

Synthesis and Reactivity of an Iridium Hydroxo Complex. Insertion of Ethylene into a Metal-Oxygen Bond

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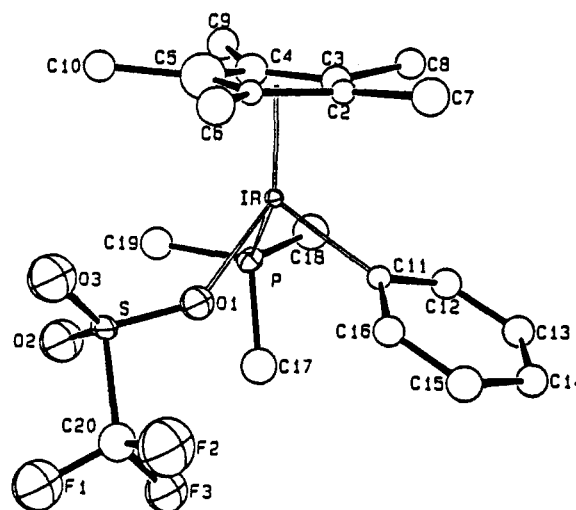
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Alkoxo and hydroxo complexes of the late transition metals have generated interest because the reactivity of this combination of soft metal and hard ligand is not well documented.¹ The hydroxo complexes have been studied in detail only for coordinatively unsaturated palladium and platinum complexes.^{2,3} The reactivity of coordinatively saturated metal hydroxo complexes, however, has received little attention, although ligand metathesis reactions with acidic reagents such as H₂S have been documented.⁴ As a complement to our studies of late metal alkoxides and amides,⁵ we have now successfully prepared the coordinatively saturated iridium hydroxo complex Cp*(PMe₃)Ir(Ph)OH (**1**). This complex undergoes hydroxide ligand metathesis and reacts at the M-O bond with electrophilic and nucleophilic reagents. Furthermore, we have demonstrated that both dimethyl acetylenedicarboxylate and ethylene insert into the metal-oxygen bond. The latter transformation is analogous to a critical step proposed in the Wacker oxidation of ethylene to acetaldehyde.⁶

Complex **1** was prepared from Cp*(PMe₃)Ir(Ph)OSO₂CF₃ (**2**). This material was obtained in 94% yield by treatment of Cp*(PMe₃)Ir(Ph)Cl with AgOTf, in analogy to the preparation of Cp*(PMe₃)Ir(OTf)₂.⁷ The triflate was demonstrated to be covalent in the solid state by X-ray crystallography.⁸ An ORTEP diagram of this material is shown in Figure 1, and details of the structure determination are provided as supplementary material. Treatment of **2** with cesium hydroxide afforded **1** in 72% yield as a pentane-soluble, air-sensitive solid.⁹ When the iridium triflate **2** was treated with potassium *tert*-butoxide, **1** was obtained in 87% yield.^{10,11} We do not yet know whether this reaction proceeds by formation of the *tert*-butoxo complex, followed by elimination of 2-methylpropene, or by nucleophilic attack of KO^tBu at sulfur; however, so far we have been unable to detect the alkene by

Scheme I



NMR spectrometry. The preparation using cesium hydroxide is preferable since it affords crystalline **1** in analytically pure form.

The spectral properties of the hydroxo complex **1** confirm its structure. The hydroxyl proton resonance appears at -3.1 ppm (CD₂Cl₂) in the ¹H NMR spectrum as a broad singlet ($\Delta\nu_{1/2} = 5$ Hz) at 25 °C. Although its chemical shift is independent of temperature from 25 to -90 °C, the OH resonance sharpens at lower temperatures and appears as a doublet at -60 °C ($^3J_{P-OH} = 1$ Hz). The resonances attributed to the phenyl group broaden at -80 °C, suggesting that there is restricted rotation of the phenyl ring. The ¹⁷O NMR spectrum of an isotopically enriched sample of **1** displays a single resonance at -114 ppm (relative to H₂O),¹² and the O-H stretch in the infrared spectrum appears as a weak absorbance at 3610 cm⁻¹.¹³

The hydroxo complex **1** is a favorable compound for the study of the Ir-OH functionality because its reactions are confined to this moiety. For example, **1** undergoes facile metathesis reactions of the hydroxyl ligand (Scheme I).^{4,5} Treatment of **1** with 1 equiv of phenol in C₆D₆ resulted in a 1:5 mixture of **1** and Cp*(PMe₃)Ir(Ph)OPh (**3**); the phenoxide was isolated in 96% yield from this mixture after the equilibrium was shifted to favor **3** by azeotropic removal of the water with benzene. When the metathesis reaction was performed using THF-*d*₈ as solvent, only **3** was observed by ¹H and ³¹P {¹H} NMR spectroscopy. The observation of a solvent effect on the equilibrium suggests that bond energies as well as solvation are important in determining

(1) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163-1188. (b) For recent studies of late metal alkoxides, see: Alsters, P. L.; Baesjou, P. J.; Janssen, M. D.; Kooijman, H.; Sicherer-Roetman, A.; Spek, A. L.; van Koten, G. *Organometallics* **1992**, *11*, 4124-4135, and references cited therein.

(2) These hydroxides undergo ligand metathesis reactions with protic electrophiles such as phenols and insertion reactions of CO, CO₂, and SO₂ into the metal-oxygen bond. For example, see: Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175*, 239-255.

(3) The reactions of CO₂ with coordinatively unsaturated rhodium(I) and iridium(I) hydroxides have been reported: (a) Flynn, B. R.; Vaska, L. *J. Chem. Soc., Chem. Commun.* **1974**, 703-704. (b) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibeis, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212-4221.

(4) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444-1456.

(5) (a) Glueck, D. S.; Winslow, L. J. N.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462-1479. (b) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875-1887. (c) Simpson, R. D.; Bergman, R. G. *Organometallics* **1992**, *11*, 3980-3993. We have also recently prepared two coordinatively saturated hydroxoruthenium complexes, cf.: (d) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875-5876.

(6) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411-2416, and references cited therein.

(7) Stang, P. J.; Huang, Y.-H.; Arif, A. M. *Organometallics* **1992**, *11*, 231-237.

(8) Crystals grown from diethyl ether at -40 °C. Crystal data for **2**: C₂₀H₂₉F₃IrO₃PS, *P*1, *V* = 1156(1) Å³, Mo Kα ($\lambda = 0.71073$ Å), $\mu_{\text{calc}} = 59.5$ cm⁻¹, $d_{\text{calc}} = 1.81$ g cm⁻³, $a = 8.665(3)$ Å, $b = 9.669(2)$ Å, $c = 14.205(4)$ Å, $\alpha = 92.10(2)^\circ$, $\beta = 99.35(2)^\circ$, $\gamma = 99.51(2)^\circ$, $T = -114$ °C, $Z = 2$, $2\theta_{\text{max}} = 45^\circ$. The final residuals for 132 variables refined against the 2657 data for which $F^2 > 3\sigma(F^2)$ were $R = 6.2$, $R_w = 8.9$, and GOF = 3.83. The *R* value for all 3022 data was 7.0.

(9) Few monomeric iridium hydroxides have been reported, and little is known about their chemistry: (a) Vaska, L.; Peone, J., Jr. *J. Chem. Soc., Chem. Commun.* **1971**, 418-419. (b) James, B. R.; Preece, M.; Robinson, S. D. *Adv. Chem. Ser.* **1982**, *196*, 145-161. (c) Stevens, R. C.; Bau, R.; Milstein, D.; Blum, O.; Koetzle, T. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1429-1432. (d) Green, L. M.; Meek, D. W. *Organometallics* **1989**, *8*, 659-666. (e) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003-2008.

(10) The reaction of (Ph₃P)₃RhCl with potassium *tert*-butoxide resulted in the preparation of (Ph₃P)₃RhOH: Gregorio, G.; Pregaglia, G.; Ugo, R. *Inorg. Chim. Acta* **1969**, *3*, 89-93.

(11) Recently Merola and co-workers reported that the reaction of 1,1-dimethylethanol with an iridium(I) salt leads to 2-methylpropene and an iridium(III) hydroxy hydride: Ladipo, F. T.; Kooti, M.; Merola, J. S. *Inorg. Chem.* **1993**, *32*, 1681-1688.

(12) (a) The ¹⁷O NMR chemical shifts have not been reported for late metal hydroxides, but Hillhouse and Bercaw have reported chemical shifts of +140 to +230 ppm for zirconium and hafnium hydroxides: Hillhouse, G. L.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5472-5478. The downfield shifts of early metal oxo and hydroxo complexes are attributed to the removal of electron density at oxygen by π -bonding to the electron-deficient metal. For a general discussion, see: Klemperer, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246-254. (b) Recently, Parkin has reported ¹⁷O NMR chemical shifts of -8 to -36 ppm for tris(pyrzoly)hydroboratozinc hydroxo complexes: Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4690-4697.

(13) It has been noted that late metal hydroxides have characteristically weak O-H absorbances at about 3600 cm⁻¹ (see ref 4).

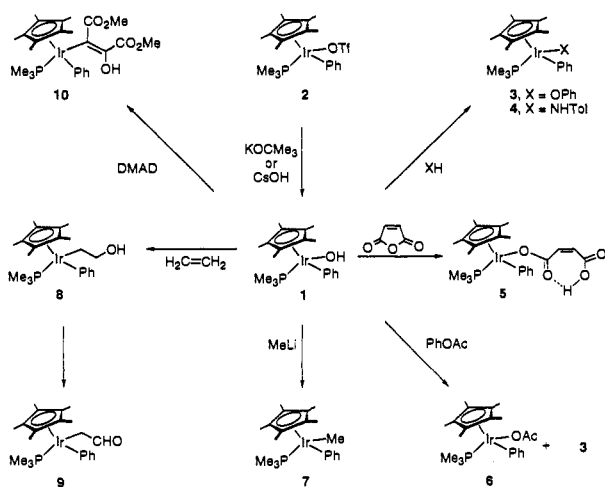


Figure 1. ORTEP diagram of $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Ph})\text{OSO}_2\text{CF}_3$ (**2**).

the equilibrium constants of this metathesis reaction. The structure of **3** was confirmed by X-ray crystallography, although there were indications of disorder (details of the structure are provided as supplementary material). The metathesis reaction of **1** with 2 equiv of *p*-toluidine in C_6D_6 resulted in a 1:4 mixture of **1** and $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Ph})\text{NH}(p\text{-C}_6\text{H}_4\text{CH}_3)$ (**4**), from which **4** could be isolated in 100% yield after azeotropic removal of water (as for **3**) followed by recrystallization. A similar equilibrium mixture was observed when $\text{THF}-d_8$ was used as the solvent.

Complex **1** undergoes reactions with electrophilic⁵ and nucleophilic reagents. Treatment with maleic anhydride afforded the hydrogen maleate complex **5** (88% yield), which possesses two IR stretching frequencies at 1726 and 1550 cm^{-1} . We believe that the shifted C–O stretch (about 70 cm^{-1} relative to other iridium acetates¹⁴) is indicative of an intramolecularly hydrogen-bonded hydrogen maleate ligand.¹⁵ Subjection of **1** to the poorer electrophile phenyl acetate at 60 °C for 36 h resulted in an equimolar mixture of phenoxide **3** and the $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Ph})\text{-O}_2\text{CCH}_3$ (**6**) in quantitative yield by ^1H NMR spectroscopy. Only decomposition of the starting material was observed when the hydroxo complex **1** was heated with ethyl acetate at 100 °C. In addition to the nucleophilicity of the hydroxyl ligand of **1**, the iridium atom behaves as an electrophilic center. Treatment of **1** with methyl lithium in THF at 0 °C afforded a quantitative yield of the corresponding iridium methyl complex **7**.¹⁶

Migratory insertion reactions of fluoroalkenes into platinum alkoxides are known,^{1a,17} but direct observation of the insertion

of unfunctionalized alkenes into metal–oxygen bonds has no precedent. In contrast, coordinatively saturated **1** underwent an apparent insertion reaction with ethylene at 25 °C to afford $\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{Ph})\text{CH}_2\text{CH}_2\text{OH}$ (**8**) (65% yield by ^1H NMR spectroscopy after 2 days). This compound is related to the hydroxyethyl palladium complexes implicated as intermediates in the Wacker oxidation.⁶ Over the course of the insertion reaction, the formylmethyl complex **9** was detected, and over prolonged reaction times (1 week at 25 °C or 2 days at 45 °C), the amount of hydroxyethyl complex **8** was diminished and more **9** was formed along with two minor products.¹⁸ The complex **8** decomposed slowly in the absence of ethylene to afford a similar mixture of **9** and a minor material. We are currently studying the transformation of **8** to **9** to determine the fate of the removed hydrogen atoms. Insertion of dimethyl acetylenedicarboxylate (DMAD) afforded the enol **10** as a single stereoisomer in 76% yield.¹⁹ The stereochemistry of the product was determined to be (*Z*) by X-ray crystallography; details of the structure determination are provided as supplementary material. At present, we do not know whether the stereochemistry of **10** is a kinetic result of cis addition of the metal–oxygen bond or whether the olefin geometry is a result of equilibration of the (*E*)- and (*Z*)-enols.

In summary, we have demonstrated that the iridium hydroxo complex **1** reacts with a variety of reagents and undergoes ligand metathesis and electrophilic and nucleophilic attack. Furthermore, insertions of alkenes and alkynes into the metal–oxygen bond are observed. Experiments designed to elucidate the mechanisms of these reactions, with particular focus on the alkene insertion reactions and the conversion of **8** to **9**, are underway and will be reported in a full paper.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **1**–**10**; X-ray diffraction data (ORTEP diagrams, crystal and data collection parameters, positional parameters, and intramolecular distances and angles) for **2**, **3**, and **10** (16 pages). This material is provided with the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

(14) The absorbance at 1625 cm^{-1} in acetate **5** has been assigned as the carbonyl stretching frequency. See also ref 9e.

(15) (a) Döppert, K.; Sanchez-Delgado, R.; Klein, H.-P.; Thewalt, U. J. *Organomet. Chem.* **1982**, *233*, 205–213. (b) Olson, J. R.; Yamauchi, M.; Butler, W. M. *Inorg. Chim. Acta* **1985**, *99*, 121–128. (c) Gupta, M. P.; Geise, H. J.; Lenstra, A. T. H. *Cryst. Struct. Commun.* **1984**, *40*, 1152–1154.

(16) This compound has been reported previously: Diversi, P.; Iacopini, S.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1993**, 351–352.

(17) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603–1604.

(18) Other iridium formylmethyl complexes are known: Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 3773–3774.

(19) A similar insertion reaction of a palladium amide has been observed: Villanueva, L. A.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1992**, *11*, 2963–2965.