir(1)-N(1)	76.34(9)	C(13)-P(1)-Ir(1)	112.98(10)
C(1)-Ir(1)-P(1)	77.64(8)	C(8)-P(2)-C(21)	101.70(13)
C(29)#1-Ir(1)-P(1)	98.63(7)	C(8)-P(2)-C(17)	100.06(13)
N(1)-Ir(1)-P(1)	100.12(6)	C(21)-P(2)-C(17)	110.62(13)
C(1)-Ir(1)-P(2)	79.66(8)	C(8)-P(2)-Ir(1)	100.82(9)
C(29)#1-Ir(1)-P(2)	102.45(7)	C(21)-P(2)-Ir(1)	118.71(9)
N(1)-Ir(1)-P(2)	102.87(6)	C(17)-P(2)-Ir(1)	120.24(9)
P(1)-Ir(1)-P(2)	151.81(2)	C(25)-N(1)-Ir(1)	117.20(17)
C(1)-Ir(1)-H(1)	84.5(14)	N(1)-C(25)-C(25)#1	113.5(3)
C(29)#1-Ir(1)-H(1)	172.9(13)	C(29)-C(25)-C(25)#1	119.0(3)
N(1)-Ir(1)-H(1)	96.7(14)	C(25)-C(29)-Ir(1)#1	113.94(18)
P(1)-Ir(1)-H(1)	83.7(14)		
P(2)-Ir(1)-H(1)	77.7(14)		
C(7)-P(1)-C(9)	100.16(13)		
C(7)-P(1)-C(13)	106.86(14)		
C(9)-P(1)-C(13)	107.94(13)		

 Table 10.2.
 Selected bond lengths [Å] and angles [°] for 10-1a.





C66 H100 Ir2 N3 P4 Empirical formula 1443.77 Formula weight 100(2) K Temperature 0.71073 Å Wavelength Crystal system Orthorhombic Space group Pbca Unit cell dimensions a = 16.0396(10) Åa= 90°. b = 19.5703(12) Å b= 90°. c = 39.404(2) Å $g = 90^{\circ}$. 12369.0(13) Å³ Volume 8 Ζ 1.551 Mg/m³ Density (calculated) 4.445 mm⁻¹ Absorption coefficient 5848 F(000) 0.32 x 0.23 x 0.07 mm³ Crystal size Theta range for data collection 1.03 to 29.13°. Index ranges -21<=h<=21, -26<=k<=26, -53<=l<=53 Reflections collected 129507 Independent reflections 16640 [R(int) = 0.0946]Completeness to theta = 29.13° 100.0 % Absorption correction Semi-empirical from equivalents Max. and min. transmission 0.7461 and 0.3304 Refinement method Full-matrix least-squares on F² Data / restraints / parameters 16640 / 1063 / 706 Goodness-of-fit on F² 1.027 Final R indices [I>2sigma(I)] R1 = 0.0880, wR2 = 0.2036R indices (all data) R1 = 0.1015, wR2 = 0.20895.747 and -6.321 e.Å-3 Largest diff. peak and hole

Table 10.3. Crystal data and structure refinement for 10-3.

Ir(1)-C(50)	2.105(9)	Ir(2)-C(25)	2.045(9)
Ir(1)-C(1)	2.107(9)	Ir(2)-C(52)	2.109(9)
Ir(1)-N(2)	2.158(7)	Ir(2)-N(3)	2.142(8)
Ir(1)-P(2)	2.315(2)	Ir(2)-P(4)	2.311(2)
Ir(1)-P(1)	2.329(2)	Ir(2)-P(3)	2.330(2)
Ir(1)-H(1)	1.589(19)	Ir(2)-H(2)	1.596(19)
P(1)-C(7)	1.831(10)	P(3)-C(31)	1.832(10)
P(1)-C(9)	1.893(10)	P(3)-C(33)	1.895(10)
P(1)-C(13)	1.907(10)	P(3)-C(37)	1.912(11)
P(2)-C(8)	1.848(10)	P(4)-C(32)	1.841(10)
P(2)-C(21)	1.886(10)	P(4)-C(41)	1.888(11)
P(2)-C(17)	1.899(10)	P(4)-C(45)	1.904(11)
N(2)-C(54)	1.367(11)	N(3)-C(59)	1.340(12)
C(49)-C(54)	1.473(12)	C(53)-C(59)	1.495(12)
C(49)-C(50)	1.410(12)	C(52)-C(53)	1.409(12)
C(50)-Ir(1)-C(1)	174.3(4)	C(7)-P(1)-Ir(1)	104.3(3)
C(50)-Ir(1)-N(2)	78.6(3)	C(9)-P(1)-Ir(1)	112.1(4)
C(1)-Ir(1)-N(2)	95.7(3)	C(13)-P(1)-Ir(1)	124.1(3)
C(50)-Ir(1)-P(2)	100.3(2)	C(8)-P(2)-C(21)	102.7(5)
C(1)-Ir(1)-P(2)	80.5(3)	C(8)-P(2)-C(17)	103.5(5)
N(2)-Ir(1)-P(2)	100.2(2)	C(21)-P(2)-C(17)	107.6(5)
C(50)-Ir(1)-P(1)	99.3(2)	C(8)-P(2)-Ir(1)	103.0(3)
C(1)-Ir(1)-P(1)	81.6(3)	C(21)-P(2)-Ir(1)	123.9(3)
N(2)-Ir(1)-P(1)	98.9(2)	C(17)-P(2)-Ir(1)	113.5(3)
P(2)-Ir(1)- $P(1)$	154.89(9)	C(54)-N(2)-Ir(1)	114.9(6)
C(50)-Ir(1)-H(1)	91(3)	N(2)-C(54)-C(49)	115.1(7)
C(1)-Ir(1)-H(1)	95(3)	C(50)-C(49)-C(54)	117.4(8)
N(2)-Ir(1)-H(1)	163(2)	C(49)-C(50)-Ir(1)	113.7(6)
P(2)-Ir(1)-H(1)	68(3)		
P(1)-Ir(1)-H(1)	96(3)	C(25)-Ir(2)-C(52)	89.3(3)
C(7)-P(1)-C(9)	103.9(5)	C(25)-Ir(2)-N(3)	167.6(3)
C(7)-P(1)-C(13)	101.5(5)	C(52)-Ir(2)-N(3)	78.3(3)
C(9)-P(1)-C(13)	108.4(4)	C(25)-Ir(2)-P(4)	81.8(3)

 Table 10.4.
 Selected bond lengths [Å] and angles [°] for 10-3.

C(52)-Ir(2)-P(4)	102.2(2)	C(32)-P(4)-C(41)	104.4(4)
N(3)-Ir(2)-P(4)	101.2(2)	C(32)-P(4)-C(45)	103.2(5)
C(25)-Ir(2)-P(3)	82.8(3)	C(41)-P(4)-C(45)	108.5(5)
C(52)-Ir(2)-P(3)	98.8(3)	C(32)-P(4)-Ir(2)	102.1(3)
N(3)-Ir(2)-P(3)	98.4(2)	C(41)-P(4)-Ir(2)	121.8(3)
P(4)-Ir(2)-P(3)	153.70(9)	C(45)-P(4)-Ir(2)	114.4(4)
C(25)-Ir(2)-H(2)	95(3)	C(59)-N(3)-Ir(2)	115.6(6)
C(52)-Ir(2)-H(2)	171(2)	N(3)-C(59)-C(53)	116.2(8)
N(3)-Ir(2)-H(2)	98(3)	C(52)-C(53)-C(59)	114.9(8)
P(4)-Ir(2)-H(2)	86(2)	C(53)-C(52)-Ir(2)	114.8(6)
P(3)-Ir(2)-H(2)	74.0(18)		
C(31)-P(3)-C(33)	103.5(4)	Torsion angles:	
C(31)-P(3)-C(37)	103.9(4)	C(50)-C(49)-C(54)-N(2)	-0.4(11)
C(33)-P(3)-C(37)	106.8(4)	N(1)-C(49)-C(54)-C(55)	2.3(13)
C(31)-P(3)-Ir(2)	100.5(3)		
C(33)-P(3)-Ir(2)	124.4(3)	C(52)-C(53)-C(59)-N(3)	-3.5(12)
C(37)-P(3)-Ir(2)	114.9(3)	N(1)-C(53)-C(59)-C(60)	1.1(13)

Chapter 11

Reaction of (PCP)Ir with Other Polycyclic Aromatic Substrates

Abstract

Cyclometalation reactions involving (PCP)Ir have yielded many interesting results as shown in chapters 3 – 10 of this thesis. While several general classes of reactivity have been explored, assorted substrates have been utilized which have not yielded the expected products, or have unique reactivity that sets them apart from the well defined data sets already reported in previous chapters. Some of these were analyzed in order to test the limits of cyclometalation reactions, i.e., to look beyond the favorable five-member metallacycle product to see if four- or six-member rings could be generated. In some cases, even larger metallacycles were anticipated, but syntheses were not successful.

Results are presented in this chapter for a series of polycyclic aromatic substrates that do not fit neatly into the previous chapters of this thesis. Azulene has yielded particularly interesting results, exhibiting one preferential position for C-H activation. Several other substrates were chosen for their unique conformations, but yielded mixtures of C-H activation products.

11.1 Introduction

As mentioned previously, the theme of this thesis concerns the quest for a thorough understanding of the factors affecting selectivity in C-H activation reactions. Quite unexpectedly, several polycyclic aromatic substrates have given fascinating insight regarding the effects of steric and electronic conditions on C-H activation by the (PCP)Ir fragment. A mechanism involving cyclometalation has figured prominently with aromatic substrates whenever there is the possibility of forming a stable, five-member metallacycle. It has been observed that (PCP)Ir will activate multiple C-H bonds in order to generate the thermodynamically preferred metallacycle product – even when steric and electronic conditions are less than optimal.

In order to test the limits of the geometrical comformation of the metallacycle products, several polycyclic aromatic substrates were tested. The goal was to encourage the formation of four or six-member rings via C-H activation by (PCP)Ir. These attempts were unsuccessful; the mechanism of cyclometalation through either single or double C-H activation is *strongly* inhibited when the product cannot be a five-member ring.

For example, the reaction of (PCP)Ir with azulene did not yield a four-member cyclometalated product. Instead, C-H activation took place preferentially at the 2 position on the smaller, cyclopentadienyl ring. Reaction with indene also failed to produce a four-member ring, and instead gave a variety of labile C-H addition products. Reactions with fluorene and fluoranthene were analyzed in order to see if geometrically strained five-member rings could be formed, but these too, yielded labile C-H addition products. No evidence of cyclometalation was found.

Finally, sterically congested substrates such as 1,3,5-triphenylbenzene and hexaphenylbenzene were also tested under the standard reaction conditions. It was observed that these substrates yield thermodynamically unfavorable C-H addition products – comparable to results seen with unsubstituted benzene - when the reaction stoichiometry was 1:1 ((PCP)Ir:substrate). It is possible that pinwheel-type complexes containing multiple (PCP)Ir units may be accessible for these substrates, but to date, these reactions have not been attempted.

11.2.1 Synthesis and characterization of products from the reaction of (PCP)Ir with azulene

Azulene is an interesting analog of naphthalene: it is aromatic, but instead of having two fused six-member rings, there are seven- and five-member rings. Since no cyclometalation was observed during the reaction of (PCP)Ir with naphthalene, it was not surprising that the reaction with azulene failed to yield (four-member ring) products of double C-H activation. What *was* surprising, however, was that unlike naphthalene, azulene yielded a single C-H activation product (eq. 1).



Product **10-1** was formed exclusively, despite the presence of three viable locations on the larger, seven-member ring for potential C-H activation by (PCP)Ir. While rigorous studies of the kinetics of reductive elimination have not yet been conducted, the C-H activation product **10-1** seems to be exchanging much less rapidly than the corresponding products from benzene and naphthalene, implying an electronic effect at the 2-position of azulene's five-member ring. Addition of CO to trap the product as **10-2** was successful, as was subsequent crystallization. The x-ray crystal structure and selected data are included at the end of this chapter.

11.2.2 Synthesis and characterization of products from the reaction of (PCP)Ir with other polycyclic aromatic substrates

What follows is a very brief survey of reactions with substrates that yielded typical products of C-H activation, but no special additional reactivity. There are precedents for interesting applications of these substrates in the literature, but rigorous treatment of the data gathered with (PCP)Ir, is beyond the scope of the results presented in this thesis. Some of these reactions may prove interesting for future studies under different reaction conditions.

11.2.2.1 Indene

The reaction of (PCP)Ir with indene produced several labile products of C-H activation (**10-3**, eq. 2). Cyclometalation to form a four-member ring apparently does not take place, even after extended heating. It may be useful in the future to generate the aromatic indenyl anion in order to see what kind of reactivity it displays in conjunction with the (PCP)Ir fragment.


11.2.2.2 Fluorene and fluoranthene

Fluorene and fluoranthene were analyzed in order to see if the (PCP)Ir fragment would generate a cyclometalated product via a double C-H activation mechanism, despite less than optimal geometric constraints. Both of these substrates have C-H bonds available for biphenyl-type cyclometalation reactions, but the geometries are slightly different in each case. Detailed geometric analysis is not included here, since neither of these substrates produced the desired cyclometalated products. The reaction of (PCP)Ir with both fluorene and fluoranthene produced several labile products of C-H activation (**10-4** and **10-5**, eq. 3, 4). Cyclometalation reactions to form strained five-member rings apparently do not take place, even after extended heating.





11.2.2.3 1,3,5-Triphenylbenzene and hexaphenylbenzene

1,3,5-Triphenylbenzene and hexaphenylbenzene were analyzed in order to see if the (PCP)Ir fragment would generate a cyclometalated product via a double C-H activation mechanism in sterically crowded environments. As was discussed in chapter 5, (PCP)Ir is reluctant to oxidatively add C-H bonds on the 'interior' side of *meta*terphenyl, instead giving exclusive activation at 'exterior' positions. The only available positions for the substrate 1,3,5-triphenylbenzene, are crowded positions similar to the 'interior' side of *meta*-terphenyl (eq. 5). Unfortunately, cyclometalation did not occur, and labile C-H activation products (**10-6**) similar to those seen for naphthalene and benzene were observed. Hexaphenylbenzene is even more crowded. This substrate has been used with other metal complexes (typically, platinum), to generate pinwheel-type trimer and hexamer complexes with 3 or 6 metals per complex, respectively. The (PCP)Ir fragment only generated labile C-H activation products (**10-7**, eq. 6), though more complicated complexes cannot be ruled out; additional experiments would be necessary to explore this possibility. Cyclometalation reactions apparently do not take place for either of these substrates, even after extended heating.







11.3 Experimental

General Methods. Unless otherwise noted, all reactions, recrystallizations and routine manipulations were performed at ambient temperature in an argon-filled glove box, or by using standard Schlenk techniques. Anhydrous hexane, pentane, octane, and benzene were purchased from Aldrich and were deoxygenated by purging with argon gas. Mesitylene- d_{12} , *p*-xylene, and *p*-xylene- d_{10} were dried with sodium/potassium alloy and vacuum transferred under argon. Norbornene (NBE) was purified by sublimation. Reagents used as substrates for reations with (PCP)Ir were purchased from commercial suppliers and either dried over Na/K alloy and vacuum transferred or subjected to three freeze-pump-thaw cycles prior to use. Stock solutions of all reagents were made with *p*xylene and stored in the freezer in the glove box, except where noted. (PCP)IrH_n (PCP = κ^3 -2,6-(^tBu₂PCH₂)₂C₆H₃, n = 2 or 4) was prepared as described in the literature.

All NMR spectra were obtained on 400 MHz or 500 MHz Varian instruments. The residual peak of the protiated (¹H) or deuterated solvent was used as a reference for ¹H NMR chemical shifts. ³¹P NMR chemical shifts were referenced to an 85% H₃PO₄ external standard and/or P(CH₃)₃ in mesitylene. Kinetic experiments and equilibrium measurements were carried out in J-Young NMR tubes in deuterated solvents and were monitored by ¹H and ³¹P NMR spectroscopy.

Reaction of (PCP)IrH₂/H₄ with norbornene to yield the 14-electron fragment

(PCP)Ir: Since the (PCP)Ir catalyst is synthesized as a mixture of hydride complexes (dihydride and tetrahydride), a minimum of two equivalents of norbornene are required in

solution for the purpose of fully dehydrogenating the starting complex to yield the reactive 14-electron fragment (PCP)Ir. Since one product of this reaction is norbornane, all reaction mixtures contain small concentrations of norbornane (generated *in situ*) and unreacted norbornene. A full discussion of the NBE complex, including NMR characterization, is included in the Experimental section of Chapter 2 (section 2.3).

General remarks concerning these attempts to synthesize cyclometalated products: Substrates in this chapter were studied in the context of exploring cyclometalation reactions involving single or double C-H activation processes. Since the labile products all resulted from single C-H activation, many of the NMR data are broad and/or overlapping. In addition, most of these substrates have many hydrogens, resulting in very complicated spectra. Therefore, the data reported here include the ³¹P NMR signals only, except where specific ¹H NMR signals are uniquely relevant.

Reaction of (PCP)Ir with azulene (11-1): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Azulene (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the solution remained deep blue from the azulene substrate. After heating at 75 °C for 24 hr, there was no change in the appearance of the solution. ³¹P NMR (121.4 MHz, -20 °C, mesitylene- d_{12}): δ 71.1 (d, $J_{PH} = 11.5$ Hz). ¹H NMR (400 MHz, -20 °C, mesitylene- d_{12}): δ 8.05 – 7.05 (multiple peaks corresponding to substrate *H*), 3.33 (d of vt, $J_{HH} = 16.8$ Hz,

 $J_{\text{HP}} = 4.0 \text{ Hz}, 4\text{H}, CH_2$, 0.93 (t, $J_{\text{HH}} = 6.2 \text{ Hz}, 18\text{H}, C(CH_3)_3$), 0.92 (t, $J_{\text{HH}} = 6.2 \text{ Hz}, 18\text{H}, C(CH_3)_3$), -44.65 (t, $J_{\text{HP}} = 13.1 \text{ Hz}, 1\text{H}, \text{Ir-}H$).

Reaction of 11-1 with CO to form 11-2: A solution of **11-1** in a J-Young NMR tube was frozen in liquid nitrogen and evacuated. CO (0.5 atm) was added, and the tube was allowed to slowly warm to room temperature. The color of the deep blue solution became slightly greenish. The solvent was evacuated and the resulting solid was redissolved in and recrystallized from pentane and benzene; pale blue-green prisms were obtained. ³¹P NMR (121.4 MHz, 25 °C, mesitylene- d_{12}): δ 56.3 (s). ¹H NMR (400 MHz, 25 °C, mesitylene- d_{12}): δ 8.16 – 7.07 (multiple peaks corresponding to substrate *H*), 3.26 (d of vt, $J_{\text{HH}} = 16.3$ Hz, $J_{\text{HP}} = 3.9$ Hz, 4H, CH_2), 1.10 (t, $J_{\text{HH}} = 6.5$ Hz, 18H, $C(CH_3)_3$), 1.02 (t, $J_{\text{HH}} = 6.5$ Hz, 18H, $C(CH_3)_3$), -8.88 (t, $J_{\text{HP}} = 17.0$ Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with indene (11-3): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Indene (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark brown. After heating at 75 °C for 24 hr, there was no change in the appearance of the solution. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): Three products: δ 71.6 (br d, 20%), 69.2 (br d, 80%). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): δ -44.24 (t, J_{HP} = 13.5 Hz, 1H, Ir-H, 80%), -45.60 (t, J_{HP} = 12.5 Hz, 1H, Ir-H, 20%).

Reaction of (PCP)Ir with fluorene (11-4): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Fluorene (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark brown. After heating at 75 °C for 24 hr, there was no change in the appearance of the solution. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): δ 67.2 (s). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): three overlapping triplets δ -45.36 (t, J_{HP} = 14.5 Hz, 1H, Ir-H), -45.42 (t, J_{HP} = 13.8 Hz, 1H, Ir-H), -45.47 (t, J_{HP} = 13.2 Hz, 1H, Ir-H).

Reaction of (PCP)Ir with fluoranthene (11-5): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Fluoranthene (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark brown. After heating at 75 °C for 24 hr, there was no change in the appearance of the solution. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): six products δ 72.3 (d, $J_{PH} = 12.6$ Hz), 67.5 (br d), 67.3 (br d), 66.9 (br d), 65.8 (br d), 64.2 (d, $J_{PH} = 12.5$ Hz). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): six products, δ -41.74 (t, $J_{HP} = 15.7$ Hz, 1H, Ir-H), -42.87 (t, $J_{HP} = 13.6$ Hz, 1H, Ir-H), -43.01 (t, $J_{HP} = 15.7$ Hz, 1H, Ir-H), -45.27 (t, $J_{HP} = 13.8$ Hz, 1H, Ir-H), -45.35 (t, $J_{HP} = 13.8$ Hz, 1H, Ir-H), -45.41 (t, $J_{HP} = 13.8$ Hz, 1H, Ir-H).

Reaction of (PCP)Ir with 1,3,5-triphenylbenzene (11-6): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. 1,3,5-Triphenylbenzene (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, the dark red-orange solution turned dark brown. After heating at 75 °C for 24 hr, there was no change in the appearance of the solution. ³¹P NMR (121.4 MHz, -40 °C, mesitylene- d_{12}): two products δ 67.3 (s, 55%), 67.0 (s, 45%). ¹H NMR (400 MHz, -40 °C, mesitylene- d_{12}): two products, δ -45.40 (t, J_{HP} = 13.3 Hz, 1H, Ir-*H*), -45.53 (t, J_{HP} = 14.8 Hz, 1H, Ir-*H*).

Reaction of (PCP)Ir with Hexaphenylbenzene (11-7): 5.9 mg of PCPIrH₂ (0.010 mmol) was dissolved in 0.5 mL of mesitylene- d_{12} in a J-Young NMR tube at room temperature, and 2 equivalents of norbornene were added from a stock solution in *p*-xylene. Hexaphenylbenzene (1.1 eq; 0.011 mmol) was added to the resulting solution; after stirring for one minute, there was no color change. Hexaphenylbenzene has extremely limited solubility in mesitylene, and it is uncertain whether any substrate dissolved sufficiently for reaction with (PCP)Ir. Neither ³¹P NMR nor ¹H NMR spectra gave any evidence of C-H activation, even after heating at 75 °C for several days.

11.4 Conclusion

While the (PCP)Ir fragment facilitates cyclometalation reactions with a wide variety of aromatic substrates, there are geometric and steric limits to its utility for these transformations. Reactions presented in previous chapters showed that significant electronic and steric barriers could be overcome in order to generate a thermodynamically stable metallacycle. Perhaps the most obvious example was the generation of the double C-H activation product from reaction between (PCP)Ir and 2,2'-difluorobiphenyl, in which the fluoro substituents caused significant distortion from ideal geometry.

Despite this remarkable result (and others), (PCP)Ir was unable to cyclometalate several substrates presented in this chapter. Four-member metallacycles (azulene and indene) are apparently less favorable, in keeping with the absence of such products in previous reactions with naphthalene. In addition, five-member rings cannot be generated if the geometry of the substrate constrains the iridium metal center to an unfavorable conformation (fluorene and fluoranthene).

Finally, severe steric crowding prevents cyclometallation in substrates such as 1,3,5-triphenylbenzene. In these cases – and all of the above – labile complexes from single C-H bond activation are the only products. Azulene is a special exception, in which an apparent electronic effect contributes to a single, isolable addition product.





 Table 11.1.
 Crystal data and structure refinement for 11-2.

Empirical formula	C35 H51 Ir O P2	C35 H51 Ir O P2	
Formula weight	741.90	741.90	
Temperature	100(2) K		
Wavelength	0.71073 Å		
Crystal system	Monoclinic		
Space group	P2(1)/n		
Unit cell dimensions	a = 8.8722(5) Å	a= 90°.	
	b = 48.276(3) Å	b=101.723(1)°.	
	c = 15.8021(9) Å	g = 90°.	
Volume	6627.0(7) Å ³		
Z	8		
Density (calculated)	1.487 Mg/m ³	1.487 Mg/m ³	
Absorption coefficient	4.151 mm ⁻¹	4.151 mm ⁻¹	
F(000)	3008	3008	
Crystal size	0.31 x 0.14 x 0.03 mr	0.31 x 0.14 x 0.03 mm ³	
Theta range for data collection	1.38 to 27.48°.	1.38 to 27.48°.	
Index ranges	-11<=h<=11, -62<=k	-11<=h<=11, -62<=k<=62, -20<=l<=20	
Reflections collected	55334	55334	
Independent reflections	15061 [R(int) = 0.066	15061 [R(int) = 0.0667]	
Completeness to theta = 27.48°	98.9 %	98.9 %	
Absorption correction	Semi-empirical from	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.5074	0.7458 and 0.5074	
Refinement method	Full-matrix least-squa	Full-matrix least-squares on F ²	
Data / restraints / parameters	15061 / 1183 / 746	15061 / 1183 / 746	
Goodness-of-fit on F ²	1.008	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0	R1 = 0.0626, $wR2 = 0.1446$	
R indices (all data)	R1 = 0.0781, $wR2 = 0.1526$		
Largest diff. peak and hole	2.177 and -2.438 e.Å ⁻³		

Ir(1)-C(35)	1.929(7)	P(1)-C(13)	1.885(9)
Ir(1)-C(25)	2.111(7)	P(1)-C(9)	1.890(9)
Ir(1)-C(1)	2.115(7)	P(2)-C(8)	1.832(8)
Ir(1)-P(2)	2.3301(19)	P(2)-C(21)	1.882(8)
Ir(1)-P(1)	2.3338(19)	P(2)-C(17)	1.888(8)
Ir(1)-H(1)	1.596(10)	O(1)-C(35)	1.140(9)
P(1)-C(7)	1.844(8)		
C(35)-Ir(1)-C(25)	93.2(3)	C(7)-P(1)-C(9)	104.0(4)
C(35)-Ir(1)-C(1)	88.2(3)	C(13)-P(1)-C(9)	110.3(4)
C(25)-Ir(1)-C(1)	178.5(3)	C(7)-P(1)-Ir(1)	103.0(3)
C(35)-Ir(1)-P(2)	97.4(2)	C(13)-P(1)-Ir(1)	121.5(3)
C(25)-Ir(1)-P(2)	98.8(2)	C(9)-P(1)-Ir(1)	113.2(3)
C(1)-Ir(1)-P(2)	80.4(2)	C(8)-P(2)-C(21)	105.1(4)
C(35)-Ir(1)-P(1)	101.5(2)	C(8)-P(2)-C(17)	103.0(4)
C(25)-Ir(1)-P(1)	98.0(2)	C(21)-P(2)-C(17)	110.5(4)
C(1)-Ir(1)-P(1)	82.4(2)	C(8)-P(2)-Ir(1)	101.6(3)
P(2)-Ir(1)- $P(1)$	153.86(7)	C(21)-P(2)-Ir(1)	119.4(3)
C(35)-Ir(1)-H(1)	176(3)	C(17)-P(2)-Ir(1)	114.9(3)
C(25)-Ir(1)-H(1)	89(3)	C(34)-C(25)-C(26)	104.4(6)
C(1)-Ir(1)-H(1)	90(3)		
P(2)-Ir(1)-H(1)	85(3)		
P(1)-Ir(1)-H(1)	75(3)		
C(7)-P(1)-C(13)	102.2(4)		

 Table 11.2.
 Selected bond lengths [Å] and angles [°] for 11-2.

List of additional substrates

The information presented in this thesis has been compiled from experimental reactions between (PCP)Ir and a long list of aromatic substrates. For reasons including clarity and concision, the results of experiments with several *additional* substrates have not been discussed. Since these results may have value in the context of future studies by our research group, the additional substrates are listed below, and the respective results will be included in a separate, unpublished document.

Additional substrates

1,3-bis(trimethylsilyl)benzene 4,4"-dimethyl-1,1':3',1"-terphenyl hexafluorobenzene hexachlorobenzene iodobenzene 3-chloro-fluorobenzene 1,10-phenanthroline 2-fluoro-1,3-dimethylbenzene 2-chloro-1,3-dimethylbenzene 2-bromo-1,3-dimethylbenzene 2-methoxy-1,3-dimethylbenzene 1,3-dimethyl-2-nitrobenzene 2,6-dimethylaniline 1,2,3-trimethylbenzene 5-bromo-1,3-dimethylbenzene 1-methoxy-2,4-dimethylnaphthalene

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PUBLICATIONS

Laviska, David A.; Kanzelberger, Mira; Wang, David Y.; Krogh-Jespersen, Karsten; Goldman, Alan S. Aryl C-H bond activation by a pincer-ligated iridium complex: Steric and electronic effects from *ortho*, *meta*, and *para* substituents. *Manuscript in preparation*.

Laviska, David A.; Goldman, Alan S. C-H bond activation in a series of polycyclic aromatic substrates. *Manuscript in preparation*.

Laviska, David A.; Field, Kathleen D.; Sparks, Sarah M.; Goldman, Alan S. Introducing the LEEDAR Program: The pedagogical value of experimental design in the high school classroom. *Manuscript in preparation*.

Laviska, David A.; Goldman, Alan S. C-C bond activation of biphenylene. *Manuscript in preparation*.