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Investigations of Iridium-Mediated Reversible C−H Bond Cleavage: Characterization of a 16-Electron Iridium(III) Methyl Hydride Complex

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Abstract: New iridium complexes of a tridentate pincer ligand, 2,6-bis(di-*tert*-butylphosphinito)pyridine (PONOP), have been prepared and used in the study of hydrocarbon C−H bond activation. Intermolecular oxidative addition of a benzene C−H bond was directly observed with [(PONOP)Ir^{I}(cyclooctene)][PF_6] at ambient temperature, resulting in a cationic five-coordinate iridium(III) phenyl hydride product. Protonation of the (PONOP)Ir^{I} methyl complex yielded the corresponding iridium(III) methyl hydride cation, a rare five-coordinate, 16-valence electron transition metal alkyl hydride species which was characterized by X-ray diffraction. Kinetic studies of C−H bond coupling and reductive elimination reactions from the five-coordinate complexes have been carried out. Exchange NMR spectroscopy measurements established a barrier of 17.8(4) kcal/mol (22 °C) for H−C_{aryl} bond coupling in the iridium(III) phenyl hydride cation and of 9.3(4) kcal/mol (−105 °C) for the analogous H−C_{alkyl} coupling in the iridium(III) methyl hydride cation. The origin of the higher barrier of H−C_{aryl} relative to H−C_{alkyl} bond coupling is proposed to be influenced by a hindered rotation about the Ir−C_{aryl} bond, a result of the sterically demanding PONOP ligand.

Introduction

Investigations of homogeneous catalytic systems for the selective oxidation of methane and higher alkanes to functionalized organic compounds have been ongoing since the initial discoveries of intermolecular C−H bond activation reactions by transition metal complexes.[1] Technologies to convert alkanes directly to functionalized organic molecules would allow the use of relatively inexpensive and abundant saturated hydrocarbons as direct chemical feedstocks.[2,3] The selective functionalization of saturated hydrocarbons, however, is a challenging transformation. The C−H bond dissociation enthalpies in alkanes are quite high, and the C−H bonds of the products of alkane oxidation are typically more reactive than those of the alkane itself, leading to undesirable overoxidation products.[2,3] Despite these difficulties, there has been remarkable progress in this field during the past several decades, and numerous promising transition metal systems for alkane functionalization have been identified and investigated.[1−3]

The two main types of homogenously catalyzed alkane oxidation reactions to emerge have been alkane dehydrogenation and oxygen atom incorporation.[2−4] The dehydrogenation of alkanes to olefins has been accomplished with variable efficiency by several different metal complexes.[5,6] Among the most widely studied systems have been Ir(I) catalysts supported by pincer ligands such as PCP and POCOP (PCP = 2,6-bis(di-*tert*-butylphosphinomethyl)benzene; POCOP = 2,6-bis(di-*tert*-butylphosphinito)benzene).[6] Dehydrogenation reactions both with and without hydrogen acceptors can be achieved with these catalysts, and thorough mechanistic studies have provided insight into the C−H activation and β-hydride elimination steps.[6,7] Experimental and computational results point to the involvement

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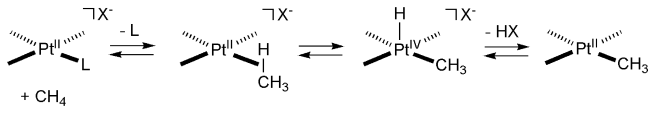

Figure 1. Mechanism for the electrophilic activation of methane by platinum(II).

of a three-coordinate iridium(I) intermediate which undergoes oxidative addition of a C−H bond to form a transient iridium(III) alkyl hydride species.[8]

The other well-known type of homogenously catalyzed alkane functionalization involves the incorporation of an oxygen atom into the oxidized products. In this realm, the platinum(II)-catalyzed oxidations of methane to methanol,[9] methyl bisulfate,[10] and acetic acid,[11] first discovered decades ago, remain among the highest yielding and most thoroughly studied reactions for methane functionalization. In the original Shilov process, $PtCl_4^{2-}$ was used as a catalyst with $PtCl_6^{2-}$ as the sacrificial oxidant to convert methane to methanol in aqueous solution.[9] The mechanism of Pt(II)-catalyzed alkane oxidations has been intensively investigated, and a variety of model systems have been used to study the key C−H bond activation step.[12] Studies of inter- and intramolecular C−H bond activation at Pt(II), C−H bond reductive elimination from Pt(IV), and protonolysis of Pt(II) alkyl complexes are all consistent with the proposal that electrophilic methane activation occurs via a sequence where (1) CH_4 coordinates to a Pt(II) center generating a σ-alkane complex, (2) oxidative addition of the C−H bond affords a five-coordinate Pt(IV) methyl hydride species, and (3) deprotonation of the hydridomethylplatium(IV) species generates a platinum(II) methyl complex (Figure 1).[12]

Notably, neither the platinum(II) σ-methane complex nor the five-coordinate Pt(IV) methyl hydride has been directly observed. Their existence has been inferred on the basis of mechanistic and computational investigations of model complexes.[3,12−15] Intermolecular oxidative addition of alkane C−H bonds to Pt(II) centers has been directly observed to form platinum(IV) alkyl hydride products but only when chelating ligands are present to trap the intermediate as a six-coordinate, 18-valence electron species.[16] Additionally, mechanistic investigations of C−H bond reductive eliminations from the majority of octahedral platinum(IV) complexes suggest ancillary ligand dissociation prior to C−H bond coupling from a five-coordinate platinum(IV) intermediate.[15]

Significantly, five-coordinate d^6 transition metal alkyl hydride species are proposed as the immediate product of C−H bond activation in both Pt(II)- and Ir(I)-catalyzed alkane functionalization, despite the difference in the final oxidized products.[7,8,12] Recently isolable, five-coordinate iridium(III) aryl hydride species have been reported, and mechanistic studies of reductive elimination from these complexes have provided insight into the mechanism of arene C−H bond activation by Ir(I) centers.[17] However, no isolable five-coordinate alkyl hydride complexes of either iridium(III) or platinum(IV) have yet been reported. Such species would serve as direct models for the highly reactive alkyl hydride intermediates in both Ir(I)-catalyzed alkane dehydrogenation reactions and Pt(II)-catalyzed alkane oxidations.[18]

Herein we report the synthesis and use of a new pincer ligand, 2,6-bis(di-*tert*-butylphosphinito)pyridine (PONOP), to stabilize reactive iridium complexes relevant to hydrocarbon C−H bond activation. Protonation of $(PONOP)Ir^{I}$ phenyl and methyl complexes yields, respectively, isolable cationic five-coordinate iridium(III) phenyl hydride and methyl hydride complexes. The $(PONOP)Ir^{III}$ methyl hydride cation was crystallographically characterized. The dynamic behavior of these rare five-coordinate, 16-electron iridium(III) aryl and alkyl hydride complexes was studied by ^{1}H NMR spectroscopy. Rapid, reversible C−H bond reductive coupling and oxidative cleavage prior to release of the hydrocarbon were established in each case. These results implicate an iridium(I) σ-methane adduct and an iridium(I) arene complex as intermediates in the dynamic processes. The barriers to $H-C_{alkyl}$ and $H-C_{aryl}$ bond coupling

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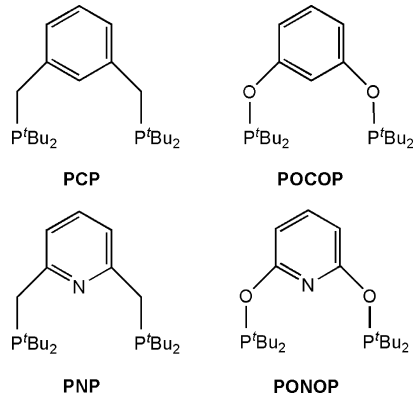


Figure 2. PCP, POCOP, PNP, and PONOP pincer ligands.

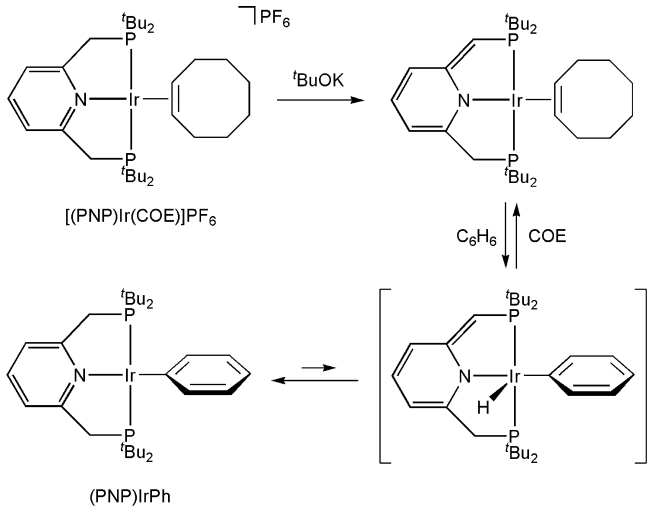


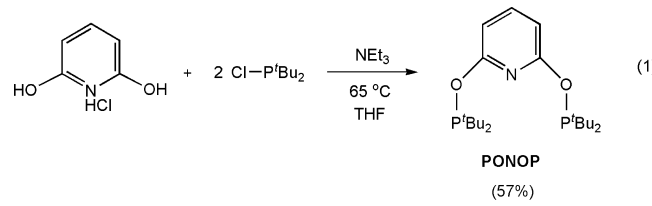
Figure 3. Ligand deprotonation and benzene C−H activation by [(PNP)Ir(COE)]PF_6.

were measured and rationalized with respect to geometric constraints within the molecules.

Results and Discussion

Synthesis of PONOP Iridium Aryl and Alkyl Complexes. Recently, Milstein and co-workers have reported a family of iridium complexes supported by the neutral pincer ligand 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine (PNP) (Figure 2).[19] These species have demonstrated a range of intriguing reactivities including selective ketone and haloarene C−H bond cleavage,[20] methanol decarbonylation,[21] and intermolecular benzene activation.[20b] Thorough mechanistic investigations indicated that the methylene groups on the PNP ligand play an important role in the reactivity of the metal complex.[22] These CH_2 groups are susceptible to deprotonation by external base or the transition metal itself resulting in dearomatization of the ligand (Figure 3).[17d,20b]

Several years ago, we reported that POCOP ligands increased the productivity of iridium catalysts for some alkane transfer dehydrogenations over their PCP counterparts (Figure 2).[6i] A similar alteration of the PNP ligand would yield a new pincer ligand, 2,6-bis(di-*tert*-butylphosphinito)pyridine (PONOP). In addition to factors that could change the thermodynamics and kinetics of C−H activation reactions, the PONOP ligand offers the advantage of exchanging the reactive $-CH_2-$ sites on PNP for an $-O-$ linking unit which avoids the possibility of ligand deprotonation. The neutral, tridentate PONOP ligand was prepared in a straightforward manner by the treatment of 2,6-dihydroxypyridine hydrochloride with di-*tert*-butylchlorophosphine in the presence of excess triethylamine at 65 °C in THF (eq 1). The PONOP ligand was characterized by multinuclear NMR spectroscopy and elemental analysis.[23]



Coordination of PONOP to iridium was accomplished by treatment of the ligand with either $[Ir(C_2H_4)_2Cl]_2$[24] or $[Ir(COE)_2(acetone)_2]PF_6$[25] (COE = cyclooctene), affording good yields of (PONOP)IrCl (**1-Cl**) and [(PONOP)Ir(COE)]PF_6 (**1-COE**$^+$), respectively (Figure 4). Complex **1-Cl** was isolated as an orange powder and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and combustion analysis. The ^1H NMR spectrum of **1-Cl** in methylene chloride-d_2 solution exhibits the number of resonances consistent with a C_{2v} symmetric molecule. The $^{31}P\{^1H\}$ NMR spectrum of **1-Cl** displays a singlet at 175.7 ppm. Cationic **1-COE**$^+$ was obtained as a bright red solid and also identified by multinuclear NMR spectroscopy. An acetone-d_6 solution of **1-COE**$^+$ exhibits a multiplet at 4.66 ppm in the ^1H NMR spectrum assigned to the olefinic protons of the cyclooctene bound to iridium. The $^{31}P\{^1H\}$ NMR spectrum of the PF_6^- salt of **1-COE**$^+$ displays a singlet at 183.1 ppm and a septet at −142.7 ppm.

Complex **1-Cl** was readily converted to the corresponding methyl and phenyl derivatives. Addition of an ethereal methyl lithium solution to a toluene slurry of **1-Cl** and subsequent heating afforded (PONOP)IrCH_3 (**1-Me**), which was isolated as a dark red solid (eq 2).[23] The iridium(I) methyl complex was characterized by NMR spectroscopy and elemental analysis. The presence of an Ir-CH_3 moiety was confirmed by observation of a 3H triplet at 2.11 ppm ($^3J_{P-H}$ = 5.0 Hz) in the ^1H NMR spectrum. Additionally, the $^{31}P\{^1H\}$ NMR spectrum of **1-Me** displays a singlet at 186.4 ppm, shifted downfield relative to that for **1-Cl**. In a similar manner, the phenyl-substituted iridium(I) complex, (PONOP)Ir(C_6H_5) (**1-Ph**), was prepared by treatment of **1-Cl** with a phenyl lithium solution.[23] Complex **1-Ph** was obtained as a red solid in modest yield and identified by NMR spectroscopy and single-crystal X-ray diffraction.[23] The solid state structure of **1-Ph** is depicted in Figure 5, with relevant metrical parameters listed in Table 1. The X-ray diffraction data indicate a generalized square planar geometry about the metal center, with the plane of the phenyl substituent nearly orthogonal to that of the pyridine backbone. The

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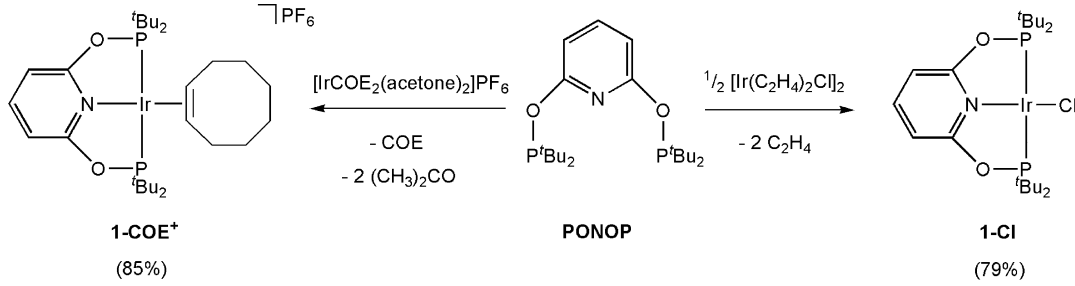


Figure 4. Preparation of **1-COE** and **1-Cl**.

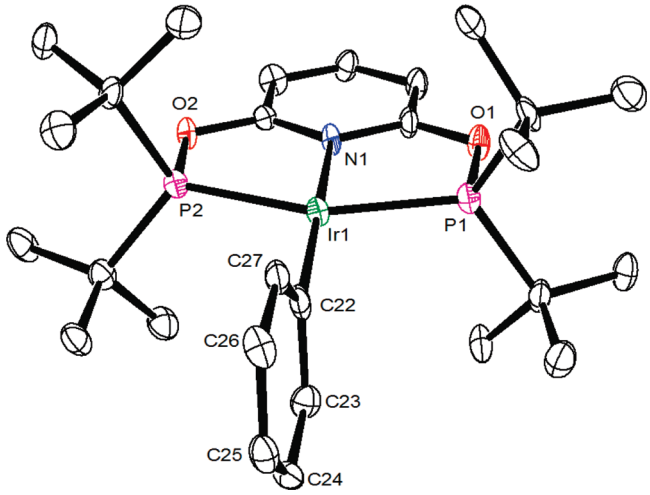
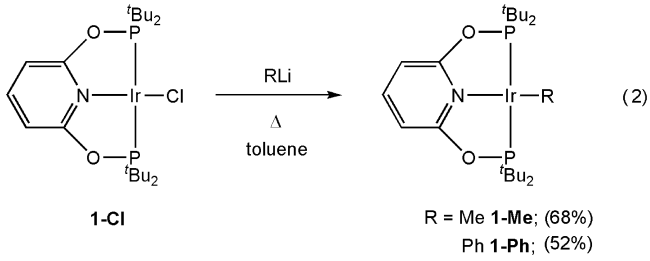


Figure 5. Molecular structure of **1-Ph** at 30% probability ellipsoids. All hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (°) for **1-Ph**

Ir(1)−P(1)	2.248(3)	P(1)−Ir(1)−P(2)	160.08(10)
Ir(1)−P(2)	2.218 (3)	N(1)−Ir(1)−C(22)	175.1 (4)
Ir(1)−N(1)	2.035 (8)	P(1)−Ir(1)−C(22)	100.6 (3)
Ir(1)−C(22)	2.051 (11)	P(2)−Ir(1)−C(22)	98.7 (3)

Ir(1)−C(22) bond length of 2.051(11) Å is comparable to a previously reported analogue using the PNP pincer ligand.[17b]



(2)

Ir−Aryl and Ir−Alkyl H/D Exchange with Protic Reagents. With methyl- and phenyl-substituted PONOP iridium(I) complexes in hand, an investigation into the stability and reactivity of these species was undertaken. Both **1-Me** and **1-Ph** were found to be thermally stable in benzene-d_6 solutions at 125 °C over 2 days. No H/D exchange with solvent or significant decomposition was observed by NMR spectroscopy. Likewise, these species were unchanged by treatment with large excesses (>50 equiv) of protic reagents such as methanol or water. However, upon addition of deuterated methanol (CD_3OD) or water (D_2O), significant ^2H incorporation was detected in the methyl and phenyl substituents of **1-Me** and **1-Ph**, respectively (Figure 6).[26] In the case of **1-Me**, deuterium incorporation into the $-CH_3$ group was conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy at ambient temperature where each isotopologue (d_0−d_3) displays a distinct chemical shift ranging from 186.36 (d_0) to 186.65 (d_3) ppm.[27] The presence of deuterium in the methyl substituent was also confirmed by ^2H NMR experiments. For **1-Ph**, conveniently measurable ^2H incorporation required warming to 40 °C and was monitored by the disappearance of the three phenyl resonances observed in the ^1H NMR spectrum. Significantly, the peaks assigned to the *ortho*, *meta*, and *para* sites diminished at nearly the same rate, suggesting that an exchange process equilibrating those sites is as or more rapid than deuterium incorporation (vide infra).

Unexpectedly, parallel experiments in which **1-Me** and **1-Ph** were treated with 50 equiv of CD_3OD at 40 °C indicated H/D exchange was faster for the methyl substituent than the phenyl substituent. The half-life for ^2H incorporation under these conditions was 4 h for **1-Me**, while exchange with **1-Ph** required slightly over 3 days to reach the same level of ^2H incorporation. Thus **1-Me** appears to undergo H/D exchange with CD_3OD ca. 12 times faster (statistically corrected) than **1-Ph** (vide infra).

A mechanistic hypothesis for the proton-assisted reversible C−H bond cleavage observed in **1-Me** and **1-Ph** is presented in Figure 7. In analogy to the pathway proposed for hydrogen−deuterium exchange in the protonation of alkyl platinium(II) species (Figure 1),[12] it is proposed that either alcohol or water protonates the iridium(I) alkyl or aryl complex to generate a five-coordinate alkyl/aryl iridium(III) deuteride cation (**A**). If the conjugate base is sufficiently coordinating under the reaction conditions, a six-coordinate iridium(III) species (**B**) could subsequently form. The relative free energies of **A** and **B** will be dictated largely by the binding enthalpy of the anionic ligand X ($X = {}^-OD$, $^-OCD_3$) under the reaction conditions.[28] Notably, while neither **A** nor **B** is observed in the H/D exchange reactions, based on significant literature precedent for C−H bond reductive elimination reactions from Pt(IV) and Ir(III) centers, reductive coupling would be expected to occur from the five-coordinate species.[12,15,16] Reversible formation of a new C−D bond would afford either a transient σ-methane complex (**C**) in the case of **1-Me** or an arene complex (**D**) for **1-Ph**.[29] Both **C** and **D** may be highly fluxional, resulting in scrambling of the C−D and C−H bond positions.[12,30,31] Oxidative addition of a C−H bond in the σ-methane or arene complex followed by regeneration

(26) Control experiments using CH_3CH_2OD indicate that ^2H incorporation is derived from the −OD source not the $-CD_3$ position in H/D change reaction with CD_3OD.
(27) See Supporting Information.
(28) Blum, O.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 229.
(29) The arene intermediate **D** may be coordinated to the iridium center either through a C−H σ-bond or a C−C σ-bond (see ref 41).
(30) Yung, C. M.; Skaddan, M. B.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *126*, 13033.

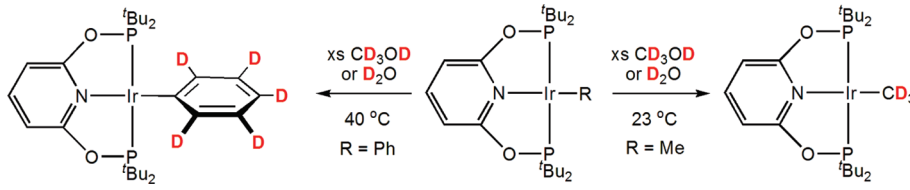


Figure 6. H/D exchange of **1-Me** and **1-Ph** with protic reagents.

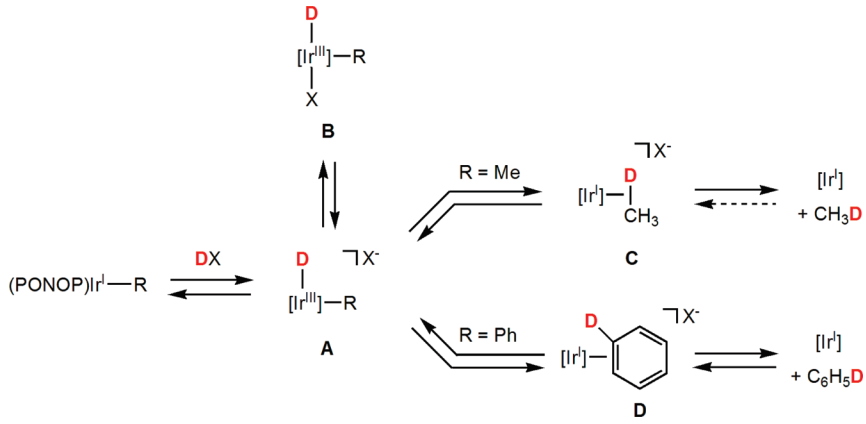
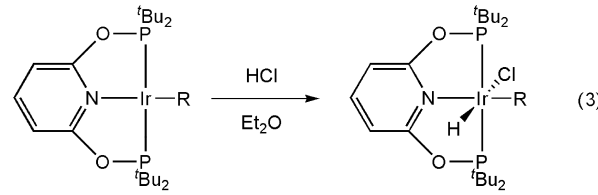


Figure 7. Proposed mechanism for proton-assisted reversible C−D/H bond activation from **1-Me** and **1-Ph**.

of the iridium(I) alkyl or aryl species would complete the observed deuterium incorporation reaction.

Mechanism of H/D Exchange from 1-Me and 1-Ph. Mechanistic investigations of the H/D exchange observed for **1-Me** and **1-Ph** in the presence of deuterated water or methanol began by attempting to isolate intermediates in the proposed mechanism for proton-assisted reversible C−H bond cleavage (Figure 7). The protonolysis of (PONOP)IrR (R = Me, Ph) was probed by addition of a strong acid containing a coordinating anion. Treatment of **1-Me** and **1-Ph** with 1 equiv of HCl gas afforded the six-coordinate iridium(III) complexes (PONOP)IrH(CH_3)Cl (**1-MeHCl**) and (PONOP)IrH(C_6H_5)Cl (**1-PhHCl**), respectively (eq 3).[23] Treatment of **1-MeHCl** or **1-PhHCl** with additional HCl yielded the dichloroiridium(III) hydride species, (PONOP)Ir(H)Cl_2 (**1-HCl$_2$**).[23] These compounds were characterized by multinuclear NMR spectroscopy and elemental analysis, and the stereochemistry about the metal center was established by 2D NOESY NMR experiments. The ^{1}H NMR spectra of **1-MeHCl** and **1-PhHCl** exhibit the number of signals expected for C_s symmetric molecules. Additionally, the proton NMR spectrum of **1-MeHCl** displays triplet signals at 1.55 ($^3J_{P-H}$ = 5.0 Hz) and −19.34 ppm ($^2J_{P-H}$ = 16.5 Hz) assigned to the Ir-CH_3 and Ir−H fragments, respectively. The corresponding spectrum of **1-PhHCl** also shows an upfield shifted Ir−H resonance at −19.62 ppm ($^2J_{P-H}$ = 16.8 Hz). The 2D NOESY spectra of both **1-MeHCl** and **1-PhHCl** exhibit strong NOE correlations between the iridium−alkyl/aryl signals and both P−^{t}Bu resonances, indicating the alkyl/aryl group is symmetrically disposed with respect to the phosphine substituents and likely positioned *trans* to the N_{py} of the PONOP ligand. The iridum−hydride signals in both spectra show NOE correlations to the iridium−alkyl/aryl signals but only one P−^{t}Bu resonance, suggesting a *trans* orientation between the Ir−H and Ir−Cl moieties in **1-MeHCl** and **1-PhHCl**.



R = Me **1-MeHCl**; (69%)
Ph **1-PhHCl**; (50%)

Isolation of the alkyl and aryl hydridochloride iridium(III) species offers strong evidence for the viability of the proposed species **B** described in Figure 7. Since the relative ground state stabilization of **B** compared to the five-coordinate alkyl/aryl iridium (III) cation, **A**, is largely dependent on the binding ability of the anion, isolation of a model complex of intermediate **A** was attempted by replacing the strongly bound chloride anion in **1-MeHCl** with a weakly coordinating anion. Addition of silver hexafluoroantimonate to a methylene chloride solution of **1-MeHCl** resulted in immediate precipitation of AgCl salt. Quick filtration and cooling of the solution to −35 °C overnight afforded the cationic iridium(III) methyl hydride complex, [(PONOP)Ir(H)Me](SbF_6) (**1-(H)Me$^+$**), as a yellow powder. Conversely, the borate salt of **1-(H)Me$^+$** may be prepared by addition of H[B(Ar^F)$_4$]•(Et_2O)$_2$ directly to a solution of **1-Me** (Figure 8).[23]

Characterization of (PONOP)Ir(H)Me Cation. Both salts of **1-(H)Me$^+$** display limited thermal stability in solution, undergoing methane elimination at ambient temperature with an approximate half-life of 3 h. Monitoring the degradation of the borate salt of **1-(H)Me$^+$** by ^{31}P NMR spectroscopy afforded a rate constant for methane loss of 3.8(7) × 10^{-4} s^{-1} at 29 °C,[27]

(31) (a) Chin, R. M.; Dong, L.; Duckett, S. B.; Partidge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685. (b) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846. (c) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724. (d) Norris, C. M.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **2002**, *21*, 5649. (e) Wik, B. J.; Lersch, M.; Krivokapic, A.; Tilset, M. *J. Am. Chem. Soc.* **2006**, *128*, 2682.

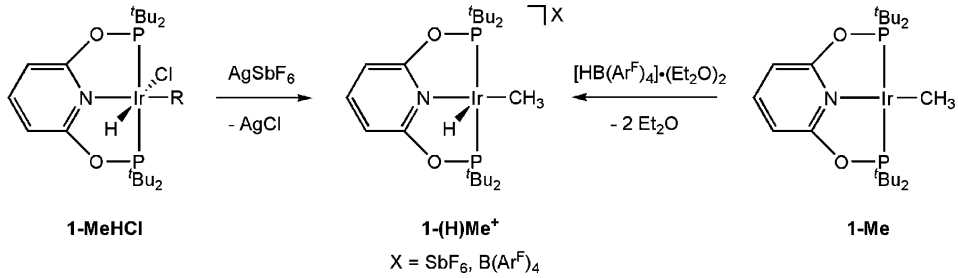


Figure 8. Routes for the preparation of **1-(H)Me**$^+$.

corresponding to a barrier for methane elimination from **1-(H)Me**$^+$ of $\Delta G^{\ddagger} = 22.4(2)$ kcal/mol. The surprising stability of **1-(H)Me**$^+$ permitted characterization via multinuclear, low-temperature NMR spectroscopy as well as low-temperature X-ray diffraction experiments. At −132 °C in $CDCl_2F$ solution, the ^{1}H NMR spectrum of **1-(H)Me**$^+$ displays a triplet resonance at −41.82 ppm ($^2J_{P-H} = 13.0$ Hz) assigned to the Ir−H[32] and a broad signal at 1.92 ppm assigned to the Ir-CH_3 moiety. Warming the sample to −86 °C results in substantial broadening of both the Ir−H and Ir−CH_3 resonances along with a small change in the chemical shifts to −41.79 and 1.82 ppm, respectively. At this temperature, a qualitative 2D NOESY NMR spectrum with a mixing time of 500 ms indicated rapid exchange between the protons of the iridium−methyl and the iridium−hydride groups. The rate of site exchange between the iridium−hydride and iridium−methyl positions was examined by a series of quantitative EXSY NMR spectroscopy experiments.[23] At −105 °C in $CDCl_2F$ solvent, a rate constant of 4.2(8) s^{-1} was observed for the Ir−H/Ir−CH_3 exchange. This corresponds to a barrier of 9.3(4) kcal/mol for the interchange of the iridium−hydride and iridium−methyl protons. This barrier was supported by line shape analysis of ^{1}H NMR spectra of **1-(H)Me**$^+$ at low temperature, which afforded rate constants comparable to those determined by EXSY NMR spectroscopy.[33,34]

The observed site exchange between Ir−H and Ir−CH_3 protons points to a fast, reversible formation of a σ-methane complex analogous to the proposed intermediate **C** (Figure 7). Transient formation of a methane adduct provides a mechanism that equilibrates all four hydrogens, similar to the mechanism proposed for isotopic scrambling in a related 18-valence electron osmium(IV) methyl hydride complex.[35] Observation of **1-(H)Me**$^+$ by ^{1}H NMR spectroscopy at 36 °C revealed sharp resonances for the PONOP ligand and the number of peaks expected for a C_{2v} symmetric molecule. In addition, a broad peak observed at −8.95 ppm was assigned as a time-averaged signal from the rapidly exchanging Ir−H and Ir−CH_3 groups. This chemical shift is near the expected weighted average value of −9.02 ppm for a fast site exchange between a 3H resonance at 1.92 ppm and a 1H resonance at −41.82 ppm and is dramatically upfield of the chemical shift of free methane (0.17 ppm), eliminating possible assignment as a σ-methane adduct.

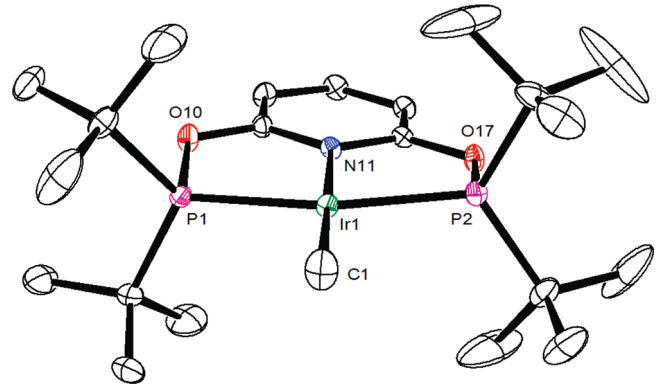


Figure 9. Molecular structure of **1-(H)Me**$^+$ at 30% probability ellipsoids. All hydrogen atoms, the $B(Ar^F)_4$ anion, and a co-crystallized solvent molecule are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (°) for **1-(H)Me**$^+$

Ir(1)−P(1)	2.2875 (9)	P(1)−Ir(1)−P(2)	160.27 (3)
Ir(1)−P(2)	2.2840 (9)	N(1)−Ir(1)−C(1)	178.73 (17)
Ir(1)−N(1)	2.084 (3)	P(1)−Ir(1)−C(1)	99.69 (13)
Ir(1)−C(1)	2.091 (4)	P(2)−Ir(1)−C(1)	100.04 (13)

Further confirmation of the identity of **1-(H)Me**$^+$ was provided by a low-temperature X-ray diffraction experiment. Crystals of the cationic iridium(III) methyl hydride complex suitable for diffraction were obtained by the slow diffusion of diethyl ether into a concentrated methylene chloride solution of the borate salt of **1-(H)Me**$^+$ at −35 °C. The solid state structure of **1-(H)Me**$^+$ is presented in Figure 9, and relevant metrical parameters are listed in Table 2. The data were not of sufficient quality to locate the metal hydride, although its presence may be inferred from the diamagnetic metal oxidation state and is supported by the NMR spectroscopic evidence. All other hydrogens in the molecular structure of **1-(H)Me**$^+$ were located. The coordination environment about the iridium center is nearly planar, with the inferred metal hydride completing a generalized square pyramidal geometry. The observed Ir(1)−C(1) bond length of 2.091(4) Å is comparable those reported for related pincer iridium(III)−methyl complexes.[36]

The isolation of a 16-valence electron iridium(III) methyl hydride complex and the observation of fluxional exchange of the hydride and methyl hydrogen positions provide strong support for proposed intermediate **C** in the mechanism of H/D exchange from **1-Me** (Figure 7). Isolation of **1-(H)Me**$^+$ and its reductive coupling/oxidative cleavage is also significant with respect to the mechanism of alkane activation by iridium(I) species. Oxidative addition of alkane to a three-coordinate

(32) The significant upfield chemical shift of the Ir−H resonance is consistent with literature precedent for a hydride ligand *trans* to a vacant site in a five-coordinate complex. See: Moulton, C. J.; Shaw, B. L. *Dalton Trans.* **1976**, 1020, and refs 6i and 17.

(33) The one-dimensional ^{1}H NMR spectrum of **1-(H)Me**$^+$ at −105 °C did not display sufficient line broadening to permit reliable rate measurements. However, the spectrum at −86 °C exhibited sufficient changes in line shape to determine a rate constant for exchange of 95(4) s^{-1}. Assuming a negligible $\Delta S^{\ddagger}$ for this intramolecular processes, extrapolation yields a rate constant of approximately 5.8 s^{-1} at −105 °C.

(34) For determining rate constants by NMR line shape analyses, see: Anet, F. A. L.; Borne, A. J. *J. Am. Chem. Soc.* **1967**, *89*, 760.

(35) Gross, C. L.; Girolami, G. S. *J. Am. Chem. Soc.* **1998**, *120*, 6605.

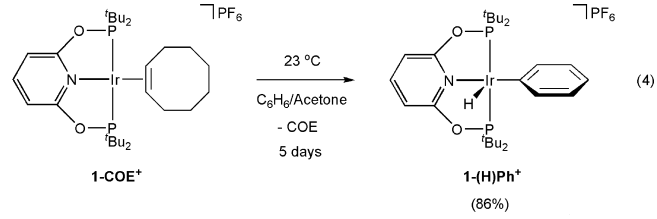
(36) Ghosh, R.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2008**, *130*, 11317.

iridium(I) species is proposed as the key C−H activation step in the PCP and POCOP iridium(I)-catalyzed alkane dehydrogenation reactions.[7,8] The resulting neutral five-coordinate iridium(III) alkyl hydride has not been observed experimentally but would be directly analogous to cationic **1-(H)Me**$^+$. The reversible reductive coupling and oxidative cleavage reactions of **1-(H)Me**$^+$ thus serve as a model for the C−H bond activation step at Ir(I) centers. Notably, the reactivity of **1-(H)Me**$^+$ also models important alkane oxidation reactions at Pt(II). The five-coordinate Pt(IV) methyl hydrides, which are proposed as intermediates in the oxidation of methane at Pt(II), have not been directly observed.[12] Instead, their involvement as intermediates has been advanced on the basis of H/D scrambling observed in the methane product released upon addition of D^+ to platinum(II) methyl species and from kinetic evidence obtained in studies of C−H reductive elimination from six-coordinate Pt(IV) methyl hydride species.[12,15,16,18] Thus, the observation of a five-coordinate, unsaturated Ir(III) methyl hydride complex and the demonstration of its reductive coupling/oxidative cleavage chemistry provide insight into two of the most studied alkane functionalization systems to date—alkane dehydrogenation by iridium and the conversion of alkanes to oxygenated substrates with platinum.[6,7,12,37]

The relative stability of **1-(H)Me**$^+$ toward methane loss is particularly unexpected as most previously reported transition metal methyl hydride species are coordinately saturated.[1a,15,35,38a] Mechanistic studies of reductive elimination from octahedral d^6 alkyl hydride complexes to form d^8 square planar products have determined that preliminary dissociation of an ancillary ligand occurs prior to C−H bond coupling in many cases.[16] It is likely not coincidental that platinum(IV) alkyl hydride complexes reported to be stable above ambient temperature all contain strongly bound and/or chelating ancillary ligands.[15o,38] For example, Templeton and co-workers have reported an 18-valence electron, six-coordinate dimethyl hydride complex, κ^3-Tp′Pt^{IV}(CH$_3$)$_2$H (Tp′ = hydridotris(3,5-dimethlpyrazolyl)borate), which requires thermolysis at 110 °C to observe facile methane elimination.[15l] For Tp′Pt^{IV}(CH$_3$)$_2$H, the high barrier to dissociation of a pyrazolyl arm to form the five-coordinate intermediate required for facile reductive coupling was proposed to enhance its thermal stability.[15l] However, the relatively slow rate of methane loss from **1-(H)Me**$^+$ does not originate from a high barrier due to ligand dissociation or C−H bond coupling, as NMR line broadening analysis and EXSY NMR experiments suggest coupling is rapid and reversible even at −105 °C (vide supra). The stability of **1-(H)Me**$^+$ may derive from the combination of a modest binding energy for the σ-methane ligand and the thermodynamic preference of the iridium(III) methyl hydride ground state over the corresponding iridium(I) methane complex. On the basis of the observed rate constant for methane loss (3.8(7) × 10^{-4} s^{-1} at 29 °C), the sum of this ground state free energy preference and the barrier for methane dissociation from the iridium(I) methane complex must be ca. 22 kcal/mol.[17a,39]

Hydrocarbon Activation by (PONOP)Ir(I) Complexes. Successful characterization of **1-(H)Me**$^+$ and **1-MeHCl** as models for intermediates **A** and **B** (Figure 7) supports the proposed mechanism for H/D exchange between CD_3OD and **1-Me**. In addition, the observed site exchange in **1-(H)Me**$^+$ is consistent with the formation of a transient σ-methane adduct. Perhaps more significant is the possibility that molecules similar to these could be expected to form along the reaction coordinate for electrophilic C−H activation of methane by Ir(I) centers. However, the initial step of such a process, intermolecular activation of a C−H bond in methane, has not been observed for any of the (PONOP)Ir^I complexes. Alternatively, the cationic iridium(I) species, **1-COE**$^+$, has proven competent for the oxidative addition of aromatic C−H bonds.

Exposure of **1-COE**$^+$ to an acetone/benzene (1:1) solvent mixture for 5 days at ambient temperature afforded the iridium(III) phenyl hydrido cation, [(PONOP)Ir(H)Ph]PF$_6$ (**1-(H)Ph**$^+$) (eq 4) in good yield.[23] A similar reaction has been reported for the analogous (PNP)Ir^I cation, which gave [(PNP)Ir(H)Ph]PF$_6$.[17b] The borate salt of **1-(H)Ph**$^+$ was alternatively prepared by the protonation of **1-Ph**, analogous to the synthesis of **1-(H)Me**$^+$.[23] The activation of benzene by the (PONOP)Ir^I fragment was reversible as exposure of **1-(H)Ph**$^+$ to a large excess of C_6D_6 at elevated temperature resulted in ^{2}H incorporation into the phenyl and hydride substituents. However, the slow decomposition fo **1-(H)Ph**$^+$ at temperatures above 60 °C prevented detailed rate measurements.



(4)

The benzene activation product, **1-(H)Ph**$^+$, was characterized by NMR spectroscopy and elemental analysis. The ^{1}H NMR spectrum of **1-(H)Ph**$^+$ in acetone-d_6 solution displays a broadened resonance at −38.47 ppm (vida infra) assigned to the iridium hydride, as well as signals at 7.57, 7.05, and 6.85 ppm corresponding to the iridium phenyl group. Further confirmation of the identity of **1-(H)Ph**$^+$ was provided by its reaction with base. Treatment of a tetrahydrofuran solution of the iridium(III) phenyl hydride cation with 1 equiv of potassium *tert*-butoxide afforded the neutral iridium(I) phenyl complex, **1-Ph**, suggesting the hydride ligand maintains a degree of acidity. A similar transformation has also been reported for the (PNP)Ir(H)(C$_6$H$_5$) cation.[20b]

Activation of benzene by **1-COE**$^+$ at ambient temperature proceeded without direct observation of an intermediate arene adduct (**D**, Figure 7). However, the viability of an iridium(I) benzene intermediate is supported by prior reports of related arene adducts[31] and is consistent with the dynamic NMR behavior of **1-(H)Ph**$^+$ in solution. In dry tetrahydrofuran-d_8 solution, the ^{1}H NMR spectrum of **1-(H)Ph**$^+$ exhibits a triplet

(37) Eisenstein, O.; Crabtree, R. H. *New J. Chem,* **2001**, *25*, 665.

(38) (a) O'Reilly, S.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 5684. (b) Canty, A. J.; Dedieu, A.; Jin, H.; Milet, A.; Richmond, M. K. *Organometallics* **1996**, *15*, 2845. (c) Hill, G. S.; Vittal, J. J.; Puddephatt, R. J. *Organometallics* **1997**, *16*, 1209. (d) Prokopchuk, E. M.; Jenkins, H. A.; Puddephatt, R. J. *Organometallics* **1999**, *18*, 2861. (e) Haskel, A.; Keinan, E. *Organometallics* **1999**, *21*, 247. (f) Puddephatt, R. J. *Coord. Chem. Rev.* **2001**, *219*−*221*, 157. (g) Reinartz, S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2002**, *18*, 4677. (h) Iron, M. A.; Lo, H. C.; Martin, J. M. L.; Keinan, E. *J. Am. Chem. Soc.* **2002**, *124*, 7041.

(39) For precedents of dissociative ligand substitution at Ir(I) pincer complexes, see: (a) Cartwright Sykes, A.; White, P.; Brookhart, M. *Organometallics* **2006**, *25*, 1664. (b) Bernskoetter, W. H.; Brookhart, M. S. *Organometallics* **2008**, *27*, 2036.

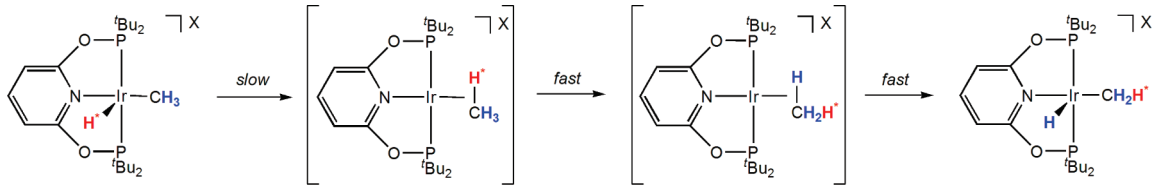


Figure 10. Proposed mechanism for site exchange in **1-(H)Me**$^+$.

resonance at −41.43 ppm ($^2J_{P-H}$ = 13.0 Hz; $\upsilon_{1/2}$ = 28 Hz)[32,40] at ambient temperature assigned to the Ir−H moiety. Upon warming the sample to 73 °C, the Ir−H resonance broadens significantly to a $\upsilon_{1/2}$ = 66 Hz. The *ortho*, *meta*, and *para* proton resonances of the phenyl substituent also show significant broadening at this temperature, displaying peak widths at half-height of 62, 63, and 79 Hz, respectively. The observed line broadening of the metal hydride and phenyl resonances suggests a rapid site exchange process among the four positions. This hypothesis is supported by the observation of exchange correlations between all four sites in the ambient temperature 2D NOESY NMR spectrum (mixing time = 500 ms).

The intramolecular site exchange between Ir−H and Ir−Ph protons was examined more closely by a series of quantitative EXSY NMR experiments on **1-(H)Ph**$^+$.[23] At 22 °C, magnetization transfer was detected between the metal hydride and all three phenyl resonances. Exchange correlations between the Ir−H and the *ortho*-Ph positions were considerably more intense than those to the *meta*- and *para*-Ph sites, suggesting that reversible C−H coupling is slightly faster than scrambling between the arene positions. A rate constant of 0.35(7) s^{-1} at 22 °C was measured for the exchange of the Ir−H and the *ortho*-Ph sites. This corresponds to a barrier of 17.8(4) kcal/mol in solution. The interchange of the iridium hydride and phenyl protons of **1-(H)Ph**$^+$, as well as the intermolecular exchange with benzene-d_6, suggests an iridium(I) arene complex (**D**) as an intermediate in both C−H bond reductive coupling and benzene oxidative addition.

Relative Rates of Aryl and Alkyl C−H Bond Coupling. The proposed mechanism for H/D exchange with protic reagents in **1-(H)Me**$^+$ or **1-(H)Ph**$^+$ (Figure 7) invokes a key step in which a C−H bond is reversibly formed. Significantly, quantitative EXSY NMR experiments probing the site exchange between the Ir−H and Ir−Me or Ir−Ph permit a comparison of the relative ease of alkyl and aryl C−H bond coupling from a d^6 metal center. The absence of an observable quantity of alkane or arene adduct in solutions of **1-(H)Me**$^+$ or **1-(H)Ph**$^+$ supports the assumption that the C−H bond coupling event is rate-limiting in the site exchange processes (Figure 10). Surprisingly, the barrier of 9.3(4) kcal/mol at −105 °C measured by EXSY NMR experiments for site exchange in **1-(H)Me**$^+$ is substantially lower than the 17.8(4) kcal/mol barrier at 22 °C found for an analogous process in **1-(H)Ph**$^+$ in which the Ir−H and *ortho*-Ph protons were interchanged. The difference in barriers for C−H bond coupling may also be the origin of the dramatically faster rate for H/D exchange in **1-Me** with CD_3OD compared to **1-Ph** (vide supra).

Previous studies have suggested that the coupling of a metal−hydride with an sp^3-hybridized carbon such as a methyl substituent may have an intrinsically higher barrier than similar couplings with sp^2-hybridized carbon centers.[41] The greater degree of directionality of the sp^3-hybridized orbital in a metal−methyl bond is predicted to "prevent the carbon atom from simultaneously forming strong C−H and C−C bonds while retaining a strong M−C bond in the transition state."[41] For sp^2-hybrids, the higher degree of spherical s-orbital character is believed to attenuate this effect by limiting orbital directionality. However, the rate of C_{sp^2}−H bond coupling in **1-(H)Ph**$^+$ was found to be dramatically slower than the analogous C_{sp^3}−H bond coupling in **1-(H)Me**$^+$. Thus, the relative facility of benzene and methane formation from cationic iridium(III) centers does not appear to be dominated by an intrinsic property of the orbital hybridization about the carbon atom.

Recently, Goldman, Krogh-Jespersen, and co-workers have examined factors influencing a range of C−C bond couplings at related iridium(III) pincer complexes.[36] Similar to the observations of C−H bond coupling in the (PONOP)Ir^{III} species reported here, no rate enhancement for sp^2-hybridized carbons was reported for reductive elimination from (PCP)Ir(R)(R′) (R/R′ = Ph/Vi, Me/Me, Me/Vi, Me/CCPh, Vi/CCPh) (Vi = *trans*-CH=CH(Ph)). Instead, reductive couplings involving C_{sp^3}−C_{sp^3} pairs were found to occur with rates similar to or greater than those involving C_{sp^3}−C_{sp^2} or C_{sp^2}−C_{sp^2} pairs. The impact of carbon atom hybridization on reductive coupling was proposed to originate not from an intrinsic property of the sp^2-orbital but rather from orientation constraints of the hydrocarbon substituents imposed by the sterically encumbered PCP ligand framework.[36]

For example, (PCP)Ir(Me)(Ph) was found to resist reductive elimination at 45 °C, while (PCP)Ir(Me)$_2$ underwent ethane elimination with a rate constant of 9.94 × 10^{-4} s^{-1} at 15 °C.[36] X-ray diffraction and computational studies indicate that the plane of the phenyl substituent in (PCP)Ir(Me)(Ph) is nearly orthogonal to that of the aromatic ligand backbone and aligned coplanar with the Ir−Me bond. This relative orientation of the phenyl and methyl ligands is computed to dramatically raise the energy of the transition state for coupling when the two groups approach each other in a sterically encumbered "edge-on" or planar transition structure (Figure 11).[36] The calculated pathway in which the phenyl substituent is rotated 90° prior to the approach of the methyl group in a sterically less hampered "face-on" transition structure is considerably lower in energy, although the barrier for rotating the phenyl group into the sterically demanding environment created by the ^{t}Bu$_2$P moieties is still significant. It is this substantial barrier to rotation of the iridium−phenyl substituent prior to the face-on C−C coupling event in (PCP)Ir(Me)(Ph) which is postulated to account for the greater barrier for reductive elimination of toluene in comparison to the analogous elimination of ethane in (PCP)Ir(Me)$_2$.[36]

The requirement of an analogous rotation about the iridium−phenyl substituent prior to coupling in **1-(H)Ph**$^+$, in addition to any ground state stabilization imparted by the thermodynamic

(40) $\upsilon_{1/2}$ corresponds to the observed peak width at half-height.
(41) (a) Low, J. J.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 8321. (b) Low, J. J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609.

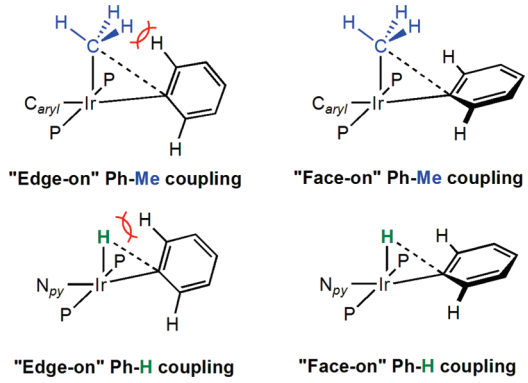


Figure 11. Transition structures for "face-on" and "edge-on" reductive couplings for (PCP)Ir(Me)(Ph) and **1-(H)Ph**$^+$.

preference for oxidative addition of benzene over methane,[42] may explain why H−C_{aryl} bond formation is substantially more difficult than H−C_{alkyl} coupling in **1-(H)Me**$^+$ (Figure 11). Although the small hydride substituent is likely to be less sensitive to steric pressure than a methyl group in the transition state for reductive coupling, preference for the face-on transition structure relative to an edge-on approach may be sufficient to require a rotation of the phenyl ligand (Figure 11). The crystal structure of the related complex **1-Ph** (Figure 5) suggests that the aryl substituent in **1-(H)Ph**$^+$ is oriented in an edge-on fashion with respect to the hydride ligand in the ground state structure. Similar to the observations for (PCP)Ir(Me)(Ph), hindered rotation about the Ir−Ph bond prior to C−H bond coupling may be a source of both the slower site exchange in **1-(H)Ph**$^+$ compared to **1-(H)Me**$^+$ and the reduced rate of H/D exchange between **1-Ph** and CD_3OD.

Concluding Remarks

A new neutral, tridentate pincer ligand, 2,6-bis(di-*tert*-butylphosphinito)pyridine, has been developed as a platform for the examination of the mechanism of hydrocarbon activation by d^8 Ir(I) complexes. The mechanism of benzene and methane reductive coupling was explored using isotopic labeling experiments and NMR spectroscopy, and viable intermediates along the reaction pathway were isolated. For methane, direct observation of C−H bond cleavage via an intermolecular reaction of the unsaturated iridium pincer complex with methane was not observed. However, protonolysis of **1-Me** permitted detailed study of reductive coupling and oxidative cleavage, implicating an iridium(I) σ-methane complex as an intermediate. The protonated complex **1-(H)Me**$^+$ is a very rare example of a 16-valence-electron, d^6 transition metal methyl hydride cation. Remarkably, this Ir(III) species was isolated and crystallographically characterized. The synthesis of complex **1-(H)Me**$^+$ and its reductive coupling/oxidative cleavage reactivity involving a d^8 transition metal σ-methane complex serve to model the key C−H activation steps in both Ir(I)-mediated alkane dehydrogenation and Pt(II)-catalyzed Shilov-type alkane oxidations.

Intermolecular oxidative addition of benzene was directly observed for the pincer iridium(I) olefin cation, **1-COE**$^+$. The five-coordinate Ir(III) complex **1-PhH**$^+$, produced via C−H activation of benzene, was also accessed by protonation of **1-Ph**. These Ir(III) and Ir(I) complexes were isolated and characterized, including the solid state structure determination of the iridium(I) phenyl complex, **1-Ph**. Mechanistic investigations indicate that the C−H activation event proceeds through a transient iridium(I) arene complex.

Contrary to reports that suggest orbital directionality may dominate reductive elimination at transition metals,[41] rate measurements of site exchange processes in **1-(H)Me**$^+$ and **1-(H)Ph**$^+$ suggest that H−C_{aryl} bond coupling proceeds with a dramatically higher barrier than the analogous H−C_{alkyl} coupling. In the sterically demanding (PONOP)Ir environment, coupling of the phenyl and hydrogen substituents may be slowed by the requirement of a hindered rotation about the Ir−C_{aryl} bond. This hypothesis is inspired by a recent report by Goldman, Krogh-Jespersen, and co-workers,[36] where similar hindered rotations about Ir−C_{sp^2} bonds are predicted to slow reductive coupling. Further studies into the factors influencing reductive coupling and oxidative addition at sterically encumbered transition metals may lead to new developments in many C−C and C−H bond forming transformations. In addition, studies of the relative stabilities of transition metal methyl hydride complexes versus the corresponding σ-methane adducts are currently ongoing in our laboratory. Understanding the factors impacting the kinetics and thermodynamics of these equilibria and the binding strength of σ-alkane adducts may facilitate the development of new catalysts for alkane activation and functionalization.

Experimental Section

General Considerations. All manipulations were carried out using standard vacuum, Schlenk, cannula, or glovebox techniques. Argon gas was purified by passage through columns of BASF R3-11 and 4 Å molecular sieves. THF was distilled from sodium benzophenone ketyl under nitrogen. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over 4 Å molecular sieves (benzene-d_6, methylene chloride-d_2, tetrahydrofuran-d_8, and cyclohexane-d_{12}) or calcium sulfate (acetone-d_6) and distilled prior to use. All other solvents were dried and deoxygenated using literature procedures.[43] Freon ($CDCl_2F$),[44] $[Ir(COE)_2Cl]_2$,[25] $[Ir(COE)_2(acetone)_2]PF_6$,[45] and $H[B(Ar^F)_4]\bullet(Et_2O)_2$[46] were prepared as previously described. All other reagents were purchased from Aldrich, Acros, Alpha Aesar, or Strem chemicals and used as received.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DPX 200, AV 300, DRX 400, and 500 MHz spectrometers. ^1H and ^{13}C chemical shifts are referenced to residual solvent signals; ^{31}P chemical shifts are referenced to an external standard of H_3PO_4. Probe temperatures were calibrated using ethylene glycol and methanol as previously described.[47] Due to strong $^{31}P-^{31}P$ coupling in the pincer ligand, many ^1H and ^{13}C NMR signals appear as virtual triplets (vt) and are reported as such with the apparent coupling noted. The ^1H and ^{13}C NMR spectral data for the $B(Ar^F)_4$ anion ($B(Ar^F)_4$ = $B[3,5\text{-}(CF_3)_2C_6H_3)]_4$) in CD_2Cl_2 are identical for all complexes and are therefore not repeated below. **$B(Ar^F)_4$.** ^1H NMR: δ 7.56 (s, 4H, *p*-Ar), 7.72 (s, 8H, *o*-Ar). ^{13}C {^1H} NMR: δ 117.9 (*p*-Ar), 125.0 (q, 273 Hz, CF_3), 129.3 (q, 31 Hz, *m*-Ar), 135.2 (*o*-Ar), 162.2 (q, 37 hz, *ipso*-Ar). Elemental analyses were performed by Robertson Microlit Laboratories Inc. in Madison, NJ, or Atlantic Microlab Inc. in Norcross, GA.

Preparation of $(2,6\text{-}(OP^tBu_2)_2C_5H_3N)$ (PONOP). 2,6-Dihydroxypyridine hydrochloride (378.3 mg, 2.56 mmol), di-*tert*-butylchlo-

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(47) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

rophosphine (860 μL, 4.53 mmol), triethylamine (1.92 mL, 13.78 mmol), and THF (50 mL, 0.617 mol) were combined in a glass vessel equipped with a Teflon stopcock. The reaction mixture was heated at 65 °C for 1 week. The volatiles were removed under vacuum, leaving an oily yellow solid. The solid was extracted into toluene and filtered through a Teflon syringe filter. The solvent was then removed under vacuum, leaving an off-white oil, which became an oily solid at −35 °C. Yield: 511 mg (57%). Anal. Calcd for $C_{12}H_{39}IrNO_2P_2$: C, 63.14; H, 9.84; N, 3.51. Found: C, 63.00; H, 9.71; N, 3.59. ^{1}H NMR (C_6D_6): δ 7.10 (t, 1H, J = 8.1 Hz, Py), 6.48 (d, 2H, J = 8.1 Hz, Py), 1.20 (d, 36 H, J = 11.4 Hz, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 155.0 (s). ^{13}C {^{1}H} NMR (C_6D_6): δ 164.55, 141.70, 105.40 (C_6H_3N), 36.00 (d, J = 28.9 Hz, P-C(CH$_3$)$_3$), 28.12 (d, J = 16.3 Hz, P−C(CH_3)$_3$).

Preparation of {C$_6$H$_3$N-2,6-[OP(^{t}Bu)$_2$]$_2$}IrCl (1-Cl). A 50 mL Schlenk flask was charged with 0.201 g (0.223 mmol) of [Ir(COE)$_2$Cl]$_2$[25] and 10 mL of diethyl ether. On a vacuum line, the orange solution was stirred under 1 atm of ethylene at −40 °C until the solution became very pale yellow. Then a solution of 0.185 g (0.463 mmol) of PONOP dissolved in 5 mL of diethyl ether was added via syringe to the reaction mixture, resulting in immediate formation of an orange precipitate. The reaction vessel was warmed to ambient temperature, and the volatiles were removed in vacuo. The resulting orange powder was extracted with toluene, filtered, and the solvent removed. The red-orange powder was washed with 5 mL of cold pentane yielding 0.223 g (79%) of **1-Cl**. Anal. Calcd for $C_{21}H_{39}IrNP_2O_2Cl$: C, 40.22; H, 6.27; N, 2.23. Found: C, 39.98; H, 6.21; N, 2.09. ^{1}H NMR (CD_2Cl_2): δ 1.43 (vt, J = 7.2 Hz, 36H, P−C(CH_3)$_3$), 6.38 (d, J = 8.0 Hz, 2H, m-C$_6H_3$N), 7.82 (t, J = 8.0 Hz, 1H, p-C$_6H_3$N). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 175.7. ^{31}P{^{1}H} NMR (23 °C, C_6D_6): δ 180.7. ^{13}C{^{1}H} NMR (C_6D_6): δ 27.9 (vt, J = 3.6 Hz, P−C(CH_3)$_3$), 41.4 (vt, J = 9.0 Hz, P-C(CH$_3$)$_3$), 102.0, 131.7, 166.6 (C_6H_3N).

Preparation of [{C$_6$H$_3$N-2,6-[OP(^{t}Bu)$_2$]$_2$}Ir(COE)]PF$_6$ (1-COE$^+$). In a round-bottom flask, PONOP (192 mg, 0.480 mmol) and [Ir(COE)$_2$(acetone)$_2$]PF$_6$[44] (320 mg, 0.480 mmol) were combined in acetone (4 mL). After mixing, the reaction turned a cherry-red color, and all the solids were dissolved. The solvent was removed under vacuum, and the remaining red solid was washed with pentane (2 × 3 mL) to yield 348 mg (85%) of **1-COE**$^+$. ^{1}H NMR (acetone-d_6): δ 1.50 (vt, J = 7.5 Hz, 36 Hz, P−C(CH_3)$_3$), 1.68−1.53 (m, 8H, COE), 1.80 (m, 2H, COE), 2.65 (m, 2H, COE), 4.66 (m, 2H, COE), 7.26 (d, J = 8.1 Hz, 2H, m-C$_6H_3$N), 8.30 (t, J = 8.1 Hz, 1H, p-C$_6H_3$N). ^{31}P{^{1}H} NMR (acetone-d_6): δ 183.14 (br s, Ir-P), −142.7 (sept, J = 707 Hz, PF$_6$).

Preparation of {C$_6$H$_3$N-2,6-[OP(^{t}Bu)$_2$]$_2$}IrCH$_3$ (1-Me). A heavy-walled glass reaction vessel was charged with 0.133 g (0.212 mmol) of **1-Cl**, 265 μL of 1.6 M methyl lithium in diethyl ether (0.424 mmol), and 15 mL of toluene. The solution was heated at 90 °C for 2 days, yielding a dark red solution. The volatiles were removed in vacuo, and the dark residue was extracted with pentane, filtered through Celite, and recrystallized at −35 °C, affording 0.088 g (68%) of **1-Me** as dark red blocks. Anal. Calcd for $C_{22}H_{42}IrNP_2O_2$: C, 43.55; H, 6.98; N, 2.31. Found: C, 43.27; H, 7.06; N, 2.31. ^{1}H NMR (C_6D_6): δ 1.41 (vt, J = 7.0 Hz, 36H, P−C(CH_3)$_3$), 2.11 (t, J = 5.0 Hz, 3H, Ir−CH_3), 6.11 (d, J = 8.0 Hz, 2H, m-C$_6H_3$N), 7.41 (t, 8.0 Hz, 1H, p-C$_6H_3$N). ^{31}P{^{1}H} NMR (C_6D_6): δ 186.4. ^{13}C{^{1}H} NMR (C_6D_6): δ −24.8 (Ir-CH$_3$), 28.2 (vt, J = 3.7 Hz, P−C(CH_3)$_3$), 40.9 (vt, J = 8.8 Hz, P-C(CH$_3$)$_3$), 101.9, 130.8, 164.0 (C_6H_3N).

Preparation of {C$_6$H$_3$N-2,6-[OP(^{t}Bu)$_2$]$_2$}Ir(C$_6$H$_5$) (1-Ph). Method A: In a glass vessel equipped with a Teflon stopcock, **1-(H)Ph**$^+$ (30 mg, 0.037 mmol) and potassium *tert*-butoxide (6.0 mg, 0.054 mmol) were dissolved in THF (5 mL). The solution turned red instantly. The volatiles were removed under vacuum, leaving a red solid. The solid was then extracted into benzene and the solution filtered through a Teflon syringe filter. The benzene was then removed under vacuum, leaving 9.0 mg (31%) of **1-Ph** as a red solid. **Method B**: A heavy-walled glass reaction vessel was charged with 0.100 g (0.159 mmol) of **1-Cl**, 120 μL of 1.6 M (0.192 mmol) phenyl lithium in cyclohexane/diethyl ether, and 15 mL of toluene. The solution was stirred at ambient temperature for 1 h then heated at 80 °C overnight, yielding a dark red solution. The volatiles were removed in vacuo, and the dark residue was extracted with pentane, filtered through Celite, and recrystallized at −35 °C, affording 0.054 g (52%) of **1-Ph** as red blocks. ^{1}H NMR (THF-d_8): δ 1.30 (vt, J = 7.5 Hz, 36 H, P−C(CH_3)$_3$), 6.40 (m, 1H, Ir-Ph), 6.51 (d, J = 9.0 Hz, 2H, m-C$_6H_3$N), 6.71 (t, J = 7.5 Hz, 2H, Ir-Ph), 7.46 (d, J = 9.0 Hz, 2H, Ir-Ph), 7.96 (t, J = 9.0 Hz, 1H, p-C$_6H_3$N). ^{31}P{^{1}H} NMR (THF-d_8): δ 190.14. ^{13}C{^{1}H} NMR (C_6D_6): δ 28.4 (vt, J = 3.8 Hz, P−C(CH_3)$_3$), 41.9 (vt, J = 8.7 Hz, P-C(CH$_3$)$_3$), 101.5, 143.5, 163.8 (C_6H_3N), 120.0, 127.0, 128.9, 133.7 (Ir-C_6H_5).

Preparation of [{C$_6$H$_3$N-2,6-[OP(^{t}Bu)$_2$]$_2$}Ir(C$_6$H$_5$)H]PF$_6$ (1-(H)Ph$^+$). In a glass vessel with a Teflon stopcock, **1-COE**$^+$ (50 mg, 0.0595 mmol) was dissolved in a mixture of benzene (5 mL) and acetone (5 mL). Over the course of 5 days, the solution changed color from bright orange to yellow. The solvent was removed under vacuum, leaving an orange solid, which was washed with pentane (3 × 2 mL) and dried under vacuum to yield 42 mg (86%) of **1-(H)Ph**$^+$. The borate salt of **1-(H)Ph**$^+$ may be prepared by a procedure identical to that for **1-(H)Me**$^+$ (Method B) using **1-Ph** and H[B(Ar^F)$_4$]•(Et$_2$O)$_2$. Anal. Calcd for $C_{27}H_{45}F_6NO_2P_3Ir$: C, 39.80; H, 5.57; N, 1.72. Found: C, 39.57; H, 5.55; N, 1.68. ^{1}H NMR (acetone-d_6): δ 1.37 (vt, J = 7.8 Hz, 36 H, P−C(CH_3)$_3$), 6.83 (t, J = 6.9 Hz, 1H, p-Ph), 7.05 (t, J = 7.5 Hz, 1H, m-Ph), 7.33 (d, J = 8.7 Hz, 2H, m-C$_6H_3$N), 7.57 (d, J = 8.7 Hz, 2H, o-Ph), 8.23 (t, J = 8.4 Hz, 1H, p-C$_6H_3$N), −38.47 (br s, 1H, Ir-H). ^{31}P{^{1}H} NMR (acetone-d_6): δ 180.16 (s, Ir-P), −142.7 (sept, J = 707 Hz, PF$_6$).

Preparation of [{C$_6$H$_3$N-2,6-[OP(^{t}Bu)$_2$]$_2$}Ir(CH$_3$)H]X (1-(H)Me$^+$) (X = SbF$_6$, B(Ar^F)$_4$). Method A: An 8 mL vial was charged with 0.041 g (0.064 mmol) of **1-MeHCl**, 0.023 g (0.067 mmol) of silver hexafluoroantimonate, and 2 mL of methylene chloride. The mixture was shaken for 5 min, quickly filtered through Celite, and layered with approximately 3 mL of pentane. Storage of the solution at −35 °C overnight yielded 32 mg (59%) of the SbF$_6$ salt of **1-(H)Me**$^+$ as an orange powder. **Method B**: An 8 mL vial was charged with 0.018 g (0.030 mmol) of **1-Me**, 0.031 g (0.031 mmol) of H[B(Ar^F)$_4$]•(Et$_2$O)$_2$, and 2 mL of methylene chloride. The solution was allowed to stand at ambient temperature for 5 min and layered with 3 mL of pentane. Recrystallization at −35 °C afforded 26 mg (60%) of the B(Ar^F)$_4$ salt of **1-(H)Me**$^+$ as large orange blocks. ^{1}H NMR (36 °C, CD_2Cl_2): δ 1.35 (vt, J = 8.0 Hz, 36H, P−C(CH_3)$_3$), 7.07 (d, J = 8.5 Hz, 2H, m-C$_6H_3$N), 7.99 (t, J = 8.5 Hz, 1H, p-C$_6H_3$N), −8.95 (br s, 4H, Ir-H and Ir−CH_3 in fast exchange). ^{1}H NMR (20 °C, CD_2Cl_2): δ 1.35 (vt, J = 8.0 Hz, 36H, P−C(CH_3)$_3$), 7.07 (d, J = 8.5 Hz, 2H, m-C$_6H_3$N), 7.99 (t, J = 8.5 Hz, 1H, p-C$_6H_3$N), signals for Ir−H and Ir−CH_3 not observed. ^{1}H NMR (0 °C, CD_2Cl_2): δ 1.39 (vt, J = 7.8 Hz, 36H, P−C(CH_3)$_3$), 7.05 (d, J = 8.5 Hz, 2H, m-C$_6H_3$N), 8.00 (t, J = 8.5 Hz, 1H, p-C$_6H_3$N), signals for Ir−H and Ir−CH_3 not observed. ^{1}H NMR (−60 °C, CD_2Cl_2): δ 1.41 (vt, J = 7.8 Hz, 36H, P−C(CH_3)$_3$), 1.82 (br s, 3H, Ir−CH_3), 7.05 (d, J = 8.5 Hz, 2H, m-C$_6H_3$N), 7.93 (t, J = 8.5 Hz, 1H, p-C$_6H_3$N), −41.79 (br s, 1H, Ir−H). ^{1}H NMR (−86 °C, CD_2Cl_2): δ 1.21 (br s, 36H, P−C(CH_3)$_3$), 1.83 (br s, 3H, Ir−CH_3), 6.95 (d, J = 8.0 Hz, 2H, m-C$_6H_3$N), 7.82 (t, J = 8.0 Hz, 1H, p-C$_6H_3$N), −41.79 (br s, 1H, Ir−H). ^{1}H NMR (−132 °C, CD_2Cl_2): δ 1.49 (br s, 36H, P−C(CH_3)$_3$), 1.93 (br s, 3H, Ir−CH_3), 7.05 (d, J = 8.1 Hz, 2H, m-C$_6H_3$N), 7.93 (t, J = 8.1 Hz, 1H, p-C$_6H_3$N), −41.83 (t, J = 13.0 Hz, 1H, Ir−H). ^{31}P{^{1}H} NMR (23 °C, CD_2Cl_2): δ 184.2. ^{13}C{^{1}H} NMR (−86 °C, CD_2Cl_2): δ −20.6 (Ir−CH$_3$) 25.9 (P−C(CH_3)$_3$), 42.0 (P−C(CH$_3$)$_3$), 103.4, 143.6, 161.7 (C_6H_3N).

Preparation of {C$_6$H$_3$N-2,6-[OP(^{t}Bu)$_2$]$_2$}IrMe(H)Cl (1-MeHCl). A heavy-walled glass reaction vessel was charged with 0.015 g (0.025 mmol) of **1-Me** and 5 mL of pentane. On a vacuum line, the solution was frozen at −196 °C, and 16 Torr (0.025 mmol) of hydrogen chloride in a 28.9 mL calibrated gas bulb was admitted to the vessel. The solution was warmed to room temperature,

quickly changing color from dark red to colorless. The volatiles were removed in vacuo, and the residue was washed with 10 mL of pentane to afford 0.011 g (69%) of **1-MeHCl** as a beige powder. Anal. Calcd for $C_{22}H_{42}IrNP_2O_2$: C, 41.08; H, 6.74; N, 2.18. Found: C, 39.19; H, 6.32; N, 2.00. ^{1}H NMR (C_6D_6): δ 1.81 (vt, J = 7.0 Hz, 18H, P−C(CH_3)$_3$), 1.55 (t, J = 5.0 Hz, 3H, Ir−CH_3), 1.69 (vt, J = 7.0 Hz, 18H, P−C(CH_3)$_3$), 6.11 (d, J = 8.0 Hz, 2H, m-C$_6H_3$N), 6.43 (t, J = 8.0 Hz, 1H, p-C$_6H_3$N), −19.34 (t, J = 16.5 Hz, 1H, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6): δ 162.6. ^{13}C{^{1}H} NMR (C_6D_6): δ −36.6 (t, J = 4.4 Hz, Ir−CH$_3$), 28.1 (vt, J = 3.1 Hz, P−C(CH$_3$)$_3$), 30.3 (vt, J = 3.1 Hz, P−C(CH$_3$)$_3$), 42.2 (vt, J = 6.9 Hz, P−C(CH$_3$)$_3$), 45.3 (vt, J = 6.9 Hz, P−C(CH$_3$)$_3$), 101.9, 140.3, 162.7 (C_6H_3N).

Preparation of {C$_6$H$_3$N-2,6-[OP(^{t}Bu)$_2$]$_2$}IrPh(H)Cl (1-PhHCl). A heavy-walled glass reaction vessel was charged with 0.014 g (0.028 mmol) of **1-Ph** and 5 mL of pentane. On a vacuum line, the solution was frozen at −196 °C, and 19 Torr (0.029 mmol) of hydrogen chloride in a 28.9 mL calibrated gas bulb was admitted to the vessel. The solution was warmed to room temperature, quickly changing color from dark red to colorless. The volatiles were removed in vacuo, and the residue was washed with 10 mL of pentane affording 0.010 g (50%) of **1-PhHCl** as a beige powder. ^{1}H NMR (C_6D_6): δ 1.78 (vt, J = 7.0 Hz, 18H, P−C(CH_3)$_3$), 1.50 (vt, J = 7.0 Hz, 18H, P−C(CH_3)$_3$), 6.11 (d, J = 8.0 Hz, 2H, m-C$_6H_3$N), 6.64 (t, J = 8.0 Hz, 1H, p-C$_6H_3$N), 7.06 (t, J = 7.3 Hz, 1H, Ir-p-C$_6H_5$), 7.21 (m, 2H, Ir−m-C$_6H_5$), 8.60 (d, J = 3.5 Hz, 2H, Ir−o-C$_6H_5$), −19.62 (t, J = 16.8 Hz, 1H, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6): δ 161.3. ^{13}C{^{1}H} NMR (C_6D_6): δ 28.3 (vt, J = 3.1 Hz, P−C(CH$_3$)$_3$), 33.3 (vt, J = 3.1 Hz, P−C(CH$_3$)$_3$), 43.2 (vt, J = 6.9 Hz, P−C(CH$_3$)$_3$), 46.0 (vt, J = 6.9 Hz, P−C(CH$_3$)$_3$), 102.3, 141.5, 162.7 (C_6H_3N), 121.8, 127.3, 144.3 (Ir−C_6H_5), one Ir−C_6H_5 signal not located.

Preparation of {C$_6$H$_3$N-2,6-[OP(^{t}Bu)$_2$]$_2$}Ir(H)Cl$_2$ (1-HCl$_2$). A heavy-walled glass reaction vessel was charged with 0.050 g (0.080 mmol) of **1-Cl** and 5 mL of diethyl ether. On a vacuum line, the solution was frozen at −196 °C, and 55 Torr (0.086 mmol) of hydrogen chloride in a 28.9 mL calibrated gas bulb was admitted to the vessel. The solution was warmed to room temperature, quickly changing from dark red to colorless. The volatiles were removed in vacuo, and the residue was washed with 10 mL of pentane to afford 0.038 g (72%) of **1-HCl$_2$** as colorless powder. Anal. Calcd for $C_{22}H_{42}IrNP_2O_2$: C, 38.01; H, 6.08; N, 2.11. Found: C, 39.62; H, 6.26; N, 1.78. ^{1}H NMR (C_6D_6): δ 1.25 (vt, J = 7.0 Hz, 18H, P−C(CH_3)$_3$), 1.74 (vt, J = 7.0 Hz, 18H, P−C(CH_3)$_3$), 5.94 (d, J = 8.2 Hz, 2H, m-C$_6H_3$N), 6.48 (t, J = 8.2 Hz, 1H, p-C$_6H_3$N), −19.71 (t, J = 14.0 Hz, 1H, Ir−H). ^{31}P{^{1}H} NMR (C_6D_6): δ 161.5. ^{13}C{^{1}H} NMR (C_6D_6): δ 27.9 (vt, J = 2.5 Hz, P−C(CH$_3$)$_3$), 30.3 (vt, J = 2.5 Hz, P−C(CH$_3$)$_3$), 42.2 (vt, J = 6.9 Hz, P-C(CH$_3$)$_3$), 45.6 (vt, J = 6.9 Hz, P-C(CH$_3$)$_3$), 102.4, 140.2, 164.9 (C_6H_3N).

General Procedure for Kinetic Determination of Site Exchange in 1-(H)Me$^+$ and 1-(H)Ph$^+$. In a J. Young tube, a sample of iridium complex of known concentration was prepared in dry $CDCl_3$ or $CDCl_2F$ under an Ar atmosphere. The tube was inserted into a temperature-calibrated probe, and quantitative EXSY NMR spectra were acquired on a Bruker DRX 500 spectrometer with mixing times of 800, 500, 300, and 3 ms. Cross peak integration was performed in MestReNova;[48] intensities were normalized and the rates calculated using literature methods.[49] A total of 512 complex points were collected in the indirectly detected dimension with 4 scans and 1024 point per increment. The resulting matrix was zero filled to 2k × 2k complex data points, and 90 shifted squared sinusoidal window functions were applied in both dimensions prior to Fourier transform.

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Supporting Information Available: Crystal structure information files for **1-Ph** and **1-(H)Me$^+$**, sample graphs for rate measurements, sample ^{31}P and 2D EXSY NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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