Multiple C−H Activations of Methyl *tert*-Butyl Ether at Pincer Iridium Complexes: Synthesis and Thermolysis of Ir(I) Fischer Carbenes[1]

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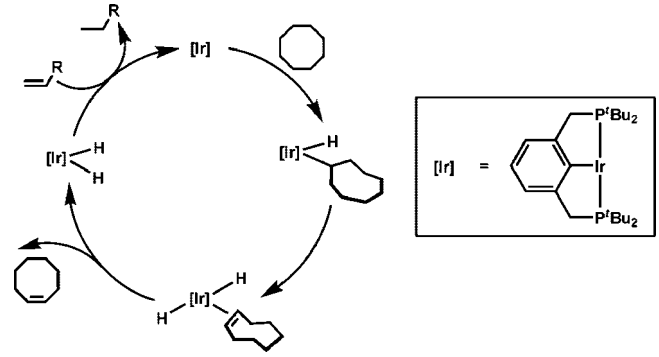
The C−H activation of methyl *tert*-butyl ether (MTBE) mediated by pincer iridium complexes derived from PNP and PCP frameworks has been studied. Double C−H activation of MTBE by these complexes leads to formation of Ir(I) Fischer carbenes of the type (pincer)Ir=C(H)O^{t}Bu via elimination of H_2. In one case, the structure of the Fischer carbene has been confirmed by single-crystal X-ray analysis. For both systems, the carbenes are obtained as kinetic products, and prolonged thermolysis leads to the formation of thermodynamically stable *trans*-(pincer)Ir(H)$_2$(CO) complexes. A mechanism for this transformation is presented along with reactivity studies supporting the proposal.

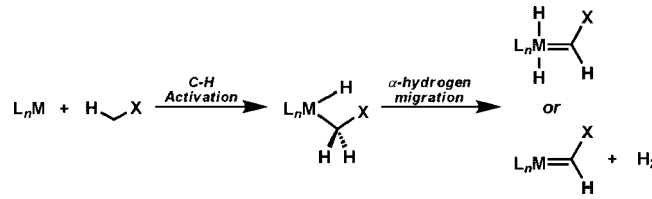
Introduction

The catalytic activation and functionalization of otherwise inert C−H bonds of discrete molecules continues to be an area of active research in organometallic chemistry.[2] One particular approach that has received increasing attention in recent years is the catalytic dehydrogenative conversion of alkanes into alkenes.[3] This transformation generates a functionalized product that can be further elaborated, but due to its thermodynamically uphill nature, it is usually accomplished in the presence of a sacrificial olefin that functions as a hydrogen acceptor. In recent years, significant progress has been made in this area due the introduction of thermally robust pincer-type complexes, and iridium variants in particular have been found to be exceptionally active catalysts.[3,4] The commonly accepted mechanism for this transformation involves (1) C−H oxidative addition of the alkane at a highly reactive 14-electron iridium intermediate, (2) β-hydrogen elimination with formation of the corresponding alkene, (3) release of the alkene and regeneration of the metal dihydride precursor, and (4) transfer of hydrogen from the latter to a sacrificial olefin to regenerate the active catalytic species (Scheme 1, cyclooctane as substrate).[3,5] Tuning of the steric bulk around the metal center and reaction conditions have a major impact on catalytic activity and catalyst lifetime, and in some cases such tuning has allowed the dehydrogenation of alkanes to occur in the absence of a hydrogen acceptor.[3b]

Scheme 1



Scheme 2



In comparison to alkane dehydrogenation, progress in the dehydrogenation of heteroatom-containing substrates has lagged.[6] This is somewhat surprising given the high versatility demonstrated by pincer-type complexes in several areas of catalysis.[4,7]

As outlined above, β-hydrogen elimination allows for the generation of an alkene from an alkane. In the absence of β-hydrogens, α-hydrogen migration is likely to ensue, giving access to unsaturated Fischer-type carbenes, which could be further elaborated (Scheme 2). While most C−H activation

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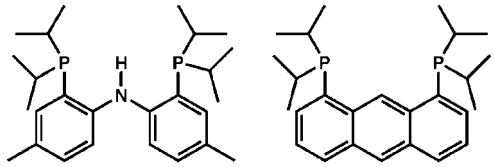

1 **2**

Figure 1

protocols rely on the generation of an M−C_{sp^3} bond for potential functionalization,[2] the construction of a reactive M=C_{sp^2} fragment via direct C−H activation provides new mechanisms for entry into C−C coupling and other bond-forming reactions.

We have begun to explore this subject and have selected pincer iridium platforms as a starting point for the generation of Fischer-type carbenes from methyl ethers. In this contribution we present our initial efforts in this area using the pincer ligands **1** and **2** (Figure 1).

Results and Discussion

I. Preparation of Anthraphos Ligands. Although originally claimed by Haenel et al. in the context of alkane dehydrogenation,[8] neither synthetic details nor characterization for **2** or its complexes has been furnished. Therefore, we start by discussing some of the details of the preparation of **2**, with full details given in the Experimental Section. As reported, the key 1,8-difluoroanthraquinone can be conveniently prepared from commercially available 1,8-dichloroanthraquinone and subsequently reduced to 1,8-difluoroanthracene in good yields.[9] Additionally, we have found that both 1,8-difluoroanthraquinone and 1,8-difluoroanthracene can be conveniently purified by sublimation, circumventing the need for chromatographic purification. Subsequent reaction of $^{i}Pr_2PK$ (obtained from metathesis of $^{i}Pr_2PSiMe_3$ and $^{t}BuOK$) with 1,8-difluoroanthracene in a 1:1 mixture of THF/dioxane affords the desired ligand (ca. 75−80% yield), which can also be readily purified by sublimation. Anthraphos ligand **2** is an air-stable solid and can be routinely prepared on a 3−5 g scale (Scheme 3).

II. Preparation of Iridium Precursors. Hydrido chloride complex **3**, bearing a diarylamido unit, has been prepared by Ozerov and co-workers by reaction of the free ligand with $[IrCl(COD)]_2$ (Scheme 4),[10] and dihydride complex **8** can be obtained by direct reaction of **3** with $LiEt_3BH$.[11] Anthraphos complex **4** was prepared in high yield by direct metalation of the ligand with $[IrCl(COE)_2]_2$ in refluxing toluene (Scheme 4). Multinuclear NMR spectroscopy analysis revealed a complex of C_s symmetry with a diagnostic triplet hydride signal at −35.9 ppm ($^2J_{PH}$ = 12 Hz) and a singlet resonance in the ^{31}P NMR spectrum (61 ppm). The high-field position of the Ir-*H* resonance in the ^{1}H NMR spectrum, as well as the symmetry displayed, is consistent with a square-pyramidal geometry with the apical site occupied by the hydride and a mirror plane bisecting the backbone anthracene ligand. Red complex **4** is air-sensitive in solution but can be handled in air as a solid.

Haenel et al. have prepared the dihydride ($^{t\mathrm{Bu}}$Anthraphos)IrH_2 complex, which can be used as a precatalyst for the C−H activation of alkanes,[8] from the corresponding hydrido chloride precursor. Alternatively, access to the 14-electron unsaturated intermediate responsible for C−H activation is possible directly from the hydrido chloride precursor. Following a protocol reported by Brookhart and co-workers,[12] reductive dehydrochlorination of **4** with the soluble base ^{t}BuONa proceeds smoothly in aromatic solvents. When this procedure is carried out under an atmosphere of N_2, dinitrogen complex **5** forms rapidly (Scheme 5). Although generation of **5** in solution is quantitative as judged by NMR, isolation of pure compound is difficult due to its lack of crystallinity. Therefore, **5** was characterized in solution. The ^{1}H NMR spectrum of dark green complex **5** showed a complex of C_{2v} symmetry consistent with a symmetrical environment around the iridium center, and the ^{31}P NMR spectrum revealed a single resonance at 64 ppm. Solution IR spectroscopy (C_6H_6) of **5** showed a band at 2096 cm^{-1} assigned to the bound dinitrogen ligand. This value is slightly higher than the previously reported complex ($^{t\mathrm{Bu}}$PCP)IrN_2 (ν_{NN} = 2079 cm^{-1}).[13]The observed $\Delta\nu$ of 17 cm^{-1} is likely a reflection of the weaker donor ability of the ligand **2** due to the presence of less basic phosphines (^{i}Pr versus ^{t}Bu) and a more electron-withdrawing anthracene backbone (compared to *o*-xylyl). This translates into a lower dπ−pπ* back-bonding from the (PCP)Ir center to the terminal N_2 ligand. The appearance of an IR-active band for **5** also indicates that, in solution, the product corresponds to the terminal dinitrogen adduct since the symmetric Ir−N≡N−Ir dimer should be IR silent.

The identity of dinitrogen complex **5** has also been inferred by derivatization with CH_3I (Scheme 5). Oxidative addition to the iridium(I) center in **5** occurs smoothly at room temperature to give **6** in 96% isolated yield. Air- and moisture-stable **6** shows a diagnostic triplet at 1.37 ppm in the ^{1}H NMR spectrum corresponding to the iridium-bound methyl group ($^3J_{PH}$ = 6.0 Hz, CD_2Cl_2) along with C_s symmetry for the ligand environment and a single ^{31}P NMR resonance at 39.6 ppm. IR spectroscopy showed the disappearance of the N≡N stretch observed in **5**.

X-ray characterization of a single crystal of **6** obtained by slow evaporation of a CH_2Cl_2 solution confirmed the proposed structure. The structure shows a distorted square-pyramidal configuration wherein the apical methyl group is slightly canted toward the ligand backbone with a C(13)−Ir−C(27) angle of 83.3(1)°, while the vector defined by C(13)−Ir−I deviates from linearity with an angle of 168.65(8)°. This is likely a consequence of the rigid geometry imposed by the ligand, which distorts the square-pyramidal structure to avoid unfavorable steric interactions with the isopropyl groups. The iridium atom resides slightly above the mean plane defined by C(13)−P(1)−I−P(2) by 0.22 Å. Both the CH_3−Ir (2.086(3) Å) and the C(13)−Ir (2.017(3) Å) distances are unremarkable and compare well with related complexes.[13,14] The anthracene ligand backbone deviates from planarity and is slightly puckered in the solid state.

III. Dehydrogenation of Methyl *tert*-Butyl Ether. To access the desired Fischer carbenes, reaction of the (PCP)Ir and (PNP)Ir fragments with methyl *tert*-butyl ether (MTBE) was investigated. MTBE is an ideal candidate since it can be used as both reacting partner and solvent. Furthermore, the bulky *tert*-butyl group

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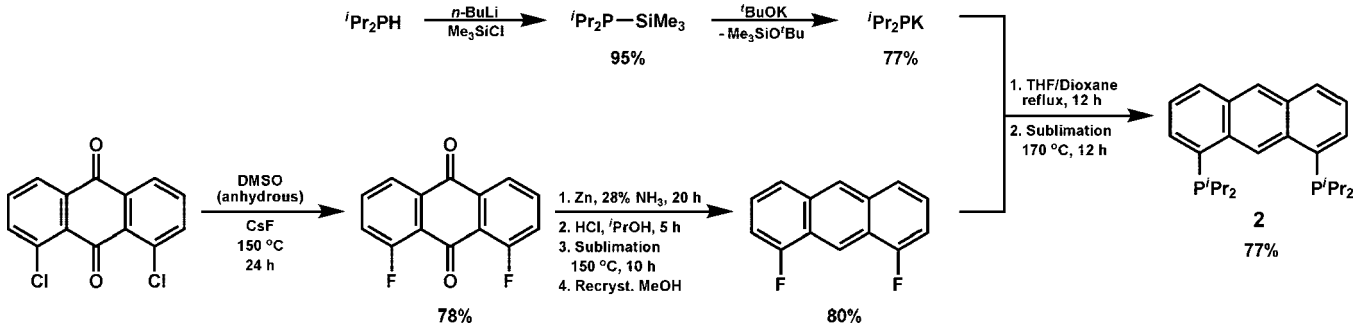
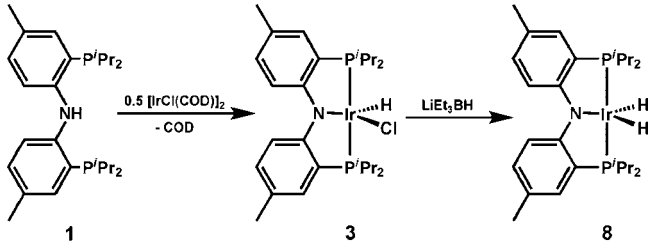
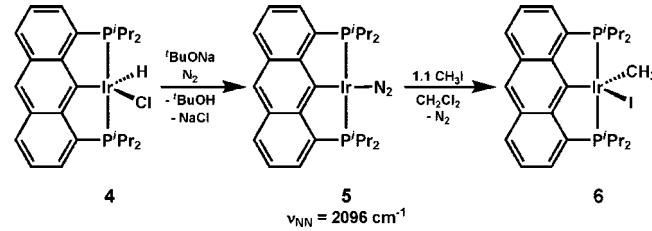
Scheme 3

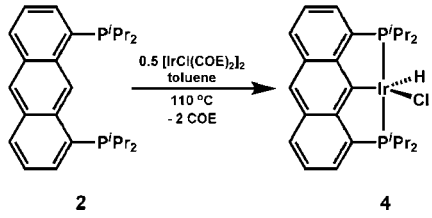


Scheme 4



Scheme 5





should bias C−H activation events toward the desired and more accessible CH_3 group.

Initial experiments showed that the dinitrogen complex **5** was inactive toward C−H activation of MTBE, consistent with previous observations that the catalytic activity of PCP-supported catalysts in alkane dehydrogenation is strongly inhibited by the presence of dinitrogen.[3,5,13] Despite rigorous exclusion of N_2 from the system, formation of **5** was also observed under an atmosphere of argon. Therefore, subsequent experiments were performed in evacuated systems using carefully degassed solvents.

Vacuum transfer of MTBE onto a mixture of **4** and ^{t}BuONa, followed by brief heating, generated a clear brown solution, from which an orange powder was isolated. ^{1}H NMR analysis of this material showed clean formation of a complex evidencing C_{2v} symmetry along with a diagnostic triplet hydride signal at −9.45 ppm ($^2J_{PH}$ = 15.0 Hz), and the ^{31}P NMR spectrum showed a single resonance at 66.1 ppm. Solution IR spectroscopy (THF) showed a strong absorption in the carbonyl region at 1989 cm^{-1}. An absorption band assigned to the H−Ir−H asymmetric stretch was also observed at 1763 cm^{-1}, consistent with *trans*-disposed hydride ligands.[15] On the basis of the spectroscopic evidence, the structure of this material was assigned as the *trans*-dihydrido carbonyl complex **7** (Scheme 6).

The identity of **7** was further confirmed by single-crystal X-ray diffraction. The analysis showed a carbonyl ligand located in the plane of the PCP ligand, although the hydride atoms could not be located. Bond distances and angles in **7** are unremarkable, and selected metrical parameters are shown in Figure 3.

In contrast to (PCP)Ir complexes, pincer derivatives of PNP ligand **1** show no tendency to form dinitrogen adducts, facilitating the study of C−H activation processes.[7,11,16] Complex **8** reacts cleanly with norbornene in MTBE at room temperature to generate the iridium(I)−MTBE adduct, which is observable by ^{31}P NMR spectroscopy (45 ppm). The ether adduct gradually converts to the desired Fischer carbene, (PNP)Ir=C(H)O^{t}Bu (**9**), over a period of 16 h (Scheme 7).[1] This outcome is indicative of a slow and rate-determining first C−H activation step followed by rapid formation of **9** with liberation of H_2. Two equivalents of norbornene are necessary to ensure complete conversion because regeneration of **8** occurs readily upon exposure of the ether adduct to the generated dihydrogen. The ^{1}H NMR spectrum of **9** contains a characteristic triplet shifted far downfield that represents the carbene proton (13.8 ppm, $^3J_{PH}$ = 7.5 Hz).

Single-crystal XRD analysis confirmed the identity of **9** as the Fischer carbene and revealed a square-planar Ir(I) center with the carbene situated *trans* to the amido donor (Figure 4). The short Ir=C bond length (1.88 Å) is consistent with those of previously reported iridium−carbon double bonds.[17] Although a number of Fischer-type iridium carbenes are known, most examples feature an Ir(III) center.[17,18] Complex **9** represents an unusual example of a square-planar Ir(I) center featuring

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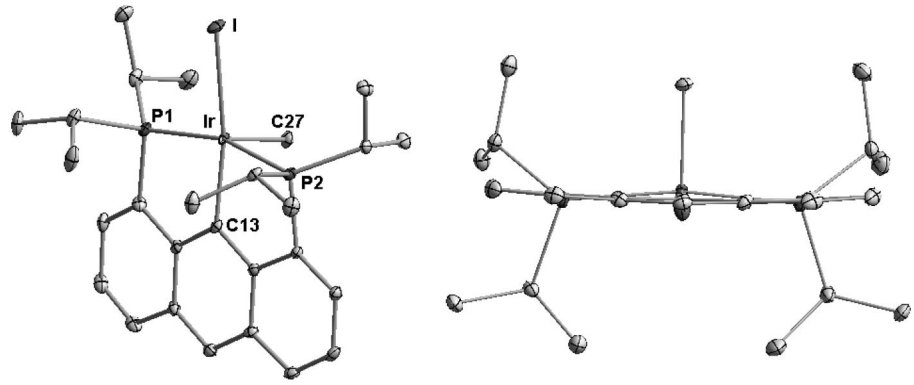
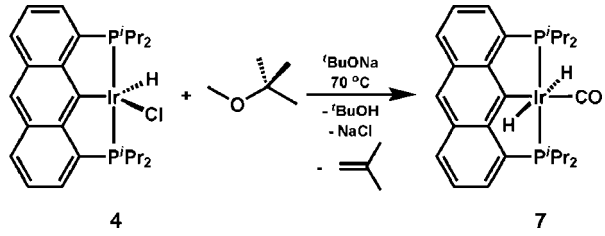
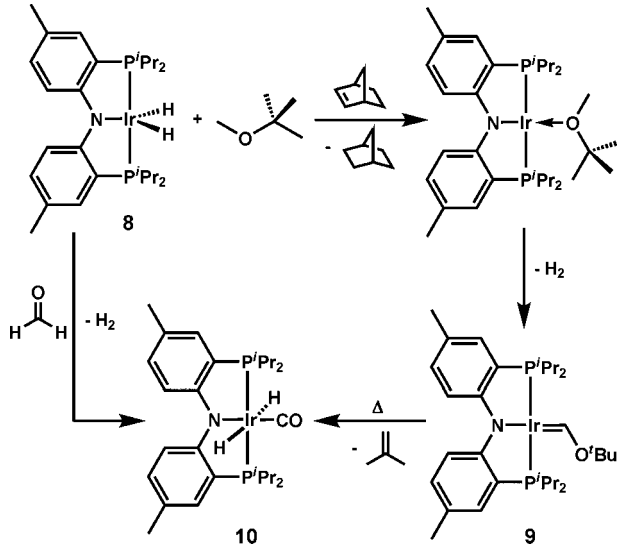


Figure 2. Displacement ellipsoid (35%) representation of **6** (top and side view) with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Ir−C13 2.017(3), Ir−P1 2.3009(8), Ir−P2 2.3119(8), Ir−C27 2.086(3), Ir−I 2.6935(2), C13−Ir−I 168.65(8), P1−Ir−P2 163.78(3), C13−Ir−C27 83.3(1), C27−Ir−I 107.99(8).

Scheme 6



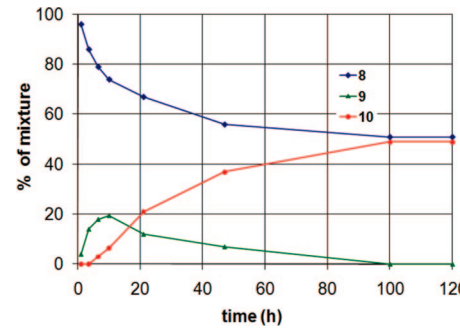
Scheme 7



this moiety.[19] Interestingly, though the carbene substituents and C−N−C linkage are canted slightly out of the square plane, they are precisely aligned with each other, allowing a strong interaction between the filled pπ orbital of the amido donor and the empty pπ orbital of the *tert*-butoxymethylidene ligand (Figure 4).

Carbene **9** undergoes smooth conversion to the *trans*-dihydrido carbonyl complex **10** upon thermolysis in C_6D_6 over a period of hours with concomitant elimination of isobutylene (detected by ^{1}H NMR spectroscopy). We have observed that **9** is thermally unstable both in solution and in the solid state, and crystalline samples of **9** are stored at −35 °C to avoid

Chart 1. Thermolysis of 8 in Neat MTBE



decomposition. The thermolysis of complex **8** in the presence of MTBE without a hydrogen acceptor can be readily monitored by NMR spectroscopy. The initial formation of carbene **9** and its subsequent decomposition to **10** are graphically shown in Chart 1. Under these conditions (sealed system), the reaction reaches a maximum of 50% conversion into the final product **10** due to reaction inhibition by generated hydrogen (vide supra). The identity of **10** was confirmed by XRD analysis. The Ir−C(14) bond length (1.84 Å) is slightly shorter than the Ir−C(27) bond of Fischer carbene complex **9** (1.88 Å), indicating that the effective bond orders in these complexes are similar. The infrared spectrum of compound **10** features a prominent carbonyl stretch (ν_{CO} = 1990 cm^{-1}) similar to that observed for the isostructural **7**.

IV. Mechanism of MTBE Decarbonylation. Complexes **7** and **10** are structurally related to Milstein's (^{iPr}PCP)Ir(H)$_2$(CO)[15a] and Goldberg's [(^{tBu}PNP)Ir(H)$_2$(CO)]$^+$,[20] with the latter being obtained by decarbonylation of methanol. This decarbonylation is thought to occur by β-hydrogen elimination of a metal-bound methoxide, followed by C−H activation of the newly formed formaldehyde.[20]

In analogy with the results of Goldberg, we find that exposure of **8** to formaldehyde (37 wt % solution in H_2O) results in the immediate formation of **10** with loss of H_2 (Scheme 7). On the basis of this observation, we propose that the decarbonylation processes mediated by pincer systems **1** and **2** share common intermediates. Thus, thermodynamically favored **7** likely arises from a series of C−H activation events involving the intermediacy of an unobserved iridium Fischer carbene complex. A plausible mechanism is depicted in Scheme 8.

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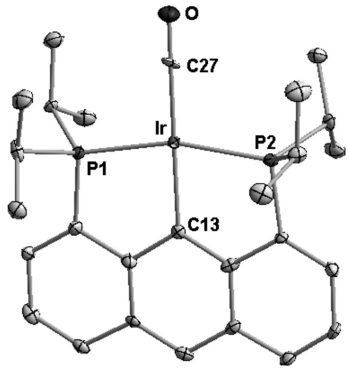
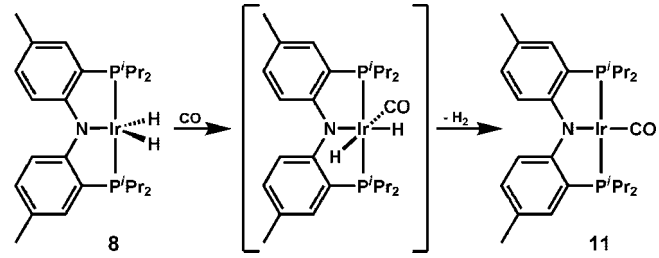


Figure 3. Structural representation of **7** with thermal ellipsoids at 35% probability. Selected bond distances (Å) and angles (deg): Ir−C13 2.094(6), Ir−P1 2.2941(15), Ir−P2 2.3041(15), Ir−C27 1.876(6), C13−Ir−C27 178.7(2), P1−Ir−P2 163.29(5).

Either reductive dehydrochlorination of **4** or dihydrogen elimination from **8** leads to the active 14-electron species, which undergoes C−H oxidative addition, followed by α-hydrogen migration and H_2 elimination to yield a Fischer carbene. The fact that the hydride ligands in **7** and **10** are in a *trans* arrangement suggests a mechanism with a predisposition of the carbene fragment to afford this geometry. Therefore, we propose that the decarbonylation of **9** (as well as that of the unobserved carbene derived from **4**) occurs via an oxocarbenium-type zwitterionic species, where proton transfer from the *tert*-butyl substituent in a rigid intermediate leads to elimination of isobutylene. In solution we observe only a single resonance in the ^{31}P NMR spectrum, indicating that the out-of-plane rotation required by this mechanism is facile. Even at −80 °C, only broadening of the ^{31}P NMR resonance is observed, suggesting a low barrier for rotation. The mechanism proposed in Scheme 8 is further supported by the fact that the X-ray structure of carbene **9** shows a C(27)−O distance of 1.351(5) Å, suggesting a sizable degree of multiple bond character and therefore a significant contribution of the oxocarbenium-type canonical form. The unobserved formyl complex undergoes further stereoselective C−H activation, yielding the *trans*-dihydrido carbonyl species, in line with the observation that reaction of **8** and H_2CO yields **10** cleanly. Notably, a potential α-alkoxy migration is not a competitive pathway after the first C−H activation event, and only α-hydrogen migration is observed to occur.

Milstein and co-workers have reported that, under certain conditions, *cis*-(^{iPr}PCP)Ir(H)$_2$(CO) undergoes thermal isomerization into the thermodynamically favored *trans*-(^{iPr}PCP)Ir(H)$_2$(CO) isomer.[15a] The intermediacy of a *cis*-dihydride for these systems was ruled out by a separate experiment. Reaction of **8** with CO leads to the exclusive formation of Ir(I) carbonyl complex **11** via formation of an unstable *cis*-dihydride, which slowly eliminates H_2 (Scheme 9).[21] This dihydride intermediate is characterized by a prominent IR band (ν_{CO} = 1960 cm^{-1}) and distinct high-field triplets of doublets in the ^{1}H NMR spectrum at −9.1 ppm ($^2J_{PH}$ = 18 Hz, $^2J_{HH}$ = 3.9 Hz) and −16.5 ppm ($^2J_{PH}$ = 11 Hz, $^2J_{HH}$ = 3.9 Hz). Carbonyl complex **11** shows a strong CO absorption at 1930 cm^{-1}.

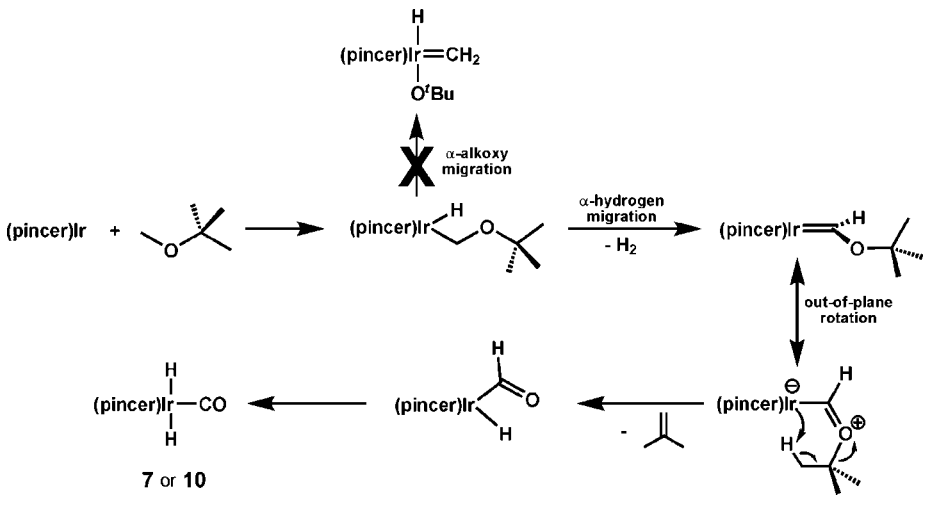
Scheme 9



Alternatively, a second decarbonylation mechanism could also be operative. The Fischer carbene in both systems could undergo a second α-hydrogen migration event to give a Fischer-type alkoxycarbyne (Scheme 10). This step would install the first hydride in place followed by hydrogen delivery from the ^{t}Bu group on the opposite side of the metal center, with elimination of isobutylene.

Terminal alkoxycarbynes are rare and certainly unknown for group 9 metals, but recent work by Templeton and co-workers has shown that for certain tungsten complexes they are indeed isolable species.[22] Protonation of Templeton's alkoxycarbyne leads to formation of a tungsten Fischer carbene, and the carbene proton engages in an agostic interaction with the metal center, suggesting an intermediate situation where the hydrogen is shared by both the metal and the carbene carbon.[22] In the solid state, we find no evidence of an agostic contact in carbene **9**. This is largely because, as mentioned above, the carbene fragment is found in the plane of the pincer framework due to conjugation with the amido group. Such an agostic interaction would be expected to precede the proposed formation of the hydrido-alkoxycarbyne intermediate in Scheme 10. Although in solution the Ir=C bond is indeed fluxional, no evidence for a C−H agostic interaction is observed in the ^{1}H NMR spectrum. Although we cannot rule out this mechanism at this point, on

Scheme 8



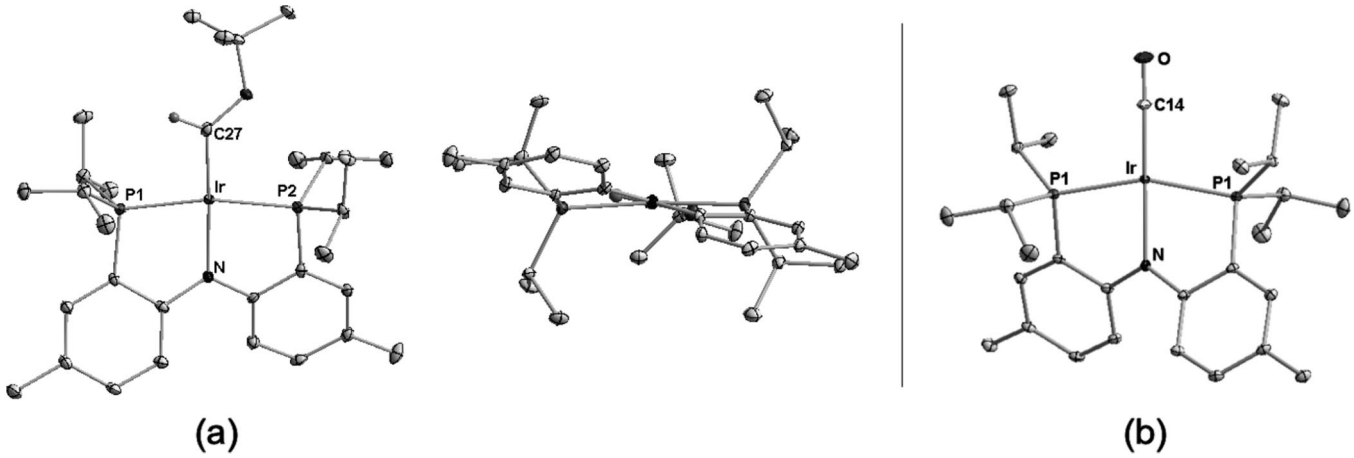
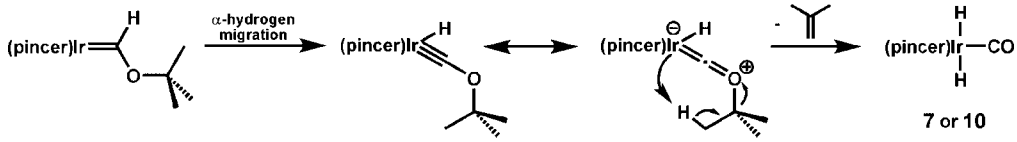


Figure 4. Displacement ellipsoid (35%) representations of (a) (PNP)Ir=C(H)O^{t}Bu (**9**) (top and side views) and (b) *trans*-(PNP)Ir(CO)$(H)_2$ (**10**) with hydrogen atoms and solvent molecules omitted for clarity. Selected bond lengths (Å) and angles (deg), for **9**: Ir−N 2.067(3), Ir−C27 1.882(4), Ir−P1 2.273(1), Ir−P2 2.280(1), P1−Ir−P2 165.80(4), N−Ir−C27 177.4(1). For **10**: Ir−N 2.109(2), Ir−P1 2.3057(6), Ir−C14 1.841(2), N−Ir−C14 180.000, P1−Ir−P1 160.18(2).

Scheme 10



the basis of the available evidence, we favor the path delineated in Scheme 8.

Conclusions

Pincer iridium complexes derived from ligands **1** and **2** are suitable platforms for the C−H activation of methyl *tert*-butyl ether (MTBE). Although anthraphos ligand **1** proved to be unsuitable for the stabilization of MTBE-derived Fischer carbenes, dehydrogenation of $(PNP)IrH_2$ (**8**) in MTBE afforded a square-planar, formally d^8 iridium(I) carbene in high yield as a kinetic product. For both systems, the final thermodynamic product is a *trans*-(pincer)Ir$(H)_2(CO)$ complex arising from thermal decomposition of the corresponding Fischer carbene. A mechanism involving an oxocarbenium intermediate has been proposed on the basis of structural evidence and indirect experiments. In the case of the thermodynamic products **7** and **10** it is unclear at this point why a *trans*-dihydride configuration is preferred. This geometry is at first counterintuitive given the positioning of two strongly *trans*-influencing hydride ligands, but recent results by Milstein, Goldberg, and others suggest this to be a general trend for these architectures.[15a,20,23]

In general, the reactivity of Fischer carbenes stabilized by group 9 metals has received little attention.[17,18] The synthesis of **9** as an unusual example of an Ir(I) carbene opens the possibility of studying a number of reactions at this motif. Simple molecular orbital considerations indicate that complex **9** should possess a HOMO of largely Ir(d_{z^2})-parentage due to its formally d^8, square-planar configuration. The orientation of this orbital perpendicular to the plane of the complex may lead to metal-based reactivity rather than the ligand-based reactivity more commonly discussed for metal-bound carbenes.[1,24] In addition to providing fundamental information and interesting structural possibilities, this work opens new catalytic pathways for hydrocarbon functionalization.

Experimental Section

General Considerations. All operations were performed under inert atmosphere in a nitrogen-filled drybox or by using standard Schlenk techniques unless otherwise specified. All commercial reagents were used without further purification. Complex **11** was synthesized according to a published procedure.[1] Solvents were dried by passage through activated alumina columns[25] and stored in evacuated bombs. NMR spectra were obtained at ambient temperature on a Mercury-300 (299.8 MHz, ^{1}H; 121.4 MHz, ^{31}P) spectrometer. ^{31}P NMR chemical shifts are reported relative to an external standard of 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were carried out at Desert Analytics, Tucson, AZ. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

Notes on the Preparation of 1,8-Difluoroanthraquinone and 1,8-Difluoroanthracene. Although good yielding and reliable protocols for both of these starting materials have been reported,[9] we have also found that they can be readily purified by sublimation under dynamic vacuum (10^{-3} Torr, 1,8-difluoroanthraquinone = 150 °C; 1,8-difluoroanthracene = 100 °C) without the need for chromatographic purification. 1,8-Difluoroanthracene can be further purified by recrystallization from hot methanol followed by cooling at −35 °C.

Synthesis of ^{i}Pr$_2$PSiMe$_3$. This phosphine was prepared according to the method developed by Werner and co-workers[26] with some

(21) The preparation and characterization of complex **11** have been previously reported in ref 1.

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modifications. Under nitrogen, $^{i}Pr_2PH$ (5.00 g, 42.3 mmol) was loaded into a two-neck round-bottom flask fitted with a rubber septum, and the flask was connected to a swivel frit apparatus. The flask was cooled to −78 °C, and THF (30 mL) was vacuum-transferred to the system. At this temperature, *n*-BuLi (31.9 mL, 51 mmol, 1.6 M in hexanes) was added dropwise and the system was allowed to warm to room temperature and stirred for 2 h. During this time a bright yellow solution developed. The system was cooled to −78 °C, chlorotrimethylsilane (7.0 mL, 55 mmol) was added dropwise, and the solution was stirred overnight. The volatiles were removed under vacuum, and pentane (20 mL) was transferred onto the mixture. The LiCl was separated by filtration, and upon removal of the solvent, the product was obtained as a clear, viscous oil (7.6 g, 95%).

Synthesis of $^{i}Pr_2PK$. In a N_2-filled glovebox, freshly sublimed ^{t}BuOK (2.03 g, 18.1 mmol) was dissolved in dry THF (20 mL) and placed into a sealable glass bomb. To this solution was added in one portion $^{i}Pr_2PSiMe_3$ (3.28 g, 17.2 mmol) dissolved in dry THF (20 mL). The bomb containing the homogeneous yellow solution was removed from the glovebox and heated in an oil bath at 70 °C overnight. The resulting orange solution was transferred under nitrogen to a swivel frit apparatus via cannula, and the volatiles were removed in vacuo. Ten milliliters of dry toluene was added to the mixture, followed by 40 mL of pentane, causing the precipitation of solid $^{i}Pr_2PK$. The mixture was stirred for 30 min and filtered. The creamy solid was washed with fresh pentane until the washes became colorless and dried in vacuo (2.06 g, 77%). The ^{1}H NMR spectrum matched those previously reported.[27] The ^{31}P NMR resonance did not match the reported value, as it was recorded in a different solvent. ^{1}H NMR (THF-d_8): δ 2.31 (m, 2H, $-CH(CH_3)_2$), 1.06 (dd, 12H, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 11.4 Hz, $-CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (THF-d_8): δ 21.3 (s).

Synthesis of Anthraphos Ligand 2. 1,8-Difluoroanthracene (1.7 g, 7.94 mmol) was dissolved in dry dioxane (20 mL) and placed in a sealable glass bomb. To this solution was added via cannula at room temperature a solution of $^{i}Pr_2PK$ (2.48 g, 15.87 mmol) in 20 mL of dry THF. The flask was closed, and the resulting red solution was heated at 105 °C for 5 h, then cooled to room temperature. The system was opened to air, the solution was transferred to a round-bottom flask, and the volatiles were removed under vacuum. The solid residue was transferred to a sublimation apparatus and heated to 170 °C under dynamic vacuum (10^{-3} Torr) overnight. Pure ligand deposited as a bright yellow solid on the coldfinger. Although this material is adequate for preparative purposes, it separated as a very fine powder that was difficult to handle. Recrystallization from hot ethanol followed by cooling at −30 °C afforded a crystalline, manageable solid (2.60 g, 80%). Spectral features match those reported in the literature.[28]

Synthesis of Complex 4. $[IrCl(COE)_2]_2$ (164 mg, 0.183 mmol) and **2** (158 mg, 0.365 mmol) were weighed into a 20 mL glass bomb fitted with a Kontes valve and suspended in 8 mL of toluene. The sealed bomb was then placed in an oil bath and the mixture heated at 120 °C overnight. Under nitrogen, the red solution obtained was transferred to a round-bottom flask and the solvent removed under vacuum. In air, pentane was added to the residue and the solid was broken up with a spatula. Filtration through a medium-porosity frit afforded a bright red solid, which was washed with several portions of pentane and dried under high vacuum (203 mg, 83%). This complex is sensitive to air in solution but can be handled as a solid in air. ^{1}H NMR (C_6D_6): δ 7.93 (m, 1H, Ar-*H*), 7.86 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ar-*H*), 7.35−7.29 (m, 2H, Ar-*H*), 7.22 (m, 2H, Ar-*H*), 3.24 (m, 2H, $-CH(CH_3)_2$), 2.56 (m, 2H, $-CH(CH_3)_2$), 1.43 (dd, 6H, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 16 Hz, $-CH(CH_3)_2$), 1.08 (dd, 6H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 13 Hz, $-CH(CH_3)_2$), 1.01 (dd, 6H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 17 Hz, $-CH(CH_3)_2$), 0.85 (dd, 6H, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 17 Hz, $-CH(CH_3)_2$), −35.9 (t, 1H, $^2J_{PH}$ = 12 Hz, Ir-*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 61.1 (s). Anal. Calc for $C_{26}H_{36}ClIrP_2$: C, 48.93; H, 5.29. Found: C, 48.76; H, 5.54.

Characterization of Complex 5 and Isolation of Methyl Iodide Derivative 6. In a N_2-filled glovebox, a 50 mL round-bottom flask was charged with a mixture of **4** (150 mg, 0.216 mmol), ^{t}BuONa (23 mg, 0.24 mmol), and 15 mL of benzene. The solution was stirred under nitrogen for 3 h at room temperature, during which time a dark green color developed. ^{1}H and ^{31}P NMR as well as IR analysis of this mixture indicates the presence of a single species, assigned as the monomeric dinitrogen complex **5**. ^{1}H NMR (CD_2Cl_2): δ 7.96−7.94 (m, 2H, Ar-*H*), 7.92 (s, 1H, Ar-*H*), 7.65−7.60 (m, 2H, Ar-*H*), 7.42−7.37 (m, 2H, Ar-*H*), 2.82 (m, 4H, $-CH(CH_3)_2$), 1.32 (dd, 12H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 15.7 Hz, $-CH(CH_3)_2$), 1.24 (dd, 12H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 14.5 Hz, $-CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 64 (s). IR (C_6H_6, KBr, cm^{-1}) $\nu(N_2)$: 2096.

To the above solution containing **5** was added MeI (20 μL, 0.32 mmol), causing an immediate color change to red-purple. The solution was stirred at room temperature for 1 h, and the volatiles were removed under vacuum. The solid residue was dissolved in 15 mL of CH_2Cl_2 and filtered through Celite. The solvent was removed under high vacuum, and the solid residue was triturated with pentane (15 mL) and filtered to afford **6** (154 mg, 96%). This material is of sufficient quality for preparative purposes. Analytically pure material can be obtained by recrystallization from toluene at −35 °C. ^{1}H NMR (CD_2Cl_2): δ 8.14 (m, 1H, Ar-*H*), 8.12 (s, 1H, Ar-*H*), 8.09 (s, 1H, Ar-*H*), 7.77−7.72 (m, 2H, Ar-*H*), 7.54−7.49 (m, 2H, Ar-*H*), 3.38−3.26 (m, 2H, $-CH(CH_3)_2$), 3.22−3.13 (m, 2H, $-CH(CH_3)_2$), 1.81 (dd, 6H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 15.1 Hz, $-CH(CH_3)_2$), 1.37 (t, 3H, $^3J_{PH}$ = 6.0 Hz, Ir-*Me*), 1.25 (dd, overlap, 12H, $-CH(CH_3)_2$), 0.62 (dd, 6H, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 16.2 Hz, $-CH(CH_3)_2$).$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.6 (s). Anal. Calc for $C_{27}H_{38}IIrP_2$: C, 43.61; H, 5.15. Found: C, 43.76; H, 5.38.

Synthesis of Complex 7. In a N_2-filled glovebox, **4** (120 mg, 0.188 mmol) and ^{t}BuONa (22 mg, 0.23 mmol, 1.2 equiv) were weighed into a 20 mL glass bomb. The system was fully evacuated and refilled with argon. The process was repeated twice, and the bomb was left under full vacuum and cooled to −78 °C. Dry, N_2-free methyl *tert*-butyl ether (ca. 10 mL) was condensed onto the solids, and the system was closed under vacuum. The solution was heated to 70 °C for 2.5 h, causing a brown color to develop. The volatiles were removed under vacuum, and the resulting solid residue was dissolved in CH_2Cl_2 (10 mL) and filtered through Celite. The solvent was removed under vacuum and the mixture triturated with pentane. The supernatant was decanted, yielding an orange powder, which was dried under vacuum (101 mg, 85%). ^{1}H NMR (C_6D_6): δ 7.91 (s, 1H, Ar-*H*), 7.85−7.81 (m, 2H, Ar-*H*), 7.27−7.18 (m, 4H, Ar-*H*), 2.08 (m, 4H, $-CH(CH_3)_2$), 1.27 (dd, 12H, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 17 Hz, $-CH(CH_3)_2$), 0.90 (dd, 12H, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 16 Hz, $-CH(CH_3)_2$), −9.45 (t, 2H, $^2J_{PH}$ = 15 Hz, Ir-*H*).$^{13}C\{^1H\}$ NMR (C_6D_6): 149.3 (s, Ir-*CO*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 66.1 (s). IR (THF, KBr, cm^{-1}) ν(CO): 1989. Anal. Calc for $C_{27}H_{37}IrOP_2$: C, 51.33; H, 5.90. Found: C, 49.46; H, 5.56. HRMS (FAB+): found *m*/*z* 631.1876 for (M + H) − 2H, calcd for $C_{27}H_{37}IrOP_2$ 631.1870.

Synthesis of Complex 9. To a red solution of (PNP)IrH_2 (**8**) (175.8 mg, 0.2823 mmol) in methyl *tert*-butyl ether (6 mL) was added norbornene (49.0 mg, 0.520 mmol) in methyl *tert*-butyl ether (6 mL). After several hours, the solution gradually darkened and gained a purple hue. After 18 h, volatiles were removed in vacuo to yield a dark red film, which was redissolved in pentane (10 mL), filtered, and dried to afford **9** as a purple solid. Analytically pure crystals of **9** were obtained by slow evaporation of pentane from a concentrated solution at −35 °C (107.0 mg, 54%). Compound **9**

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was stored at −35 °C to prevent decomposition. ^{1}H NMR (C_6D_6): δ 13.78 (t, $^3J_{HP}$ = 7.5 Hz, 1H, −C(*H*)O^{t}Bu), 7.80 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-*H*), 7.17 (s, 2H, Ar-*H*), 6.82 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-*H*), 2.62 (m, 4H, −C*H*(CH_3)$_2$), 2.24 (s, 6H, Ar-C*H*$_3$), 1.30 (m, 12H, CH(C*H*$_3$)$_2$), 1.21 (m, 12H, −CH(C*H*$_3$)$_2$), 1.10 (s, 9H, −C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 210.0 (Ir=*C*HO^{t}Bu). ^{31}P{^{1}H} NMR (C_6D_6): δ 40.8 (s). Anal. Calcd for $C_{31}H_{50}IrNOP_2$: C, 52.67; H, 7.13; N, 1.98. Found: C, 52.74; H, 7.05; N, 2.04.

Synthesis of Complex 10. A dark purple solution of **9** (20.0 mg, 0.0283 mmol) in C_6D_6 (600 μL) was heated at 80 °C in a sealed NMR tube for 48 h, causing a color change to dark golden. Volatiles were removed in vacuo, leaving a golden film. **10** was isolated in analytically pure crystalline form as yellow needles by slow evaporation of pentane at −35 °C (13.7 mg, 71%). ^{1}H NMR (C_6D_6): δ 7.68 (d, $^3J_{HH}$ = 8.7 Hz, 2H, Ar-*H*), 6.86 (s, 2H, Ar-*H*), 6.70 (d, $^3J_{HH}$ = 8.7 Hz, 2H, Ar-*H*), 2.18 (s, 6H, Ar-C*H*$_3$), 2.02 (m, 12H, −CH(C*H*$_3$)$_2$), 1.21 (m, 12H, −CH(C*H*$_3$)$_2$), 1.07 (m, 12H, −CH(C*H*$_3$)$_2$), −7.25 (t, $^3J_{PH}$ = 15.3 Hz, 2H, Ir-*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 174.6 (t, $^2J_{PC}$ = 7 Hz, Ir-*C*O). ^{31}P{^{1}H} NMR (C_6D_6): δ 51.2 (s). IR (THF, KBr, cm^{-1}) ν(CO): 1990. Anal. Calcd for $C_{27}H_{42}IrNOP_2$: C, 49.83; H, 6.50; N, 2.15. Found: C, 50.23; H, 6.73; N, 2.03.

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Supporting Information Available: Crystallographic details for complexes **6**, **7**, **9**, and **10** are provided in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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