cyclohexyl) and 2.6573 (5) Å for the formally double bond in $(PCy_2)_2Re(\mu\text{-}PCy_2)_2Ir(PMe_3)_2$.[23] These species are rather chemically different from 3. The Re–Ir distance of 2.8081 (6) Å for 3 (not corrected for thermal motion[24]) is more comparable to the Ir–Ir single covalent bond in $[Cp^*Ir(CO)_2]_2^{2+}$ (2.8349 (12) Å).[25]

The carbonyl groups (C(3)–O(3), C(4)–O(4)) can be described as primarily bound to the Re atom and semibridging to the Ir atom. This is a feature that has been previously observed in the structures of two related molecules of the type (arene)(CO)M(μ_2-CO)$_2$M′(CO)(arene′), but in each previous case, M has been a 3d metal bound to a 4d metal M′. Here we see the same structural feature occuring where both metals are 5d metals. The previous examples are $Cp(CO)Mn(\mu_2\text{-}CO)_2Rh(CO)Cp^*$[8] and ($\eta^6$-$C_6H_6$)(CO)Cr($\mu_2$-CO)$_2$Rh(CO)Cp*.[6h] While the reaction can be envisaged to proceed by displacement of the weakly bonded THF ligand from $CpRe(CO)_2(THF)$ by the basic $Cp^*Ir(CO)_2$ with the formation of a dative bond from Ir to Re in $Cp(CO)_2Re \leftarrow Ir(CO)_2Cp^*$, clearly CO rearrangement occurs and the structure of 3 that results may be visualized to be built from a dative bond[6l] from an 18-electron $CpRe(CO)_3$ moiety to the 16-electron fragment Cp*Ir(CO), assisted by return of electron density from Ir via the semibridging CO groups in order to mitigate the charge imbalance, as proposed by Cotton for the similar situation in $Cp_2V_2(CO)_3(\mu_2\text{-}CO)_2$.[26] Since this structural pattern is now so well established for this type of binuclear complex, there is every reason to expect that complexes 1 and 2 also are structurally analogous to 3 and also possess semibridging CO groups as illustrated. In fact, complex 2 was also investigated by single-crystal X-ray diffraction, but the structure solution was abandoned at a point where it was clear that there was severe disorder between the rhenium and iridium atom positions and their associated carbonyl and η^5-C_5Me_5 groups, in a molecular structure similar to that of 3.

Thus, these structures may be compared directly with the structures of the corresponding homometallic analogues $[Cp^*M(CO)_2]_2$ (M = Fe, Ru, Os). Although no crystallographic determinations appear to have been reported for these, the IR spectrum in each case displays a single ν(CO) absorption at 1908–1922 cm^{-1} for terminal carbonyls and a single ν(CO) absorption at 1707–1745 cm^{-1} for bridging carbonyls. Such a simple spectrum is consistent with a trans structure, with both terminal and bridging CO groups, and inversion symmetry.

Acknowledgment. This work was supported by NSERC Canada. We are grateful to Johnson-Matthey Co. for a generous loan of iridium compounds.

Supplementary Material Available: Tables of full crystallographic data (Table SI), hydrogen atom coordinates and isotropic thermal parameters (Table SII), and anisotropic thermal parameters for Ir and Re (Table SIII) (3 pages); a table of observed and calculated structure factors for 3 (7 pages). Ordering information is given on any current masthead page.

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Formation of Carbon–Hydrogen and Oxygen–Hydrogen Bonds at Iridium Centers: Addition of H_2 and HCl to *trans*-$RIr(CO)L_2$ (R = Me, OMe; L = PPh_3, P(*p*-tolyl)$_3$)

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Received February 7, 1990

Reaction of *trans*-$RIr(CO)L_2$ with HX (R = Me, L = P(*p*-tolyl)$_3$, X = H, Cl; R = OMe, L = PPh_3, X = H; R = OMe, L = P(*p*-tolyl)$_3$, X = Cl results in RH and $HIr(X)_2(CO)L_2$. Low-temperature NMR spectra (^1H and ^{31}P) show that these reactions occur through oxidative-addition, reductive-elimination sequences. A normal deuterium isotope effect is observed ($k_H/k_D = 1.4$). Formation of the carbon (sp^3)–hydrogen bond occurs more readily than formation of the carbon (sp^2)–hydrogen bond or the oxygen–hydrogen bond. The nature of the hydrogen source (HX; X = H, Cl) does not significantly affect CH_4 formation but is significant for CH_3OH formation. Considering the geometric and product differences, however, the three types of bonds are formed with remarkably similar barriers.

Formation of bonds to hydrogen is central in many catalytic reactions.[1] Although the ready formation of carbon–hydrogen bonds initially limited modeling these reactions, there have now appeared several studies of C–H bond formation.[2] Formation of O–H bonds has received much less attention.[3]

Table I. NMR Data (ppm) for $RIr(H)(Cl)(CO)L_2$

	^1H			
R	Me(*p*-tolyl)	R	H^-	$^{31}P\{^1H\}$
Me	2.25 (s)	–0.04 (t)	–18.7 (t)	–0.05 (s)
Ph	2.25 (s)		–17.8 (t)	–1.0 (s)
OMe	2.25 (s)	3.2 (s)	–15.7 (t)	–3.0 (s)
Cl	2.25 (s)		–16.2 (t)	–2.7 (s)

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For C–H bond formation both intramolecular and intermolecular reactions have been observed.[2] Several theoretical studies have examined effects of geometry, phosphine ligands, and possible reaction coordinates.[2b,4] Rate changes with the alkyl group have shown the order Ph > Et > Me > C_3H_5 for elimination from *cis*-Pt(H)(R)$(PPh_3)_2$.[2d] This order does not appear to be general, since elimination from Pt(H)(R)$(PEt_3)_2Cl_2$ shows CH_4 elimination to be more rapid than C_6H_6 elimination.[5] Elimination of a C–H bond following oxidative addition of H_2 is not as common. We reported that *trans*-MeIr(CO)$(PPh_3)_2$ reacts with H_2 to form CH_4 and H_3Ir(CO)$(PPh_3)_2$.[6] Low solubility precluded a more detailed analysis. Sweany and Russell have reported that CH_4 is eliminated when $CH_3Co(CO)_4$ is irradiated in the presence of H_2 in an argon matrix.[7]

Examples of hydrogenolysis of metal–alkoxide bonds are limited. Goeden and Caulton reported that reaction of $[Cu(O\text{-}t\text{-}Bu)]_4$ with H_2 in the presence of phosphine gives *t*-BuOH and $[HCuP]_6$.[3] These authors pointed out that formally hydrogenolysis of a metal alkoxide involves heterolytic splitting of the hydrogen.[3] Whether this is mechanistically significant has not yet been ascertained.

In this paper we report the reactions of H_2 and HCl with the complexes *trans*-RIr(CO)L_2 (R = Me, Ph, OMe; L = PPh_3, P(*p*-tolyl)$_3$). These reactions, which result in formation of C–H and O–H bonds, have been examined by low-temperature ^{31}P and ^1H NMR spectroscopies to establish the intermediates in these bond-forming reactions.

Experimental Section

Iridium trichloride was purchased or borrowed from Johnson Matthey, Inc. Gases (H_2, HCl, and HI) were purchased from Matheson. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer utilizing NaCl solution cells or a KBr disk. ^1H NMR and ^{31}P NMR spectra were recorded on a Varian EM-390, a JEOL FX-90Q, a Varian Gemini-300, or a Varian VXR-400 spectrometer. Gas chromatography was performed with a Varian 2440-FID gas chromatograph. All syntheses were accomplished under an argon or nitrogen atmosphere (unless noted otherwise), with use of an argon-filled glovebox, Schlenk, or vacuum line techniques.

The complexes *trans*-Ir(CO)(P(*p*-tolyl)$_3$)$_2$Cl, *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$, and *trans*-MeOIr(CO)(P(*p*-tolyl)$_3$)$_2$ were prepared by previously described procedures.[8]

Reaction of Hydrogen with *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$. In the inert-atmosphere glovebox, *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ (0.010 g) was added to an NMR tube equipped with a vacuum adaptor. The tube was removed from the box, placed on a vacuum line, and evacuated. Deuteriomethylene chloride (1 mL) was vacuum-distilled into the NMR tube and warmed to allow dissolution of the *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$. The sample was frozen in N_2(l) and H_2 added at 1 atm. The NMR tube was flame-sealed and monitored in the NMR probe from −60 °C to room temperature. MeIr(H)$_2$(CO)(P(*p*-tolyl)$_3$)$_2$ with the hydride at −10.8 (m) ppm and the methyl at −0.6 (t) ppm was the only intermediate observed.

Reaction of H_2 with *trans*-MeOIr(CO)$(PPh_3)_2$. *trans*-MeOIr(CO)$(PPh_3)_2$ (0.25 g) was dissolved in 25 mL of benzene under an inert atmosphere and the solution transferred to a pressure bottle equipped with a stirbar. The pressure bottle was sealed under an inert atmosphere, flushed, and charged with 5 atm of H_2 gas. After 14 h an IR spectrum of the solution showed approximately 50% reaction with starting material still evident. The reactor was filled with 5 atm of H_2 gas, and the reaction was allowed to continue for 5 days, after which an IR spectrum was taken in benzene, which showed sharp peaks at 2080 and 1776 cm^{-1}. Broad peaks were evident between 1950 and 1980 cm^{-1}. The solvent was removed, and the resulting solid was redissolved in cyclohexane. The IR spectrum showed absorptions at 2085 (sharp), 2050 (w, sharp), 1993 (w, sharp), 1975 (vs), 1943 (s, sharp), and 1782 (w, br) cm^{-1}. Since a mixture of compounds was evident, the solid was redissolved in benzene and the solution placed under H_2 again and allowed to react at 65 °C. The IR spectrum after 14 h still showed a mixture of products.

Reaction of H_2 with *trans*-(*n*-PrO)Ir(CO)$(PPh_3)_2$. *trans*-(*n*-PrO)Ir(CO)$(PPh_3)_2$ (0.25 g) was suspended in 30 mL of cyclohexane and the excess solid filtered off. The saturated solution was placed in an autoclave reactor under an inert atmosphere and brought out of the drybox. The reactor was pressurized with 500 psi of H_2. The reaction was allowed to proceed at room temperature and was monitored by IR spectroscopy. The IR spectrum after $^1/_2$, 2, 6, 8, and 20 h showed a mixture with peaks at 2075, 1997, 1950, and 1808 cm^{-1} in cyclohexane. The only noticeable change over the time intervals appeared to be a decrease in starting material (1951 cm^{-1}) and an increase in intensity of the other peaks. After 20 h, the mixture was heated to 75 °C and allowed to react for 3 h. An IR spectrum after 3 h in cyclohexane showed the clean formation of H_3Ir(CO)$(PPh_3)_2$[9] with peaks at 2085 (s), 1974 (s), and 1782 (br, w) cm^{-1}.

Reaction of H_2 with *trans*-ROIr(CO)$(PPh_3)_2$ Where R = H, *t*-Bu, and Ph. In a typical experiment, 0.05 g of the iridium complex in 20 mL of benzene was placed in the pressure bottle under an inert atmosphere, the bottle was flushed and charged with 5 atm of H_2, and the solution was stirred in a 70 °C oil bath for 3 days, after which the solvent was removed and an IR spectrum of the solid in cyclohexane showed absorptions at 2085 (s), 1974 (s), and 1782 (m, br) cm^{-1} consistent with formation of H_3Ir(CO)$(PPh_3)_2$. For R = Ph, formation of phenol was detected by IR spectroscopy (3610 cm^{-1}).

Reaction of D_2 with *trans*-PhOIr(CO)$(PPh_3)_2$. In 25 mL of cyclohexane was placed 0.5 g of *trans*-PhOIr(CO)$(PPh_3)_2$ in a pressure bottle under an inert atmosphere. Five atmospheres of deuterium was introduced into the pressure bottle and the bottle flushed. The reaction mixture under deuterium was stirred for 24 h at 75 °C, after which an IR spectrum of the solution in cyclohexane showed a band at 2010 cm^{-1} (vs). The solvent was removed in vacuo, and an IR spectrum of the solid in KBr showed peaks at 1992 (m) and 1982 cm^{-1} (vs), consistent with the formulation D_3Ir(CO)$(PPh_3)_2$.[9]

Reaction of Hydrogen Chloride with *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$. In an inert-atmosphere glovebox, *trans*-MeIr-

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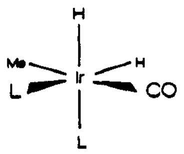

Figure 1. Geometry established for $MeIr(H)_2(CO)(P(p\text{-tolyl})_3)_2$ by NMR spectroscopy ($L = P(p\text{-tolyl})_3$).

$(CO)(P(p\text{-tolyl})_3)_2$ (0.010 g) was added to an NMR tube equipped with a vacuum adaptor. The tube was removed from the box, placed on a vacuum line, and evacuated. CD_2Cl_2 (1 mL) was vacuum-distilled into the NMR tube and warmed to allow dissolution of the *trans*-$MeIr(CO)(P(p\text{-tolyl})_3)_2$. The sample was frozen in $N_2(l)$, and 2×10^{-4} mol of HCl(g) was added. The NMR tube was flame-sealed and monitored in the NMR probe from −80 °C to room temperature. The same procedure was used for examination of the reaction between HCl and *trans*-$MeOIr(CO)(P(p\text{-tolyl})_3)_2$ and *trans*-$PhIr(CO)(P(p\text{-tolyl})_3)_2$.

Kinetics Studies. Kinetic examinations of the reductive elimination of RH from $Ir(R)(H)(CO)(P(p\text{-tolyl})_3)_2Cl$ were accomplished by ^{31}P NMR spectroscopy. In an inert-atmosphere glovebox, *trans*-$RIr(CO)(P(p\text{-tolyl})_3)_2$ (0.010 g; R = Me, Ph) was added to an NMR tube equipped with a vacuum adaptor. The tube was removed from the glove box, placed on a vacuum line, and evacuated. CD_2Cl_2 (1 mL) was vacuum-distilled onto the sample. The tube was warmed to allow dissolution to occur and then refrozen with $N_2(l)$. HCl (or DCl) (2×10^{-4} mol) was added and the tube flame-sealed. The reaction was monitored at the appropriate temperature (R = Me, −10 °C; R = Ph, 18 °C) until completion. The disappearance of $Ir(R)(H)(CO)(P(p\text{-tolyl})_3)_2Cl$ and appearance of $Ir(H)(CO)(P(p\text{-tolyl})_3)_2Cl_2$ were monitored by integration of their ^{31}P resonances (listed in Table I). The reactions were first order in $Ir(H)(R)(CO)(P(p\text{-tolyl})_3)_2Cl$ with the rate constants listed in Table II.

Results and Discussion

The reactions described in this paper can be represented as in reaction 1. Each of these reactions will be described separately.

$$trans\text{-}RIr(CO)L_2 + HX \rightarrow HIr(X)_2(CO)L_2 + RH \quad (1)$$

$$HX = H_2, HCl; R = Me, Ph, OMe; \quad L = P(p\text{-tolyl})_3, PPh_3$$

Reaction of H_2 with *trans*-$MeIr(CO)(P(p\text{-tolyl})_3)_2$. The reaction of H_2 with *trans*-$MeIr(CO)(P(p\text{-tolyl})_3)_2$ at room temperature results in CH_4 and $H_3Ir(CO)(P(p\text{-tolyl})_3)_2$. $H_3Ir(CO)(P(p\text{-tolyl})_3)_2$ is a mixture of the facial and the meridional isomers.[9] Low-temperature ^1H NMR examination shows formation of $MeIr(H)_2(CO)(P(p\text{-tolyl})_3)_2$ with the phosphines trans to the hydrides as shown in Figure 1. This corresponds to the perpendicular adduct in Crabtree's terminology,[10] clearly shown by the AA′XX′ pattern centered at −10.8 ppm. This stereochemistry is maintained until CH_4 elimination occurs at ~10 °C.

Reaction of H_2 with *trans*-$ROIr(CO)(PPh_3)_2$. Addition and/or elimination reactions of the alkoxy complexes *trans*-$ROIr(CO)(PPh_3)_2$ (R = Me, Ph, *n*-Pr, *t*-Bu) require heating:

$$trans\text{-}ROIr(CO)(PPh_3)_2 + H_2 \xrightarrow[5\text{ atm}]{70\text{ °C}} H_3Ir(CO)(PPh_3)_2 + ROH \quad (2)$$

These reactions were clean for alkoxy groups lacking a hydrogen β to the metal. Competing β-elimination led to more complicated product mixtures.[11] The X group in *trans*-$Ir(CO)L_2X$ is very important for oxidative addition of H_2,[12] and the alkoxy group is not a sufficiently good donor to readily activate H_2. We see no evidence for intermediates of H_2 addition. We do note that reaction 2 corresponds formally to a heterolytic splitting of H_2, with H^+ forming the alcohol and H^- on the metal.[3] Hydrogenolysis of a metal–alkoxy bond has been reported for a copper alkoxide.[3] However, on the basis of the known facility of Ir(I) complexes for activation of H_2 through oxidative addition and the results for reaction with HCl (to be described in the following section) an oxidative addition of H_2 and reductive elimination with formation of the oxygen–hydrogen bond seems the most likely mechanism.

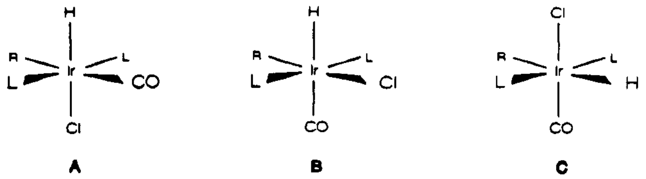

Figure 2. Geometries suggested for $RIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ formed by low-temperature oxidative addition of HCl to *trans*-$RIr(CO)(P(p\text{-tolyl})_3)_2$ ($L = P(p\text{-tolyl})_3$).

Table II. Rate Constants for Reductive Elimination of RH from $Ir(R)(H)(CO)(P(p\text{-tolyl})_3)_2Cl$

product	k, s^{-1}	temp, °C
CH_4	$(1.8 \pm 0.4) \times 10^{-4}$	−10
C_6H_6	$(9.7 \pm 0.6) \times 10^{-7}$	18
CH_3D	$(1.3 \pm 0.2) \times 10^{-4}$	−10

HCl Addition to *trans*-$RIr(CO)(P(p\text{-tolyl})_3)_2$ (R = Me, Ph). Addition of HCl to *trans*-$RIr(CO)(P(p\text{-tolyl})_3)_2$ leads to elimination of RH (R = Me, Ph):

$$trans\text{-}RIr(CO)(P(p\text{-tolyl})_3)_2 + 2HCl \rightarrow HIr(CO)(P(p\text{-tolyl})_3)_2Cl_2 + RH \quad (3)$$

$$R = Me, Ph$$

The iridium product is identical with the product of addition of HCl to *trans*-$Ir(CO)(P(p\text{-tolyl})_3)_2Cl$. When HCl is added at −78 °C and the reaction followed by NMR spectroscopy an intermediate is observed. For R = Me the NMR spectral characteristics of the intermediate (Ir–Me, −0.04 (t) ppm, $J_{P-H} = 7.2$ Hz; Ir–H, −18.7 (t) ppm, $J_{P-H} = 17.2$ Hz; Ir–P ($^{31}P\{^1H\}$), −0.05 (s) ppm) are consistent with the HCl oxidative-addition product, $CH_3Ir(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$. When the two $P(p\text{-tolyl})_3$ ligands are kept trans as required by the NMR spectral data, the three isomers shown in Figure 2 are possible. Oxidative addition of HCl in nonpolar solvents has been previously demonstrated to proceed stereospecifically cis.[13] Thus, A is not likely as the geometry for $RIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$. B and C both involve a cis addition of HCl. Usually the chemical shift of a hydride is significantly affected by the trans ligand. As shown in Table I, the chemical shifts of the hydride of $RIr(H)(Cl)(CO)L_2$ are relatively unaffected by the R group. Thus, we favor B as the geometry for

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[16] Addition of HCl to *trans*-$Ir(CO)(I)(P(p\text{-tolyl})_3)_2$ at low temperature (−70 °C) leads to four isomers. These isomers do not interconvert as the temperature is raised to room temperature. After the mixture is stored overnight at room temperature, one isomer is greatly increased while the other three are decreased, suggesting that isomerization does occur at room temperature.

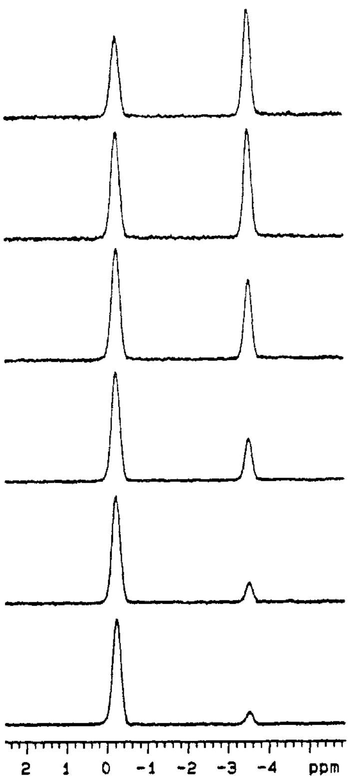

Figure 3. Sample ^{31}P NMR spectral results used for kinetic analysis. These spectra were recorded at -10 °C for the conversion of $MeIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ (-0.2 ppm) to $HIr(Cl)_2(CO)(P(p\text{-tolyl})_3)_2$ (-3.6 ppm). At completion the -0.2 ppm resonance is gone and only $HIr(Cl)_2(CO)(P(p\text{-tolyl})_3)_2$ is observed.

$RIr(H)(Cl)(P(p\text{-tolyl})_3)_2$. We see no evidence for any other isomer in the oxidative addition or during the subsequent warmup. At 0 °C we begin to see the product of a methane reductive elimination followed by addition of a second HCl, $HIr(CO)(P(p\text{-tolyl})_3)_2Cl_2$. In the sealed NMR tube we see the resonances of both HCl (1.4 ppm) and CH_4 (0.06 ppm). Addition to the phenyl complex occurs analogously, through the intermediate $PhIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$. For both R = Me and Ph the reactions are quantitative. Only $HIr(CO)(P(p\text{-tolyl})_3)_2Cl_2$, RH, and HCl are observed in the final solution.

Kinetic studies of RH elimination from $RIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ were evaluated from ^{31}P NMR data. Spectral changes are illustrated in Figure 3. The rates were first order in iridium complex with rate constants of $1.9 \times 10^{-4}\ s^{-1}$ at -10 °C for R = Me and $9.7 \times 10^{-7}\ s^{-1}$ at 18 °C for R = Ph. Thus, elimination of CH_4 occurs about 10^3 more rapidly than elimination of C_6H_6. A normal deuterium isotope effect of $k_H/k_D = 1.4$ was observed for CH_4 elimination.

HCl Addition to *trans*-MeOIr(CO)(P(*p*-tolyl)$_3$)$_2$. Reaction of HCl with *trans*-$MeOIr(CO)(P(p\text{-tolyl})_3)_2$ occurs cleanly to form MeOH and $HIr(CO)(P(p\text{-tolyl})_3)_2Cl_2$:

$$trans\text{-}MeOIr(CO)(P(p\text{-tolyl})_3)_2 + HCl \rightarrow HIr(CO)(P(p\text{-tolyl})_3)_2Cl_2 + MeOH \quad (4)$$

We considered a direct protonation of the oxygen of the methoxy as quite likely; however, addition of HCl at -78 °C, studied by NMR spectroscopy showed an oxidative-addition, reductive-elimination mechanism completely analogous to that for the methyl and phenyl complexes. At -70 °C the intermediate hydride $MeOIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ (Ir-OMe, 3.2 (s) ppm; Ir-H, -15.7 (t) ppm, J_{P-H} = 6.0 Hz; ^{31}P (proton decoupled), Ir-P ($^{31}P\{^1H\}$, -3.0 (s) ppm) becomes apparent and remains as the sole intermediate observable until the elimination of CH_3OH occurs at 20 °C. We cannot exclude a mechanism that involves protonation of the methoxy ligand of $MeOIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$, but we see no evidence for such a mechanism. The methoxy signal in the ^1H NMR spectrum remains unchanged, and the free HCl signal is not broadened or shifted from that for the methyl and phenyl analogues. Indeed the similarity to the reactions of HCl with the methyl and phenyl analogues strongly supports an oxidative-addition, reductive-elimination reaction in formation of MeOH from *trans*-$MeOIr(CO)(P(p\text{-tolyl})_3)_2$ and HCl. The similarity of ^{31}P chemical shifts for $MeOIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ and $HIr(CO)(P(p\text{-tolyl})_3)_2Cl_2$ prohibited a kinetic study.

Bond Formation. There have been a number of studies of carbon-hydrogen bond formation, yet simple questions such as the relative ease of elimination of benzene from a phenyl hydride versus the elimination of methane from a methyl hydride are not fully understood. Several studies of reductive elimination have shown the importance of dissociation of a phosphine ligand.[2] In the studies reported in this paper, there is no evidence for dissociation of a ligand being involved in the reductive elimination. Free phosphine is not observed, and the coupling is retained. The rate of conversion from $CH_3Ir(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ to $HIr(Cl)_2(CO)(P(p\text{-tolyl})_3)_2$ and CH_4 is decreased by about a factor of 2 ($k_{obs} = 9 \times 10^{-5}\ s^{-1}$) by the presence of excess (1:1 ratio) $P(p\text{-tolyl})_3$. A similar inhibition is observed when Et_2O is present or if the amount of HCl is halved. It is most likely that these slower rates in the presence of excess phosphine arise from interactions of the phosphine with HCl and not from inhibition of a possible phosphine dissociation. The similar complex $HIr(Cl)_2(CO)(P(p\text{-tolyl})_3)_2$ undergoes exchange with $PMePh_2$ only slowly (over a 24-h period) at room temperature. Thus, it seems likely that the six-coordinate complex $CH_3Ir(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ is undergoing reductive elimination to a four-coordinate complex. Such a scheme is also most consistent with the observation of $HIr(CO)(P(p\text{-tolyl})_3)_2Cl_2$ as the only product.

The reductive-elimination reaction appears to be relatively insensitive to the hydrogen source and the nature of R. Both $CH_3Ir(H)_2(CO)(P(p\text{-tolyl})_3)_2$ and $CH_3Ir(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ eliminate methane at approximately 0 °C. This is despite the rather different geometries for these complexes as shown in Figures 1 and 2B. Theoretical studies have provided a rationale for more ready elimination of groups with an sp^2 carbon than for those with an sp^3 carbon.[17] Literature reports on the reductive elimination of C_6H_6 and CH_4 provide no consensus on the relative rates. Our results on $RIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ show that CH_4 is eliminated more readily than C_6H_6 by a factor of 1000. Feher and Jones have suggested that reductive elimination of CH_4 and C_6H_6 from a rhodium complex occurs with approximately equal energy barriers because of the η^2 coordination of the arene to the rhodium.[14] In the absence of η^2 coordination the barrier to elimination of C_6H_6 would be 7 kcal/mol greater than the barrier for elimination of CH_4.[14] Such a barrier difference would lead to a ratio of rate constants ($k(CH_4)/k(C_6H_6)$) of 1×10^5. Whether the ratio of rate constants of 1×10^3 for the iridium system arises from weaker interaction (η^2) to the benzene, possible interaction of CH_4, or another source is unclear. There is no evidence for interaction of CH_4 with *trans*-$Ir(CO)(P(p\text{-tolyl})_3)_2Cl$ (the product of reductive elimination). Olefins do interact with *trans*-$Ir(CO)(P(p\text{-tolyl})_3)_2Cl$, although unactivated olefins have a

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[17] Low, J. J.; Goddard, W. A., III. *Organometallics* **1986**, *5*, 609.

small binding constant.[15] However, either of these interactions could provide a 3-4 kcal/mol transition-state interaction important to the greater facility for CH_4 elimination than for C_6H_6. The previous two studies that compare reductive elimination of CH_4 and C_6H_6 offer some evidence supporting the Feher and Jones postulate of η^2-C_6H_6 coordination.[14] For elimination from $Pt(R)(H)(PEt_3)_2Cl_2$, methane was eliminated more readily than benzene.[5] In this case the Pt(II) complex $Pt(PEt_3)_2Cl_2$ would probably not bind C_6H_6 strongly. However, for elimination from *cis*-$Pt(R)(H)(PPh_3)_2$, where the Pt(0) complex should bind strongly to C_6H_6, reductive elimination of benzene is favored over that of CH_4.[2d] Elimination of CH_3OH by formation of an oxygen-hydrogen bond from $CH_3OIr(H)(Cl)(CO)(P(p\text{-tolyl})_3)_2$ occurs at approximately the same temperature as elimination of CH_4 and C_6H_6. There is very little literature precedence for O-H bond formation. The relative insensitivity of the reductive-elimination reactions of RH to R or to the structure of the six-coordinate complex suggests that the activation barrier is dominated by a process that is independent of electronic factors. Two possibilities were considered for such a process: (1) a bending of the Ir-H bond for incipient formation of the bond from hydrogen to R or (2) an isomerization of the six-coordinate iridium complex. Either process would be consistent with the deuterium isotope effect. Isomerization of $Ir(CO)(Cl)(I)(H)(P(p\text{-tolyl})_3)_2$ occurs overnight at room temperature (under conditions similar to those of phosphine exchange).[16] Thus, the isomerization is considerably slower than the reductive-elimination reactions. Also, the dihydrogen addition product does not require isomerization before elimination; the most likely geometry for $Ir(CO)(Me)(H)(Cl)(P(p\text{-tolyl})_3)_2$ (Figure 2B) also does not require isomerization.

The most likely activation process for elimination of RH that is not very sensitive to R or other groups on iridium is a bending of the Ir-H bond. For reductive elimination the Ir-H bond bends to move into a position to interact with R. This bend should be relatively unaffected by the groups bound to iridium. Low and Goddard have calculated that reductive elimination of CH_4 from Pt(II) involves a change of the H-Pt-CH_3 angle from 90° in the ground state to 51° for the transition state.[17] Thus, a significant component of Ir-H bond bending to the activation energy has precedent.

Kinetic deuterium isotope effects have been reported for carbon-hydrogen bond formation for several complexes with values ranging from 0.7 to 3.3.[18,19] For a rate-determining step that involves a significant component of Ir-H bond bending, the observed value of 1.4 for k_H/k_D is reasonable.

An inverse isotope effect is observed for systems that exhibit carbon-hydrogen activation.[18,19] Interestingly, those systems that show inverse isotope effects involve donor ligands, η^5-C_5Me_5 and PMe_3, while those that show normal isotope effects involve arylphosphines.[18,19] The exception to this is a rhodium-PMe_3 complex that has a small, normal isotope effect.[16b] It has been suggested for a number of years that donor ligands promote reductive-elimination reactions or, in the Parkin and Bercaw scheme,[19] would lower the energy of the barrier between the alkyl-hydride complex and an alkane complex and might promote an inverse kinetic deuterium isotope effect for C-H elimination.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-8709563) for support of this work and Professor J. B. Keister for helpful discussions. The NMR instruments were purchased from funds provided by NSF Grant No. CHE-8613066 and Department of Education Grant No. 2-2-01011. A loan of $IrCl_3{\cdot}xH_2O$ was provided by Johnson Matthey, Inc.

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