upon treatment with a nonnucleophilic base, and we are currently investigating this chemistry.

Diynes. $[RuClH(CO)(PPh_3)_3]$ reacts with diphenylbutadiyne or bis(phenylethynyl)mercury to provide the α-phenylethynyl-*trans*-β-styryl complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$,[3] and part of our characterization of this complex involved its reaction with BSD to provide the purple complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(BSD)(PPh_3)_2]$. This compound is also the exclusive product of the reaction of $[RuClH(CO)(BSD)(PPh_3)_2]$ with diphenylbutadiyne (Scheme VII).

Reactions with Isonitriles. The reactions of $[M(C_6H_4Me\text{-}4)Cl(CO)(BSD)(PPh_3)_2]$ (M = Ru, Os) with carbon monoxide lead to rapid displacement of the heterocycle and formation of the dicarbonyl complexes $[M(C_6H_4Me\text{-}4)Cl(CO)_2(PPh_3)_2]$.[6] In a similar reaction, we find that the vinyl complexes described above react rapidly with 1 equiv of (2,6-dimethylphenyl)isonitrile to liberate the heterocycle with formation of the isonitrile complex $[Ru(vinyl)Cl(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$. The reactions of $[Ru(CH{=}CHR)Cl(CO)(PPh_3)_2(L)]$ (L = pyridine, 3,5-dimethylpyrazole) with ^{t}BuNC also lead to replacement of the heterocycle.[10]

Acknowledgment. We are grateful to Johnson Matthey Ltd. for a generous loan of ruthenium salts.

Registry No. $[Ru(CH{=}CHC_4H_9)Cl(CO)(BSD)(PPh_3)_2]$, 136570-77-9; $[Ru(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BSD)(PPh_3)_2]$, 136570-78-0; $[Ru(CH{=}CH_2)Cl(CO)(BSD)(PPh_3)_2]$, 136570-79-1; $[Ru(CH{=}CHCMe_2OH)Cl(CO)(BSD)(PPh_3)_2]$, 136570-80-4; $[Ru\{C(C{\equiv}CC_6H_5){=}CHC_6H_5\}Cl(CO)(BSD)(PPh_3)_2]$, 136570-81-5; $[Ru\{CH{=}CHCH_2CH(CO_2Et)PO(OEt)_2\}Cl(CO)(BSD)(PPh_3)_2]$, 136570-82-6; $[RuClH(CO)(BSD)(PPh_3)_2]$, 128817-72-1; $HC{\equiv}CC_6H_4Me\text{-}4$, 766-97-2; $HC{\equiv}CC_4H_9$, 693-02-7; $HC{\equiv}CH$, 74-86-2; $HC{\equiv}CMe_2OH$, 115-19-5; $C_6H_5C{\equiv}CC{\equiv}CC_6H_5$, 886-66-8; $HC{\equiv}CCH_2CH(CO_2Et)PO(OEt)_2$, 26199-74-6; $CNC_6H_3Me_2\text{-}2,6$, 2769-71-3.

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(10) Montoya, J.; Santos, A.; Eschavarren, A. M.; Ros, J. *J. Organomet. Chem.* **1990**, *390*, C57.

Bond-Forming Reactions to a Coordinated Hydroxo Group: Reaction of *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ with MeI, EtI, HCl, CH$_3$C(O)Cl, and H$_2$

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Reactions of *trans*-$Ir(CO)(OH)(P(p\text{-tolyl})_3)_2$ with MeI, EtI, HCl, and $CH_3C(O)Cl$ lead to the formation of bonds between the hydroxide and the adding group. For MeI and EtI addition, where the alcohols are formed, the reactions occur by oxidative addition followed by reductive elimination to form the carbon–oxygen bond. Reaction with HCl proceeds very rapidly by protonation of the hydroxide to eliminate H_2O. The reaction of *trans*-$Ir(CO)(OH)(P(p\text{-tolyl})_3)_2$ with acetyl chloride gives a mixture of products from initial attack of acetyl chloride on the hydroxide to produce acetic acid. Subsequent oxidative addition of the acid produces an acetate complex. Reaction of *trans*-$Ir(CO)(OH)(P(p\text{-tolyl})_3)_2$ with H_2 produces the trihydride $H_3Ir(CO)(P(p\text{-tolyl})_3)_2$ and H_2O. This reaction is partially reversible; treatment of the trihydride with H_2O produces the hydroxy complex. The reactions reported here are among the first that exhibit bond formation to a metal-bound hydroxo group.

Hydroxide complexes are central to catalytic reactions such as the Wacker process[1] and water–gas shift reactions.[2] Despite this importance relatively few hydroxide complexes of low oxidation state transition metals have been prepared.[3] One synthetic route to hydroxide complexes involves hydrolysis of alkoxide complexes.[4,5]

$$Pt(CCl{=}CCl_2)(OMe)(PPh_3)_2 + H_2O \rightarrow Pt(CCl{=}CCl_2)(OH)(PPh_3)_2 + MeOH \quad (1)$$

$$Ir(CO)(OMe)(PPh_3)_2 + H_2O \rightarrow Ir(CO)(OH)(PPh_3)_2 + MeOH \quad (2)$$

A second route involves displacement of coordinated solvent with hydroxide.[6,7]

$$Pt(Cl)(Me)L_2 \xrightarrow[\text{acetone}]{AgBF_4} [Pt(\text{acetone})(Me)L_2{}^+] \xrightarrow{KOH} Pt(OH)(Me)L_2 \quad (3)$$

L = a tertiary phosphine

$$Ir(CO)(CH_3CN)(PPh_3)_2{}^+ + OH^- \rightarrow Ir(CO)(OH)(PPh_3)_2 + CH_3CN \quad (4)$$

Reactivity studies of such hydroxide complexes have been limited to reactions with weak acids to eliminate H_2O[4,6-8]

$$Pt(OH)(Me)L_2 + HX \rightarrow Pt(X)(Me)L_2 + H_2O \quad (5)$$

L = a tertiary phosphine, X = $CH_2C(O)CH_3$, CH_2NO_2, etc.

and reaction with CO forming a carboxylic acid that may decompose to a hydride and CO_2.[9,10]

$$Pt(OH)(Ph)(PEt_3)_2 + CO \rightarrow Pt(CO_2H)(Ph)(PEt_3)_2 \quad (6)$$

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(1) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971, Vol. 2.

(2) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139.

(3) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163.

(4) Yoshida, T.; Okano, T.; Otsuka, S. *J. Chem. Soc., Dalton Trans.* **1976**, 993.

(5) Rees, W. M.; Atwood, J. D. *Organometallics* **1985**, *3*, 402.

(6) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119.

(7) Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1370.

(8) Green, L. M.; Meek, D. W. *Organometallics* **1989**, *8*, 659.

0276-7333/91/2310-3906$02.50/0

Reaction 6 is probably similar to those involved in water–gas shift reactions. Alkoxide complexes have been used in several carbon–oxygen and hydrogen–oxygen bond formation reactions.[11,12]

$$trans\text{-}\mathrm{Ir(CO)(OR)(P(}p\text{-}\mathrm{tolyl)_3)_2} + \mathrm{R'X} \rightarrow [\mathrm{Ir(CO)(X)(P(}p\text{-}\mathrm{tolyl)_3)_2}] + \mathrm{R'OR} \quad (7)$$

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

$$\mathrm{R'X = H_2, HCl, CH_3C(O)Cl, SiMe_3I, Si(H)(Me)(Ph)_2}$$

In all cases of R′X except $SiMe_3Cl$, the reaction occurred by oxidative addition giving the six-coordinate Ir(III), Ir(CO)(R′)(OR)(X)(P(*p*-tolyl)$_3$)$_2$. Reductive elimination produced the products.[11,12] A few examples of displacement of an alkoxide from a soft center by soft ligands have also been reported.[10,11,13]

$$\mathrm{Ir(CO)(OMe)(PPh_3)_2 + CO} \rightarrow [\mathrm{Ir(CO)_3(PPh_3)_2^+}][\mathrm{OMe^-}] \rightarrow \mathrm{Ir(C(O)OMe)(CO)_2(PPh_3)_2} \quad (8)$$

In this manuscript we report on the formation of oxygen–hydrogen and oxygen–carbon bonds by reaction of molecules with *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$.

$$trans\text{-}\mathrm{Ir(CO)(OH)L_2 + RX} \rightarrow [\mathrm{Ir(CO)XL_2}] + \mathrm{ROH} \quad (9)$$

$$\mathrm{RX = HCl, MeI, EtI, H_2,\ and\ CH_3C(O)Cl}$$

In each case the hydroxide is removed from the metal by formation of a new bond.

Experimental Section

Iridium trichloride was purchased or borrowed from Johnson Matthey, Inc. 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. MeI and EtI (Aldrich) were run down an activated alumina column and stored under a nitrogen atmosphere until needed. H_2 and HCl were purchased from Matheson and used as received.

All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer or on a Mattson Polaris FTIR utilizing NaCl solution cells. ^1H 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_3PO_4. The ^1H spectra recorded for the P(*p*-tolyl)$_3$ complexes have absorptions at ~2.2 and 6–7.5 from the P(*p*-tolyl)$_3$ ligands in addition to those listed. 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.

Preparation of *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$. In an inert-atmosphere glovebox, *trans*-Ir(CO)(OMe)(P(*p*-tolyl)$_3$)$_2$, 0.50 g, was placed in a Schlenk flask and dissolved in 25 mL of THF. The flask was removed from the glovebox and placed on a Schlenk line. With N_2(g) purge, 20 mL of deaerated H_2O was added. The solution was stirred at room temperature under N_2 for 16 h. The solvent was removed, giving a light yellow powder, and the flask was returned to the glovebox. The solid was dissolved in toluene (30 mL), the solution was transferred to an Erlenmeyer flask, and the toluene was removed by vacuum. The solid was extracted with benzene and filtered through a fine frit. The volume of the filtrate was reduced to 10 mL. Hexanes were used in a slow addition apparatus to effect crystallization. The yellow crystals were collected and washed with hexanes (yield = 0.34 g, 65%). IR (C_6H_6): 1925 cm^{-1}. NMR (C_6D_6), δ: ^1H 1.12 (t) ppm, J_{P-H} = 8.4 Hz; ^{31}P 24.9 (s) ppm. NMR (CD_2Cl_2), δ: ^1H 0.4 (t) ppm, J_{P-H} = 8.4 Hz; ^{31}P 26.1 (s) ppm. Microanalysis calc.: C, 61.06; H, 5.09; Ir, 22.74; P, 7.33. Obs: C, 61.03; H, 5.00; Ir, 23.60; P, 6.59.

Preparation of Ir($C_2H_3O_2$)(CO)(P(*p*-tolyl)$_3$)$_2$. In an inert-atmosphere glovebox, 0.5 g of *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ was suspended in 15 mL of THF. To this was added a suspension of 0.5 g of Ag($C_2H_3O_2$) in 35 mL of THF, and the mixture was stirred for 24 h. The solution was filtered through a medium frit and the solvent removed from the filtrate. The light yellow solid was extracted with C_6H_6 and filtered through a fine frit. The filtrate was reduced in volume to 10 mL on a rotary evaporator, and hexanes were added by slow addition to crystallize the product. The solid was collected by filtration and washed with hexanes. IR (KBr): 1950 (vs), 1630 (s) cm^{-1}. NMR (CD_2Cl_2), δ: ^1H 0.02 (s) ppm; ^{31}P 26.3 (s) ppm.

Addition of RX to *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$. In an inert-atmosphere glovebox, *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ (0.01 g) was added to an NMR tube equipped with a vacuum adapter. The tube was removed from the glovebox, placed on a vacuum line, and evacuated. CD_2Cl_2 (1.0–1.5 mL) was vacuum-distilled into the NMR tube. The tube was warmed to allow dissolution of the iridium complex and then refrozen in N_2(l). RX (RX = HCl, MeI, EtI, and $CH_3C(O)Cl$) was vacuum-distilled (~4 molar excess) into the frozen sample, and the NMR tube was flame-sealed. The NMR spectrum was monitored from −80 °C to room temperature.

Reaction of H_2 with *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$. In an inert-atmosphere glovebox, 0.28 g of *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ was placed in 100 mL of toluene in a Schlenk flask. An initial infrared spectrum had only the ν_{CO} of *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$. The flask was sealed, removed from the inert-atmosphere glovebox, and placed under H_2. The infrared spectrum was monitored for 5 weeks as the starting complex slowly disappeared and absorbances appeared at 2083, 1966, and 1786 cm^{-1}. An absorption at 1943 cm^{-1} was also observed. At the conclusion of the reaction, the toluene was removed by vacuum and the solid was returned to the glovebox. During solvent removal the solution turned green. An infrared spectrum (KBr) of the green solid showed H_3Ir(CO)(P(*p*-tolyl)$_3$)$_2$[14] (2086 (s), 2026 (w), 1958 (s), and 1803 (s) cm^{-1}), *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ (1922 (w) cm^{-1}), and an absorbance at 1978 (s) cm^{-1}. These products were also identified by ^1H and ^{31}P NMR spectra in toluene-d_8: H_3Ir(CO)(P(*p*-tolyl)$_3$)$_2$[14] ^{31}P 14.1 and 5.1 ppm, ^1H, −10.6 (second-order dd), −10.0 (tt), −9.6 (t), −9.4 (td), 1.90 (s); *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ ^{31}P 24.5, ^1H, 0.8 (t), 1.92 (s). In the ^{31}P spectrum a resonance at 5.6 (s) ppm is also observed. The resonance for H_2O is observed at 4.3 ppm in the ^1H spectrum.

Reaction of $H_3Ir(CO)(PPh_3)_2$ with H_2O. A solution of 0.081 g of $H_3Ir(CO)(PPh_3)_2$ in 50 mL of toluene was placed in a Schlenk flask in an inert-atmosphere glovebox. The flask was removed from the glovebox, and 1 mL of deaerated, distilled H_2O was added under N_2 purge. The initial light yellow solution turned green in 4 days. After 6 days, the volatile materials were removed by vacuum and the flask returned to the glovebox. Extraction with toluene produced a blue solid with no CO stretches and a green solution. Vacuum removal of the toluene gave a green solid. Infrared analysis (KBr) showed this to be composed of $H_3Ir(CO)(PPh_3)_2$ (2076, 1963, and 1781 cm^{-1}), the hydroxy complex (1924 cm^{-1}), and an unknown product with an absorption at 1987 cm^{-1}.

Results

Methyl Iodide Addition. From −70 to −50 °C only *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ and MeI are observed. At −40 °C the oxidative addition product, Ir(CO)(OH)(I)(Me)(P(*p*-tolyl)$_3$)$_2$ is formed. The NMR spectrum (^1H 0.59 (t), *J* = 7 Hz, and −2.7 (s), ^{31}P −6.0 (s) ppm) is quite similar

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[9] Bennett, M. A.; Robertson, G. B.; Rokicki, A.; Wickramasinghe, W. A. *J Am. Chem. Soc.* **1988**, *110*, 7098.

[10] Randall, S. L.; Thompson, J. S.; Buttrey, L. A.; Ziller, J. A.; Churchill, M. R.; Atwood, J. D. *Organometallics* **1991**, *10*, 683.

[11] Bernard, K. A.; Atwood, J. D. *Organometallics* **1989**, *8*, 795 and references therein.

[12] Thompson, J. S.; Bernard, K. A.; Rappoli, B. J.; Atwood, J. D. *Organometallics* **1990**, *9*, 2727.

[13] (a) Rees, W. M.; Churchill, M. R.; Fettinger, J. C.; Atwood, J. D. *Organometallics* **1985**, *4*, 2179. (b) Rees, W. M.; Atwood, J. D. *Organometallics* **1985**, *4*, 402.

[14] Harrod, J. F.; Yorke, W. J. *Inorg. Chem.* **1981**, *20*, 1156.

to that observed for MeI addition to *trans*-$Ir(CO)(OMe)(P(p\text{-tolyl})_3)_2$.[11]

$$trans\text{-}Ir(CO)(OH)L_2 + MeI \xrightarrow{-40\ °C} Ir(CO)(OH)(I)(Me)L_2 \xrightarrow[MeI]{0\ °C} MeOH + Ir(CO)(I)_2(Me)L_2 \quad (10)$$

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

$Ir(CO)(OH)(I)(Me)(P(p\text{-tolyl})_3)_2$ remains unchanged until ~0 °C where CH_3OH elimination occurs (3.4 (s), 4.25 (s) ppm) and another MeI adds to give $Ir(CO)(I)_2(Me)(P(p\text{-tolyl})_3)_2$[15] ($^1H$ NMR 1.05 (t) ppm, J_{P-H} = 6 Hz; ^{31}P NMR = −26.9 (s) ppm) as the final product.

Ethyl Iodide Addition. Addition of EtI is not as clean a reaction as is addition of MeI, but the major products are very similar. The oxidative addition has a larger activation barrier; the six-coordinate adduct is formed at ~0 °C. NMR spectral data (^1H −2.7 (s), 0.56 (t), 1.62 (q), J_{H-H} = 8 Hz; ^{31}P −12.0 ppm) are consistent with the six-coordinate product with a coordinated Et and OH.

$$trans\text{-}Ir(CO)(OH)L_2 + EtI \xrightarrow{0\ °C} Ir(CO)(Et)(OH)(I)L_2 \xrightarrow[EtI]{25\ °C} EtOH + Ir(CO)(I)L_2 + Ir(CO)(Et)(I)_2L_2 \quad (11)$$

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

This hydroxy, ethyl complex is moderately stable at room temperature; during 2 h, EtOH elimination occurs (1.24 (t) and 3.4 (q) ppm, J_{H-H} = 7 Hz). Both $Ir(CO)(I)(P(p\text{-tolyl})_3)_2$ (^{31}P 19.0 (s) ppm) and $Ir(CO)(Et)(I)_2(P(p\text{-tolyl})_3)_2$[15] ($^1H$ 1.31 (t) and 2.42 (q) ppm, J_{H-H} = 7.4 Hz; ^{31}P −20.6 (s) ppm) are observed as iridium products.

HCl Addition. At −75 °C the reaction was complete with formation of H_2O (5.3 (s) ppm) and $Ir(CO)Cl_2(H)(P(p\text{-tolyl})_3)_2$, which was fully characterized previously.[12]

$$trans\text{-}Ir(CO)(OH)(P(p\text{-tolyl})_3)_2 + 2HCl \rightarrow Ir(CO)Cl_2(H)(P(p\text{-tolyl})_3)_2 + H_2O \quad (12)$$

Acetyl Chloride Addition. Addition of acetyl chloride occurs at −75 °C. The ^1H spectrum has too many resonances between 2 and 3 ppm to be useful; however the ^{31}P spectrum is diagnostic. Sample spectra are shown in Figure 1. At −75 °C most of the *trans*-$Ir(CO)(OH)(P(p\text{-tolyl})_3)_2$ remains (25.0 (s) ppm) although some *trans*-$Ir(CO)(Cl)(P(p\text{-tolyl})_3)_2$ (22.5 (s) ppm), $Ir(OC(O)Me)(CO)(P(p\text{-tolyl})_3)_2$ (26.3 (s) ppm), and $Ir(CO)(Cl)_2(H)(P(p\text{-tolyl})_3)_2$ (−3.5 (s) ppm) are formed. As this mixture is warmed, the starting hydroxy complex, the chloride, and the acetate eventually are converted to the hydride (^1H −15.5 (t) ppm; ^{31}P −3.5 (s) ppm).

Dihydrogen Addition. Dihydrogen reacts slowly with *trans*-$Ir(CO)(OH)L_2$ (L = $P(p\text{-tolyl})_3$ or PPh_3) to give $H_3Ir(CO)L_2$. A small amount of H_2O is observed (4.3 δ, compared to an authentic sample at a similar concentration) during the reaction. To check the possibility that H_2O reacts with the formed trihydride, $H_3Ir(CO)L_2$, we examined the reactions between $H_3Ir(CO)(PPh_3)_2$ and H_2O and between the product from the reaction of H_2 with *trans*-$Ir(CO)(OH)(P(p\text{-tolyl})_3)_2$ and H_2O. In both cases the hydroxy complex, *trans*-$Ir(CO)(OH)L_2$, was formed. Thus the reaction of H_2 with *trans*-$Ir(CO)(OH)L_2$ is reversible.

$$trans\text{-}Ir(CO)(OH)L_2 + 2H_2 \rightleftharpoons H_3Ir(CO)L_2 + H_2O$$

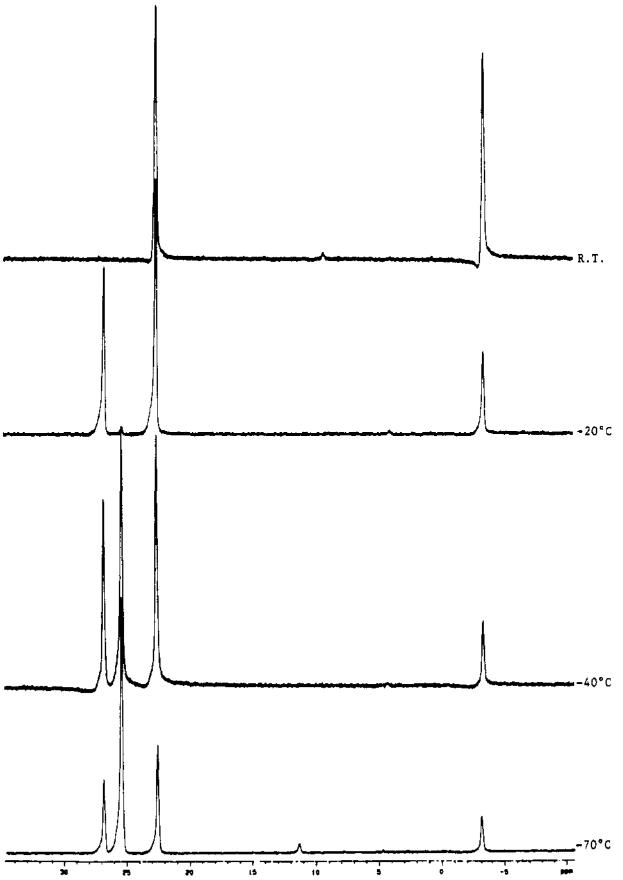

Figure 1. ^{31}P NMR spectra for the reaction of acetyl chloride with *trans*-$Ir(CO)(OH)(P(p\text{-tolyl})_3)_2$. The resonance at 25 ppm is from the starting hydroxy complex. The resonance at 22.5 ppm is for the chloride, *trans*-$Ir(CO)(Cl)(P(p\text{-tolyl})_3)_2$, and that at 26.3 ppm is from the acetate, *trans*-$Ir(C_2H_3O_2)(CO)(P(p\text{-tolyl})_3)_2$. The final hydride, $Ir(CO)(Cl)_2(H)(P(p\text{-tolyl})_3)_2$, has the singlet at −3.5 ppm that dominates at room temperature.

Some decomposition accompanies the reaction of the trihydride with H_2O, making quantitative studies difficult. In the reaction from either direction an intermediate is observed with a ν_{CO} at 1978 cm^{-1} and a ^{31}P resonance at 5.6 ppm. The CO stretch approximately 50 cm^{-1} higher than that of *trans*-$Ir(CO)(OH)(P(p\text{-tolyl})_3)_2$ and the position of the ^{31}P resonance are consistent with the dihydride, $Ir(CO)(H)_2(OH)(P(p\text{-tolyl})_3)_2$.

Discussion

Complexes that contain hard and soft ligands in some cases display unusual reactivity.[10,16–21] The alkoxy complexes of iridium, *trans*-$Ir(OR)(CO)L_2$, however, display remarkably similar reactions to the analogous alkyl complexes, *trans*-$Ir(R)(CO)L_2$.[22,23] Only in the mechanism for

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[15] Reaction of MeI with independently prepared *trans*-$Ir(CO)(I)(P(p\text{-tolyl})_3)_2$ produces $Ir(CO)(I)_2(Me)(P(p\text{-tolyl})_3)_2$. This species has ν_{CO} = 2039 cm^{-1}, a ^1H NMR (CD_2Cl_2) resonance of 1.05 (t), J_{P-H} = 6 Hz, and a ^{31}P NMR (CD_2Cl_2) resonance at −26.9 ppm.

[16] Stebler-Röthlisberger, M.; Hummel, W.; Pittet, P.-A.; Bürgi, H.-B.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1358.

[17] Hartley, F. R.; Murray, S. G.; Wilkinson, A. *Inorg. Chem.* **1989**, *28*, 549.

[18] Bauer, H.; Beck, W. *J. Organomet. Chem.* **1986**, *308*, 73.

[19] Harding, P. A.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1987**, 947.

[20] Harding, P. A.; Preece, M.; Robinson, S. D.; Henrick, K. *Inorg. Chim. Acta* **1986**, *118*, L31.

[21] Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297.

[22] (a) Bernard, K. A.; Atwood, J. D. *Organometallics* **1988**, *7*, 235. (b) Bernard, K. A.; Atwood, J. D. *Organometallics* **1987**, *6*, 1133. (c) Janik, T. S.; Bernard, K. A.; Churchill, M. R.; Atwood, J. D. *J. Organomet. Chem.* **1987**, *323*, 247. (d) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Organometallics* **1988**, *7*, 1939.

reaction with CO, where the alkoxide is displaced,[13] is there marked difference in reactions for the alkyl- and alkoxyiridium complexes. In a variety of bond-forming reactions, the reductive elimination occurs with similar activation barriers for the alkyl and alkoxy complexes.[11,12] The hydroxy complexes, in contrast, show two quite different routes to formation of bonds.

Oxidative Addition and Reductive Elimination. Reaction of *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ with MeI and EtI shows clear evidence for the oxidative addition intermediate, Ir(CO)(OH)(R)(I)(P(*p*-tolyl)$_3$)$_2$. These complexes have the OH resonance at ~-3 ppm, similar to the resonance of hydroxides coordinated to platinum,[4] and show the typical resonances for R. That EtI adds more slowly than MeI is consistent with an oxidative addition process.[24] Elimination of MeOH is somewhat more rapid than elimination of EtOH, but the rates of both processes are in the range observed for reductive elimination of carbon-hydrogen, carbon-carbon, carbon-oxygen, and oxygen-hydrogen bonds from six-coordinate iridium complexes.[11,12,22,23] In all respects the formation of MeOH and EtOH is similar to other reductive elimination reactions. To our knowledge this is the first report of reductive elimination of an alcohol from an alkyl, hydroxide complex.

Two aspects of the reductive elimination should be noted: (1) The reductive elimination of MeOH by formation of the carbon-oxygen bond occurs under nearly the same conditions as elimination of MeOH by formation of the oxygen-hydrogen bond from a similar methoxy, hydride complex.[12] Thus, if these iridium complexes are useful models of a reaction where MeOH is a product, the relative reductive elimination rates for O-H versus C-O bond formation cannot be used to assign a mechanism. (2) The reductive elimination of MeOH from the methyl, hydroxide complex occurs under conditions where dimethyl ether is not eliminated from the methyl, methoxy complex.[22a] The greater facility for formation of the carbon-hydroxy bond versus the carbon-methoxy bond indicates that the substituents on groups to be coupled are very important. Estimates indicate that a metal-hydroxide bond is ~15 kcal/mol stronger than a metal-methoxide bond.[25] Thus kinetic control of the reductive elimination is indicated.

Addition of H_2 to *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ results in elimination of H_2O in a reaction very similar to the reaction of the alkoxides, *trans*-Ir(OR)(CO)(PPh$_3$)$_2$, with H_2. In both cases the oxidative addition of H_2 is fairly slow; for the hydroxy complex evidence of the oxidative addition intermediate is observed. The reaction is partially reversible, with reaction of the trihydride and H_2O producing the intermediate and the hydroxy complex. The mechanism of reaction of H_2O with $H_3Ir(CO)L_2$ (L = PPh$_3$ or P(*p*-tolyl)$_3$) is not clear, but involves activation of water and elimination of H_2.

Attack on the Hydroxide. In contrast to the reactions of MeI and EtI with *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$, reactions with HCl and CH$_3$C(O)Cl occur very rapidly with no evidence for an oxidative addition intermediate. Reaction with HCl produces, at -75 °C, Ir(CO)(Cl)$_2$(H)(P(*p*-tolyl)$_3$)$_2$ and H_2O. This reaction probably occurs by protonation of the hydroxide,[26] weakening the iridium-oxygen bond and giving *trans*-Ir(CO)(Cl)(P(p-tolyl)$_3$)$_2$, which is known to rapidly add HCl.[12] No further reaction is observed on warming to room temperature. The fact that this reaction occurs by protonation of the hydroxide again points to different reactivity for the methoxy and hydroxy analogues. The methoxy complex undergoes an oxidative addition, reductive elimination sequence in reaction with HCl.[12]

$$trans\text{-}Ir(CO)(OH)L_2 + CH_3C(O)Cl \rightarrow trans\text{-}Ir(CO)(Cl)L_2 + CH_3C(O)OH$$

$$trans\text{-}Ir(CO)(OH)L_2 + CH_3C(O)OH \rightarrow trans\text{-}Ir(C_2H_3O_2)(CO)L_2 + H_2O$$

$$trans\text{-}Ir(CO)(Cl)L_2 + CH_3C(O)Cl \rightarrow Ir(C(O)Me)(CO)(Cl)_2L_2$$

$$Ir(C(O)Me)(CO)(Cl)_2L_2 + H_2O\ (\text{or } CH_3C(O)OH) \rightarrow Ir(CO)(Cl)_2(H)L_2$$

Figure 2. Suggested reactions that produce the product mixture for reaction of acetyl chloride with *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$.

Reaction of acetyl chloride with *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ provides a mixture of products at -75 °C. Both *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ and the acetate, *trans*-Ir(C$_2$H$_3$O$_2$)(CO)(P(*p*-tolyl)$_3$)$_2$, are formed in similar amounts even at -75 °C. These products must result from formation of acetic acid with subsequent reactions, as shown in Figure 2. The hydride, Ir(CO)(Cl)$_2$(H)(P(*p*-tolyl)$_3$)$_2$, is present in a small amount at -75 °C and grows steadily to be the only product at room temperature. The low activation barrier and lack of observable intermediates indicate an attack of the acetyl chloride directly on the hydroxide, not oxidative addition followed by reductive elimination. In this respect the reaction with acetyl chloride is quite similar to reaction with HCl. The analogous methoxy complex reacts much more slowly through an oxidative addition, reductive elimination sequence.[22a] Attack of the acetyl on the hydroxide results in formation of acetic acid and *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$. The acetic acid is not observed but must rapidly react with *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ to produce H_2O and the acetate complex, *trans*-Ir(C$_2$H$_3$O$_2$)(CO)(P(*p*-tolyl)$_3$)$_2$. The acetate complex is observed at -75 °C. Reaction of acetic acid with *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ (by comparison to reaction with HCl) may be expected to occur readily, as observed. The water would react readily with CH$_3$C(O)Cl to form more acetic acid and HCl. Further known reactions would result in Ir(CO)(Cl)$_2$(H)(P(*p*-tolyl)$_3$)$_2$ as the final product.

Attack on the oxygen of *trans*-Ir(CO)(OMe)(P(*p*-tolyl)$_3$)$_2$ was observed only for the reaction with Si(Cl)Me$_3$.[22d] This reaction also occurred very rapidly under conditions where oxidative addition of Si(Cl)Me$_3$ was not observed. Attack on the oxygen atom of a coordinated hydroxide or alkoxide is characteristically very rapid, and there is no evidence for oxidative addition intermediates. For the iridium complexes in each reaction that occurs by oxidative addition, the oxidative addition intermediate is observed and the rates are consistent with known oxidative addition abilities. The hydroxy complexes undergo much more facile attack on the oxygen, which may indicate a role for hydrogen bonding.

Conclusion

Different mechanisms have been observed for formation of bonds to the hydroxide of *trans*-Ir(CO)(OH)(P(*p*-

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[23] (a) Rappoli, B. J.; McFarland, J. M.; Thompson, J. S.; Atwood, J. D. *J. Coord. Chem.* **1990**, *21*, 147. (b) Churchill, M. R.; Fettinger, J. C.; Janik, T. S.; Rees, W. M.; Thompson, J. S.; Tomazewski, S.; Atwood, J. D. *J. Organomet. Chem.* **1987**, *323*, 233. (c) Churchill, M. R.; Fettinger, J. C.; Rees, W. M.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *301*, 99.

[24] Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985.

[25] Brynzda, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

[26] Hydrogen bonding of alcohols to coordinated alkoxo groups have been previously reported.[27]

[27] (a) Braga, D.; Sabatino, P.; DiBugno, C.; Leoni, P.; Pasquali, M. *J. Organomet. Chem.* **1987**, *334*, C46. (b) Kegley, S. E.; Schaverien, C. J.; Freudenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563. (c) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096.

tolyl)$_3$)$_2$: (1) For the acidic species, HCl and $CH_3C(O)Cl$, direct attack on the oxygen occurs with no evidence for an intermediate. (2) For MeI and EtI, oxidative-addition leads to an observable six-coordinate intermediate, which then reductively eliminates the alcohol providing the first example of carbon–hydroxide coupling on a metal center. In terms of bond formation reactions by reductive elimination, the hydroxide is more similar to a hydride and the methoxide is more similar to the methyl than the hydroxide and methoxide are to each other. (3) Reaction of H_2 with *trans*-Ir(CO)(OH)(P(*p*-tolyl)$_3$)$_2$ results in elimination of H_2O and formation of $H_3Ir(CO)$(P(*p*-tolyl)$_3$)$_2$ in a reaction that is partially reversible.

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Lewis-Base-Free Cationic Zirconocene Complexes Containing an Alkenyl Ligand

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Electrophilic cations $[Cp'_2ZrMe(NMe_2Ph)_n][B(4\text{-}C_6H_4F)_4]$ (1) (n = 1, $Cp'_2 = (C_5H_5)_2$ (**a**), $\{(Me_3Si)C_5H_4\}_2$ (**b**), $\{(Me_3C)C_5H_4\}_2$ (**c**), *rac*-C_2H_4(indenyl)$_2$ (**d**); n = 0, $Cp' = C_5Me_5$ (**e**)), generated in situ by protonolysis, react with internal alkynes to give Lewis-base-free alkenyl complexes $[Cp'_2ZrC(R^1){=}C(R^2)Me][B(4\text{-}C_6H_4F)_4]$ ($R^1 = SiMe_3$, R^2 = Me, **2a–d**; $R^1 = R^2$ = Ph, **3a–e**). ^1H, ^{13}C, and ^{29}Si NMR spectroscopy suggests that agostic coordination of a Si–Me group to the zirconium center occurs for complexes **2** in solution. The structure of **2d**·CH_2Cl_2 has been determined by X-ray crystallography. Crystal data: $C_{52}H_{49}BCl_2F_4SiZr$, M = 950.99, monoclinic, $P2_1/n$, a = 15.402 (3) Å, b = 17.606 (3) Å, c = 16.960 (3) Å, Z = 4, and R = 0.050 for 5392 "observed" reflections. The alkenyl ligand in **2d** interacts with electron-poor zirconium via agostic coordination of a Si–C and a C–H bond of the α-$SiMe_3$ group (Zr–Si = 2.935 (2) Å; Zr–C = 2.578 (5) Å; Zr–H = 2.26 (7) Å). ^{19}F NMR spectroscopy shows that the anion is noncoordinating in complexes **2**, **3c**, and **3e**; labile fluorine coordination to zirconium in complexes **1**, **3a**, **3b**, and **3d** results in upfield-shifted ^{19}F NMR resonances for the anion.

Introduction

The high reactivity of group 4 metallocene/alkylaluminoxane catalysts for alkene polymerization[1] is attributed to the presence of an electrophilic cationic active species, $[Cp'_2MR]^+$, in combination with a poorly coordinating anion.[2] Although insertion reactions of unsaturated molecules with model Lewis base complexes, $[Cp'_2MR(L)][BPh_4]$ (M = Ti, Zr), have been extensively investigated,[3] more electrophilic base-free complexes, closely related to the proposed catalyst active spcies, have been less well studied.[4,5] Because of the coordinating ability and facile degradation of $[BPh_4]^-$,[4,6,7] alternative anions such as fluorinated $[BPh_4]^-$ or carboranes are required for the stabilization of reactive base-free complexes.[6,8] Incorporation of fluorine in the 4-positions of $[BPh_4]^-$ was expected to suppress π-coordination of a benzene ring[7] and result in reactive cationic complexes. We report here the reaction of highly electrophilic methylzirconocene cations with bulky disubstituted alkynes and the unusual structure of a highly electron-deficient alkenyl product.

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(1) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189.

(2) (a) Dyachkovskii, F. S.; Shilova, A. K.; Shilov, A. E. *J. Polym. Sci., Part C* **1967**, *16*, 2333. (b) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. J.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219. (c) Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875. (d) Jolly, C. A.; Marynick, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 7968.

(3) (a) Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 778. (b) Jordan, R. F.; Bradley, P. K.; Baenziger, N.; LaPointe, R. E. *Organometallics* **1989**, *8*, 2892. (c) Guram, A. S.; Jordan, R. F. *Organometallics* **1990**, *9*, 2190. (d) Guram, A. S.; Jordan, R. F.; Taylor, D. F. *J. Am. Chem. Soc.* **1991**, *113*, 1833. (e) Alelyunas, Y. W.; Jordan, R. F.; Echols, S. F.; Borkowsky, S. L.; Bradley, P. K. *Organometallics* **1991**, *10*, 1406. (f) Jordan, R. F.; Taylor, D. F.; Baenziger, N. C. *Organometallics* **1990**, *9*, 1546. (g) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (h) Taube, R.; Krukowka, L. *J. Organomet. Chem.* **1988**, *347*, C9.

(4) (a) Bochmann, M.; Jaggar, A. J.; Nicholls, N. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780. (b) Lin, Z.; Le Marechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127.

(5) (a) Christ, C. S.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 596. (b) Christ, C. S.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 4778.

(6) (a) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (b) Turner, H. W. European Patent Application 0277004 assigned to Exxon.

(7) (a) Isolated complexes $Cp'_2Zr(Me)\{B(C_6H_5)_4\}$ (Cp'_2 = *rac*-C_2H_4(indenyl)$_2$, *rac*-C_2H_4(tetrahydroindenyl)$_2$, $\{(Me_3Si)C_5H_4\}_2$, $\{(Me_3C)C_5H_4)\}_2$ contain anions coordinated via the meta and para carbons of one phenyl group.[7b] (b) Horton, A. D.; Frijns, J. H. G. *Angew. Chem., Int. Ed. Engl.*, in press.

(8) (a) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840. (b) *Ibid. J. Am. Chem. Soc.* **1991**, *113*, 3623.