Alcohol Complexes of Tungsten Prepared by Ionic Hydrogenations of Ketones

Jeong-Sup Song,[†] David J. Szalda,[‡] and R. Morris Bullock*

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000

Ionic hydrogenation of acetone by $Cp(CO)_3WH$ and HOTf (OTf = OSO_2CF_3) gives the 2-propanol complex $[Cp(CO)_3W(HO^iPr)]^+OTf^-$. ^{1}H NMR data suggest O−H⋯O hydrogen bonding between the alcohol OH and an oxygen of the triflate anion in solution, and a crystal structure of this complex shows that hydrogen bonding also exists in the solid state. The short O⋯O distance of 2.63(1) Å indicates a strong hydrogen bond. Hydrogenation of other ketones and aldehydes gives related $[Cp(CO)_3W(alcohol)]^+OTf^-$ complexes. Aldehydes are selectively hydrogenated over ketones, and alkyl ketones are selectively hydrogenated over aromatic ketones. Hydrogenation of acetophenone gives ethylbenzene, with no intermediate tungsten complexes being observed. Reaction of 1-phenyl-1,3-butanedione with $Cp(CO)_3WH$ and HOTf gave $\{Cp(CO)_3W[CH_3CH(OH)CH_2C(=O)Ph]\}^+OTf^-$, the structure of which was determined by X-ray diffraction. The alcohol complexes $[Cp(CO)_3W(alcohol)]^+OTf^-$ decompose in solution to give free alcohols and $Cp(CO)_3WOTf$. The cationic dihydride $[Cp(CO)_2(PMe_3)-W(H)_2]^+OTf^-$ hydrogenates aldehydes and ketones; in these reactions a metal hydride serves as both the proton and hydride donor.

Alcohol ligands on low-valent transition metals are involved in several homogeneously catalyzed reactions.[1] Facile displacement of the methanol ligands of [Rh-(diphosphine)(MeOH)$_2$]$^+$ provides a site for coordination of the unsaturated substrate in the catalytic cycle for hydrogenation of olefins.[2] Iridium complexes with alcohol ligands, such as [IrH$_2$(PPh$_3$)$_2$(EtOH)$_2$]$^+$, are used in the homogeneous catalysis of olefin hydrogenation[3] and the catalytic alcoholysis of hydrosilanes.[4] Alcohol complexes are proposed as intermediates in the catalytic hydrogenation of ketones catalyzed by Rh complexes.[5]

Hydrogenations of ketones can proceed through ionic pathways. Hydride transfer from a metal hydride to a protonated ketone appears to be involved in several previously reported examples of stoichiometric hydrogenation of C=O bonds. In most of these cases the product is a free alcohol rather than a metal complex with an alcohol ligand. Kinetic studies of the hydrogenation of acetone by [Ru(bpy)$_2$(CO)H]$^+$ in aqueous solution support preequilibrium protonation of the acetone followed by hydride transfer from the metal.[6] Darensbourg and co-workers reported[7] hydrogenation

of aldehydes and ketones by acetic acid and a series of anionic metal hydrides such as HCr(CO)$_5^-$. Aldehydes are selectively reduced in the presence of ketones[8] using acetic acid and the bridging anionic hydride complex [Mo$_2$(CO)$_{10}$(μ-H)]$^+$. The molybdenum dihydride complex Cp$_2$MoH$_2$ can be used with acetic acid to hydrogenate ketones.[9] Bakhmutov and co-workers recently reported the characterization by low-temperature NMR of alcohol complexes of rhenium formed by ionic hydrogenation of ketones by ReH$_2$(CO)(NO)(PR$_3$)$_2$ (R = ^{i}Pr, CH$_3$, O^{i}Pr) and CF$_3$CO$_2$H.[10] In a few cases there is evidence for hydrogenation of ketones in which both the proton and the hydride are supplied from a metal. The tantalum dihydride [Cp$_2$(CO)TaH$_2$]$^+$ reacts with acetone to produce a 2-propanol complex,[11] [Cp$_2$(CO)Ta(HO^{i}Pr)]$^+$. Hydrogenation of acetone by the η^2-dihydrogen complex [(NH$_3$)$_5$-Os(η^2-H$_2$)]$^{3+}$ may proceed through an ionic mechanism.[12]

Our research on ionic hydrogenations has shown that unsaturated organic substrates can be hydrogenated using a strong acid (typically CF$_3$SO$_3$H, abbreviated as HOTf) as a proton source and a metal hydride as a hydride donor. The C=C bonds of tetrasubstituted, trisubstituted, and 1,1-disubstituted alkenes are hydrogenated at −50 °C using HOTf and metal carbonyl

---

(1) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Boston, 1994.

(2) Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* **1987,** *109,* 1746−1754.

(3) Crabtree, R. H.; Demou, P. C.; Eden, D.; Mihelcic, J. M.; Parnell, C. A.; Quirk, J. M.; Morris, G. E. *J. Am. Chem. Soc.* **1982,** *104,* 6994−7001.

(4) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989,** *111,* 2527−2535.

(5) Schrock, R. R.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1970,** 567−568.

(6) Geraty, S. M.; Harkin, P.; Vos, J. G. *Inorg. Chim. Acta* **1987,** *131,* 217−220.

(7) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985,** *107,* 2428−2434.

(8) Gibson, D. H.; El-Omrani, Y. S. *Organometallics* **1985,** *4,* 1473−1475.

(9) (a) Ito, T.; Koga, M.; Kurishima, S.; Natori, M.; Sekizuka, N.; Yoshioka, K. *J. Chem. Soc., Chem. Commun.* **1990,** 988−989. (b) Minato, M.; Fujiwara, Y.; Koga, M.; Matsumoto, S.; Kurishima, S.; Natori, M.; Sekizuka, N.; Yoshioka, K.; Ito, T. *J. Organomet. Chem.* **1998,** *569,* 139−145.

(10) Bakhmutov, V. I.; Vorontsov, E. V.; Antonov, D. Y. *Inorg. Chim. Acta* **1998,** *278,* 122−126.

(11) Reynoud, J.-F.; Leboeuf, J.-F.; Leblanc, J.-C.; Moïse, C. *Organometallics* **1986,** *5,* 1863−1866.

(12) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990,** *112,* 2261−2263.

---

hydrides.[13] The C≡C bonds of some alkynes can also be hydrogenated using HOTf and $Cp(CO)_3WH$; such cases involve a double hydrogenation, converting $PhC≡CH$ to $PhCH_2CH_3$, for example.[14] In this paper we report the synthesis and characterization of a series of alcohol complexes of tungsten. The alcohol ligand is produced in these reactions through ionic hydrogenation of an aldehyde or ketone.[15] In contrast, most previously reported examples where alcohol complexes were prepared and isolated involved adding an intact alcohol molecule to a metal complex with a weakly bound ligand. Examples include Beck's synthesis of alcohol complexes of tungsten[16] and ruthenium[17] by displacement of weakly coordinating BF_4 or SbF_6 ligands and the synthesis of a series of chiral rhenium alcohol complexes by Gladysz and co-workers through displacement of weakly bound CH_2Cl_2 ligands.[18]

Results

Synthesis and Characterization of $[Cp(CO)_3W$-(alcohol)]$^+OTf^-$ Complexes. Addition of triflic acid (HOTf) to a CH_2Cl_2 solution of $Cp(CO)_3WH$ and acetone produces the 2-propanol complex $[Cp(CO)_3W$-$(HO^iPr)]^+OTf^-$, which was isolated as a dark red microcrystalline solid in 78% yield (eq 1). The OH of the bound 2-propanol ligand appears as a doublet ($J = 7.4$ Hz) at δ 7.34 in the ^1H NMR spectrum in CD_2Cl_2. This OH resonance for the bound 2-propanol ligand appears at least 5 ppm downfield from that of free 2-propanol, indicating substantial hydrogen bonding of the alcohol. (The OH resonance of free alcohols varies somewhat depending on concentration, presence of water, etc.) The structure of $[Cp(CO)_3W(HO^iPr)]^+OTf^-$ was determined by single-crystal X-ray diffraction; Figure 1 shows the O–H···O hydrogen bonding observed in the solid state. Table 1 provides data collection and refinement details, and Table 2 lists selected bond distances and angles. The short O···O distance of 2.63(1) Å is indicative of a strong hydrogen bond.
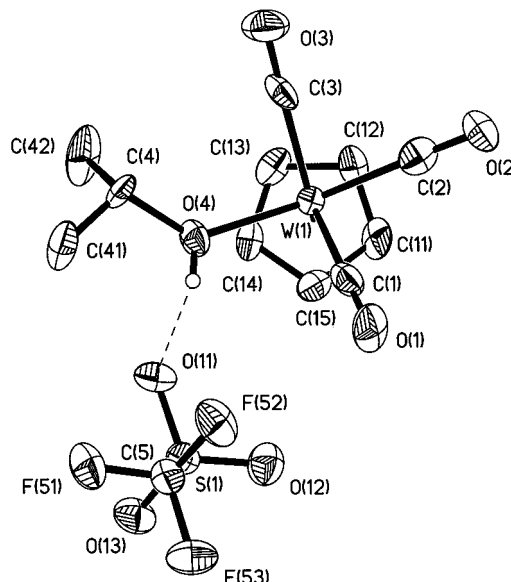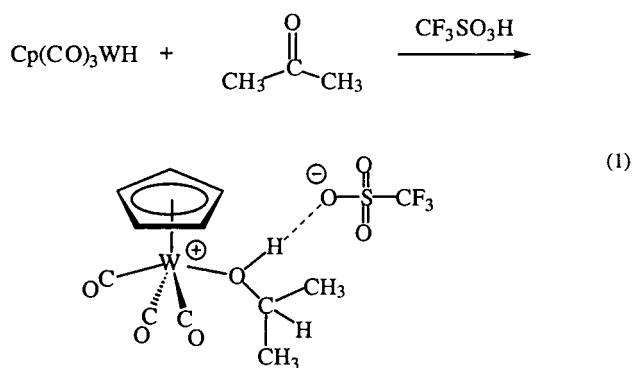
Figure 1. Drawing of $[Cp(CO)_3W(HO^iPr)]^+OTf^-$. The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms (except H4) are omitted.

Ionic hydrogenations of propionaldehyde, 2-adamantanone, and cyclohexanone gave tungsten alcohol complexes that were also isolated and fully characterized by ^1H NMR, ^{13}C NMR, IR, and elemental analysis (eqs 2–4). ^1H NMR chemical shifts of the OH resonances were in the range δ 6.94–7.75 for these compounds, indicating hydrogen bonding to OTf in all of these cases.
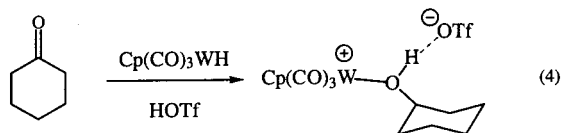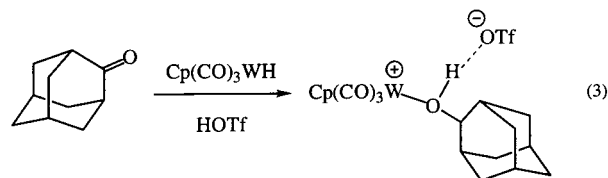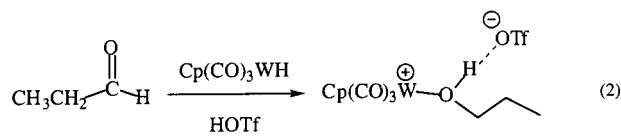
Hydrogenations of 2-butanone, pivaldehyde [^tBuC-(=O)H], and 4-phenyl-2-butanone by $Cp(CO)_3WH$ and HOTf were carried out in NMR tubes. The $[Cp(CO)_3W$-(alcohol)]$^+OTf^-$ products from these reactions were characterized by ^1H NMR and appear entirely analogous to the examples that were fully characterized; details are provided in the Experimental Section. Even though 1,3,5-trioxane, $[(CH_2O)_3]$, has little solubility in CD_2Cl_2, it reacted with $Cp(CO)_3WH$ and HOTf to give the methanol complex $[Cp(CO)_3W(HOCH_3)]^+OTf^-$. Apparently ring-opening occurs in the presence of the acid, resulting in the chemical equivalent of hydrogenation of formaldehyde to methanol.

When hydrogenation of acetophenone is attempted with 1 equiv each of $Cp(CO)_3WH$ and HOTf, only half

(13) Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602–8612.

(14) Luan, L.; Song, J.-S.; Bullock, R. M. *J. Org. Chem.* **1995**, *60*, 7170–7176.

(15) Some of these results were published in a communication: Song, J.-S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1233–1235.

(16) Sünkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 231–240.

(17) Milke, J.; Missling, C.; Sünkel, K.; Beck, W. *J. Organomet. Chem.* **1993**, *445*, 219–227.

(18) Agbossou, S. K.; Smith, W. W.; Gladysz, J. A. *Chem. Ber.* **1990**, *123*, 1293–1299.

**Table 1. Crystallographic Data for
[Cp(CO)₃W(HOⁱPr)]⁺OTf⁻ and
{Cp(CO)₃W[CH₃CH(OH)CH₂C(=O)Ph]}⁺OTf⁻**

	[Cp(CO)₃W-(HOⁱPr)]⁺OTf⁻	{Cp(CO)₃W[CH₃CH-(OH)CH₂C(=O)Ph]}⁺OTf⁻
formula	$C_{12}H_{13}F_3O_7SW$	$C_{19}H_{17}F_3O_8SW$
mol wt	542.13	646.24
space group	$P2_1/n$	$P\bar{1}$
a, Å	8.139(1)	10.391(2)
b, Å	20.906(5)	12.000(2)
c, Å	10.516(2)	8.768(2)
α (deg)	90.00	95.68(2)
β (deg)	113.22(2)	98.43(2)
γ (deg)	90.00	96.53(2)
V, Å³	1644.4(5)	1067.0(4)
Z	4	2
ρ(calcd) g cm⁻³	2.190	2.011
temp (K)	200	200
radiation	Mo Kα	Mo Kα
μ, cm⁻¹	0.7215	0.5581
abs corr	empirical	Gaussian
no. of reflns collected	4798	5180
no. of unique reflns	4798	4910
2θ limits (deg)	60.0	55.0
no. of variables	218	290
$R_1{}^a$ $(I>2\sigma(I))$	0.0541	0.0479
wR_2	0.1389	0.1382
max. shift/error, final cycle	0.001	<0.001

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(|F_o{}^2| - |F_c{}^2|)^2]/\Sigma[w|F_o{}^4|]\}^{1/2}$.

**Table 2. Selected Bond Lengths (Å) and Angles
(deg) for [Cp(CO)₃W(HOⁱPr)]⁺OTf⁻**

W(1)−C(3)	1.994(14)
W(1)−C(1)	2.012(14)
W(1)−C(2)	2.015(15)
W(1)−O(4)	2.176(8)
W−Cp^a	1.99(1)
C(3)−W(1)−C(1)	110.5(6)
C(3)−W(1)−C(2)	76.8(6)
C(1)−W(1)−C(2)	76.0(5)
C(3)−W(1)−O(4)	83.8(4)
C(1)−W(1)−O(4)	78.6(4)
C(2)−W(1)−O(4)	140.0(5)

^{a} Cp designates the centroid of the cyclopentadienyl ring.

of the acetophenone is consumed, and ethylbenzene is produced. The reaction does proceed cleanly to completion when 2 equiv each of Cp(CO)₃WH and HOTf are used (eq 5), but it proceeds more slowly than hydrogenation of aliphatic ketones. No *sec*-phenethyl alcohol is observed as an intermediate in these reactions, indicating that the rate of its conversion to ethylbenzene is faster than that of acetophenone. Separate experiments starting with this alcohol verified that it is converted to ethylbenzene by Cp(CO)₃WH and HOTf (eq 6).
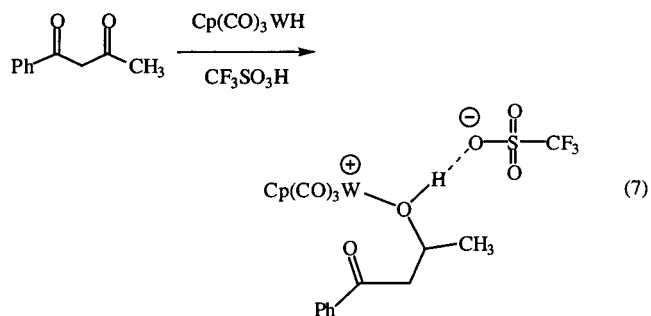
$$
\text{Ph}-\overset{\displaystyle O}{\underset{\displaystyle }{C}}-\text{CH}_3 \xrightarrow[\substack{\text{2 HOTf} \\ -\text{H}_2\text{O}}]{\text{2 Cp(CO)}_3\text{WH}} \text{PhCH}_2\text{CH}_3 \quad (5)
$$

$$
\overset{\displaystyle H}{\underset{\displaystyle Ph}{}}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}} \xrightarrow[\substack{\text{HOTf} \\ -\text{H}_2\text{O}}]{\text{Cp(CO)}_3\text{WH}} \text{PhCH}_2\text{CH}_3 \quad (6)
$$
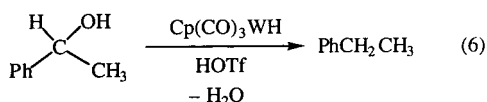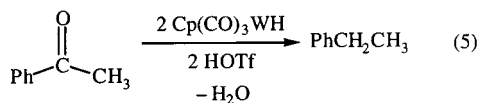
Selectivity of C=O Hydrogenation. The possibility of selective hydrogenations by Cp(CO)₃WH and HOTf
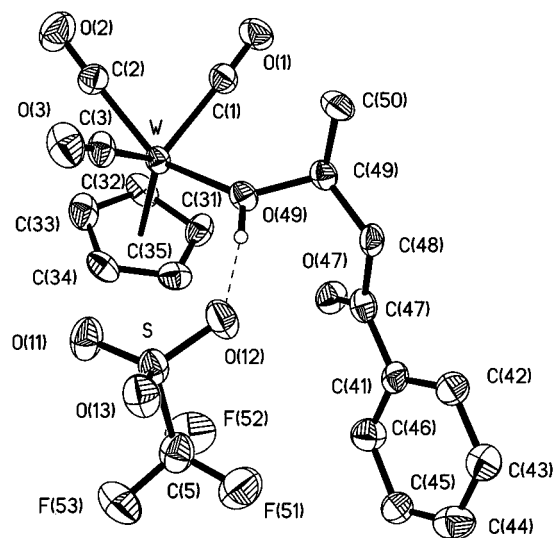
Figure 2. View of {Cp(CO)₃W[CH₃CH(OH)CH₂C(=O)-Ph]}⁺OTf⁻. The thermal ellipsoids are at the 50% probability level. The hydrogen atoms are omitted, except for H49.

was assessed. When acetone and pivaldehyde in the same NMR tube were reacted with Cp(CO)₃WH and HOTf, only the aldehyde was hydrogenated. The formation of the neopentyl alcohol complex {Cp(CO)₃W-[HOCH₂C(CH₃)₃]}⁺OTf⁻ indicates a strong preference for hydrogenation of the aldehyde over the ketone. None of the 2-propanol complex that would have resulted from hydrogenation of acetone was detected. The ¹H NMR resonance for acetone shifted from δ 2.12 to 2.15, suggesting that some of the acetone was protonated by HOTf.

A similar competition between acetone and acetophenone resulted in hydrogenation of the acetone, with no product from hydrogenation of acetophenone being detected. This is thought to be due to stabilization of the protonated acetophenone by the phenyl group, making it a weaker hydride acceptor. An intramolecular competition between aliphatic and aromatic ketone functional groups was carried out, as shown in eq 7. The

$$
\text{Ph}-\overset{\displaystyle O}{\underset{\displaystyle }{C}}\text{CH}_2\overset{\displaystyle O}{\underset{\displaystyle }{C}}-\text{CH}_3 \xrightarrow[\text{CF}_3\text{SO}_3\text{H}]{\text{Cp(CO)}_3\text{WH}}
$$

(7)

product of this reaction was fully characterized by ¹H NMR, ¹³C NMR, IR, and elemental analysis as well as a crystal structure. The structure found in the solid (Figure 2) is similar to that found for the 2-propanol complex with hydrogen bonding of the OH to the triflate counterion. Table 1 provides data collection and refinement details, and Table 3 lists selected bond distances and angles. The O···O distance of 2.63(1) Å is indicative of a strong hydrogen bond; this distance is the same as that found for [Cp(CO)₃W(HOⁱPr)]⁺OTf⁻. This complex

**Table 3. Selected Bond Lengths (Å) and
Angles (deg) for
{Cp(CO)$_3$W[CH$_3$CH(OH)CH$_2$C(=O)Ph]}$^+$OTf$^-$**

| W−C(2)	1.978(12)
W−C(1)	2.017(12)
W−C(3)	2.038(12)
W−O(49)	2.169(8)
W−Cp[a]	1.99(1)
C(2)−W−C(1)	75.6(5)
C(2)−W−C(3)	76.6(5)
C(1)−W−C(3)	112.9(5)
C(2)−W−O(49)	140.3(4)
C(1)−W−O(49)	85.5(4)
C(3)−W−O(49)	79.3(4)

[a] Cp designates the centroid of the cyclopentadienyl ring.

might have been able to form an intramolecular hydrogen bond between the C=O of the aromatic ketone and the OH of the alcohol. Such a hydrogen bond would form a six-membered ring that might be expected to be stable. In the crystal structure, however, hydrogen bonding to OTf$^-$ is found, so this mode of hydrogen bonding is preferred, at least in the solid. Another diketone that was hydrogenated was diacetyl, CH$_3$(C=O)$_2$CH$_3$, giving the alcohol complex {Cp(CO)$_3$W[CH$_3$CH(OH)C(=O)-CH$_3$]}$^+$OTf$^-$, which was isolated and fully characterized.

We previously found that ether complexes of tungsten could be isolated from reactions of acetals with Cp-(CO)$_3$WH and HOTf.[19] Two examples were crystallographically characterized, including one having an oxygen-bound ether and another in which a vinyl acetal was converted to a vinyl ether bound to tungsten through the C=C bond. Results from an NMR tube reaction of 1,1-dimethoxyacetone with Cp(CO)$_3$WH and HOTf (eq 8) provided evidence for the formation of an alcohol complex, indicating selective C=O hydrogenation in the presence of an acetal functionality.
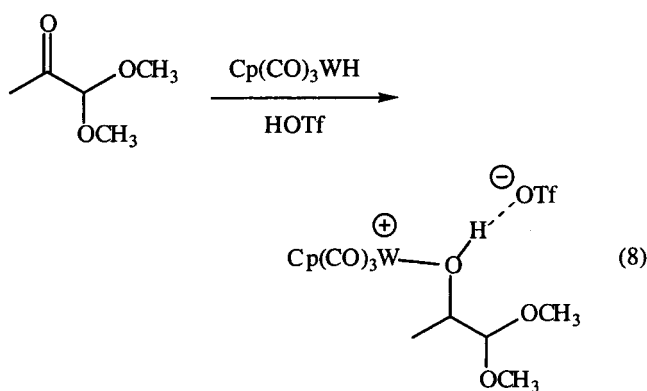
Release of Free Alcohols by Displacement of Bound Alcohol by Triflate. These alcohol complexes are sufficiently stable to be isolated, but they decompose over the course of several hours at room temperature in solution. Equation 9 shows the decomposition of the 2-propanol complex, which gives free 2-propanol and Cp-(CO)$_3$WOTf due to displacement of the alcohol by the triflate counterion. For the 2-propanol complex, the reaction is about half completed in 14 h at room temperature. Qualitatively, this reaction is unaffected by the presence of excess free 2-propanol or by acetone. Other

$t_{1/2} \approx 14$ h at 22°C
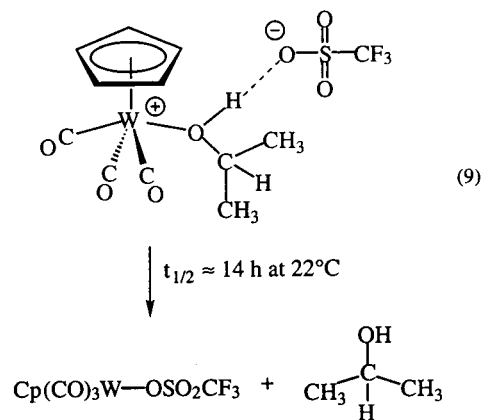
alcohol complexes with triflate counterion also decomposed in a similar manner, but the rates of these reactions were not studied in detail. The alcohol ligand can be quickly and cleanly displaced by addition of NEt$_4$Br, resulting in the release of free alcohol and formation of Cp(CO)$_3$WBr.

An Alcohol Complex of Tungsten with a BAr′$_4$$^-$ Counterion. These complexes with triflate counterion may be compared to a related alcohol complex with a noncoordinating counterion. Reaction of acetone with Cp(CO)$_3$WH and [H(OEt$_2$)$_2$]$^+$BAr′$_4$$^-$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] gave [Cp(CO)$_3$W(HO^{i}Pr)]$^+$BAr′$_4$$^-$, which was isolated in 69% yield as an analytically pure solid. A notable feature in the ^{1}H NMR spectrum of this complex is the appearance of the OH resonance as a doublet ($J = 7.9$ Hz) at δ 2.41. The substantial upfield shift of this resonance, compared to the OH in the triflate complex [Cp(CO)$_3$W(HO^{i}Pr)]$^+$OTf$^-$, suggests little or no hydrogen bonding of the OH in the complex with the BAr′$_4$$^-$ counterion. This 2-propanol complex with the BAr′$_4$$^-$ counterion is much more stable than [Cp(CO)$_3$W(HO^{i}Pr)]$^+$OTf$^-$. A solution of [Cp(CO)$_3$W-(HO^{i}Pr)]$^+$BAr′$_4$$^-$ that was left at room temperature for 1 day showed only 16% free HO^{i}Pr (cf. eq 9 for much faster decomposition of [Cp(CO)$_3$W(HO^{i}Pr)]$^+$OTf$^-$).

Addition of acetone (1 equiv) to a solution of [Cp-(CO)$_3$W(HO^{i}Pr)]$^+$BAr′$_4$$^-$ in CD$_2$Cl$_2$ causes a downfield shift of the ^{1}H NMR resonance of the OH doublet to δ 6.74, suggesting that acetone serves as a hydrogen bond acceptor in an O−H···O hydrogen bond. Over the course of several days, the 2-propanol ligand of [Cp(CO)$_3$W-(HO^{i}Pr)]$^+$BAr′$_4$$^-$ is displaced by acetone, giving [Cp-(CO)$_3$W(η^1-O=CMe$_2$)]$^+$BAr′$_4$$^-$. After 5 days, about a 1:1 ratio of 2-propanol and acetone complexes were observed by NMR, but the equilibrium constant was not determined. This acetone complex, [Cp(CO)$_3$W(η^1-O=CMe$_2$)]$^+$-BAr′$_4$$^-$, was not isolated, but it is closely related to ketone complexes that were fully characterized.[20] We previously reported the isolation and characterization of a series of [Cp(CO)$_3$W(η^1-ketone)]$^+$ complexes by ionic hydrogenation of α,β-unsaturated ketones.[20]

Ionic Hydrogenation of Ketones with Mo, Mn, and Re Hydrides. Most of our efforts have focused on the use of Cp(CO)$_3$WH as a hydride donor, since it forms alcohol complexes that can be isolated. We reported the kinetics of hydride transfers for a series of metal

(19) Song, J.-S.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 11134−11141.

(20) Song, J.-S.; Szalda, D. J.; Bullock, R. M. *Inorg. Chim. Acta* **1997**, *259*, 161−172.

hydrides,[21] and several of these metal hydrides have also been found to be effective hydride donors in these ionic hydrogenations. Addition of HOTf to a CD_2Cl_2 solution containing acetone and the molybdenum hydride $Cp(CO)_3MoH$ resulted in the formation of $[Cp(CO)_3Mo(HO^iPr)]^+OTf^-$ and free HO^iPr. The molybdenum alcohol complex was less stable than the analogous tungsten complex, with about half of it having decomposed in 30 min at 22 °C. The rhenium complex $(CO)_5ReH$ also reacted with acetone and HOTf to give a high yield of HO^iPr; less than 10% of the alcohol complex $[(CO)_5Re(HO^iPr)]^+OTf^-$ was detected by NMR. Reaction of the manganese hydride $(CO)_5MnH$ with acetone and HOTf at 22 °C resulted in a high yield of HO^iPr and the triflate complex $(CO)_5MnOTf$, with no evidence for a 2-propanol complex.

Limitations on Substrates to be Hydrogenated. A variety of ketone and aldehydes can be hydrogenated by this method, but we found a few cases where $Cp(CO)_3WH$ and HOTf at room temperature fail to hydrogenate C=O bonds. Addition of HOTf and $Cp(CO)_3WH$ to 4,4'-dimethoxybenzophenone, $(MeO-p-C_6H_4)_2C=O$, resulted in a downfield shift of 0.24−0.27 ppm of the NMR resonances of the ketone, suggesting it was protonated. No hydrogenation product was detected after a day at 22 °C. Similar observations were made from attempted hydrogenation of xanthone by $Cp(CO)_3WH$ and HOTf.

Esters are much more difficult to hydrogenate than ketones,[22] and we found that methyl acetate was not hydrogenated by $Cp(CO)_3WH$ and HOTf at room temperature. Both methyl resonances of $CH_3CO_2CH_3$ were shifted 0.36 ppm downfield upon addition of HOTf, but no evidence for hydrogenation was obtained. These substrates that are more difficult to hydrogenate provide impetus for future studies using different reaction conditions and different metal hydrides than those examined here.

Hydrogenations by Cationic Dihydrides. The hydrogenations presented above involve use of HOTf as the proton source and a neutral metal hydride as the hydride donor. A more attractive proton source would be a highly acidic metal hydride. The cationic tungsten dihydride $[Cp(CO)_2(PMe_3)W(H)_2]^+OTf^-$ can be isolated and has been fully characterized, including a crystal structure.[23] This complex reacts quickly with propionaldehyde at 22 °C to give an *n*-propanol complex (eq 10) which exists as a mixture of cis and trans isomers.

Several prior studies established ^1H NMR criteria to distinguish cis from trans isomers in these types of phosphine-substituted W (or Mo) compounds with a four-legged piano stool geometry.[24] The Cp resonance for the cis isomers appears about 0.2−0.3 ppm downfield of the resonance for the Cp of the trans isomer. The Cp
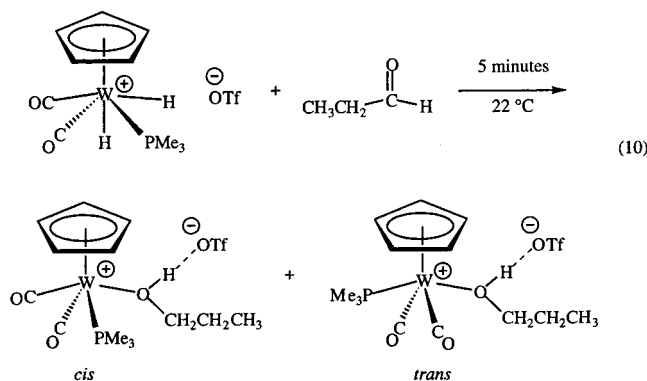
resonance of the trans isomer appears as a doublet ($J_{PH} \approx 2$ Hz) rather than the singlet of the cis isomer. After 5 min at 22 °C, the trans isomer of $[Cp(CO)_2(PMe_3)W(HO^nPr)]^+OTf^-$ (70%) predominated over *cis*-$[Cp(CO)_2(PMe_3)W(HO^nPr)]^+OTf^-$ (17%). After 1.5 h, <2% of *cis*-$[Cp(CO)_2(PMe_3)W(HO^nPr)]^+OTf^-$ remained, since it decomposed to *cis*-$Cp(CO)_2(PMe_3)WOTf$, but *trans*-$[Cp(CO)_2(PMe_3)W(HO^nPr)]^+OTf^-$ is stable under these conditions.

A similar hydrogenation of acetone by $[Cp(CO)_2(PMe_3)W(H)_2]^+OTf^-$ was observed. Both cis and trans isomers of the alcohol complex $[Cp(CO)_2(PMe_3)W(HO^iPr)]^+OTf^-$ were initially formed. They decompose to release free HO^iPr, with 83% *cis*-$Cp(CO)_2(PMe_3)WOTf$ being observed after 20 h at 22 °C. This demonstration that both H^+ and H^- could be delivered from a metal-based system to an organic substrate is significant since it constitutes a critical step in the development of catalytic ionic hydrogenations using complexes of Mo and W. We have recently reported that a series of ketone complexes $[Cp(CO)_2(PR_3)M(\eta^1-O=CEt_2)]^+BAr'_4^-$ (M = Mo, W) are catalyst precursors for hydrogenation of ketones under mild conditions (23 °C, < 4 atm H_2).[25]

The hydrogenation of ketones by this tungsten dihydride may proceed through direct metal-to-oxygen proton transfer from the cationic dihydride $[Cp(CO)_2(PMe_3)W(H)_2]^+OTf^-$ to the ketone, followed by hydride transfer from the neutral hydride $Cp(CO)_2(PMe_3)WH$. An alternative that cannot be ruled out is that OTf^- serves as a kinetically competent proton carrier. Darensbourg has shown that Cl^- and other "hard" anions can mediate deprotonations of metal hydrides and influence kinetics of proton transfers.[26] In our case, this would involve proton transfer to OTf^- from $[Cp(CO)_2(PMe_3)W(H)_2]^+OTf^-$ to give HOTf, which would then protonate the ketone.

Discussion

Mechanistic Considerations. A study of the kinetics of ionic hydrogenation of isobutyraldehyde by $CpMo(CO)_3H$ using CF_3CO_2H as the acid[15] showed that the apparent rate decreases as the reaction proceeds, since acid is consumed. But with a buffer present, the reaction was first-order in acid and first-order in metal hydride. These kinetics are consistent with the mechanism

(21) (a) Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121−13137. (b) Cheng, T.-Y.; Bullock, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 3150−3155.

(22) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 557.

(23) Bullock, R. M.; Song, J.-S.; Szalda, D. J. *Organometallics* **1996**, *15*, 2504−2516.

(24) (a) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618−2626. (b) Smith, K.-T.; Tilset, M. *J. Organomet. Chem.* **1992**, *431*, 55−64. (c) Kalck, P.; Poilblanc, R. *J. Organomet. Chem.* **1969**, *19*, 115−121. (d) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852−5860.

(25) Bullock, R. M.; Voges, M. H. *J. Am. Chem. Soc.* **2000**, *122*, 12594−12595.

(26) (a) Hanckel, J. M.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1983**, *105*, 6979−6980. (b) Darensbourg, M. Y.; Ludvig, M. M. *Inorg. Chem.* **1986**, *25*, 2894−2898.

Scheme 1
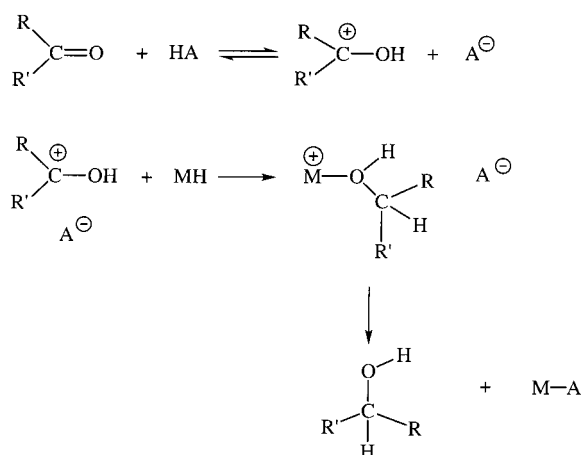
shown in Scheme 1, involving preequilibrium protonation of the substrate, followed by rate-determining hydride transfer.

Norton's group has extensively studied the kinetic and thermodynamic acidity of metal hydrides,[27] and they recently determined a pK_a of 5.6 in CH_3CN for $[Cp(CO)_2(PMe_3)W(H)_2]^+$.[28] Since the pK_a of protonated acetone in CH_3CN is about -0.1,[29,30] proton transfer from the tungsten dihydride to acetone is uphill thermodynamically. The hydrogenation still proceeds smoothly, since fast hydride transfer follows the unfavorable proton transfer. Norton and co-workers reported a rate constant of $k = 1.2 \times 10^4 \, M^{-1} \, s^{-1}$ at 25 °C in CH_3CN for hydride transfer from $Cp(CO)_2(PPh_3)MoH$ to protonated acetone.[30] Their kinetics and mechanistic studies led to the conclusion that these were single-step hydride transfers, rather than the alternative pathway of electron transfer followed by hydrogen atom transfer.

In our reactions, hydride transfer occurs from $CpW(CO)_3H$ to protonated ketones. In the absence of acid, no reaction is observed between ketones and $CpW(CO)_3H$ or other metal hydrides studied here. In contrast, Berke and co-workers found that tungsten hydride complexes such as $WH(CO)_2(NO)(PMe_3)_2$ readily insert aldehydes and ketones into the metal−hydrogen bond.[31] The reactivity of metal hydride complexes with nitrosyl ligands has been reviewed.[32]

In the absence of ketone, each of the metal hydrides $Cp(CO)_3MoH$, $(CO)_5ReH$, and $(CO)_5MnH$ reacts quickly with HOTf at 22 °C to give H_2 and the corresponding metal triflates.[13] The successful use of metal hydrides in these reactions shows that hydride transfer can occur in the presence of acid and requires that H^+ and H^- be transferred to the ketone faster than the formation of H_2 gas. Instead of direct cleavage of the M−H by H^+ to produce H_2, protonation of the metal hydride can occur. Protonation directly at the metal would give a dihydride $[M(H)_2]^+$, or protonation at the metal−hydrogen bond will produce a dihydrogen complex $[M(\eta^2\text{-}H_2)]^+$.[33] The stability of the cationic dihydride or dihydrogen complex can influence the reaction by favoring proton transfer from the MH_2^+ species, rather than elimination of H_2 from it. We found earlier that protonation of $Cp(CO)_3WH$ by HOTf ($\sim$1 equiv) proceeds to only partial completion.[23] The resultant tungsten dihydride, $[Cp(CO)_3W(H)_2]^+OTf^-$, not only is highly acidic but has moderate thermal stability as well, being incompletely decomposed to H_2 and $Cp(CO)_3WOTf$ after two weeks. The phosphine-substituted dihydride $[Cp(CO)_2(PMe_3)W(H)_2]^+OTf^-$ is stable enough to be isolated and crystallographically characterized,[23] but such stability is certainly not a requirement. The molybdenum dihydrides implicated as intermediates in catalytic ionic hydrogenations have not been directly observed.[25]

The C−H bond of the alcohol is formed through a hydride transfer from metal to carbon. The formation of the alcohol complexes $[Cp(CO)_3W(ROH)]^+OTf^-$ as the kinetic product indicates that some W−O bond formation must be occurring in the transition state for hydride transfer, before W−H rupture is complete. If this were not the case, then the thermodynamically more stable product $Cp(CO)_3WOTf$ would have been the kinetic product.

Studies of the kinetics and thermodynamics of cis−trans interconversions of the neutral metal hydride complexes $Cp(CO)_2(PR_3)MH$ (M = Mo, W) have been reported, with the equilibria generally favoring the cis isomer.[21a,24d] Related cationic complexes also tend to exhibit a thermodynamic preference for the cis isomer: Tilset and co-workers found that isomerization of a cis/trans mixture of $[Cp(CO)_2(PMe_3)W(NCCH_3)]^+BF_4^-$ to the thermodynamic isomer ratio of 95:5 cis:trans was very slow ($t_{1/2} \approx 40$ h at ambient temperature).[24a] In our hydrogenations of acetone and propionaldehyde by the phosphine-substituted tungsten dihydride $[Cp(CO)_2(PMe_3)W(H)_2]^+OTf^-$, both cis and trans isomers of the alcohol complexes $[Cp(CO)_2(PMe_3)W(HO^iPr)]^+$ and $[Cp(CO)_2(PMe_3)W(HO^nPr)]^+$ were observed. In both cases, the *trans*-$[Cp(CO)_2(PMe_3)W(alcohol)]^+$ complexes persisted after 1−2 days and were significantly more stable than the cis isomers. Our cis alcohol complexes may be thermodynamically favored over the trans alcohol isomers, as found in the examples cited above. We have no direct evidence for trans to cis isomerization of our $[Cp(CO)_2(PMe_3)W(alcohol)]^+$ complexes, however. The higher kinetic lability of the cis alcohol isomers toward displacement by triflate means that the formation of the observed *cis*-$Cp(CO)_2(PMe_3)WOTf$ product predominantly results from displacement of the alcohol by triflate anion from the *cis*-$[Cp(CO)_2(PMe_3)W(alcohol)]^+OTf^-$ isomers.

The relative trend of stability observed for these alcohol complexes, with the W complexes being more stable than those of Mo or Re, is due to both the strength of the metal−alcohol bond being displaced, as well as the strength of the metal−triflate bond being formed.

(27) For a review of proton-transfer reactions of metal hydrides, see: Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 9; pp 309−359.

(28) Papish, E. T.; Rix, F. C.; Spetseris, N.; Norton, J. R.; Williams, R. D. *J. Am. Chem. Soc.* **2000**, *122*, 12235−12242.

(29) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8539−8546.

(30) Smith, K.-T.; Norton, J. R.; Tilset, M. *Organometallics* **1996**, *15*, 4515−4520.

(31) (a) van der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *11*, 2051−2057. (b) van der Zeijden, A. A. H.; Berke, H. *Helv. Chim. Acta* **1992**, *75*, 513−522. (c) van der Zeijden, A. A. H.; Veghini, D.; Berke, H. *Inorg. Chem.* **1992**, *31*, 5106−5116.

(32) Berke, H.; Burger, P. *Comments Inorg. Chem.* **1994**, *16*, 279−312.

(33) For reviews of dihydrogen complexes, see: (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913−926. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155−284.

Mayer and co-workers reported extensive studies of oxygen atom transfers between a series of d^2 oxo complexes of W, Mo, and Re.[34] On the basis of the relative directions of inter-metal oxygen transfers, they concluded the relative metal−oxygen bond strengths for $M(O)Cl_xL_{5-x}$ to be W > Mo > Re. Their ordering of bond strengths agrees with the qualitative relative stability of our alcohol complexes, despite the significant differences in ligand sets and formal oxidation states.

Structural Comparisons. The X-ray structural data for both $[Cp(CO)_3W(HO^iPr)]^+OTf^-$ and $\{Cp(CO)_3W-[CH_3CH(OH)CH_2C(=O)Ph]\}^+OTf^-$ show evidence for hydrogen bonding between the OH of the bound alcohol ligands and an oxygen of the OTf^- anion. The coordination sphere about the tungsten is remarkably similar in the two structures (Table 2). The short O···O separation of 2.63(1) Å found in the two examples reported here are indicative of strong[35] hydrogen bonding. This O···O separation is comparable to that determined (2.62 Å) for the unusually strong hydrogen bond of $(PMe_2-Ph)_3Rh(Otol)(HOtol)^{36}$ [tol = *p*-tolyl], in which an alcohol is hydrogen bonded to the rhodium alkoxide. In addition to the crystallographic study, a calorimetric determination showed $\Delta H = -9.7 \pm 0.5$ kcal/mol for association of the alcohol to the rhodium alkoxide.[36] Spectroscopic evidence was reported[37] for hydrogen bonding of an oxygen of the perchlorate counterion to the bound alcohol ligand in $[ReH(CO)(NO)(PPh_3)_2(MeOH)]^+ClO_4^-$. Beck and co-workers reported[17] a crystal structure of the ruthenium alcohol complex $[Cp(CO)(PPh_3)Ru-(EtOH)]^+BF_4^-$ that indicated O−H···F hydrogen bonding. In contrast, Gladysz and co-workers prepared[18] a series of low-valent rhenium alcohol complexes of formula $[CpRe(NO)(PPh_3)(ROH)]^+BF_4^-$ and noted that their spectroscopic data did not provide a strong case for hydrogen bonding.

Compared to alcohol complexes, far more structural data are available on H_2O ligands exhibiting hydrogen bonding. The aqua ligand of $[IrH_2(THF)(H_2O)(PPh_3)_2]^+-SbF_6^-\cdot THF$ exhibits hydrogen bonding to both the F of the SbF_6^- and the O of a THF molecule in the lattice (O···O separation of 2.70(2) Å).[38] The H_2O bound to tungsten in $W(CO)_3(P^iPr_3)_2(H_2O)\cdot THF$ exhibits hydrogen bonding, with the crystal structure[39] showing both a hydrogen bond to lattice THF and an unusual O−H···O hydrogen bond of the OH to the oxygen of a carbonyl ligand of an adjacent molecule (O···O separation of 2.792 Å). In some cases different oxygens of the same OTf^- anion form hydrogen bonds to different water molecules on the same metal.[40] Clearly a variety

of interesting hydrogen-bonding patterns are adopted by alcohol and water molecules[41] bound to low-valent transition metals. The importance of hydrogen bonding in biological compounds has long been appreciated,[42] and recent interest has focused on hydrogen-bonding patterns in organometallic and organic compounds for crystal engineering.[43]

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. ^{1}H NMR chemical shifts were referenced to the residual proton peak of $CHDCl_2$ at δ 5.32. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory (Woodside, NY). NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz for ^{1}H). IR spectra were recorded on a Mattson Polaris FT-IR spectrometer.

The metal hydrides $Cp(CO)_3WH$,[44] $Cp(CO)_3MoH$,[44] $(CO)_5-MnH$,[45] $(CO)_5ReH$,[46] and $[Cp(CO)_2(PMe_3)W(H)_2]^+OTf^{-23}$ were prepared by literature methods. THF, Et_2O, and hexane were distilled from Na/benzopheneone, and CH_2Cl_2 was distilled from P_2O_5. The organic substrates were purchased from commercial sources and used as received. HOTf was purified by distillation. $[H(OEt_2)_2]^+BAr'_4^-$ [Ar' = 3,5-bis(trifluoromethyl)phenyl] was prepared as previously reported.[47]

Preparation of $[Cp(CO)_3W(HO^iPr)]^+OTf^-$. HOTf (100 μL, 1.13 mmol) was added to a solution of $Cp(CO)_3WH$ (300 mg, 0.90 mmol) and acetone (80 μL, 1.1 mmol) in CH_2Cl_2 (10 mL) at 22 °C. The solution was stirred for 30 min, during which time it became burgundy-red. Et_2O (20 mL) and hexane (10 mL) were added by vacuum transfer, and the dark red microcrystalline precipitate was collected by filtration. Yield of $[Cp(CO)_3W(HO^iPr)]^+OTf^-$: 380 mg (78%). Crystals suitable for diffraction studies were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the product at −75 °C. This alcohol complex was unstable in solution at 22 °C, and after 14 h 50% of it decomposed to yield $Cp(CO)_3WOTf$ and free HO^iPr. ^{1}H NMR (CD_2Cl_2): δ 7.34 (d, $J = 7.4$ Hz, 1H, OH), 6.04 (s, 5H, Cp), 3.58 (d of septets, $J = 7.3$ Hz, 6.3 Hz, 1H, CH), 1.15 (d, $J = 6.3$ Hz, 6H, CH_3). ^{13}C NMR (CD_2Cl_2, −73 °C): 225.0 (CO), 222.3 (2 CO), 94.9 (Cp), 83.8 (CH), 22.2 (CH_3). IR (KBr): $\nu(OH)$ 3444 (w, br); $\nu(CO)$ 2062 (vs), 1983 (vs), 1954 (vs); $\nu(C-O)$ 1022 (s) cm^{-1}. IR (CH_2Cl_2): $\nu(CO)$ 2061 (vs), 1982 (s), 1954 (vs) cm^{-1}. Anal. Calcd for $C_{12}H_{13}F_3O_7SW$: C, 26.58; H, 2.42. Found: C, 26.71, H, 2.25.

Preparation of $[Cp(CO)_3W(HO^nPr)]^+OTf^-$. HOTf (55 μL, 0.62 mmol) was added to a solution of $Cp(CO)_3WH$ (150 mg, 0.45 mmol) and propionaldehyde (40 μL, 0.55 mmol) in CH_2Cl_2 (10 mL) at −78 °C. The solution was stirred for 2 h, during which time the color changed from pale yellow to burgundy-red. Addition of Et_2O (30 mL) resulted in precipitation of a dark red solid, which was collected by filtration and washed with Et_2O (10 mL). Recrystallization from $CH_2Cl_2/$

(34) Over, D. E.; Critchlow, S. C.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4643−4648.

(35) Gilli, P.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Am. Chem. Soc.* **1994**, *116*, 909−915. This article discusses bonding in O−H···O hydrogen bonds in the context of structural data and refers to the loose definitions of bond strength according to O···O distances as very strong (<2.50 Å), strong (2.50−2.65 Å), medium (2.65−2.80 Å), and weak (>2.80 Å).

(36) Kegley, S. E.; Schaverien, C. J.; Freundenberger, J. H.; Bergman, R. G.; Nolan, S. P.; Hoff, C. D. *J. Am. Chem. Soc.* **1987**, *109*, 6563−6565.

(37) Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1985**, *24*, 3898−3903.

(38) Luo, X.-L.; Schulte, G. K.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 682−686.

(39) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390−3404.

(40) Svetlanova-Larsen, A.; Zoch, C. R.; Hubbard, J. L. *Organometallics* **1996**, *15*, 3076−3087.

(41) Numerous citations to low-valent aqua complexes are given in ref 39. A more recent article (Takahashi, Y.; Akita, M.; Hikichi, S.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3186−3194) presents a series of Ru aqua complexes hydrogen bonded to OTf^- and THF; this article has a discussion of the various hydrogen-bonding modes encountered.

(42) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: New York, 1991.

(43) (a) Braga, D.; Grepioni, F.; Sabatino, P.; Desiraju, G. R. *Organometallics* **1994**, *13*, 3532−3543. (b) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311−2327. (c) Braga, D.; Grepioni, F.; Desiraju, G. R. *Chem. Rev.* **1998**, *98*, 1375−1405.

(44) Keppie, S. A.; Lappert, M. F. *J. Chem. Soc. (A)* **1971**, 3216−3220.

(45) Bullock, R. M.; Rappoli, B. J. *J. Organomet. Chem.* **1992**, *429*, 345−368.

(46) Urbancic, M. A.; Shapley, J. R. *Inorg. Synth.* **1989**, *26*, 77−80.

(47) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922.

hexane at −78 °C gave [Cp(CO)$_3$W(HO^{n}Pr)]$^+$OTf$^−$ as a micro-crystalline solid (210 mg, 86% yield). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.75 (t, br, J = 4.6 Hz, 1H, OH), 6.06 (s, 5H, Cp), 3.56 (dt, J = 7.4 Hz, 4.6 Hz, 2H, OCH_2), 1.50 (sextet, J = 7.4 Hz, 2H, OCH$_2$CH_2), 0.84 (t, J = 7.4 Hz, 3H, CH$_3$). ^{13}C NMR (CD$_2$Cl$_2$, −73 °C): 224.4 (CO), 221.9 (2 CO), 94.5 (Cp), 80.3 (OCH$_2$), 23.3 (OCH$_2$$CH_2$), 8.5 (CH$_2$$CH_3$). IR (KBr): ν(OH) 3449 (w, br), ν(CO) 2051 (s), 1977 (s, sh), 1953 (vs), ν(C−O) 1026 (s) cm$^{−1}$. IR (CH$_2$Cl$_2$): ν(CO) 2061 (vs), 1981 (s), 1958 (vs) cm$^{−1}$. Anal. Calcd for C$_{12}$H$_{13}$F$_3$O$_7$SW: C, 26.58; H, 2.42. Found: C, 26.07, H, 2.38.

Preparation of [Cp(CO)$_3$W(HOC$_6$H$_{11}$)]$^+$OTf$^−$. HOTf (70 μL, 0.79 mmol) was added to a solution of Cp(CO)$_3$WH (215 mg, 0.644 mmol) and cyclohexanone (80 μL, 0.77 mmol) in CH$_2$Cl$_2$ (10 mL) at 22 °C. The solution was stirred for 30 min, during which time it became burgundy-red. Et$_2$O (20 mL) and hexane (10 mL) were added by vacuum transfer to yield the a dark red microcrystalline precipitate, which was collected by filtration, washed with Et$_2$O (10 mL) and hexane (30 mL), and dried under vacuum to give [Cp(CO)$_3$W(HOC$_6$H$_{11}$)]$^+$OTf$^−$ (213 mg, 57% yield). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.35 (d, J = 7.3 Hz, 1H, OH), 6.05 (s, 5H, Cp), 3.16 (m, 1H, OCH), 1.88−1.76 (m, 4H), 1.53−1.06 (m, 6H). ^{13}C NMR (CD$_2$Cl$_2$, −33 °C): 225.4 (CO), 222.3 (2 CO), 95.3 (Cp), 89.3, 33.1, 24.5 (cyclohexyl carbons). IR (KBr): ν(OH) 3443 (w,br), ν(CO) 2064 (vs), 1985 (s), 1948 (vs), ν(C−O) 1024 (s) cm$^{−1}$. IR (CH$_2$Cl$_2$): ν(CO) 2060 (vs), 1982 (s), 1953 (vs) cm$^{−1}$. Anal. Calcd for C$_{15}$H$_{17}$F$_3$O$_7$SW: C, 30.94; H, 2.94. Found: C, 30.67, H, 2.81.

Preparation of [Cp(CO)$_3$W(2-adamantanol)]$^+$OTf$^−$. HOTf (60 μL, 0.68 mmol) was added to a solution of Cp(CO)$_3$WH (200 mg, 0.600 mmol) and 2-adamantanone (110 mg, 0.73 mmol) in CH$_2$Cl$_2$ (10 mL) at 22 °C. The solution was stirred for 30 min, during which time it became burgundy-red. Et$_2$O (30 mL) was added by vacuum transfer to yield the dark red solid, which was collected by filtration, washed with Et$_2$O (30 mL), and dried under vacuum to give [Cp(CO)$_3$W(2-adamanta-nol)]$^+$OTf$^−$ (270 mg, 71% yield). ^{1}H NMR (CD$_2$Cl$_2$): δ 6.96 (d, J = 4.6 Hz, 1H, OH), 6.08 (s, 5H, Cp), 3.51 (m, 1H, OCH), 2.00−1.52 (m, 14H). ^{13}C NMR (CD$_2$Cl$_2$, −33 °C): 224.9 (CO), 221.7 (2 CO), 94.9 (Cp), 93.6 (1C, OCH), 35.9 (1C), 35.3 (2C), 31.9 (2C), 29.4 (2C), 25.9 (2C). IR (KBr): ν(OH) 3449 (w,br), ν(CO) 2051 (vs), 1977 (s, sh), 1952 (vs), ν(C−O) 1026 (s) cm$^{−1}$. IR (CH$_2$Cl$_2$): ν(CO) 2061 (vs), 1984 (s), 1950 (vs) cm$^{−1}$. Anal. Calcd for C$_{19}$H$_{21}$F$_3$O$_7$SW: C, 35.98; H, 3.50. Found: C, 36.27, H, 3.50.

Preparation of {Cp(CO)$_3$W[CH$_3$CH(OH)C(=O)CH$_3$]}$^+$-OTf$^−$. HOTf (100 μL, 1.13 mmol) was added to a solution of Cp(CO)$_3$WH (200 mg, 0.600 mmol) and 2,3-butanedione (60 μL, 0.68 mmol) in CH$_2$Cl$_2$ (10 mL) at 22 °C. The solution was stirred for 10 min, during which time it became burgundy-red. Et$_2$O (30 mL) and hexane (10 mL) were added by vacuum transfer to yield a dark red solid, which was collected by filtration, washed with Et$_2$O (10 mL), and dried under vacuum to give [Cp(CO)$_3$W{CH$_3$CH(OH)C(=O)CH$_3$}]$^+$OTf$^−$ (147 mg, 43% yield). ^{1}H NMR (CD$_2$Cl$_2$): δ 8.61 (br s, 1H, OH), 6.10 (s, 5H, Cp), 3.93 (br s, 1H, OCH), 2.09 (s, 1H, CH_3C=O), 1.35 (d, J = 6.9 Hz, 3 H, CH_3CH). ^{13}C NMR (CD$_2$Cl$_2$, −53 °C): 224.1 (CO), 223.2 (CO), 203.9 (C=O), 95.0 (Cp), 86.5 (OCH), 25.1 (CH$_3$C=O), 17.5 (CH$_3$CH). IR (KBr): ν(OH) 3442 (w,br), ν(CO) 2064 (s), 1964 (s, sh), 1957 (vs); ν(C=O) 1725; ν(C−O) 1025 (s) cm$^{−1}$. IR (CH$_2$Cl$_2$): ν(CO) 2062 (vs), 1985 (s), 1951 (vs); ν(C=O) 1735 (m) cm$^{−1}$. Anal. Calcd for C$_{13}$H$_{13}$F$_3$O$_8$-SW: C, 27.38; H, 2.30. Found: C, 27.59, H, 2.14.

Preparation of [Cp(CO)$_3$W(HO^{i}Pr)]$^+$[BAr′$_4$]$^−$. Cp(CO)$_3$WH (80 mg, 0.24 mmol), [H(Et$_2$O)$_2$]$^+$[BAr′$_4$]$^−$ (200 mg, 0.20 mmol), and toluene (10 mL) were placed in a Schlenk flask, which was cooled to −78 °C. Acetone (22 μL, 0.30 mmol) was added, and the reaction mixture was warmed to 22 °C and stirred for 1 h. No color change was observed. The solvent was removed under vacuum, and the color slowly darkened. The purple-red residue was dissolved in Et$_2$O (10 mL), and hexane

(30 mL) was slowly added. The resulting precipitate was isolated, washed with hexane (50 mL), and dried under vacuum to give [Cp(CO)$_3$W(HO^{i}Pr)]$^+$[BAr′$_4$]$^−$ as a purple-red solid (171 mg, 69%). This reaction can also be carried out in CH$_2$Cl$_2$, but as in this reaction in toluene, no reaction appears to occur until the solvent was removed. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.73 (br, 8H, o-H), 7.58 (br, 4H, p-H), 5.99 (s, 5H, Cp), 3.71 (d of septets, J = 7.9 Hz, 6.3 Hz, 1H, CH), 2.41 (d, J = 7.9 Hz, 1H, OH), 1.18 (d, J = 6.3 Hz, 6H, CH$_3$). ^{13}C NMR (CD$_2$Cl$_2$, −13 °C): 222.4 (2 CO), 221.8 (CO), 161.6 (1:1:1:1 quartet, J_{CB} = 48.2 Hz, *ipso*-C), 134.7 (*o*-C), 128.7 (br, q, $^2J_{CF}$ = 30.5 Hz, *m*-C), 124.5 (q, $^1J_{CF}$ = 272 Hz, CF$_3$), 117.5 (*p*-C), 95.7 (Cp), 65.6 (CH), 14.5 (CH$_3$). IR (CH$_2$Cl$_2$): ν(CO) 2062 (s), 1986 (m), 1964 (vs) cm$^{−1}$. Anal. Calcd for C$_{43}$H$_{25}$BF$_{24}$O$_4$W: C, 41.13; H, 2.01. Found: C, 40.78; H, 1.98.

Preparation of {Cp(CO)$_3$W[CH$_3$CH(OH)CH$_2$C(=O)Ph]}$^+$OTf$^−$. HOTf (100 μL, 1.13 mmol) was added to a solution of Cp(CO)$_3$WH (150 mg, 0.45 mmol) and 1-phenyl-1,3-butane-dione (100 mg, 0.62 mmol) in CH$_2$Cl$_2$ (10 mL) at 22 °C. The solution was stirred for 30 min, during which time it became burgundy-red. Et$_2$O (30 mL) and hexane (10 mL) were added by vacuum transfer to yield a dark red solid, which was collected by filtration, washed with Et$_2$O (10 mL), and dried under vacuum to give {Cp(CO)$_3$W[CH$_3$CH(OH)CH$_2$C(=O)-Ph]}$^+$OTf$^−$ (173 mg, 59% yield). Crystals suitable for diffraction studies were grown by slow diffusion of hexane into a CH$_2$Cl$_2$ solution of the product at −35 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.97−7.47 (m, 5H, Ph), 6.00 (s, 5H, Cp), 4.14 (br s, 1H, OCH), 3.56 (dd, J = 18.6 Hz, 8.5 Hz, 1H, CH_2), 2.96 (dd, J = 18.6 Hz, 3.5 Hz, 1H, CH_2), 1.21 (d, J = 6.5 Hz, 3H, CH_3). ^{13}C NMR (CD$_2$Cl$_2$, −53 °C): 225.3 (CO), 224.7 (CO), 220.2 (CO), 195.8 (PhC(=O)), 135.0 (*ipso*-C), 133.5 (*p*-C), 128.3 (*o*-C), 127.5 (*m*-C), 95.0 (Cp), 81.1 (CH(OH)), 45.3 (C(=O)CH$_2$), 19.7 (CH$_3$). IR (KBr): ν(OH) 3443 (w, br); ν(CO) 2059 (vs), 1968 (vs), 1942 (vs); ν(C=O) 1678 (s); ν(C−O) 1023 (s) cm$^{−1}$. IR (CH$_2$Cl$_2$): ν(CO) 2059 (vs), 1981 (s), 1955 (vs); ν(C=O) 1686 (m) cm$^{−1}$. Anal. Calcd for C$_{19}$H$_{17}$F$_3$O$_8$SW: C, 35.31; H, 2.65. Found: C, 35.46, H, 2.85.

General Procedure for Reactions Carried Out in NMR Tubes. Reactions between ketones (or aldehydes) and metal hydrides carried out in NMR tubes were prepared by adding a measured quantity of Cp(CO)$_3$WH or other metal hydride, the ketone (or aldehyde), and an internal integration standard (1,2-dichloroethane or bibenzyl) to a screw-capped NMR tube in a drybox. CD$_2$Cl$_2$ was added, and the volume of the solution was calculated from the height of the solution in the NMR tube using a reported formula.[48] After measuring the initial NMR spectrum, HOTf was added to the solution, and spectra were taken over the course of the reaction and integrated vs the internal standard. ^{1}H NMR (CD$_2$Cl$_2$) spectrum of Cp(CO)$_3$-WOTf (observed as a decomposition product of these alcohol complexes): δ 5.99 (s).

Ionic Hydrogenation of 2-Butanone by Cp(CO)$_3$WH and HOTf. Using the general procedure described above for NMR tube reactions, HOTf (3 μL, 0.034 mmol) was added to a solution of Cp(CO)$_3$WH (19 mg, 0.057 mmol), 2-butanone (3.5 μL, 0.039 mmol), and 1,2-dichloroethane (3 μL) in CD$_2$Cl$_2$ (0.60 mL). After 30 min at 22 °C, the ^{1}H NMR spectrum of the burgundy-red solution showed the formation of [Cp(CO)$_3$W-(2-butanol)]$^+$OTf$^−$ in 83% yield. After 1 h at 22 °C, [Cp(CO)$_3$W-(2-butanol)]$^+$OTf$^−$ (93%) and Cp(CO)$_3$WOTf (4%) were ob-served. [Cp(CO)$_3$W(CH$_3$CH$_2$CH(OH)CH$_3$)]$^+$OTf$^−$: ^{1}H NMR (CD$_2$Cl$_2$): δ 6.03 (s, 5H, Cp), 5.66 (d, J = 7.8 Hz, 1H, OH), 3.37 (septet, J = 6.9 Hz, 1H, CH), 1.57−1.34 (m, 2H, CH_2), 1.11 (d, J = 6.4 Hz, 3H, CH(OH)CH_3), 0.86 (t, J = 7.4 Hz, 3H, CH_3CH$_2$).

Ionic Hydrogenation of Pivalaldehyde by Cp(CO)$_3$WH and HOTf. Using the general procedure described above for

---

(48) Bryndza, H. E.; Calabrese, J. C.; Marsi, M.; Roe, D. C.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4805−4813.

NMR tube reactions, HOTf (6 μL, 0.068 mmol) was added to a solution of Cp(CO)$_3$WH (18 mg, 0.054 mmol), pivalaldehyde (4 μL, 0.036 mmol), and 1,2-dichloroethane (3 μL) in CD$_2$Cl$_2$ (0.55 mL). After 5 min at 22 °C, the ^{1}H NMR spectrum of the resulting burgundy-red solution showed the formation of [Cp-(CO)$_3$W(2,2-dimethyl-1-propanol)]$^+$OTf$^-$ in 94% yield. After 16 h at 22 °C, [Cp(CO)$_3$W(2,2-dimethyl-1-propanol)]$^+$OTf$^-$ (31%) and free 2,2-dimethyl-1-propanol (69%) were observed. {Cp-(CO)$_3$W[HOCH$_2$C(CH$_3$)$_3$]}$^+$OTf$^-$: ^{1}H NMR (CD$_2$Cl$_2$): δ 7.30 (t, J = 5.4 Hz, 1H, OH), 6.11 (s, 5H, Cp), 3.33 (d, J = 5.4 Hz, 2H, CH$_2$), 0.83 (s, 9H, CH$_3$).

Ionic Hydrogenation of 4-Phenyl-2-butanone by Cp-(CO)$_3$WH and HOTf. Using the general procedure described above for NMR tube reactions, HOTf (3 μL, 0.034 mmol) was added to a solution of Cp(CO)$_3$WH (7 mg, 0.021 mmol), 4-phenyl-2-butanone (3 μL, 0.020 mmol), and 1,2-dichloroethane (4 μL) in CD$_2$Cl$_2$ (0.61 mL). After 30 min at 22 °C, the ^{1}H NMR spectrum showed the formation of [Cp(CO)$_3$W(4-phenyl-2-butanol)]$^+$OTf$^-$ in 88% yield. After 40 h at 22 °C, [Cp-(CO)$_3$W(4-phenyl-2-butanol)]$^+$OTf$^-$ had decomposed to give Cp(CO)$_3$WOTf (81%) and 4-phenyl-2-butanol (81%).
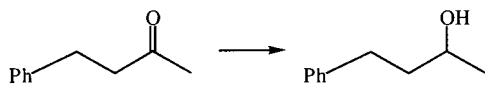
[Cp(CO)$_3$W(PhCH$_2$CH$_2$CH(OH)CH$_3$)]$^+$OTf$^-$: ^{1}H NMR (CD$_2$-Cl$_2$): δ 7.33−7.14 (m, 5H, Ph), 6.36 (d, J = 7.9 Hz, 1H, OH), 5.99 (s, 5H, Cp), 3.39 (m, 1H, C*H*), 2.56 (t, J = 6.8 Hz, 2H, PhC*H*$_2$), 1.90−1.64 (m, 2H, PhCH$_2$C*H*$_2$), 1.16 (d, J = 6.3 Hz, 3H, C*H*$_3$). 4-Phenyl-2-butanol: ^{1}H NMR (CD$_2$Cl$_2$): δ 7.29−7.14 (m, 5H, Ph), 4.33 (sextet, J = 6.4 Hz, 1H, C*H*), 2.71 (m, 2H, PhC*H*$_2$), 2.04 (m, 2H, PhCH$_2$C*H*$_2$), 1.42 (d, J = 6.4 Hz, 3H, C*H*$_3$).

Ionic Hydrogenation of Acetophenone by Cp(CO)$_3$WH and HOTf. Using the general procedure described above for NMR tube reactions, HOTf (14 μL, 0.16 mmol) was added to a solution of Cp(CO)$_3$WH (32 mg, 0.096 mmol), acetophenone (4 μL, 0.034 mmol), and 1,2-dichloroethane (4 μL) in CD$_2$Cl$_2$ (0.57 mL). After 1 h at 22 °C, the ^{1}H NMR spectrum of the resulting wine-red solution showed the formation of ethylbenzene in 50% yield, along with Cp(CO)$_3$WOTf. After 3 h at 22 °C, the yield of ethylbenzene had increased to 91%, and only 8% acetophenone remained (the remaining acetophenone is apparently partially protonated; its CH$_3$ resonance appears at δ 3.17, vs δ 2.59 for free acetophenone in the absence of HOTf).

Ionic Hydrogenation of 1,3,5-Trioxane by Cp(CO)$_3$WH and HOTf. Using the general procedure described above for NMR tube reactions, HOTf (6 μL, 0.068 mmol) was added to a solution of Cp(CO)$_3$WH (15 mg, 0.045 mmol), 1,3,5-trioxane (5.4 mg, 0.060 mmol), and 1,2-dichloroethane (3 μL) in CD$_2$Cl$_2$ (0.64 mL). After 5 min at 22 °C, the ^{1}H NMR spectrum showed the formation of [Cp(CO)$_3$W(HOMe)]$^+$OTf$^-$ (86% yield). [Cp(CO)$_3$W(HOMe)]$^+$OTf$^-$: ^{1}H NMR (CD$_2$Cl$_2$): δ 7.40 (v br, 1H, OH), 6.05 (s, 5H, Cp), 3.57 (s, 3H, CH$_3$).

Ionic Hydrogenation of Acetone by Cp(CO)$_3$MoH and HOTf. Using the general procedure described above for NMR tube reactions, HOTf (10 μL, 0.11 mmol) was added to a solution of Cp(CO)$_3$MoH (19 mg, 0.077 mmol), acetone (4 μL, 0.054 mmol), and 1,2-dichloroethane (4 μL) in CD$_2$Cl$_2$ (0.56 mL). After 5 min at 22 °C, the ^{1}H NMR spectrum of the resulting purple solution showed the formation of [Cp(CO)$_3$-Mo(HO^{i}Pr)]$^+$OTf$^-$ (77%) and 2-propanol (23%) along with Cp-(CO)$_3$MoOTf (δ 5.88). After 30 min at 22 °C, approximately equal amounts of [Cp(CO)$_3$Mo(HO^{i}Pr)]$^+$OTf$^-$ and HO^{i}Pr were present, and after 20 h at 22 °C, no alcohol complex was detected, and Cp(CO)$_3$MoOTf and free HO^{i}Pr were the predominant products. [Cp(CO)$_3$Mo(HO^{i}Pr)]$^+$OTf$^-$: ^{1}H NMR (CD$_2$Cl$_2$): δ 5.90 (s, 5H, Cp), 4.90 (br, 1H, OH), 3.46 (br, 1H, CH), 1.18 (d, J = 6.3 Hz, 6H, CH$_3$).

Ionic Hydrogenation of Acetone by (CO)$_5$MnH and HOTf. Using the general procedure described above for NMR tube reactions, HOTf (10 μL, 0.11 mmol) was added to a solution of (CO)$_5$MnH (19 mg, 0.097 mmol), acetone (4 μL, 0.054 mmol), and 1,2-dichloroethane (3.5 μL) in CD$_2$Cl$_2$ (0.52 mL). After 5 min at 22 °C, the ^{1}H NMR spectrum of the resulting yellow solution showed the formation of HO^{i}Pr in a quantitative yield. The integration over the hydride region indicated that 1.06 equiv of (CO)$_5$MnH was consumed. A separate experiment monitored by IR spectroscopy confirmed the formation of (CO)$_5$MnOTf [49] as the organometallic product.

Ionic Hydrogenation of Acetone by (CO)$_5$ReH and HOTf. Using the general procedure described above for NMR tube reactions, HOTf (15 μL, 0.17 mmol) was added to a solution of (CO)$_5$ReH (80 mg, 0.24 mmol), acetone (8 μL, 0.11 mmol), and 1,2-dichloroethane (4 μL) in CD$_2$Cl$_2$ (0.65 mL). After 5 min at 22 °C, an ^{1}H NMR spectrum showed the formation of HO^{i}Pr and [(CO)$_5$Re(HO^{i}Pr)]$^+$OTf$^-$ in a 91:9 ratio. After 20 min at 22 °C, only ~3% of [(CO)$_5$Re(HO^{i}Pr)]$^+$OTf$^-$ and 97% of HO^{i}Pr were observed in the ^{1}H NMR spectrum. ^{1}H NMR (CD$_2$Cl$_2$) of [(CO)$_5$Re(HO^{i}Pr)]$^+$OTf$^-$: δ 7.00 (br, OH, tentative assignment), δ 3.97 (br, 1H, CH), 1.33 (d, J = 6.2 Hz, 6H, CH$_3$).

Reaction of [Cp(CO)$_3$W(HO^{i}Pr)]$^+$[BAr′$_4$]$^-$ with Acetone. The reaction between acetone (1 μL, 0.015 mmol) and [Cp(CO)$_3$W(HO^{i}Pr)]$^+$[BAr′$_4$]$^-$ (19 mg, 0.015 mmol) in CD$_2$Cl$_2$ (0.65 mL) was monitored by ^{1}H NMR. Slow displacement of the alcohol ligand by acetone was observed. After 5 days at 22 °C, a 53:47 mixture of [Cp(CO)$_3$W(HO^{i}Pr)]$^+$[BAr′$_4$]$^-$ and [Cp(CO)$_3$W(acetone)]$^+$[BAr′$_4$]$^-$ was observed, along with free HO^{i}Pr. ^{1}H NMR (CD$_2$Cl$_2$) of [Cp(CO)$_3$W(acetone)]$^+$[BAr′$_4$]$^-$: δ 6.07 (s, 5H, Cp), 2.39 (s, 6H, Me). ^{1}H NMR (CD$_2$Cl$_2$) of 2-propanol: δ 3.93 (m, 1H, CH), 2.12 (br, 1H, OH), 1.23 (d, J = 6.2 Hz, 6H, CH$_3$).

Reaction of [Cp(CO)$_2$(PMe$_3$)W(H)$_2$]$^+$OTf$^-$ with Propionaldehyde. Propionaldehyde (2 μL, 0.028 mmol) was added to a solution of [Cp(CO)$_2$(PMe$_3$)W(H)$_2$]$^+$OTf$^-$ (16 mg, 0.030 mmol) and 1,2-dichloroethane (2 μL) in CD$_2$Cl$_2$ (0.60 mL) in an NMR tube. After 5 min at 22 °C, the ^{1}H NMR spectrum of the wine-red solution showed the formation of *trans*-[Cp(CO)$_2$-(PMe$_3$)W(HO^{n}Pr)]$^+$OTf$^-$ (70%), *cis*-[Cp(CO)$_2$(PMe$_3$)W(HO^n-Pr)]$^+$OTf$^-$ (17%), and *cis*-Cp(CO)$_2$(PMe$_3$)WOTf (3%). After 1.5 h, *cis*-[Cp(CO)$_2$(PMe$_3$)W(HO^{n}Pr)]$^+$OTf$^-$ (1%) and *cis*-Cp(CO)$_2$-(PMe$_3$)WOTf (23%) were observed along with free HO^{n}Pr, while *trans*-[Cp(CO)$_2$(PMe$_3$)W(HO^{n}Pr)]$^+$OTf$^-$ remained. Little change in the amount of *trans*-[Cp(CO)$_2$(PMe$_3$)W(HO^{n}Pr)]$^+$OTf$^-$ was observed after 2 days. *trans*-[Cp(CO)$_2$(PMe$_3$)W(HO^n-Pr)]$^+$OTf$^-$: ^{1}H NMR (CD$_2$Cl$_2$): δ 6.77 (t, J = 4.7 Hz, 1H, O*H*), 5.53 (d, J_{PH} = 2.6 Hz, 5H, Cp), 3.54 (br, q, J = 7.0 Hz, 2H, OC*H*$_2$), 1.68 (d, J_{PH} = 9.8 Hz, 9H, PMe$_3$), 1.48 (sextet, J = 7.2 Hz, 2H, OCH$_2$C*H*$_2$), 0.82 (t, J = 7.4 Hz, 3H, C*H*$_3$). *cis*-[Cp(CO)$_2$-(PMe$_3$)W(HO^{n}Pr)]$^+$OTf$^-$: ^{1}H NMR (CD$_2$Cl$_2$): δ 6.61 (t, J = 4.7 Hz, 1H, O*H*), 5.86 (s, 5H, Cp), 3.54 (br, q, J = 7.0 Hz, 2H, OC*H*$_2$), 1.69 (d, J_{PH} = 9.8 Hz, 9H, PMe$_3$), 1.48 (sextet, J = 7.2 Hz, 2H, OCH$_2$C*H*$_2$), 0.81 (t, J = 7.4 Hz, 3H, C*H*$_3$). *cis*-Cp(CO)$_2$-(PMe$_3$)WOTf: ^{1}H NMR (CD$_2$Cl$_2$): δ 5.76 (s, 5H, Cp), 1.62 (d, J_{PH} = 10.0 Hz, 9H, PMe$_3$).

Reaction of [Cp(CO)$_2$(PMe$_3$)W(H)$_2$]$^+$OTf$^-$ with Acetone. Acetone (3 μL, 0.041 mmol) was added to a solution of [Cp(CO)$_2$(PMe$_3$)W(H)$_2$]$^+$OTf$^-$ (22 mg, 0.041 mmol) and 1,2-dichloroethane (2.5 μL) in CD$_2$Cl$_2$ (0.60 mL). After 5 min at 22 °C, the reaction was only partially complete and showed *cis*-[Cp(CO)$_2$(PMe$_3$)W(HO^{i}Pr)]$^+$OTf$^-$ (47%), *trans*-[Cp(CO)$_2$-(PMe$_3$)W(HO^{i}Pr)]$^+$OTf$^-$ (11%), and *cis*-Cp(CO)$_2$(PMe$_3$)WOTf (8%). After 1 h at 22 °C, <5% acetone remained, and *cis*-[Cp-(CO)$_2$(PMe$_3$)W(HO^{i}Pr)]$^+$OTf$^-$ (32%), *trans*-[Cp(CO)$_2$(PMe$_3$)-W(HO^{i}Pr)]$^+$OTf$^-$ (16%), and *cis*-Cp(CO)$_2$(PMe$_3$)WOTf (49%) were observed in the ^{1}H NMR spectrum. After 20 h at 22 °C, <3% *cis*-[Cp(CO)$_2$(PMe$_3$)W(HO^{i}Pr)]$^+$OTf$^-$ was observed, along

(49) Nitschke, J.; Schmidt, S. P.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 1972−1978.

with *trans*-[Cp(CO)$_2$(PMe$_3$)W(HO^{i}Pr)]$^+$OTf$^-$ (14%) and *cis*-Cp-(CO)$_2$(PMe$_3$)WOTf (83%). *trans*-[Cp(CO)$_2$(PMe$_3$)W(HO^{i}Pr)]$^+$OTf$^-$: ^{1}H NMR (CD$_2$Cl$_2$): δ 6.37 (d, *J* = 7.7 Hz, 1H, O*H*), 5.52 (d, J_{PH} = 2.7 Hz, 5H, Cp), 3.57 (br, septet, *J* = 6.4 Hz, 1H, OC*H*), 1.68 (d, J_{PH} = 9.8 Hz, 9H, PMe$_3$), 1.12 (d, *J* = 6.4 Hz, 6H, C*H$_3$*). *cis*-[Cp(CO)$_2$(PMe$_3$)W(HO^{i}Pr)]$^+$OTf$^-$: ^{1}H NMR (CD$_2$Cl$_2$): δ 5.93 (t, *J* = 7.7 Hz, 1H, O*H*), 5.86 (s, 5H, Cp), 3.57 (br, septet, *J* = 6.4 Hz, 2H, OC*H$_2$*), 1.67 (d, J_{PH} = 9.8 Hz, 9H, PMe$_3$), 1.16 (dd, *J* = 6.3 Hz, *J* = 2.0 Hz, 6H, C*H$_3$*).

Selectivity in Ionic Hydrogenation. Aldehyde vs Ketone. Using the general procedure described above for NMR tube reactions, HOTf (4 μL, 0.045 mmol) was added to a solution of Cp(CO)$_3$WH (20 mg, 0.060 mmol), acetone (3 μL, 0.041 mmol), pivalaldehyde (4.5 μL, 0.041 mmol), and 1,2-dichloroethane (4 μL) in CD$_2$Cl$_2$ (0.63 mL). After 5 min at 22 °C, the ^{1}H NMR spectrum of the resulting burgundy-red solution showed the formation of [Cp(CO)$_3$W(2,2-dimethyl-1-propanol)]$^+$OTf$^-$ (88% yield). There was no evidence for hydrogenation of acetone, but it does appear to have been partially protonated as its CH$_3$ resonance moved from δ 2.12 in the absence of acid to δ 2.15.

Ionic Hydrogenation of 1,1-Dimethoxyacetone by Cp-(CO)$_3$WH and HOTf. Using the general procedure described above for NMR tube reactions, HOTf (3 μL, 0.034 mmol) was added to a solution of Cp(CO)$_3$WH (16 mg, 0.048 mmol), 1,1-dimethoxyacetone (4 μL), and 1,2-dichloroethane (3 μL) in CD$_2$Cl$_2$ (0.55 mL). After 5 min at 22 °C, the ^{1}H NMR spectrum of the resulting wine-red solution showed the formation of the alcohol complex, [Cp(CO)$_3$W(1,1-dimethoxy-2-propanol)]$^+$OTf$^-$ (60%). Free 1,1-dimethoxy-2-propanol (5%) and unreacted 1,1-dimethoxyacetone (21%) were also observed. [Cp(CO)$_3$W(1,1-dimethoxy-2-propanol)]$^+$OTf$^-$: ^{1}H NMR (CD$_2$Cl$_2$): δ 7.57 (d, *J* = 8.5 Hz, 1H, OH), 6.06 (s, 5H, Cp), 4.14 (d, *J* = 6.4 Hz, 1H, C*H*(OCH$_3$)$_2$), 3.46 (s, 3H, OC*H$_3$*), 3.39 (s, 3H, OC*H$_3$*), 3.33 (m, 1H, HOC*H*), 1.08 (d, *J* = 6.6 Hz, 3H, CHC*H$_3$*).

Collection and Reduction of X-ray Data. X-ray data sets were collected on crystals of [Cp(CO)$_3$W(HO^{i}Pr)]$^+$OTf$^-$ and {Cp(CO)$_3$W[CH$_3$CH(OH)CH$_2$C(=O)Ph]}$^+$OTf$^-$. Crystals of each of these alcohol complexes were coated with Vaseline and sealed inside a glass capillary, which was then transferred to an Enraf Nonius CAD-4 diffractometer equipped with a low-

temperature device and cooled to 200 K for the collection of diffraction data. Diffraction data indicated triclinic symmetry for [Cp(CO)$_3$W(HO^{i}Pr)]$^+$OTf$^-$ and monoclinic symmetry with systematic absences consistent with space group $P2_1/n$ for {Cp(CO)$_3$W[CH$_3$CH(OH)CH$_2$C(=O)Ph]}$^+$OTf$^-$. Space group P was used for the solution and refinement of [Cp(CO)$_3$W-(HO^{i}Pr)]$^+$OTf$^-$. Crystal data and information about the data collection are provided in Table 1 and the Supporting Information.

Determination and Refinement of the Structure. The structures[50] were solved by standard heavy atom Patterson methods. In the least-squares refinement,[50] anisotropic temperature parameters were used for all the non-hydrogen atoms. Hydrogen atoms, except the one on the alcohol oxygen in both of the two structures, which was located on a difference Fourier map and fixed in that location, were placed at calculated positions and allowed to "ride" on the atom to which they were attached. A common isotropic thermal parameter was refined for the hydrogen atoms in each structure. A Gaussian absorption correction[50] was used for [Cp(CO)$_3$W(HO^{i}Pr)]$^+$OTf$^-$. For {Cp(CO)$_3$W[CH$_3$CH(OH)CH$_2$C(=O)Ph]}$^+$OTf$^-$ the data were corrected using a Fourier absorption correction (XABS2).[51]

Supporting Information Available: Crystallographic information for [Cp(CO)$_3$W(HO^{i}Pr)]$^+$OTf$^-$ and {Cp(CO)$_3$W-[CH$_3$CH(OH)CH$_2$C(=O)Ph]}$^+$OTf$^-$: atomic coordinates, tables of complete bond lengths and angles, anisotropic displacement parameters for the non-hydrogen atoms, hydrogen coordinates, and distances and angles for hydrogen bonds. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010222L

(50) Sheldrick, G. M. *SHELXL* Version 5; Siemens Analytical Instruments, Inc.: Madison WI; 1994.
(51) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53−56.