$(Me_2PC_2H_4PMe_2)_2Cl_2$ (1.0 g, 2.4 mmol) in diethyl ether (30 mL) was cooled to −78 °C and treated with an ethereal solution of EtMgCl (11.7 mL of a 0.41 M solution, 4.8 mmol). The reaction mixture was warmed to −30 °C, stirred for 12 h, filtered at −30 °C, and evaporated to dryness in vacuo. The orange residue was extracted with precooled pentane at −30 °C and the extract cooled to −78 °C to give the compound as red crystals, which were dried at −30 °C. Yield: 0.77 g (78% theory). Anal. Calcd for $C_{16}H_{42}CrP_4$: C, 46.8; H, 10.3; Cr, 12.7; P, 30.2. Found: C, 46.9; H, 10.3; Cr, 12.5; P, 30.3. IR (KBr, −50 °C): 1455 (m), 1420 (s), 1350 (m), 935 (s), 920 (s) cm^{-1}.

Single-Crystal X-ray Diffraction Studies of 2, 6, and 9. The crystal structure analyses were carried out with an Enraf-Nonius CAD-4 diffractometer. Crystallographic data and details of the refinement are listed in Table III and in the supplementary material.

Registry No. **1**, 135943-57-6; **2**, 135943-58-7; **3**, 135943-59-8; **4**, 135943-60-1; **5**, 135943-61-2; **6**, 135943-62-3; **7**, 135943-63-4; **8a**, 135943-64-5; **8b**, 135943-65-6; **9a**, 135972-33-7; **10**, 135943-66-7; **11**, 135943-67-8; $Me_2Cr(PMe_3)_2$, 135943-68-9; $Et_2Cr(Me_2PC_2H_4PMe_2)_2$, 135943-69-0; $Cr(THF)Cl_2$, 36463-97-5; $Cr(PPh_2Me)_2Cl_2$, 135943-70-3; $CrCl_3$, 10025-73-7; $Cr(Me_2PC_2H_4PMe_2)_2Cl_2$, 135943-71-4; $Cr(PMe_3)_2Cl_2$, 135943-72-5; 2-propenylmagnesium chloride, 2622-05-1; 2-methyl-2-propenylmagnesium chloride, 5674-01-1; 2-butenylmagnesium chloride, 6088-88-6; 1,3-butadiene, 106-99-0; 2-butyne, 503-17-3.

Supplementary Material Available: Detailed information on the crystal structure determination of 2, 6, and 9 including tables of final atomic positional parameters, final thermal parameters, and interatomic distances and angles (17 pages); lists of observed and calculated structure factors (46 pages). Ordering information is given on any current masthead page.

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Formation of Carbon–Carbon Bonds by Oxidative-Addition Reactions to *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$

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Oxidative addition of various organic halides to *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ has been examined by variable-temperature NMR spectroscopy. For $PhCH_2Cl$, $CH_3C(O)Cl$, $Ph_2CHC(O)Cl$, PhC(O)Cl, and $PhCH_2C(O)Cl$ oxidative addition is followed by reductive elimination to form carbon–carbon bonds. For reaction of *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ with $CH_3C(O)Cl$ the intermediate is characterized by ^1H and ^{31}P NMR spectroscopy at −5°; acetone elimination is significant at 10 °C. For the other complexes the oxidative addition is sufficiently slow that an intermediate cannot be identified. Oxidative addition of MeI and EtI to *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ leads to complexes Ir(CO)(I)(R)(Me)(P(*p*-tolyl)$_3$)$_2$ that are characterized by ^1H and ^{31}P NMR spectroscopy. For R = Me this complex is stable; for R = Et the complex slowly undergoes β-elimination leading to C_2H_4 and CH_4. These results provide strong support for a mechanism involving halide dissociation from the iridium(III) complexes.

Formation of carbon–carbon bonds is a major focus for organic and organometallic chemists. Catalytic systems involving transition-metal complexes most often form a carbon–carbon bond through alkyl → acyl conversions with carbon monoxide.[1] However, there exist increasing examples of carbon–carbon bond formation through reductive-elimination reactions.

A theoretical study of C–C bond formation on palladium and platinum centers attributes the less facile formation of C–C bonds in comparison to C–H bonds to the directionality of the sp^3 hybrids.[2] Thus, bond formation between two sp^3 centers should be a higher energy process than between an sp^3 center and an sp^2 center or to an atom that only uses s orbitals. These studies also show that reductive elimination is favored by palladium over platinum and by M(IV) over M(II).[2] A theorectial study on the possible geometrical preferences of $Ni(L)_3(R)_2$ formed in the associative path for reductive elimination from $Ni(L)_2(R)_2$ has also been reported.[3]

Stille and co-workers reported on the reductive elimination of ethane from dimethylpalladium complexes.[4] These studies showed that the reductive elimination required a cis orientation of methyls, proceed with retention of configuration at the carbon, and were inhibited by excess phosphine ligand.[4]

Reductive-elimination reactions on palladium centers have continued to attract attention.[5] Reductive elimination of ethane from $Pd(Me)_3(bpy)I$ apparently involves dissociation of I^- prior to the reductive elimination.[5] Addition of allyl bromide to $PdMe_2$(tripod) (tripod = a tridentate nitrogen-donor ligand) led to ethane and the η^3-allyl product.[6] Cross-coupling of C_6H_5I and MeMgI catalyzed by *trans*-Pd(Ph)(I)$(PEt_2Ph)_2$ led to toluene with a selectivity of over 90%, apparently through a reductive-elimination reaction.[7] Coupling of an allyl and phenyl

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group to form allylbenzene derivatives has also been reported on a palladium center.[8] Nickel complexes have also been quite useful for coupling to aryl groups.[9] Biphenyl formation was reported for reaction of PhBr with Ni(dppe) under reducing electrochemical conditions.[9] Arylated alkenes were formed by reactions of alkenylmetals with unsaturated organic halides.[10]

Carbon–carbon bond formation has also been reported on other metal centers.[11-14] Selective elimination of toluene derivatives was observed from *cis*-Au(Me)$_2$(aryl)L (L = a phosphine ligand).[11] In this case the elimination was preceded by phosphine dissociation. There was no evidence for ethane.[11] In contrast, reductive elimination from *cis*-Au(Me)$_2$(C(O)OMe)PPh$_3$ showed no selectivity with methyl acetate and ethane formed in a 1:1 ratio.[12] Studies continue showing the preference for acetone elimination over ethane.[13] Rh(Me)$_3$(triphos) reacts with CO to produce acetone and RhMe(CO)(triphos).[13] Diarylplatinum complexes show a competition between biaryl formation and arene elimination through hydrogen transfer.[14] The carbon–carbon bond formation appears not to require loss of a ligand from platinum.[14]

For several years we have been pursuing reactions of complexes, *trans*-RIr(CO)L$_2$ (R = alkyl or alkoxy; L = PPh$_3$ or P(*p*-tolyl)$_3$), that result in formation of bonds between R and the added molecule:[15-18]

$$\textit{trans}\text{-RIr(CO)L}_2 + \text{R}'\text{X} \rightarrow \text{RR}' + [\textit{trans}\text{-Ir(CO)L}_2\text{X}]$$

$$\text{R} = \text{alkyl, alkoxy}$$

$$\text{R}'\text{X} = \text{alkyl halide, HCl, HSi(OMe)}_3\text{, SiMe}_3\text{I, acid chlorides, H}_2$$

$$\text{L} = \text{PPh}_3\text{, P(}p\text{-tolyl)}_3$$

This research has shown the formation of C–H,[17] O–H,[17] C–C,[18] C–O,[15] C–Si,[16b] and O–Si[16a] bonds. In this paper we elaborate on the formation of carbon–carbon bonds, including low-temperature identification of some intermediates.

Experimental Section

Iridium trichloride was purchased or borrowed from Johnson Matthey, Inc. Ph$_2$CHC(O)Cl (Aldrich) was used as obtained. Acetyl chloride (Aldrich) was stirred over basic alumina for 14 h prior to further purification. The acetyl chloride was vacuum-distilled onto *N,N*-dimethylaniline and stirred 5–10 min. The first one-third portion of the acid chloride was discarded, and ~90% of the remaining portion was distilled into an oven-dried glass reaction vessel fitted with a stopcock and stored until needed. PhCH$_2$Cl, MeI, MeBr, EtI, EtBr, PhC(O)Cl, and PhCH$_2$C(O)Cl (Aldrich) were run down an activated alumina column and stored under a nitrogen atmosphere until needed. The formaldehyde monomer, CH$_2$O, was generated by heating paraformaldehyde under a flowing N$_2$ atmosphere. It was collected under a N$_2$ atmosphere at N$_2$(l) temperature in a reaction vessel fitted with a vacuum adaptor and stored under N$_2$(l) until use.[19]

All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer utilizing NaCl solution cells. ^{1}H NMR and ^{31}P NMR spectra were recorded on a Varian VXR-400 spectrometer. The ^{31}P spectra reported are proton-decoupled and referenced to H$_3$PO$_4$. The ^{1}H spectra recorded have absorptions at ~2.2 and 6–7.5 ppm from the P(*p*-tolyl)$_3$ ligands in addition to those listed. Gas chromatography was performed with a Varian 2440-FID chromatograph. All syntheses were accomplished under an argon or nitrogen atmosphere (unless noted otherwise), with use of an argon-filled glovebox or Schlenk or vacuum-line techniques.

The complexes *trans*-Ir(CO)(P(*p*-tolyl)$_3$)$_2$Cl and *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ were prepared by previously described procedures.[17]

Reaction of *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ with MeI. In an inert-atmosphere glovebox, *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ (0.010 g) was added to an NMR tube equipped with a vacuum adapter. The tube was removed from the drybox, placed on a vacuum line, and evacuated. Deuteriodichloromethane (1.5 mL) was vacuum-distilled into the NMR tube and warmed to allow dissolution of *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$. The solution was frozen in N$_2$(l), and purified MeI was added (~4-fold excess). The NMR tube was flame-sealed and monitored on the NMR instrument from −80 °C to room temperature. Only Ir(CO)(I)(Me)$_2$(P(*p*-tolyl)$_3$)$_2$ (^{1}H, 0.48 (t, $J_{\text{P-H}}$ = 6.2 Hz), 1.02 (t, $J_{\text{P-H}}$ = 7.5 Hz) ppm; ^{31}P, −9.0 (s) ppm) was observed as a product.

Reaction of *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ with EtI. A procedure analogous to that for MeI was used. Oxidative addition to form Ir(CO)(Et)(I)(Me)(P(*p*-tolyl)$_3$)$_2$ (^{1}H, 0.57 (q, $J_{\text{H-H}}$ = 7.4 Hz), 0.38 (t, $J_{\text{H-H}}$ = 5.9 Hz), 0.34 (t, $J_{\text{P-H}}$ = 6.9 Hz) ppm; ^{31}P, −12.3 (s) ppm) occurred at 5 °C. This product was stable at room temperature for a few hours. Continued monitoring showed the formation of CH$_4$, C$_2$H$_4$, *trans*-Ir(CO)(I)(P(*p*-tolyl)$_3$)$_2$ (^{31}P, 23.0 (s) ppm), and Ir(CO)(Et)(I)$_2$(P(*p*-tolyl)$_3$)$_2$ (^{1}H, 1.4 (t, $J_{\text{H-H}}$ = 6.9 Hz), 2.4 (q, $J_{\text{H-H}}$ = 6.9 Hz) ppm; ^{31}P, −19.0 (s) ppm). Spectra are shown in Figure 1. After completion of the reaction, CH$_4$ and C$_2$H$_6$ were confirmed by comparison of retention times on Poropak Q to those of authentic samples.

Reaction of *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ with PhCH$_2$Cl. A procedure analogous to that for MeI was followed except that vacuum distillation of PhCH$_2$Cl required heating. The oxidative addition proceeds at room temperature. No intermediates were observed; the only products were ethylbenzene (^{1}H, 1.2 (t, $J_{\text{H-H}}$ = 7.6 Hz), 2.5 (q, $J_{\text{H-H}}$ = 7.6 Hz) ppm) and Ir(CO)(Cl)$_2$(H)(P(*p*-tolyl)$_3$)$_2$ (^{1}H, −16.2 (t, $J_{\text{P-H}}$ = 10.3 Hz) ppm; ^{31}P, −2.7 (s) ppm). After completion of the reaction, the presence of ethylbenzene was confirmed by comparison (and spiking) of its retention time on a 6′ Carbowax 20M column at 150 °C.

Reaction of *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ with CH$_3$C(O)Cl. The procedure used for MeI was followed for reaction of acetyl chloride with *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$. The oxidative addition proceeded at low temperature, and at −5 °C the only iridium complex was Ir(C(O)CH$_3$)(CO)(Cl)(Me)(P(*p*-tolyl)$_3$)$_2$ (^{1}H, 0.41 (s), 0.80 (t, $J_{\text{P-H}}$ = 9.2 Hz) ppm; ^{31}P, −14.0 (s) ppm). Between 0 and 10 °C acetone (^{1}H, 2.1 (s) ppm) was formed and a second CH$_3$C(O)Cl added to form Ir(C(O)CH$_3$)(CO)(Cl)$_2$(P(*p*-tolyl)$_3$)$_2$ (^{1}H, 0.16 (s) ppm; ^{31}P, −4.4 (s) ppm). This complex slowly converted to Ir(CO)(Cl)$_2$(H)(P(*p*-tolyl)$_3$)$_2$ (see above for characterization) at room temperature. The NMR tube was opened and acetone verified by gas chromatographic analysis on a 6′ Carbowax 20M column.

Reaction of *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ with PhCH$_2$C(O)Cl. For phenylacetyl chloride a procedure analogous to that for MeI was followed. No reaction was observed until room temperature, where *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ (^{31}P, 22.5 (s) ppm) and PhCH$_2$C(O)Me were formed. These products were separated and identified by comparison to independently prepared

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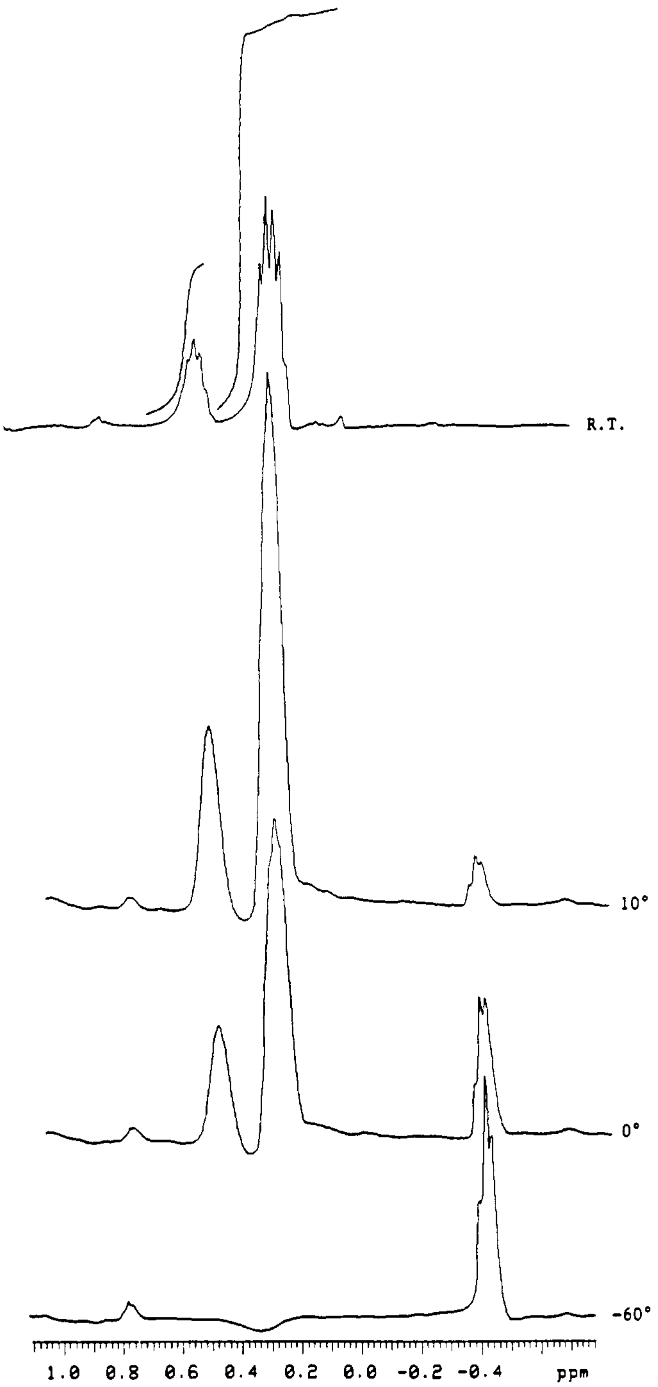

Figure 1. ^{1}H NMR spectra taken at various times during reaction of *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ with EtI. At -60 °C only the starting methyl complex was observed (-0.4 (t) ppm). At 0 °C and continuing to room temperature the oxidative-addition product is observed, Ir(CO)(Et)(I)(Me)(P(*p*-tolyl)$_3$)$_2$, with two overlapping triplets at 0.35 ppm. The integration is 1:3 as required.

samples. PhCH$_2$C(O)Me was identified by gas chromatography retention time and spiking of the sample with PhCH$_2$C(O)Me on 6′ Carbowax at 225 °C.

Reaction of *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ with Ph$_2$CHC(O)Cl. A procedure similar to that for MeI was utilized except the solid Ph$_2$CHC(O)Cl (molar excess) was stored in a side arm and added when the sample was frozen in N$_2$(l) before the NMR tube was flame-sealed. No reaction occurred until *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ and Ph$_2$CHC(O)Me were produced. These were separated and identified; Ph$_2$CHC(O)Me was determined by its infrared absorbance at 1718 cm^{-1}.

Reaction of *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ with PhC(O)Cl. The procedure used for PhCH$_2$Cl was followed for reaction of PhC(O)Cl with *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$. No reaction was observed at low temperatures. At room temperature Ir(CO)(Cl)$_2$(H)(P(*p*-tolyl)$_3$)$_2$ and acetophenone (^{1}H, 3.28 (s) ppm) were produced. Acetophenone was confirmed by gas chromatographic retention time and spiking with authentic PhC(O)Me on a 6′ Carbowax column at 250 °C.

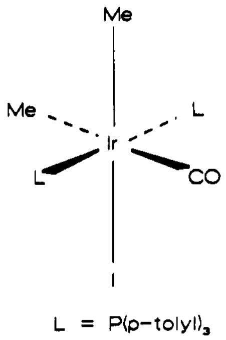

Figure 2. Suggested geometry for the product of oxidative addition of MeI to *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$).

Reaction of *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ with CH$_2$O. A procedure analogous to that for MeI addition was followed except that freshly prepared formaldehyde (2–3-mol excess) was vacuum transferred from a -78 °C dry-ice/acetone bath. No intermediates were observed; the products were Ir(CO)$_2$(H)(P(*p*-tolyl)$_3$)$_2$ (^{1}H, -12.0 (t, J_{P-H} = 10 Hz) ppm; ^{31}P, 10.0 (s) ppm) and CH$_4$ (^{1}H, 0.1 (s) ppm). A white precipitate formed that is probably paraformaldehyde, but we did not try to identify it. Methane was verified by gas chromatographic analysis at 60 °C on a 6′ Poropak Q column.

Results and Discussion

Addition of alkyl halides or acid chlorides to *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ results in formation of carbon–carbon bonds in many cases. In the reactions occurring at sufficiently low temperatures for intermediates to be identified, an oxidative-addition, reductive-elimination mechanism is indicated.

Alkyl Halide Reactions. Reaction of MeI with *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ leads to the oxidative-addition product Ir(CO)(I)(Me)$_2$(P(*p*-tolyl)$_3$)$_2$. The ^{1}H and ^{31}P NMR spectra show equivalent phosphorus atoms and inequivalent Me's. Thus, the geometry shown in Figure 2 is indicated. On the basis of electronegativity expectations and comparison to other complexes we tentatively assign the 0.48 (t) ppm resonance to the CH$_3$ trans to CO and the 1.02 (t) ppm resonance to the CH$_3$ trans to iodide. This is consistent with the results for Ir(CO)(I)(OMe)(Me)(PPh$_3$)$_2$, where the structure has been determined (Me trans to I is at 1.13 (t) ppm). The dimethyl complex does not reductively eliminate ethane.

Reaction of EtI with *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ begins similarly to the reaction of MeI with formation of Ir(CO)(Et)(I)(Me)(P(*p*-tolyl)$_3$)$_2$. The triplet for Ir–Me at 0.34 ppm (by comparison to the signal above) indicates it is trans to CO. The quartet (0.57 ppm) and triplet (0.38 ppm) for the ethyl do not show coupling to the phosphorus atoms.[20] At 20 °C this was the only species present in solution. At room temperature over several hours CH$_4$ and C$_2$H$_4$ were formed and Ir(CO)(Et)(I)(Me)(P(*p*-tolyl)$_3$)$_2$ disappeared. This decomposition probably occurs by β-hydride elimination, forming Ir(CO)(H)(I)(Me)(P(*p*-tolyl)$_3$)$_2$ and C$_2$H$_4$. The chloro analogue is known to very rapidly eliminate CH$_4$ at room temperature. Only *trans*-Ir(CO)(I)(P(*p*-tolyl)$_3$)$_2$ and the product of a second oxidative addition, Ir(CO)(Et)(I)$_2$(P(*p*-tolyl)$_3$)$_2$, could be ob-

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[20] It is possible that coupling to the phosphorus occurs but we are unable to distinguish it.

served by NMR spectroscopy. Formation of Ir(CO)(Et)(I)$_2$(P(*p*-tolyl)$_3$)$_2$ was duplicated by reaction of EtI with independently prepared *trans*-Ir(CO)(I)(P(*p*-tolyl)$_3$)$_2$. Failure to form C_3H_8 from reaction of EtI with *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ indicates that β-elimination is a lower energy process than formation of the carbon–carbon bond.

Reaction of benzyl chloride with *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ results in formation of a carbon–carbon bond, giving ethylbenzene. In this case the oxidative addition is sufficiently slow (not occurring below room temperature) that the intermediate is not observed. $PhCH_2CH_3$ was clearly observed by NMR spectroscopy and confirmed by gas chromatographic analysis. The iridium product of this reaction, Ir(CO)(Cl)$_2$(H)(P(*p*-tolyl)$_3$)$_2$, is frequently observed in these reactions. We have made no attempt to determine whether the hydride arises from traces of H_2O (in the solvent, in $PhCH_2Cl$, or adhering to the glass) or from a decomposition reaction. Addition of benzyl bromide to palladium dimethyl complexes led to mixtures of ethane and ethylbenzene showing reactions less selective than those observed for iridium.[21]

Acid Chloride Reactions. Reaction of each acid chloride with *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ results in formation of the ketone:

$$\mathrm{RC(O)Cl} + trans\text{-}\mathrm{MeIr(CO)(P(}p\text{-tolyl)}_3)_2 \rightarrow \mathrm{RC(O)Me} + [trans\text{-}\mathrm{Ir(CO)(Cl)(P(}p\text{-tolyl)}_3)_2]$$

$$\mathrm{R = Me,\ CH_2Ph,\ CHPh_2,\ Ph}$$

For two of the acid chlorides ($PhCH_2C(O)Cl$ and $Ph_2CHC(O)Cl$) a second oxidative addition does not occur and *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ is the product. For $CH_3C(O)Cl$ and PhC(O)Cl the final product is Ir(CO)(Cl)$_2$(H)(P(*p*-tolyl)$_3$)$_2$. It has previously been shown that Ir(C(O)Me)(CO)(Cl)$_2$(P(*p*-tolyl)$_3$)$_2$ is extremely susceptible to hydrolysis.

Oxidative addition of $CH_3C(O)Cl$ to *trans*-MeIr(CO)(P(*p*-tolyl)$_3$)$_2$ occurs at −5 °C, producing Ir(C(O)CH$_3$)(CO)(Cl)(Me)(P(*p*-tolyl)$_3$)$_2$. Ir–Me is a triplet, and the phosphorus atoms are equivalent from the ^{31}P spectrum. The acetyl signal, however, is at higher field than normal for an acetyl (0.41 (s) ppm). It seems likely that the CH_3 is in a position sufficiently close to the aromatic rings of the phosphines in this octahedral complex to give an unusual shift. A very similar chemical shift for the acetyl of 0.1 (s) ppm is observed for Ir(C(O)CH$_3$)(CO)(Cl)$_2$(P(*p*-tolyl)$_3$)$_2$. The integration for Ir(C(O)CH$_3$)(CO)(Cl)(Me)(P(*p*-tolyl)$_3$)$_2$ is correct, no unidentified resonances are present, only one ^{31}P signal is observed, and the resonance at 0.41 ppm disappears as acetone is formed. Thus, we are confident of our assignments and characterization for Ir(C(O)CH$_3$)(CO)(Cl)(Me)(P(*p*-tolyl)$_3$)$_2$. At 10 °C acetone is reductively eliminated and Ir(C(O)Me)(CO)(Cl)$_2$(P(*p*-tolyl)$_3$)$_2$ is formed. This complex slowly converted, at room temperature, to the hydride Ir(CO)(Cl)$_2$(H)(P(*p*-tolyl)$_3$)$_2$.

For the other three acid chlorides no reaction was observed prior to formation of the ketone. Thus, the oxidative addition does not occur as readily as for $CH_3C(O)Cl$ and no information on the relative rates of carbon–carbon bond formation in reductive elimination of ketones can be obtained.

Reductive-Elimination Reactions from Iridium(III). Formation of carbon–hydrogen, oxygen–hydrogen, carbon–carbon, carbon–oxygen, carbon–silicon, and oxygen–silicon bonds has now been reported from reductive elimination on Ir(III). Broadly, these can be divided into two categories: (1) the reductive elimination does not occur or (2) reductive elimination occurs at reasonable rates between 0 and 25 °C. There are three examples where reductive elimination does not occur. Ethane is not produced from dimethyl complexes, propane is not produced from methyl–ethyl complexes, and dimethyl ether is not produced from the methoxy–methyl complex. In all other cases the reductive-elimination reaction with bond formation occurs under remarkably similar conditions. Oxidative addition to form the iridium(III) complexes is sufficiently rapid to allow spectroscopic identification of the intermediates in five examples: (1) CH_4 is eliminated from Ir(CO)(Cl)(H)(CH$_3$)(P(*p*-tolyl)$_3$)$_2$ at 0 °C,[17] (2) acetone is eliminated from Ir(C(O)CH$_3$)(CO)(Cl)(Me)(P(*p*-tolyl)$_3$)$_2$ at 10 °C, (3) Ph_3SiOMe is eliminated from Ir(CO)(H)(OMe)(SiPh$_3$)(P(*p*-tolyl)$_3$)$_2$ at 10 °C,[16] (4) benzene is eliminated from Ir(CO(Cl)(H)(Ph)(P(*p*-tolyl)$_3$)$_2$ at 15 °C,[17] and (5) methanol is eliminated from Ir(CO)(Cl)(H)(OMe)(P(*p*-tolyl)$_3$)$_2$ at 20 °C.[17] For four additional examples the oxidative addition is sufficiently slow at room temperature that an intermediate cannot be identified. Thus, at room temperature the reductive elimination is relatively rapid for (1) ethyl benzene from Ir(CH$_2$Ph)(CO)(Cl)(Me)(P(*p*-tolyl)$_3$)$_2$, (2) ketones from Ir(C(O)R)(CO)(Cl)(Me)(P(*p*-tolyl)$_3$)$_2$ (R = Ph, CH$_2$Ph, CHPh$_2$), (3) esters from Ir(C(O)R)(CO)(Cl)(OMe)(P(*p*-tolyl)$_3$)$_2$ (R = Me, Ph, PhCH$_2$),[15] and (4) TMS from Ir(CO)(I)(Me)(SiMe$_3$)(P(*p*-tolyl)$_3$)$_2$.[16] It is remarkable that this diverse array of products is eliminated from Ir(III) with nearly equivalent activation barriers. The oxidative-addition reactions that lead to these Ir(III) complexes occur at comparable rates between −50 and +30 °C, but the reductive-elimination reactions all occur within a 20 °C range. This similarity in activation barriers suggests that the transition state for reductive elimination has only a very small component of bond formation, such that the nature of R and R′ has a small effect on the rate or a process where any stabilization is equally affecting the ground state and the transition state.

In our previous study of carbon–hydrogen bond formation we suggested that a strong component of Ir–H bending could account for the similarity of activation barriers for different groups. The new results reported in this paper indicate that a more general phenomenon is involved. Bendings of Ir–C, Ir–H and Ir–O bonds have significantly different energies, and different activation energies would be expected for formation of the different bonds reported herein.

β-elimination occurs for the ethyl complex under conditions that are similar to those for the reductive-elimination reactions. Since β-elimination requires an open coordination site,[1] the possibility of ligand dissociation as a prerequisite to reductive elimination must be considered. Ligand dissociation would account for the relative independence of the rate on the groups that are coupled. We have previously ruled out phosphine dissociation;[17] this also appears to be unlikely for the reactions reported in this paper. Reaction of Ir(CO)(I)$_2$(Me)(P(*p*-tolyl)$_3$)$_2$ with PMePh$_2$ to give phosphine exchange has a half-life of 1 day. Attempts to react *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ and *trans*-Ir(CO)(Me)(PMePh$_2$) with $CH_3C(O)Cl$ to examine possible phosphine exchange are precluded by rapid exchange of phosphine between the four-coordinate complexes.[22] We have obtained no evidence that phosphine

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dissociation is important in the reductive-elimination reactions.

Halide dissociation offers another possibility for opening a coordination site. Halide exchange on octahedral iridium(III) complexes has been recognized for a number of years.[23] $Ir(CO)(I)_2(Me)(P(p\text{-tolyl})_3)_2$ reacts readily with free Cl^- to replace one I^- (a few minutes); replacement of the second requires several days. Thus, a halide appears to be labile on an analogue of the $Ir(CO)(R)(R')(P(p\text{-tolyl})_3)_2X$ complexes. Halide dissociation as a requirement for bond coupling by reductive elimination could explain the relative independence of rate on the R and R′ groups. Previous studies have noted that ligand dissociation from a six-coordinate species facilitates reductive elimination, although in each case a phosphine ligand was lost.[24] Facilitation of reductive elimination by dissociation of halide does not appear to have been previously observed.

Why does reductive elimination not occur for $Ir(CO)(I)(Me)(R)(P(p\text{-tolyl})_3)_2$ (R = Me, Et, OMe)? Each of these species involves potential coupling of two atoms that have sp^3 hybridization. Theoretical studies have suggested that the directionality of the sp^3 hybrid inhibits bond formation. Thus, even if the two groups approach, an interaction between the atoms is insufficient to begin bond formation. Of the nine classes of bond formation from Ir(III) described above, only three involve both atoms with sp^3 hybridization. Two of these are silicon centers, and the third involves the benzyl group. The silicon centers have d orbitals that are available to accommodate the interaction from the other center. Binding of a benzyl ligand to a transition metal is complex[25] and has more s character than for an alkyl. Thus, the calculations showing that combination of two sp^3 centers is a higher energy process are consistent with the results on reductive elimination from Ir(III).[2]

One should also note that the three complexes that do not reductively eliminate have iodide as the halide; one might expect that iodide would be less likely than chloride to dissociate. However, three factors indicate that failure to dissociate iodide is not the important feature in the three complexes. (1) The ethyl complex $Ir(CO)(I)(Et)(Me)(P(p\text{-tolyl})_3)_2$ decomposes by β-elimination, which does require an open coordination site. The methoxy complex $Ir(CO)(I)(Me)(OMe)(P(p\text{-tolyl})_3)_2$ also undergoes reactions related to ligand dissociation just above room temperature.[15c] (2) Iodide is replaced by chloride in $Ir(CO)(I)_2(Me)(P(p\text{-tolyl})_3)_2$—one rapidly at room temperature, the second more slowly. (3) Abstraction of the iodide on $Ir(CO)(I)(Me)_2(PPh_3)_2$ by Ag^+ does not induce C_2H_6 elimination.[18] Thus, we conclude that formation of bonds between two sp^3 centers is not facile. Formation of other types of bonds on Ir(III) complexes occurs with nearly equal activation barriers in a process that appears to involve dissociation of halide.

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Registry No. *trans*-$MeIr(CO)(P(p\text{-tolyl})_3)_2$, 121617-18-3; MeI, 74-88-4; EtI, 75-03-6; $PhCH_2Cl$, 100-44-7; MeC(O)Cl, 75-36-5; $PhCH_2C(O)Cl$, 103-80-0; $Ph_2CHC(O)Cl$, 1871-76-7; PhC(O)Cl, 98-88-4; CH_2O, 50-00-0; $Ir(CO)(I)(Me)_2(P(p\text{-tolyl})_3)_2$, 135989-45-6; *trans*-$Ir(CO)(I)(P(p\text{-tolyl})_3)_2$, 42482-33-7; $Ir(CO)(Et)(I)_2(P(p\text{-tolyl})_3)_2$, 135989-46-7; $Ir(CO)(Cl_2)(H)(P(p\text{-tolyl})_3)_2$, 129540-38-1; $Ir(C(O)CH_3)(CO)(Cl)(Me)(P(p\text{-tolyl})_3)_2$, 135989-47-8; $Ir(C(O)CH_3)(CO)(Cl)_2(P(p\text{-tolyl})_3)_2$, 135989-48-9; *trans*-$Ir(CO)(Cl)(P(p\text{-tolyl})_3)_2$, 28195-56-4; $Ir(CO)_2(H)(P(p\text{-tolyl})_3)_2$, 38162-24-2; $PhCH_2CH_3$, 100-41-4; MeC(O)Me, 67-64-1; $PhCH_2C(O)Me$, 103-79-7; $Ph_2CHC(O)Me$, 781-35-1; PhC(O)Me, 98-86-2; $Ir(CO)(Et)(I)(Me)(P(p\text{-tolyl})_3)_2$, 135989-49-0.

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