Protonation of Metal Hydrides by Strong Acids. Formation of an Equilibrium Mixture of Dihydride and Dihydrogen Complexes from Protonation of $Cp^*Os(CO)_2H$. Structural Characterization of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$

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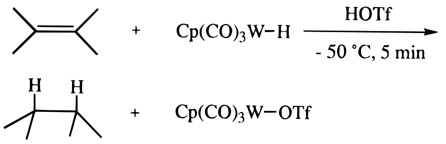
$Cp^*Os(CO)_2H$ is protonated by triflic acid (HOTf) in CD_2Cl_2 solution to give an equilibrium mixture (87:13) of the dihydride $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ and the dihydrogen complex $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$. The acidity of these protonated species is roughly comparable to HOTf, since only partial protonation was observed, e.g., 36% protonation with 1.2 equiv of HOTf. In the absence of acid, the T_1 of the hydride ligand of $Cp^*Os(CO)_2H$ is 5.9 s at −80 °C. When all of the $Cp^*Os(CO)_2H$ is protonated by excess HOTf, the T_1 (−80 °C) of the terminal hydride ligands of $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ is 2.8 s, while the T_1 of the dihydrogen ligand of $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ is 19 ms (−80 °C). The observed T_1 values of the Os−H resonance of $Cp^*Os(CO)_2H$ decreased significantly under conditions of partial protonation, indicating intermolecular proton transfer among $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$, $[Cp^*Os(CO)_2(H)_2]^+OTf^-$, $Cp^*Os(CO)_2H$, and HOTf. IR spectra indicate that the two CO ligands of $[Cp^*Os(CO)_2(H)_2]^+$ (and hence the hydrides as well) are trans to each other in the four-legged piano stool geometry. Two resonances for HOTf are observed in the NMR spectra and are assigned as $[HOTf]_n$ (hydrogen bonded to itself) and $TfOH\cdots OTf^-$ in which HOTf is hydrogen bonded to an OTf^- counterion. $[CpW(CO)_3(H)_2]^+OTf^-$ and $[Cp^*W(CO)_3(H)_2]^+OTf^-$ were formed by protonation of $CpW(CO)_3H$ and $Cp^*W(CO)_3H$. Protonation of the phosphine-substituted tungsten hydrides $CpW(CO)_2(PR_3)H$ (R = Me, Cy, Ph) by HOTf or $[H(Et_2O)_2]^+\ BAr'_4{}^-$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) gives dihydrides $[CpW(CO)_2(PR_3)(H)_2]^+$ which were isolated and fully characterized. The structure of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$ was determined by single-crystal X-ray diffraction and reveals weak hydrogen bonds between one hydride on W and two of the fluorines on the triflate anion.

Introduction

Protonation of neutral metal hydrides is frequently used to prepare cationic metal dihydrides[1] and/or dihydrogen complexes.[2] Our studies on protonation of metal hydrides arose out of our work on the ionic hydrogenation of alkenes,[3] alkynes,[4] and ketones,[5] in which a strong acid and a transition metal hydride are used to hydrogenate unsaturated organic substrates. Ionic hydrogenation of $Me_2C{=}CMe_2$ by HOTf and $CpW(CO)_3H$ (eq 1) involves formation of a carbenium ion by protonation of the alkene; subsequent hydride transfer from $CpW(CO)_3H$ produces the organic hydrogenation product along with $Cp(CO)_3WOTf$ as the organometallic product. In some cases, protonation of the metal hydride competed with protonation of the alkene. Attempted use of $CpW(CO)_2(PMe_3)H$ as a hydride donor in ionic hydrogenation failed because $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$, the cationic dihydride generated from protonation by HOTf, was not sufficiently acidic to transfer a proton to the olefin. Other metal hydrides failed to be useful as hydride donors for a different reason—$CpMo(CO)_2(PPh_3)H$, $Cp^*Fe(CO)_2H$, and $Cp^*Mo(CO)_3H$ ($Cp^* = \eta^5\text{-}C_5Me_5$) rapidly formed H_2 and M−OTf from their reaction with HOTf (eq 2). Cationic dihydrides (or dihydrogen complexes) are presumed intermediates that decompose by loss of H_2, but they were not observed for these hydrides. On the other hand, several metal hydrides were efficient hydride donors in the presence of HOTf; this is possible in cases where the cationic dihydride (or dihydrogen complex) has



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(1) For a review of polyhydride complexes, see: Hlatky, G. G.; Crabtree, R. H. *Coord. Chem. Rev.* **1985**, *65*, 1−48.

(2) 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. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95−101. (d) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120−128. (e) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17−40.

(3) (a) Bullock, R. M.; Rappoli, B. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1447−1448. (b) Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602−8612.

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

(5) 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.

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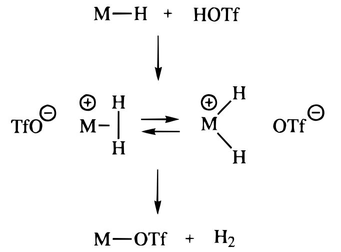

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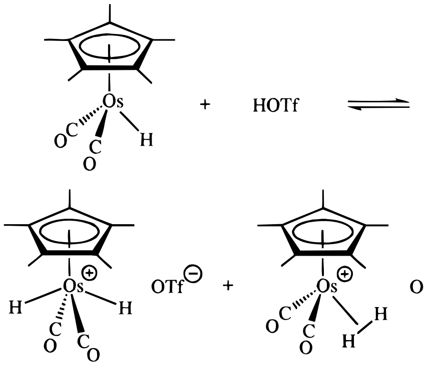
sufficient kinetic acidity to transfer a proton to the organic substrate and also has adequate thermal stability on the time scale of the hydrogenation reaction. Three such hydrides, $Cp^*Os(CO)_2H$, $CpW(CO)_3H$, and $Cp^*W(CO)_3H$, form observable protonation products. In this paper we report that protonation of $Cp^*Os(CO)_2H$ by HOTf gives an equilibrium mixture of the dihydride $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ and the dihydrogen complex $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$. Protonation of $CpW(CO)_3H$ and $Cp^*W(CO)_3H$ gives dihydrides that have also been characterized. Each of these three hydrides were only partially protonated by 1 equiv of HOTf, indicating that their protonated forms are extremely acidic. Phosphine-substituted tungsten compounds $CpW(CO)_2(PR_3)H$ (R = Me, Ph, Cy; Cy = cyclohexyl) are protonated to give dihydrides that are much less acidic; the characterization of these compounds is also reported, along with the crystal structure of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$.

Results and Discussion

Formation of $[Cp^*Os(CO)_2(H)_2]^+$ and $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+$ by Protonation of $Cp^*Os(CO)_2H$. Addition of excess HOTf to a solution of $Cp^*Os(CO)_2H$ (δ −14.21) in CD_2Cl_2 produced an 87:13 mixture of the dihydride complex $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ (δ −10.00) and the dihydrogen complex $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ (δ −7.24), as observed by ^1H NMR spectra at −80 °C (eq 3). The protonation of $Cp^*Os(CO)_2H$ was also studied by IR spectroscopy. Addition of HOTf (7 equiv) to a solution of $Cp^*Os(CO)_2H$ (0.02 M) in CH_2Cl_2 resulted in four bands in the metal carbonyl region. Figure 1 shows the observed IR spectrum along with a fitting that enabled a determination of the areas of the individual bands which are partially overlapped in the spectrum. The two most intense bands, at 2118 and 2068 cm^{-1}, are assigned as the symmetric and asymmetric carbonyl stretching vibrations of the dihydride complex $[Cp^*Os(CO)_2(H)_2]^+OTf^-$. An estimate of the OC−M−CO angle can be made from the relative areas of these bands using the relationship[6] $\tan^2\theta = I_a/I_s$, where 2θ is the OC−M−CO angle and I_a and I_s are the relative intensities of the asymmetric and symmetric bands. The experimental value of $I_a/I_s = 2.19$ leads to a predicted OC−Os−CO angle of 112°, indicating that the carbonyls (and hence the hydrides) are trans to each other, as drawn in eq 3.



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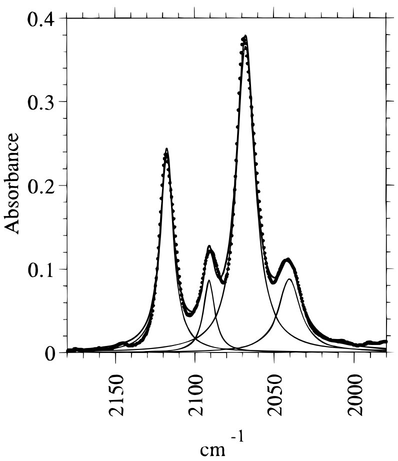

Figure 1. IR spectrum from protonation of $Cp^*Os(CO)_2H$ by excess HOTf. The dots show the observed spectrum, and the solid lines show the fitting of the four separate bands and their sum.

While we find no spectroscopic evidence for the cis isomer of our cationic Os dihydride, the isoelectronic neutral Re dihydride was shown to exist as a mixture of both isomers. Casey and co-workers[7] characterized the cis and trans isomers of $Cp^*Re(CO)_2(H)_2$; the trans isomer is thermodynamically favored over the cis isomer (97:3 ratio). From the IR intensities, the OC−Re−CO angles were estimated as 106° for the trans isomer and 92° for the cis isomer. The extensive series of Ru dihydrogen complexes of general formula $[CpRuL_2(\eta^2\text{-}H_2)]^+$ (L_2 = chelating diphosphine) studied by Heinekey[8] and by Morris[9] also convert to *trans*-dihydride isomers. A trans geometry of hydrides was verified in the crystal structures of $[CpOs(PPh_3)_2(H)_2]^+OTf^-$ [10] and $[Cp^*Fe(^iPr_2PCH_2CH_2P^iPr_2)(H)_2]^+BPh_4^-$.[11] Ab initio calculations[12] predict a greater stability for the trans forms of both $[CpOs(CO)_2(H)_2]^+$ and $[CpRu(PH_3)_2(H)_2]^+$.

The other two bands (2091 and 2040 cm^{-1}) in the IR spectrum (Figure 1) are assigned as the carbonyl stretching vibrations of the dihydrogen complex $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$. The maximum absorbance of these two bands are nearly identical, but the lower energy band has a significantly larger bandwidth. The relative areas of these two bands are in a ratio of 1.0:2.0, leading to a calculated OC−Os−CO angle of 109° based on these IR intensities.

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[6] (a) King, R. B.; Riemann, R. H. *Inorg. Chem.* **1976**, *15*, 179−183. (b) Brown, T. L.; Darensbourg, D. J. *Inorg. Chem.* **1967**, *6*, 971−977. (c) Beck, W.; Melnikoff, A.; Stahl, R. *Angew. Chem., Int. Ed. Engl.* **1967**, *4*, 692−693.

[7] Casey, C. P.; Tanke, R. S.; Hazin, P. N.; Kemnitz, C. R.; McMahon, R. J. *Inorg. Chem.* **1992**, *31*, 5474−5479; *Inorg. Chem.* **1994**, *33*, 5978.

[8] Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166−5175.

[9] Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161−171.

[10] (a) Angelici, R. J. *Acc. Chem. Res.* **1995**, *28*, 51−60. (b) Rottink, M. K.; Angelici, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 7267−7274.

[11] Jiménez-Tenorio, M.; Carmen Puerta, M.; Valerga, P. *Organometallics* **1994**, *13*, 3330−3337.

[12] Lin, Z.; Hall, M. B. *Organometallics* **1992**, *11*, 3801−3804.

The ν(CO) bands of the dihydrogen complex $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ both appear about 27 cm^{-1} lower in energy than the bands of the dihydride $[Cp^*Os(CO)_2(H)_2]^+OTf^-$. This is consistent with the higher formal oxidation state of the dihydride [Os(IV)] compared to the dihydrogen complex [Os(II)] and was observed previously in other dihydride/dihydrogen equilibria. Kubas and co-workers found[13] that the high-energy ν(CO) band of $(H)_2W(CO)_3(PCy_3)_2$ appeared at 25 cm^{-1} higher energy than the high energy ν(CO) band of the corresponding dihydrogen complex $(\eta^2\text{-}H_2)W(CO)_3(PCy_3)_2$; the lower energy bands of this dihydride/dihydrogen pair were separated by a larger amount (~60 cm^{-1}). IR spectra in liquid Xe show substantially higher energies (50−90 cm^{-1}) for the ν(CO) bands of $CpNb(CO)_3(H)_2$ compared to the dihydrogen analog $CpNb(CO)_3(\eta^2\text{-}H_2)$.[14]

High Acidity of Cationic Dihydrides and Dihydrogen Complexes. Since the hydride $Cp^*Os(CO)_2H$ is the conjugate base of both the dihydride and the dihydrogen complex, thermodynamics requires that the less abundant (more energetic) of the pair be the stronger acid. Thus the thermodynamic acidity of the dihydrogen complex $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ is greater than that of the dihydride $[Cp^*Os(CO)_2(H)_2]^+OTf^-$. Only 36% of the initial $Cp^*Os(CO)_2H$ was protonated after addition of 1.2 equiv of HOTf, indicating that the dihydride and dihydrogen species are extremely strong acids, being roughly comparable to HOTf.

Heinekey and co-workers previously reported[15] the synthesis of highly acidic cationic dihydrogen complexes by protonation of metal hydrides. Protonation of $Cp^*Re(CO)(NO)H$ with $HBF_4{\cdot}OEt_2$ produced a 7:93 mixture of the dihydride $[Cp^*Re(CO)(NO)(H)_2]^+BF_4^-$ and the dihydrogen complex $[Cp^*Re(CO)(NO)(\eta^2\text{-}H_2)]^+BF_4^-$, for which they estimated a pK_a of about −2 in CH_2Cl_2. The ruthenium dihydrogen complex $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+BF_4^-$, which is the Ru analog of the Os complex reported in this paper, was also prepared.[15] Their Ru compound exists solely as a dihydrogen complex, whereas in the Os compound we find the dihydride form predominates over the dihydrogen tautomer. As is often found for 3rd row vs 2nd row organometallic compounds, a much higher thermal stability was found for the Os compounds, where we observe slow decomposition over a period of many days at room temperature (see below). In contrast, the Ru compound $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$ begins to decompose at temperatures as low as −38 °C.[15] The Ru hydride $Cp^*Ru(CO)_2H$ was reported to be fully protonated by 1.2 equiv of $HBF_4{\cdot}OEt_2$, whereas we find only partial protonation of $Cp^*Os(CO)_2H$ by ~1.1 equiv of either $HBF_4{\cdot}OEt_2$ or HOTf. The relative thermodynamic basicities of the Ru and Os compounds are surprising, particularly in view of studies by Rottink and Angelici[10] on enthalpies of protonation of an extensive series of Ru and Os compounds of the type $CpM(PR_3)_2X$ (X = halide or hydride). They found that the Os compounds in this series were usually 6−8 kcal/mol more basic than analogous Ru compounds.

Morris and co-workers have systematically examined the pK_a values of a series of ruthenium complexes[9,16] spanning a wide range of thermodynamic acidities. Complexes with strongly electron donating phosphines have relatively low acidity; a pK_a of 16.3 ± 0.3 (aqueous pK_a scale) was found[9] for $[Cp^*Ru(PMe_3)_2(H)_2]^+$. Of most relevance to our present study is their prediction[16] of a pK_a of −6 (aqueous pK_a scale) for the dicarbonyl complex $[CpRu(CO)_2(\eta^2\text{-}H_2)]^+$. Thus, from our work and previous reports, the collective evidence indicates that extremely high acidities can result from dihydrides or dihydrogen complexes, particularly in carbonyl compounds without phosphines.

Comparison of $HBF_4{\cdot}OEt_2$ vs HOTf as Acids in the Protonation of $Cp^*Os(CO)_2H$. Relative Kinetic Acidity of Dihydride and Dihydrogen Complexes. Protonation of $Cp^*Os(CO)_2H$ by $HBF_4{\cdot}OEt_2$ was examined under conditions similar to those used with HOTf. The extent of protonation of $Cp^*Os(CO)_2H$ was comparable for the two acids, but significant differences were observed in the ^{1}H NMR line widths. Using HOTf as the acid, the line width ($\omega_{1/2}$ = 7 Hz) observed at −80 °C for the dihydride resonance of $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ was the same as that found for the hydride resonance of $Cp^*Os(CO)_2H$; the resonance for the H_2 ligand of $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ was much broader ($\omega_{1/2} \approx 70$ Hz). Similar observations were made in the partial protonation of $Cp^*Os(CO)_2H$ by $HBF_4{\cdot}OEt_2$ but only at the lowest temperature attempted (−98 °C). At −89 °C, the NMR spectrum exhibited a significantly larger line width ($\omega_{1/2} \approx 32$ Hz) for the hydride resonance of $Cp^*Os(CO)_2H$ compared to the dihydride resonance of $[Cp^*Os(CO)_2(H)_2]^+BF_4^-$ ($\omega_{1/2} \approx 10$ Hz); the dihydrogen resonance of $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+BF_4^-$ was very broad ($\omega_{1/2} \approx 200$ Hz) at this temperature. When this solution was warmed to −75 °C, the dihydrogen resonance of $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+BF_4^-$ had broadened into the baseline; the line width for the hydride resonance of $Cp^*Os(CO)_2H$ had increased to $\omega_{1/2} \approx 90$ Hz, but the dihydride resonance of $[Cp^*Os(CO)_2(H)_2]^+BF_4^-$ was not substantially broadened ($\omega_{1/2} \approx 8$ Hz). The onset of line broadening is observed at a lower temperature for the BF_4^- complex compared to the OTf^- complex, implying that kinetics of deprotonation by Et_2O (in the BF_4^- complex) are faster than deprotonation by OTf^-.

These ^{1}H NMR line-broadening experiments indicate a higher kinetic acidity of the dihydrogen complex $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+$ compared to the tautomeric dihydride complex $[Cp^*Os(CO)_2(H)_2]^+$. Microscopic reversibility thus requires that the kinetic protonation site be at the Os−H bond to give the dihydrogen complex rather than direct protonation at the metal to produce the dihydride. In several cases it was previously shown[8,9,17−19] that the initial site of protonation of a metal hydride is at the M−H bond to give a dihydrogen complex as the kinetic product, prior to isomerization to the dihydride tautomer (or an equilibrium mixture of dihydride and dihydrogen complexes). We were not successful at measuring the rate of conversion of the dihydrogen complex to the dihydride/dihydrogen equilibrium mixture; when $Cp^*Os(CO)_2H$ was protonated at −78 °C and an NMR spectrum was promptly recorded

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(13) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000−7009.

(14) George, M. W.; Haward, M. T.; Hamley, P. A.; Hughes, C.; Johnson, F. P. A.; Popov, V. K.; Poliakoff, M. *J. Am. Chem. Soc.* **1993**, *115*, 2286−2299.

(15) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824−1826.

(16) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883.

(17) Parkin, G.; Bercaw, J. E. *J. Chem. Soc., Chem. Commun.* **1989**, 255−257.

(18) Hamon, P.; Toupet, L.; Hamon, J.-P.; Lapinte, C. *Organometallics* **1992**, *11*, 1429−1431.

(19) Henderson, R. A.; Oglieve, K. E. *J. Chem. Soc., Dalton Trans.* **1993**, 3431−3439.

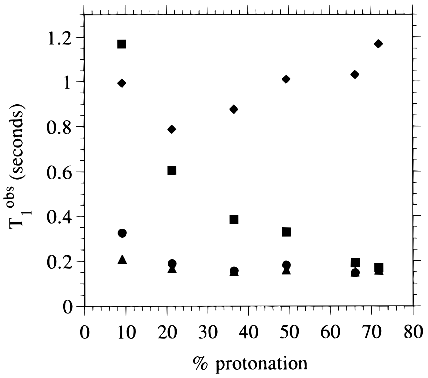


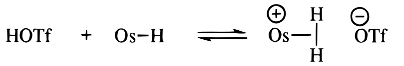
Figure 2. Observed ^{1}H NMR T_1 values (−80 °C, 300 MHz) from protonation of Cp*Os(CO)$_2$H (0.092 M) by HOTf (~0.3−2.5 equiv). ■ = Cp*Os(CO)$_2$*H*, ◆ = [Cp*Os(CO)$_2$(*H*)$_2$]$^+$, ● = TfO*H*···OTf$^-$ at δ 17.09, and ▲ = *H*OTf at δ 12.24.

at the same temperature, the equilibrium between dihydrogen complex and dihydride was established before the spectrum was completed.

Proton Exchange Processes during Partial Protonation of Cp*Os(CO)$_2$H. Observation of "T_1 Averaging". The hydride ligand of Cp*Os(CO)$_2$H has an extremely long T_1 of 51 s at 23 °C. This very slow relaxation rate requires that long pulse delays and/or small pulse angles be utilized in ^{1}H NMR studies of this and other metal hydrides in experiments where accurate integrations are needed. Most of the T_1 measurements reported in this paper were carried out at −80 °C, where relaxation is much faster than at room temperature. The true T_1 for the hydride ligand of Cp*Os(CO)$_2$H (with no added acid) is 5.9 s at −80 °C.

Information about proton exchange reactions was obtained from experiments involving partial protonation of Cp*Os(CO)$_2$H. HOTf was added at room temperature in several portions (~0.4 equiv with each addition) to a solution of Cp*Os(CO)$_2$H (0.092 M) in CD_2Cl_2; NMR spectra and T_1 values were measured at −80 °C following each incremental addition of HOTf. As the overall conversion to protonated products increased, the ratio of [Cp*Os(CO)$_2$(H)$_2$]$^+$OTf$^-$:[Cp*Os(CO)$_2$(η^2-H$_2$)]$^+$OTf$^-$ remained constant at 87(±2):13(±2). Figure 2 shows the changes in observed T_1 values at different concentrations of acid. Most notable are the substantial changes in the T_1^{obs} values of the hydride resonance of Cp*Os(CO)$_2$H. After the first addition of HOTf, only 9% of the Cp*Os(CO)$_2$H had been protonated, but the T_1^{obs} of the Os−H resonance dropped to 1.2 s (cf. 5.9 s with no acid). The T_1^{obs} continued to decrease as the amount of protonation increased, decreasing to $T_1^{obs} = 0.17$ s when 72% of the initial Cp*Os(CO)$_2$H had been protonated. When sufficient acid had been added to completely convert Cp*Os(CO)$_2$H to [Cp*Os(CO)$_2$(H)$_2$]$^+$OTf$^-$ and [Cp*Os(CO)$_2$(η^2-H$_2$)]$^+$OTf$^-$, however, a T_1 measurement of the dihydride resonance of [Cp*Os(CO)$_2$(H)$_2$]$^+$OTf$^-$ gave a value of 2.8 s. In sharp contrast to this long T_1 value, the dihydrogen ligand of [Cp*Os(CO)$_2$(η^2-H$_2$)]$^+$OTf$^-$ had a short T_1 of 19 ms.

In these spectra, separate resonances were observed at −80 °C for the hydride (δ −14.21), the dihydride (δ −10.00), and the dihydrogen complex (δ −7.24), indicating that the rate of proton exchange is slow on the chemical shift time scale.[20] The observation that the T_1^{obs} for the hydride ligand of Cp*Os(CO)$_2$H (in partially protonated samples) is much smaller than that found for pure Cp*Os(CO)$_2$H provides evidence that the rate of proton exchange is faster than its relaxation rate.[20] Exchange is apparently taking place between the hydride and one (or more) species with a lower actual T_1 value. This suggests that the dihydrogen complex [Cp*Os(CO)$_2$(η^2-H$_2$)]$^+$OTf$^-$, with a T_1 value of 19 ms, is involved in these proton transfer reactions.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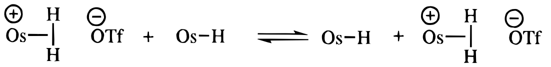
$$\mathrm{HOTf} + \mathrm{Os{-}H} \rightleftharpoons \overset{\oplus}{\mathrm{Os}}{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{|}}\ \overset{\ominus}{\mathrm{OTf}} \tag{4}$$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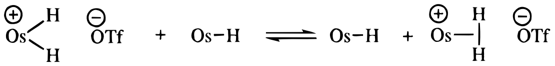
$$\overset{\oplus}{\mathrm{Os}}{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{|}}\ \overset{\ominus}{\mathrm{OTf}} + \mathrm{Os{-}H} \rightleftharpoons \mathrm{Os{-}H} + \overset{\oplus}{\mathrm{Os}}{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{|}}\ \overset{\ominus}{\mathrm{OTf}} \tag{5}$$


(6)

$$\overset{\oplus}{\mathrm{Os}}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{H}\end{smallmatrix}\ \overset{\ominus}{\mathrm{OTf}} + \mathrm{Os{-}H} \rightleftharpoons \mathrm{Os{-}H} + \overset{\oplus}{\mathrm{Os}}{-}\overset{\mathrm{H}}{\underset{\mathrm{H}}{|}}\ \overset{\ominus}{\mathrm{OTf}} \tag{6}$$

Equations 4−6 show protonation of Cp*Os(CO)$_2$H by three different proton donors, giving the dihydrogen complex as the kinetic product. The proton transfer equilibria operative in our experiments may be predominately mediated by OTf$^-$ as the base. Thus deprotonation of the dihydrogen complex by OTf$^-$ to regenerate Cp*Os(CO)$_2$H and HOTf (the reverse of eq 4), followed by reprotonation of another molecule of Cp*Os(CO)$_2$H, provides a mechanism for proton exchange among [Cp*Os(CO)$_2$(η^2-H$_2$)]$^+$, HOTf, and Cp*Os(CO)$_2$H. This mechanism can account for the "T_1 averaging" and line-broadening involving these species and avoids the requirement of a direct metal-to-metal proton transfer as shown in eq 5. The degenerate proton transfer exchange in eq 5 may occur as well but would likely involve a higher barrier[21] in view of steric requirements. Protonation of Cp*Os(CO)$_2$H by the dihydride [Cp*Os(CO)$_2$(H)$_2$]$^+$OTf$^-$ (eq 6) would presumably also involve a significant barrier to proton transfer. Furthermore, this process would not be very efficient at lowering the T_1^{obs} for the hydride, since the T_1 of the dihydride (2.8 s) is only a factor of two different from than that of the hydride. In principle, other faster processes could be occurring but not detected in our experiments; these "T_1 averaging" experiments are most sensitive for detection of exchange processes where one compound exchanges with a second species having a significantly lower T_1.

In these experiments we found "averaging" of T_1^{obs} values due to the *intermolecular* proton exchange rate being faster than the relaxation rate. T_1 averaging has been observed previously for *intramolecular* exchange of hydride and dihydrogen sites. In their study of the interconversion of dihydride and dihydrogen forms of [Cp*Ru(dppm)(η^2-H$_2$)]$^+$,[9] Morris and co-workers found averaging of the T_1 values of the Ru(η^2-H$_2$) and Ru(H)$_2$ resonances; complete averaging was observed above 40 °C, with T_1 values for both sites being 86 ms. More commonly observed than averaging between an H$_2$ ligand and the two terminal M−H ligands of its dihydride tautomer are examples where a compound exhibits averaging of the T_1 values between an η^2-H$_2$ ligand and one (or more) terminal hydrides that are present in addition to the dihydrogen ligand. Morris and co-

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[20] (20) For an informative discussion of the different exchange time scales and their effect on the observed spectrum, see: Sanders, J. K.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, U.K., 1987; pp 218−219.

[21] (21) For a weak-interaction model of proton transfer self-exchange between metals, see: Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1988**, *110*, 2418−2427.

workers reported intramolecular exchange between η^2-H_2 ligands and terminal hydrides in an extensive series of Fe, Ru, and Os complexes of general formula $[M(H)(\eta^2\text{-}H_2)(R_2PCH_2CH_2PR_2)_2]^+$.[22] Crabtree and co-workers reported an early example of T_1 averaging in $[Ir(H)(\eta^2\text{-}H_2)(PPh_3)_2(7,8\text{-benzoquinolate})]^+$.[23] Luo and Crabtree later observed averaging of T_1 values in the dihydrogen/dihydride complex $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_2Ph)_3]^+$, which exists in equilibrium with its eight-coordinate tetrahydride form $[ReH_4(CO)(PMe_2Ph)_3]^+$.[24]

Rate constants for the exchange between η^2-H_2 ligands and terminal hydrides ligands have been determined in many cases, and a recent review discusses this topic in detail.[2b] Quantitative evaluation of the observed T_1 data has been carried out in certain cases where reliable values of T_1 in the absence of exchange are available. For slower exchanges, complete line shape analysis of NMR line-broadening data can be used to obtain rate constants. For the protonation of $Cp^*Os(CO)_2H$ reported here the hydride, dihydride, and dihydrogen resonances were well-separated at −80 °C, the temperature at which our T_1 measurements were carried out, but coalescence was observed at higher temperatures. In the intramolecular exchange cases previously reported, the exchanging sites were generally limited to an η^2-H_2 ligand and hydride sites. The intermolecular proton transfer exchanges observed in our Os system are more complicated to analyze, since there are five exchanging sites: Os(H), $Os(H)_2$, $Os(\eta^2\text{-}H_2)$, and two HOTf sites (see below). We cannot determine specific rate constants for proton transfer from our data, but approximate limits on the overall rate constant for proton exchange in the system may be estimated from the relaxation rates of the $Os(\eta^2\text{-}H_2)$ and Os−H sites in the absence of exchange. The proton exchange rate must be greater than the relaxation rate of the Os−H site, or else no T_1 averaging would have been observed. For the estimated upper limit, the proton exchange rate cannot greatly exceed the relaxation rate of the $Os(\eta^2\text{-}H_2)$ site, or else the observed T_1 values would have been more similar, approaching the limit of relaxation coalescence.[25] The limits obtained in this way are $1/T_1[Os(\eta^2\text{-}H_2)] = 1/(19\text{ ms}) = 52\text{ s}^{-1}$ and $1/T_1(OsH) = 1/(5.9\text{ s}) = 0.17\text{ s}^{-1}$, corresponding to $\Delta G^{\ddagger}(-80\ °C)$ between 9.6 and 11.8 kcal mol^{-1}.

The T_1 values in the present study were measured at a single temperature, as opposed to minimum T_1 values obtained from variable-temperature studies. Notwithstanding the effect of exchange on the observed T_1 values, the large T_1 value found for $[Cp^*Os(CO)_2(H)_2]^+$ supports its assignment as a dihydride rather than a dihydrogen complex.[2]

Protonation of $CpW(CO)_3H$ and $Cp^*W(CO)_3H$. When HOTf (1.2 equiv) was added at room temperature to a CD_2Cl_2 solution of $CpW(CO)_3H$ (0.1 M), an NMR spectrum at −80 °C indicated 16% conversion to a new complex exhibiting a slightly broadened ($\omega_{1/2} = 12$ Hz) resonance at δ −2.07 that integrated as two protons. These resonances are assigned to the cationic dihydride $[CpW(CO)_3(H)_2]^+$, which was first reported[26] over 30 years ago from protonation of $CpW(CO)_3H$ by $BF_3/H_2O/CF_3CO_2H$. The T_1^{obs} for the dihydride resonance of $[CpW(CO)_3(H)_2]^+$ was 1.8 s. The T_1^{obs} for the hydride resonance of $CpW(CO)_3H$ in this partially protonated sample was 3.7 s, which is much smaller than the T_1 value of 11.2 s measured separately (with no acid added) for $CpW(CO)_3H$ at −80 °C. (For comparison, the hydride ligand of $CpW(CO)_3H$ has $T_1 = 85$ s at 29 °C.)

When a CD_2Cl_2 solution of the related Cp* complex $Cp^*W(CO)_3H$ (0.1 M) was treated at room temperature with HOTf (1.1 equiv), an NMR spectrum recorded at −78 °C indicated a 1:1 ratio of $Cp^*W(CO)_3H$ to $[Cp^*W(CO)_3(H)_2]^+OTf^-$ (eq 7). The T_1 measured at −78 °C for the W−H resonance of $Cp^*W(CO)_3H$ (δ −7.03) was 0.87 s (compared to $T_1 = 6.4$ s determined at −80 °C with no acid present), and the T_1 measured for the dihydride (δ −2.33) was 0.52 s. The protonation of $Cp^*W(CO)_3H$ was completed by the addition of more HOTf (4 equiv total). An IR spectrum of the cationic dihydride $[Cp^*W(CO)_3(H)_2]^+OTf^-$ exhibited three ν(CO) bands at room temperature in CH_2Cl_2 (2119 s, 2075 vs, 2057 s cm^{-1}), all of which appear at higher energy than the bands for the neutral hydride $Cp^*W(CO)_3H$ (2006 s, 1909 s cm^{-1}).

$$Cp^*W(CO)_3H \ + \ HOTf \ \rightleftharpoons \ [Cp^*W(CO)_3(H)_2]^+ \ OTf^- \qquad (7)$$

The observation that HOTf (1.2 equiv) caused only ∼16% protonation of $CpW(CO)_3H$ implies that the cationic dihydride $[CpW(CO)_3(H)_2]^+OTf^-$ is a stronger acid than HOTf. The analogous Cp* complex $Cp^*W(CO)_3H$ has a slightly higher basicity, since it was 50% protonated upon addition of 1.2 equiv of HOTf. The difference in basicity in $CpW(CO)_3H$ compared to $Cp^*W(CO)_3H$ is in the expected direction, but the magnitude of the effect is smaller here than in previously reported examples of Cp/Cp* pairs. The anion $[Cp^*Mo(CO)_3]^-$ is 4.4 kcal/mol more basic than $[CpMo(CO)_3]^-$ (i.e., the pK_a of $Cp^*Mo(CO)_3H$ (17.1) in CH_3CN is larger than that of $CpMo(CO)_3H$ ($pK_a = 13.9$).[27] Angelici and co-workers studied enthalpies of protonation of several classes of organometallic compounds by titration calorimetry and found that the Cp* ligand increases metal basicity (compared to Cp analogs) by 5.5−9.0 kcal/mol.[10]

Decomposition to Metal Triflates. All of the metal hydrides we have examined are very rapidly protonated by HOTf. As described earlier,[3b] H/D exchange was observed at low temperature following addition of HOTf to either $CpW(CO)_3D$ or $CpMo(CO)_3D$. Decomposition of these partially protonated metal hydrides to H_2 and metal triflates (eq 2) does occur but on a far slower time scale than that at which the proton transfer equilibrium is established. For example, formation of $Cp(CO)_3WOTf$ was incomplete after 2 weeks at room temperature following protonation of $CpW(CO)_3H$ with HOTf.[3] A CD_2Cl_2 solution of $Cp^*W(CO)_3H$ (0.1 M) that had been treated with HOTf (4 equiv) was only 48% decomposed to $Cp^*(CO)_3WOTf$ after 2.5 days at room temperature. An even slower rate of decomposition was observed when $Cp^*Os(CO)_2H$ was reacted with HOTf. When a

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[22] Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027−3039.

[23] Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032−4037.

[24] Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912−6918.

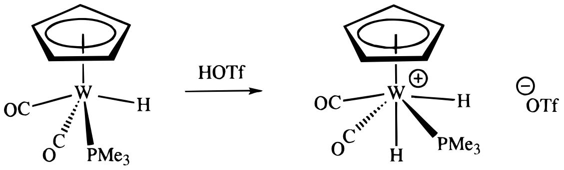
[25] Lambert, J. B.; Keepers, J. W. *J. Magn. Reson.* **1980**, *38*, 233−244.

[26] Davison, A.; McFarlane, W.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3653−3666.

[27] (a) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257−2263. (b) 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.

CD_2Cl_2 solution of $Cp^*Os(CO)_2H$ (0.10 M) was treated with HOTf (2.8 equiv), 32% of the $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ + $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ mixture remained after 20 days. The decomposition products were $Cp^*Os(CO)_2$-OTf (23%) and 41% of a second product tentatively identified as the bimetallic bridging hydride complex $\{[Cp^*Os(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ (see Experimental Section for further details).

Formation of $[CpW(CO)_2(PR_3)(H)_2]^+OTf^-$ by Protonation of $CpW(CO)_2(PR_3)H$ (R = Me, Cy, Ph). The PMe_3 ligand is a strong electron donor, and substitution of CO by PMe_3 is known to greatly increase the basicity of the metal and decrease the thermodynamic acidity of metal hydrides. The pK_a of $CpW(CO)_3H$ in MeCN is 16.1, while that of $CpW(CO)_2(PMe_3)H$ is 26.6.[27] Protonation of $CpW(CO)_2(PMe_3)H$ by HOTf gives the dihydride $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$ (eq 8). Similarly, reaction of $CpW(CO)_2(PMe_3)H$ with Brookhart's acid,[28] $[H(Et_2O)_2]^+BAr'_4{}^-$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl), led to the isolation of $[CpW(CO)_2(PMe_3)(H)_2]^+$ $BAr'_4{}^-$. The dihydride $[CpW(CO)_2(PMe_3)(H)_2]^+$ was isolated in analytically pure form with both the OTf^- and $BAr'_4{}^-$ counterions. This same dihydride was previously prepared and characterized as the BF_4^- salt by Tilset and co-workers.[29] They first observed it (along with $CpW(CO)_2(PMe_3)(NCMe)^+$) as a product of the oxidation of $CpW(CO)_2(PMe_3)H$ by Cp_2Fe^+ in MeCN; they independently prepared it by protonation of $CpW(CO)_2(PMe_3)H$ with $HBF_4{\cdot}Et_2O$. Our spectroscopic data for the OTf^- and $BAr'_4{}^-$ salts are in good agreement with those reported for the BF_4^- salt. Tilset reported that the two hydrides of $[CpW(CO)_2(PMe_3)(H)_2]^+BF_4^-$ were nonequivalent at −112 °C and suggested the structure drawn in eq 8. A fluxional process renders the two hydrides equivalent at room temperature. We measured T_1 = 2.4 s for the hydrides at 22 °C. This averaged value for the two hydrides is so large that it is clear that the compound is a dihydride in solution as well as in the solid. As suggested by Tilset,[29] the fluxional process that makes the two hydrides equivalent might involve the dihydrogen complex $[CpW(CO)_2(PMe_3)(\eta^2\text{-}H_2)]^+$ as an intermediate, but no direct evidence for this dihydrogen complex was obtained.



(8)

The dihydride $[CpW(CO)_2(PCy_3)(H)_2]^+OTf^-$, with the more sterically demanding tricyclohexylphosphine ligand, was also isolated. This compound is thermally unstable in solution, releasing H_2 and producing $Cp(CO)_2(PCy_3)WOTf$; in CD_2Cl_2 at room temperature the decomposition is half complete in about 16 h. Even as a solid, $[CpW(CO)_2(PCy_3)(H)_2]^+OTf^-$ turns dark when stored at room temperature. In contrast, $[CpW(CO)_2(PCy_3)(H)_2]^+$ $BAr'_4{}^-$, with the $BAr'_4{}^-$ counterion, is much more stable, and has been obtained in analytically pure form. A dihydride with a PPh_3 ligand, $[CpW(CO)_2(PPh_3)(H)_2]^+$ $BAr'_4{}^-$, was also isolated and characterized (see Experimental Section).

Table 1. Crystallographic Data from the X-ray Diffraction Study of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$

formula	$C_{11}H_{16}F_3O_5PSW$
mol wt	532.12
space group	$P2_12_12_1$
a, Å	8.105(3)
b, Å	13.650(3)
c, Å	15.336(2)
V, Å^3	1696.6(7)
Z	4
ρ(calcd), g cm^{-3}	2.083
temp, K	200 K
radiation	Mo Kα
μ, cm^{-1}	72.1
transm factor: max, min (ψ scans)	0.9979, 0.6594
reflcns collcd	2832
unique reflcns ($F_o > 0$)	2508
reflcns used ($F_o > 3\sigma(F_o)$)	2140
2θ limits (deg)	4−60
no. of variables	200
R^a	0.031
R_w	0.032
max shift/error, final cycle	≤0.01

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum[w(|F_o| - |F_c|)^2/\sum[w|F_o|^2]\}^{1/2}$.

As was done for the osmium compounds, the integrated intensities of the IR bands of the carbonyl ligands in these tungsten dihydrides allowed estimates[6] of the OC−W−CO angles. Estimated OC−W−CO angles were 92° for $[CpW(CO)_2(PPh_3)(H)_2]^+BAr'_4{}^-$ and 93° for $[CpW(CO)_2(PCy_3)(H)_2]^+BAr'_4{}^-$. The OC−W−CO angle estimated from the IR bands of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$ is 96°, which suggests that steric congestion in the PPh_3 and PCy_3 complexes may decrease the OC−W−CO angle, relative to the dihydride with the smaller PMe_3 ligand. The angle of 96° estimated from IR intensities is larger than the angle of 90.4(4)° found in the crystal structure (see below). Sutton and co-workers found that OC−M−CO angles estimated from IR data also exceeded those found in crystal structures.[30] For *cis*-$Cp^*Re(CO)_2I_2$ the OC−Re−CO angle of 80° estimated from the IR intensities was only slightly larger than the angle of 78(1)° determined crystallographically. For *trans*-$Cp^*Re(CO)_2Br_2$ a much larger difference was found: an OC-Re-CO angle of ∼115° was estimated from IR intensities, compared to 104.3(6)° found in the X-ray structure.[30]

Structural Characterization of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$; Observation of Weak Hydrogen-Bonding Interactions. Our structural characterization of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$ by single crystal X-ray diffraction verifies the geometry about tungsten suggested by Tilset.[29] Table 1 lists information on the data collection and refinement, and Table 2 gives selected bond distances and angles. The tungsten hydrides were located but not refined. As shown in the ORTEP diagram in Figure 3, the overall geometry can be viewed as a distorted octahedron, if the Cp ligand is thought of as occupying a single coordination site. One of the tungsten hydrides is nearly trans to the Cp, with a Cp(centroid)−W−H angle of 167°. A view from above the Cp ligand is shown in Figure 4.

The crystal structure reveals a network of weak hydrogen bonds between the tungsten complex and the triflate anions; details of angles and distances of these

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

(29) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618−2626.

(30) Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53−59.

Table 2. Selected Bond Lengths and Angles for $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$

Metal Coordination Sphere Distances (Å)			
W−C(1)	2.029(10)	W−Cp(CEN)[a]	1.983(10)
W−C(2)	2.023(10)	W−H(1)[b]	1.83
W−P	2.487(2)	W−H(2)[b]	1.62

Metal Coordination Sphere Angles (deg)			
C(1)−W−C(2)	90.4(4)	Cp(CEN)[a]−W−C(1)	110.5(4)
C(1)−W−P	131.7(3)	Cp(CEN)[a]−W−C(2)	115.4(4)
C(2)−W−P	84.7(3)	Cp(CEN)[a] −W−P	114.9(3)
H(1)−W−C(1)	61	H(2)−W−C(1)	76
H(1)−W−C(2)	76	H(2)−W−C(2)	137
H(1)−W−P	71	H(2)−W−P	75
H(1)−W−Cp(CEN)[a]	167	H(2)−W−Cp(CEN)[a]	107
H(1)−W−H(2)	63		

[a] Cp(CEN) designates the centroid of the Cp ring. [b] H(1) and H(2) were located in the final difference Fourier map but were not refined.

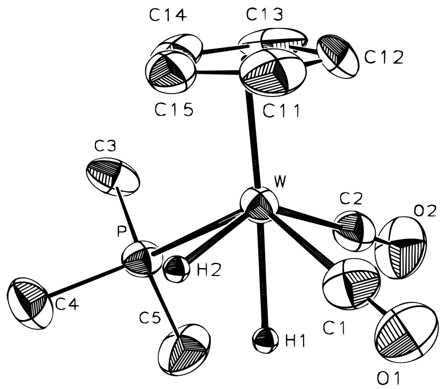

Figure 3. ORTEP drawing of $[CpW(CO)_2(PMe_3)(H)_2]^+$. The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms on the Cp and PMe_3 ligands are omitted.

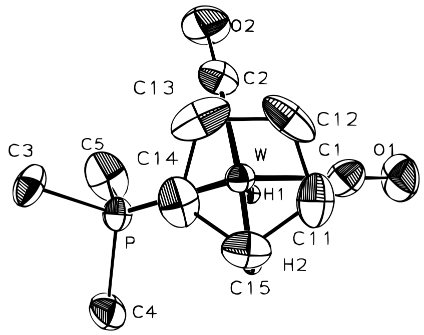

Figure 4. ORTEP drawing of $[CpW(CO)_2(PMe_3)(H)_2]^+$ viewed through the center of the Cp ring. The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms on the Cp and PMe_3 ligands are omitted.

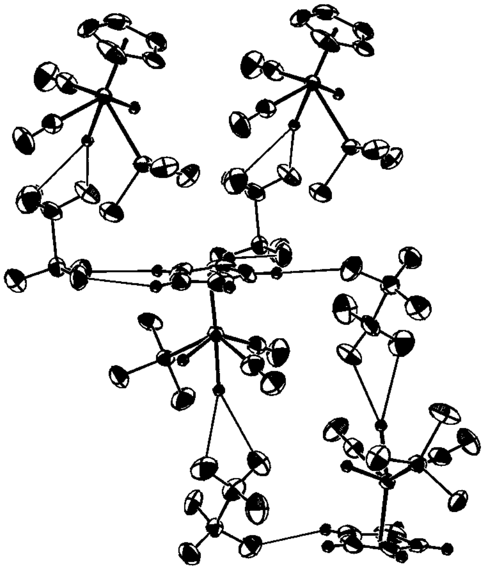

Figure 5. ORTEP drawing of the packing of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$, showing the weak hydrogen-bonding interactions (W−H···F and C−H···O). Two oxygens of one triflate form a hydrogen bond to adjacent C−H bonds on the Cp, while the remaining three C−H bonds are hydrogen bonded to oxygens on three other triflate anions. To improve the clarity of the figure, four of these hydrogen bonds are shown on the Cp near the middle of the figure, while the 5th C−H···O hydrogen bond is shown at the bottom of the figure.

are tabulated in the Supporting Information. Figure 5 is an ORTEP diagram of four $[CpW(CO)_2(PMe_3)(H)_2]^+$ cations and four OTf^- anions, showing the hydrogen bonding. The tungsten hydride trans to the Cp ligand is involved in a weak hydrogen bond with two of the fluorines on a triflate anion. The hydride is a hydrogen bond donor in this three-centered hydrogen bond, with the fluorines as hydrogen bond acceptors. The H···F separations for these interactions are 2.59 Å and 2.82 Å; the one with the shorter distance is also more linear (W−H−F angles of 162° vs 152°). The sum of the van der Waals radii for H and F is 2.55 Å, so these H···F interactions are quite weak. The tungsten hydride (H1) lies only 0.06 Å out of the plane defined by the W and the two fluorines, thus providing further evidence for the existence of this three-centered hydrogen bond.[31]

Participation of metal hydrides in hydrogen bonds has been a subject of substantial recent interest. Infrared spectroscopic data has been presented as evidence for hydrogen bonding of phosphine oxides to cationic hydride complexes of Os[32] and Re.[33] Another recent report of an O···H−M hydrogen bond involves $[(dppe)_2(\eta^1\text{-}OCOMe)WH_3]^+$, where structural and spectroscopic indicated that *one* of the hydrides of this cationic tungsten complex was involved in a hydrogen bond with an oxygen of the acetate ligand.[34] In these O···H−M interactions, as with the F···H−M interaction in $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$, the metal hydride acts as the hydrogen bond donor. All of these examples involve *cationic* metal hydrides; a Raman and IR spectroscopic study revealed no evidence for hydrogen bonding of the *neutral* hydride $HCo(CO)_4$ to amine bases prior to deprotonation.[35]

Metal hydrides have also been shown to be involved in hydrogen bonds where the metal hydride is the hydrogen bond *acceptor*. Several examples of *intra*molecular N−H···H−M hydrogen bonding have been discovered.[36,37] *Inter*molecular hydrogen bonding has been found between indole (and other N−H donors) and Re and W polyhydrides,[38] and a three-centered hydrogen bond between indole and two hydrides of $Re(PPh_3)H_5$

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(31) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: New York, 1991; p 21.

(32) Epstein, L. M.; Shubina, E. S.; Krylov, A. N.; Kreindlin, A. Z.; Rybinskaya, M. I. *J. Organomet. Chem.* **1993**, *447*, 277−280.

(33) Peris, E.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 2179−2180.

(34) Fairhurst, S. A.; Henderson, R. A.; Hughes, D. L.; Ibrahim, S. K.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1569−1570.

(35) Kristjánsdóttir, S. S.; Norton, J. R.; Moroz, A.; Sweany, R. L.; Whittenburg, S. L. *Organometallics* **1991**, *10*, 2357−2361.

was recently structurally characterized by neutron diffraction.[39] Spectroscopic data were recently published[40] for intermolecular ROH···H−M interactions between acidic alcohols and tungsten hydrides.

In addition to the hydrogen bonding of the W−H bond to the fluorines on the triflate, the crystal structure also indicates the existence of weak C−H···O hydrogen bonds,[41] where the oxygens atoms of the triflate behave as hydrogen bond acceptors. Each of the five hydrogens on the Cp ring are hydrogen bonded to an oxygen of a triflate. The C···O distances range from 3.246 to 3.497 Å; C−H···O angles range from 138 to 154°. These distances and angles are in the range found for other C−H···O hydrogen-bonding interactions. Although each of these individual hydrogen bonds is weak, collectively they can have a substantial impact on the overall crystal structure. The influence of hydrogen bonding in organometallic complexes has been recognized recently, and insightful analyses of the impact of C−H···O hydrogen bonding interactions on the crystal structures of organometallic complexes have been reported.[42]

Isotopic Effects on the Chemical Shifts of Partially Deuterated Dihydrides. We previously noted[3b] that the hydride resonance of $[CpW(CO)_3(H)(D)]^+OTf^-$ appears at δ −2.12, indicating an upfield shift of 0.05 ppm upon partial deuteration of the dihydride $[CpW(CO)_3(H)_2]^+OTf^-$ (δ −2.07). Protonation of $CpW(CO)_2(PMe_3)H$ by DOTf gives $[CpW(CO)_2(PMe_3)(H)(D)]^+OTf^-$, which exhibits a doublet (δ −2.541, $J_{PH} = 38$ Hz) at 25 °C. This resonance is 0.062 ppm upfield of the doublet for $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$ (δ −2.479). The magnitude of the isotope effects on the chemical shift, as well as the sign (upfield upon partial deuteration) that we find for these W hydrides, is similar to examples reported for a series of other dihydrides and polyhydrides. Crabtree and co-workers reported isotope effects on chemical shifts for partial deuteration of a large series of Re polyhydride complexes; upfield shifts of 0.002−0.03 ppm for each deuterium were typically observed.[43] Heinekey and co-workers found upfield shifts of up to 0.075 ppm upon partial deuteration of $[Cp^*Ir(PPh_3)(H)_3]^+$.[44] The trihydride complex $CpRu(PPh_3)(H)_3$ exhibits an upfield isotope shift of 0.023 ppm upon substitution of one H by D,[45] and the hydride resonance of *cis*-$Cp^*Re(CO)_2(H)(D)$ appears 0.056 ppm upfield of the dihydride resonance of *cis*-$Cp^*Re(CO)_2(H)_2$.[7]

In an NMR spectrum recorded at −80 °C following addition of DOTf to a CD_2Cl_2 solution of $Cp^*Os(CO)_2H$, the resonance due to $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ at δ −10.006 exhibited a shoulder at δ −9.987. This additional resonance is assigned to $[Cp^*Os(CO)_2(H)(D)]^+OTf^-$, indicating an unusual downfield shift of 0.019 ppm upon partial deuteration. This resonance assigned to the Os(H)(D) complex was not well-resolved but was reproducible. Precedent for a downfield shift of a dihydride in equilibrium with its dihydrogen tautomer comes from Heinekey's report[15] of a downfield shift of 0.027 ppm upon partial deuteration of $[Cp^*Re(CO)(NO)(H)_2]^+$, which was shown to be in equilibrium with $[Cp^*Re(CO)(NO)(\eta^2\text{-}H_2)]^+$. In both of these cases the resonance for the dihydrogen ligand is downfield of that due to the dihydride. Downfield shifts upon partial deuteration have also been reported for $Os(PTol_3)_3(H)_4$,[46] $(^tBu_3SiO)_4Ta_2(H)_4$,[47] *cis*-$IrH(\eta^2\text{-}H_2)Cl_2(P^iPr_3)_2$,[48] and $IrH_4[HB(3,5\text{-}Me_2pz)_3]$.[49]

Isotope effects on chemical shift[50] caused by geminal substitution of H for D on a metal are normally <0.1 ppm. Much larger changes in chemical shift can be observed in cases where isotopic perturbation of resonance occurs, in which there is a nonstatistical occupation of D vs H in chemically distinct sites. Partial deuteration of complexes containing both hydride and dihydrogen ligands[24,51] or dihydrides with chemically inequivalent hydride sites[52,53] can lead to observed chemical shift changes in the range of 0.2 ppm or greater due to isotopic perturbation of resonance.

Dependence of the NMR Chemical Shift of HOTf on Concentration and Temperature. NMR spectra in our experiments show resonances due to HOTf, in addition to the resonances due to the organometallic hydride complexes discussed above. The solutions of partially protonated $Cp^*Os(CO)_2H$ exhibited NMR resonances at −80 °C for HOTf at δ 12.24 and 17.09, both of which were somewhat broadened singlets ($\omega_{1/2} \approx 16$ Hz). As further additions of HOTf were made, the relative integrations of the δ 12.24:δ 17.09 resonances remained constant at 75(±3):25(±3). The acid resonances changed their chemical shift and broadened when a sufficient excess HOTf had been added to

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(36) (a) Peris, E.; Lee, J. C., Jr.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2573. (b) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014−11019. (c) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3485−3491.

(37) (a) Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2201−2202. (b) Lough, A. J.; Park, S.; Ramachandran, R.; Morris, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 8356−8357.

(38) Peris, E.; Wessel, J.; Patel, B. P.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1995**, 2175−2176.

(39) Wessel, J.; Lee, J. C., Jr.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2507−2509.

(40) Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Voronstov, E. V.; Epstein, L. M.; Gusev, D. G.; Niedermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105−1112.

(41) For leading references on C−H···O hydrogen bonds, see: (a) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063−5070. (b) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290−296. (c) Steiner, T.; Saenger, W. *J. Am. Chem. Soc.* **1992**, *114*, 10146−10154. (d) Steiner, T.; Saenger, W. *J. Am. Chem. Soc.* **1993**, *115*, 4540−4547.

(42) (a) Braga, D.; Grepioni, F.; Sabatino, P.; Desiraju, G. R. *Organometallics* **1994**, *13*, 3532−3543. (b) Braga, D.; Grepioni, F.; Biradha, K.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, *117*, 3156−3166. (c) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1994**, *27*, 51−56.

(43) (a) Hamilton, D. G.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198−3203. (b) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813−4821. (c) Luo, X.-L.; Michos, D.; Crabtree, R. H. *Organometallics* **1992**, *11*, 237−241.

(44) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909−919.

(45) Baird, G. J.; Davies, S. G.; Moon, S. D.; Simpson, S. J.; Jones, R. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1479−1486.

(46) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173−4184.

(47) Miller, R. L.; Toreki, R.; LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, *115*, 5570−5588.

(48) Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pélissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300−7312.

(49) Paneque, M.; Poveda, M.; Taboada, S. *J. Am. Chem. Soc.* **1994**, *116*, 4519−4520.

(50) Hansen, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105−234.

(51) Heinekey, D. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137−3138.

(52) Bianchini, C.; Laschi, F.; Peruzzini, M.; Ottaviani, F. M.; Vacca, A.; Zanello, P. *Inorg. Chem.* **1990**, *29*, 3394−3402.

(53) Heinekey, D. M.; Liegeois, A.; van Roon, M. *J. Am. Chem. Soc.* **1994**, *116*, 8388−8389.

protonate all of the Cp*Os(CO)$_2$H; the resonances then appeared at δ 12.01 ($\omega_{1/2} \approx$ 70 Hz) and δ 16.04 ($\omega_{1/2} \approx$ 35 Hz). An additional change is that the relative intensities had interchanged (28:72 ratio).

The T_1^{obs} for the two resonances of HOTf were typically about 0.17 s and did not undergo major changes in as the protonation proceeded (see Figure 2). After the final addition of HOTf, when all of the hydride had been protonated, the T_1^{obs} values of the two HOTf resonances increased to about 0.4 s.

The chemical shift of HOTf in CD$_2$Cl$_2$ was examined in order to help interpret these observations. A CD$_2$Cl$_2$ solution of HOTf (0.04 M) exhibited a singlet at δ 8.13. The chemical shift of HOTf was linearly dependent on concentration up to 0.22 M, increasing to δ 8.70 at [HOTf] = 0.22 M (see Figure 6 in the Experimental Section for a plot of chemical shift vs concentration). The downfield shift of the HOTf peaks with increasing concentration is consistent with the expected effect of increased hydrogen-bonding (of HOTf with itself). Above 0.22 M, the singlet for HOTf continued to move further downfield with increasing concentration, but additional broad resonances were observed at δ 11.5 and 11.8.

NMR spectra of HOTf at low temperature exhibit similar features. Whereas a singlet was observed at δ 8.37 for a solution of HOTf (0.1 M) in CD$_2$Cl$_2$ at 22 °C, the same solution at −50 °C exhibited broad resonances at δ 11.4 and 10.9, in addition to the main peak at δ 9.23. These broad resonances accounted for a total of 31% of the initial intensity of the peak observed at 22 °C, and the singlet that moved to δ 9.23 upon cooling accounted for 66% of the initial intensity.

HOTf has low solubility (~8 mM) at −80 °C, but the solubility increases in the presence of OTf$^-$ anions. A T_1 value of 1.5 s was determined at −80 °C for HOTf (0.09 M) in the presence of PPN$^+$OTf$^-$ (0.09 M). The chemical shift (δ 17.15) of this resonance is far downfield of the resonance for pure HOTf, implicating hydrogen bonding of HOTf to an OTf$^-$ counterion.

The NMR experiments on HOTf described above, carried out in the absence of metal hydrides, provide an explanation for the observation that two separate resonances were observed in the low-temperature experiments involving protonation of metal hydrides. On the basis of the similarity of the chemical shift to similar broadened resonances observed for HOTf at high concentrations or low temperatures, the resonance near δ 12 is thought to be due to excess HOTf, hydrogen-bonded to itself in aggregates [(HOTf)$_n$] or possibly not fully dissolved in solution at the low temperatures of the experiments. In our protonation experiments, OTf$^-$ counterions are present as a result of partial deprotonation of the HOTf by the metal hydrides. Thus the resonance near δ 17 is assigned as TfOH···OTf$^-$, in which HOTf is hydrogen-bonded to an OTf$^-$ counterion, based on the similarity of chemical shift to the HOTf/PPN$^+$OTf$^-$ mixture described above.

Conclusions

The tungsten hydride Cp*W(CO)$_3$H and the osmium hydride Cp*Os(CO)$_2$H are only partially protonated by 1 equiv of HOTf, giving protonated species having acidities comparable to that of HOTf. The resultant tungsten complex is a dihydride, [Cp*W(CO)$_3$(H)$_2$]$^+$OTf$^-$, while the protonation of the osmium complex gives an equilibrium mixture of the dihydride [Cp*Os(CO)$_2$(H)$_2$]$^+$OTf$^-$ and the dihydrogen complex [Cp*Os(CO)$_2$(η^2-H$_2$)]$^+$OTf$^-$. The kinetic and thermodynamic acidity of the dihydrogen complex are greater than the dihydride. Protonation of the phosphine-substituted tungsten compounds CpW(CO)$_2$(PR$_3$)H (R = Me, Cy, Ph) gives dihydrides that are much less acidic. The crystal structure of [CpW(CO)$_2$(PMe$_3$)(H)$_2$]$^+$OTf$^-$ reveals the presence of a weak hydrogen bond; one tungsten hydride is a hydrogen bond donor to two fluorines on the triflate anion.

Experimental Section

General Methods. 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 CD$_2$Cl$_2$ at δ 5.32. Solutions used for T_1 measurements were degassed by three or four freeze−pump−thaw cycles on a high-vacuum line. The T_1 measurements were carried out on a Bruker AM-300 (300 MHz for ^{1}H) using the standard inversion−recovery pulse sequence, 180°−τ−90°. Actual NMR probe temperatures were determined[54] using the measured difference in chemical shifts of the methyl and OH protons in MeOH. Line widths of NMR resonances (full width at half-maximum height) are abbreviated as $\omega_{1/2}$. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory (Woodside, NY). Cp*Os(CO)$_2$H was prepared by a modification of the method reported by Graham.[55] Cp*Os(CO)$_2$H was purified by column chromatography on silica gel using hexane as eluent and was further purified by sublimation at 65 °C. Cp*W(CO)$_3$H,[56] CpW(CO)$_3$H,[57] CpW(CO)$_2$(PMe$_3$)H,[58] and [H(Et$_2$O)$_2$]$^+$ BAr′$_4{}^-$ [28] [Ar′ = 3,5-bis(trifluoromethyl)phenyl] were prepared by literature methods. CpW(CO)$_2$(PPh$_3$)H was prepared by a minor modification of a reported method,[59] by refluxing a hexane solution of CpW(CO)$_3$H with an equimolar amount of PPh$_3$ for 5 h. HOTf was distilled and stored under Ar. PPN$^+$OTf$^-$ was prepared from reaction of AgOTf and PPN$^+$Cl$^-$ in CH$_2$Cl$_2$, followed by recrystallization from CH$_2$Cl$_2$/Et$_2$O.

Protonation of Cp*Os(CO)$_2$H To Give [Cp*Os(CO)$_2$(H)$_2$]$^+$OTf$^-$ and [Cp*Os(CO)$_2$(η^2-H$_2$)]$^+$OTf$^-$. T_1 Measurements. Cp*Os(CO)$_2$H (22.8 mg, 0.0596 mmol) was placed in an NMR tube equipped with a J. Young valve, and CD$_2$Cl$_2$ was added to give a volume of 0.65 mL. 1,2-Dichloroethane (3 μL, internal standard) was added. The chemical shifts of Cp*Os(CO)$_2$H are temperature dependent. ^{1}H NMR of Cp*Os(CO)$_2$H at 22 °C in CD$_2$Cl$_2$: δ 2.20 (s, Cp*), δ −14.08 (s, OsH). ^{1}H NMR of Cp*Os(CO)$_2$H at −80 °C in CD$_2$Cl$_2$: δ 2.13 (s, Cp*), δ −14.21 (s, OsH). The T_1 of the hydride (with no acid added) was found to be 5.9 s at −80 °C. HOTf was added at room temperature in 2 μL (0.023 mmol) increments. After each addition of HOTf, the solution

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(54) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679−680.

(55) Hoyano, J. K.; May, C. J.; Graham, W. A. G. *Inorg. Chem.* **1982**, *21*, 3095−3099.

(56) Kubas, G. J.; Kiss, G.; Hoff, C. D. *Organometallics* **1991**, *10*, 2870−2876.

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

(58) Kalck, P.; Poilblanc, R. *J. Organomet. Chem.* **1969**, *19*, 115−121.

(59) Bainbridge, A.; Craig, P. J.; Green, M. *J. Chem. Soc. A* **1968**, 2715−2718.

Table 3. T_1 Data from Protonation of $Cp^*Os(CO)_2H$

equiv of HOTf[a]	% protonation[b]	T_1^{obs} (s) δ −14.21, hydride	δ −10.00, dihydride	δ 12.24, HOTf	δ 17.09, HOTf
0.33	9	1.2	0.99	0.21	0.32
0.73	21	0.60	0.79	0.17	0.19
1.2	36	0.38	0.88	0.15	0.16
1.5	49	0.33	1.0	0.16	0.18
2.3	66	0.19	1.0	0.15	0.15
2.5	72	0.17	1.2	0.16	0.16

[a] Equiv of HOTf determined by integration of the two HOTf resonances plus the two protonated products. [b] % protonation includes dihydride and dihydrogen complexes, as a percentage of total [Os].

was freeze−pump−thawed three times on a high-vacuum line, and the tube was refilled with argon. NMR spectra were recorded at −80 °C, the intensities of the resonances were integrated vs the internal standard, and T_1 values were determined. ^1H NMR of $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ at −80 °C in CD_2Cl_2: δ 2.38 (s, Cp*), δ −10.00 (s, $Os(H)_2$). ^1H NMR of $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ at −80 °C in CD_2Cl_2: δ 1.92 (s, Cp*), δ −7.24 (br, $\omega_{1/2} \approx 70$ Hz, η^2-H_2). Typical line widths for the hydride and dihydride resonances were 7 Hz. Broad resonances ($\omega_{1/2} \approx$ 15-20 Hz) were observed for HOTf at δ 12.24 and δ 17.09. The relative integrations of the δ 12.24:δ 17.09 peaks remained constant at 75(±3):25(±3); the resonance at 12.24 typically integrated to 1.5−1.7 H compared to the sum of $[Cp^*Os(CO)_2(H)_2]^+$ and $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+$. Results of the T_1 measurements at −80 °C are found in Table 3. Addition of more HOTf (6 μL, total of 18 μL added) resulted in complete protonation of $Cp^*Os(CO)_2H$. The acid resonances moved to δ 12.01 ($T_1^{obs} = 0.37$ s) and δ 16.03 ($T_1^{obs} = 0.42$ s) (28:72 relative areas).

T_1 Measurements of $Cp^*Os(CO)_2H$ at 23 °C. In a separate experiment carried out similarly to that described above, a T_1 measurement was carried out on a solution of $Cp^*Os(CO)_2H$ in CD_2Cl_2. The T_1 of the hydride was determined to be 51 s at 23 °C, and that of the CH_3 groups of the Cp* ligand was measured as 5.1 s.

IR Spectra of $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ and $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$. $Cp^*Os(CO)_2H$ (15 mg, 0.039 mmol) was dissolved in CH_2Cl_2 (2.0 mL, volumetric flask). IR of $Cp^*Os(CO)_2H$ in CH_2Cl_2: ν(CO) 1990 (s), 1923 (s) cm^{-1}. HOTf (25 μL, 0.28 mmol, 7.2 equiv) was added, and an IR spectrum was recorded (0.1 mm path length; NaCl windows). As shown in Figure 1, IR bands (absorbance) were observed at 2118 (0.25), 2090 (0.13), 2069 (0.39), and 2042 (0.12) cm^{-1}. Fitting of these partially overlapping bands gave the following band maxima (relative areas in parentheses; arbitrary units): 2118 (3.13), 2091 (1.00), 2068 (6.87), 2040 (1.99) cm^{-1}. As described in the text, the OC−Os−CO angles estimated from the intensities of these IR bands are 112° for $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ and 109° for $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$.

Decomposition Products Formed from $Cp^*Os(CO)_2H$ + HOTf. $Cp^*Os(CO)_2H$ (23.2 mg, 0.0607 mmol) was placed in an NMR tube, and CD_2Cl_2 was added to give a volume of 0.61 mL. 1,2-Dichloroethane (2 μL, internal standard) was added. HOTf (15 μL, 0.17 mmol, 2.8 equiv) was added, giving complete protonation of $Cp^*Os(CO)_2H$. This solution decomposed slowly at 22 °C; after 20 days, the sum of $[Cp^*Os(CO)_2(H)_2]^+OTf^- + [Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ was 32% of the initial amount of $Cp^*Os(CO)_2H$. While clean decomposition to metal triflates is observed[3] from reaction of many metal hydrides with HOTf, the metal triflate $Cp^*Os(CO)_2OTf$ (δ 2.00)[60] was not the sole product observed here, since it formed in only 23% yield after 20 days in this experiment. The other decomposition product formed in 41% yield after 20 days and had ^1H NMR resonances (δ 2.20, 30 H, Cp*; δ −19.60, 1 H, μ-H) consistent with a tentative assignment as a bimetallic cation with a bridging hydride, $\{(\mu\text{-}H)[Cp^*Os(CO)_2]_2\}^+OTf^-$. This product has the same Cp* chemical shift at 22 °C as pure samples of $Cp^*Os(CO)_2H$, but it is straightforward to distinguish it from the $Cp^*Os(CO)_2H$, since, under these conditions at 22 °C with excess acid present, the Cp* peaks of $[Cp^*Os(CO)_2(H)_2]^+OTf^-$ and $[Cp^*Os(CO)_2(\eta^2\text{-}H_2)]^+OTf^-$ appear as a coalesced singlet at δ 2.44. The resonances assigned to $\{(\mu\text{-}H)[Cp^*Os(CO)_2]_2\}^+OTf^-$ are similar to those (δ 2.06, 30 H, Cp*, and −17.65, 1 H, μ-H) reported[61] for the analogous Ru complex $\{(\mu\text{-}H)[Cp^*Ru(CO)_2]_2\}^+BF_4^-$. Precedent for formation of a bridging hydride by decomposition of a dihydrogen complex comes from thermal decomposition of $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+BF_4^-$, which gives[15] $\{(\mu\text{-}H)[Cp^*Ru(CO)_2]_2\}^+BF_4^-$. Similarly, protonation of $Cp^*Re(CO)(NO)H$ with $HBF_4{\cdot}OEt_2$ gives a equilibrium mixture of dihydride and dihydrogen complexes that decompose to $\{(\mu\text{-}H)[Cp^*Re(CO)(NO)]_2\}^+BF_4^-$, while protonation of $Cp^*Re(CO)(NO)H$ with HOTf ultimately leads to $Cp^*Re(CO)(NO)OTf$ as a decomposition product.[15]

Table 4. Line Widths of Hydride, Dihydride, and Dihydrogen Resonances from Protonation of $Cp^*Os(CO)_2H$ by $HBF_4{\cdot}OEt_2$

temp (°C)	$\omega_{1/2}(HOs)$ (d −14.23)	$\omega_{1/2}((H)_2Os)$ (δ −10.00)	$\omega_{1/2}((\eta^2H_2)Os)$ (δ −7.25)
−75	90	8	very broad
−89	32	10	200
−98	16	15	100

Protonation of $Cp^*Os(CO)_2H$ by $HBF_4{\cdot}OEt_2$. $Cp^*Os(CO)_2H$ (21.0 mg, 0.0549 mmol) was placed in an NMR tube equipped with a screw cap, and CD_2Cl_2 was added to give a volume of 0.65 mL. $HBF_4{\cdot}OEt_2$ (8.5 μL, ∼0.058 mmol, ∼1.1 equiv) was added at room temperature, and NMR spectra were recorded at −75, −89, and −98 °C. Line widths ($\omega_{1/2}$ in Hz) of hydride resonances are found in Table 4.

Protonation of $CpW(CO)_3H$ To Give $[CpW(CO)_3(H)_2]^+OTf^-$. T_1 Measurements. $CpW(CO)_3H$ (21.3 mg, 0.0638 mmol) was placed in an NMR tube, and CD_2Cl_2 was added to give a volume of 0.62 mL. 1,2-Dichloroethane (4 μL, internal standard) was added. The chemical shifts of $CpW(CO)_3H$ are temperature dependent. ^1H NMR of $CpW(CO)_3H$ at 22 °C in CD_2Cl_2: δ 5.52 (s, Cp), δ −7.32 (s with W satellites; $J_{WH} = 37$ Hz, WH). ^1H NMR of $CpW(CO)_3H$ at −80 °C in CD_2Cl_2: δ 5.49 (s, Cp), δ −7.45 (s with W satellites, $J_{WH} = 37$ Hz, WH). At −80 °C, the T_1 of the hydride was determined to be 11.2 s and the T_1 of the Cp was 7.6 s. HOTf (7 μL, 0.079 mmol, 1.2 equiv) was added, and an

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[60] The metal triflate complex $Cp^*(CO)_2OsOTf$ is formed cleanly[3] from the ionic hydrogenation of $Me_2C{=}CMe_2$ by HOTf and $Cp^*(CO)_2OsH$. IR (CH_2Cl_2) of $Cp^*(CO)_2OsOTf$: 2034 (s), 1976 (s) cm^{-1}.

[61] Stasunik, A.; Malisch, W. *J. Organomet. Chem.* **1984**, *270*, C56−C62.

Table 5. T_1 Data (−80 °C) and Assignments from Protonation of $CpW(CO)_3H$ by HOTf

chem shift (δ)	T_1^{obs} (s)	assgnt
14.19	1.8	HOTf
5.92	7.2	Cp of $CpW(CO)_3H$
5.50	7.6	Cp of $[CpW(CO)_3(H)_2]^+$
−2.07	1.8	$W(H)_2$
−7.45	3.7	WH

Table 6. T_1 Data (−78 °C) and Assignments from Protonation of $Cp^*W(CO)_3H$ by HOTf (1.1 Equiv)

chem shift (δ)	T_1^{obs} (s)	assgnt
16.8	0.33	HOTf···OTf^-
12.1	0.34	HOTf
2.33	0.72	Cp* of $[Cp^*W(CO)_3(H)_2]^+$
2.11	0.78	Cp* of $Cp^*W(CO)_3H$
−2.33 ($\omega_{1/2}$ = 25 Hz)	0.52	$W(H)_2$
−7.03 ($\omega_{1/2}$ = 5 Hz)	0.87	WH

NMR spectrum recorded at −80 °C indicated that 16% of the $CpW(CO)_3H$ had been protonated to form $[CpW(CO)_3(H)_2]^+OTf^-$. ^1H NMR of $[CpW(CO)_3(H)_2]^+OTf^-$ at −80 °C in CD_2Cl_2: δ 5.92 (s, Cp), δ −2.07 (s, $\omega_{1/2}$ = 12 Hz, $W(H)_2$). The resonance observed at δ 14.19 ($\omega_{1/2}$ = 12 Hz) is assigned to HOTf. Results of T_1 measurements on this solution at −80 °C are found in Table 5.

T_1 Measurement of $CpW(CO)_3H$ at 29 °C. In a separate experiment carried out similarly to that described above, a T_1 measurement was carried out on a solution of $CpW(CO)_3H$ (0.1 M) in CD_2Cl_2. The T_1 of the hydride was determined to be 85 s at 29 °C, and that of the Cp ligand was measured as 52 s.

Protonation of $Cp^*W(CO)_3H$ To Give $[Cp^*W(CO)_3(H)_2]^+OTf^-$. T_1 Measurements. $Cp^*W(CO)_3H$ (24.0 mg, 0.0594 mmol) was placed in an NMR tube, and CD_2Cl_2 was added to give a volume of 0.63 mL. 1,2-Dichloroethane (3 μL, internal standard) was added. The chemical shifts of $Cp^*W(CO)_3H$ are temperature dependent. ^1H NMR of $Cp^*W(CO)_3H$ at 22 °C in CD_2Cl_2: δ 2.20 (s, Cp*), δ −6.86 (s, J_{WH} = 40 Hz, WH). ^1H NMR of $Cp^*W(CO)_3H$ at −80 °C in CD_2Cl_2: δ 2.12 (s, Cp*), δ −7.03 (s with W satellites, J_{WH} = 40 Hz, WH). The T_1 of the hydride was determined to be 6.4 s at −80 °C. HOTf (6 μL, 0.068 mmol, 1.1 equiv) was added, and the color of the solution turned from pale yellow to slightly darker yellow. The NMR spectrum at −36 °C exhibited a single broad ($\omega_{1/2}$ = 59 Hz) Cp* resonance at δ 2.23; separate resonances were observed for the dihydride $[Cp^*W(CO)_3(H)_2]^+OTf^-$ (δ −2.27, $\omega_{1/2}$ = 80 Hz) and for the hydride (δ −6.95, $\omega_{1/2}$ = 70 Hz). At −57 °C, separate Cp* resonances were observed for the hydride (δ 2.14) and dihydride (δ 2.36). Along with resonances for the hydride (δ −6.98) and dihydride (δ −2.29) observed at −57 °C, broad resonances were observed at δ 16.4 and 12.2. Further cooling of the solution to −78 °C and integration of the resonances indicated that the ratio of $Cp^*W(CO)_3H$ to $[Cp^*W(CO)_3(H)_2]^+OTf^-$ was 1:1. A resonance at δ 16.8 ($\omega_{1/2}$ = 25 Hz) integrated to 1.0 proton compared to the dihydride, and the resonance at δ 12.1 ($\omega_{1/2}$ = 40 Hz) integrated to 0.4 protons compared to the dihydride. Results of T_1 measurements on this solution at −78 °C are found in Table 6.

Additional HOTf (15 μL, making a total of 4 equiv of HOTf added per $Cp^*W(CO)_3H$) was added, and the NMR spectrum indicated complete conversion to $[Cp^*W(CO)_3(H)_2]^+OTf^-$. Results of T_1 measurements on this solution at −78 °C are found in Table 7. This yellow solution of $[Cp^*W(CO)_3(H)_2]^+OTf^-$ turned red as it slowly decomposed to $Cp^*(CO)_3WOTf$ (δ 2.08, 48% yield after 2.5 days at 22 °C).

Table 7. T_1 Data (−78 °C) and Assignments from Protonation of $Cp^*W(CO)_3H$ by Excess HOTf

chem shift (δ)	T_1 (s)	assgnt
13.1	1.9	HOTf
2.32	0.76	Cp* of $[Cp^*W(CO)_3(H)_2]^+$
−2.33	0.49	$W(H)_2$

IR Spectrum of $[Cp^*W(CO)_3(H)_2]^+OTf^-$. $Cp^*W(CO)_3H$ (9.7 mg, 0.024 mmol) was dissolved in CH_2Cl_2 (1.0 mL). IR of $Cp^*W(CO)_3H$: ν(CO) 2006 (s), 1909 (s) cm^{-1}. HOTf (20 μL, 0.22 mmol, 9.4 equiv) was added, and the IR spectrum of $[Cp^*W(CO)_3(H)_2]^+$ exhibited ν(CO) bands at 2119 (s), 2075 (vs), and 2057 (s) cm^{-1}.

Preparation of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$. HOTf (105 μL, 1.19 mmol) was added to a solution of $CpW(CO)_2(PMe_3)H$ (384 mg, 1.00 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 10 min at 22 °C, during which time it turned from yellow to colorless. Et_2O (10 mL) and hexane (30 mL) were added by vacuum transfer to produce a white precipitate, which was collected by filtration, washed with Et_2O (30 mL), and dried under vacuum to give $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$ (522 mg, 0.98 mmol, 98%). ^1H NMR (CD_2Cl_2): δ 5.70 (s, 5H, Cp), 1.88 (d, J_{PH} = 9.6 Hz, 9H, PMe_3), −2.48 (d, J_{PH} = 40 Hz, 2H, $W(H)_2$). ^{13}C NMR (CD_2Cl_2, 250 K): 202.0, 200.4 (br, CO), 120.7 (q, J_{CF} = 318.9 Hz, CF_3), 88.2 (Cp), 23.5 (d, J_{PC} = 38.9 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −32.3 (s, $^1J_{PW}$ = 204 Hz). IR (CH_2Cl_2): $\nu(CO)_{asym}$ 2073 (rel intensity 1.0), 2016 (rel intensity 1.25) cm^{-1}; calculated[6] OC-W-CO = 96°. Anal. Calcd for $C_{11}H_{16}F_3O_5PSW$: C, 24.83; H, 3.03. Found: C, 25.13; H, 3.24.

Collection and Reduction of X-ray Data. Crystals of $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$ were prisms grown from slow diffusion of hexane into a CH_2Cl_2 solution at −50 °C. A crystal (0.28 × 0.30 × 0.48 mm) was coated with petroleum jelly and sealed inside a glass capillary. The diffraction data measured on an Enraf Nonius CAD-4 diffractometer indicated orthorhombic symmetry with systematic absences $h00$, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$, $l = 2n + 1$ consistent with the space group $P2_12_12_1$.

Determination and Refinement of the Structure. The structure[62] was solved by standard heavy-atom Patterson methods using absorption-corrected data. In the least-squares refinement, anisotropic temperature parameters were used for all the non-hydrogen atoms and the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. Hydrogen atoms were placed at calculated (X−H = 0.95 Å) positions and allowed to "ride" on the atom to which they were attached. (The two hydrogen atoms coordinated to the tungsten were not included in the refinement.) A common isotropic thermal parameter was refined for the hydrogen atoms. In the final difference Fourier map the peaks were less than ±1 $e^-/Å^3$. Two peaks, 1.83 and 1.62 Å from the tungsten, were observed

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[62] Sheldrich, G. M. 1976, SHELX76. Crystal Structure refinement program, Cambridge University, England. Neutral atom scattering factors were taken from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99−100. Anomalous dispersion effects were taken from: Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891−1898.

in reasonable positions to be the two coordinated hydrogen atoms. The handedness of the structure was checked, and the model which resulted in the lower R_w value is reported here.

Preparation of $[CpW(CO)_2(PMe_3)(H)_2]^+BAr'_4{}^-$. CH_2Cl_2 (10 mL) was vacuum-transferred into a flask containing $CpW(CO)_2(PMe_3)H$ (82 mg, 0.21 mmol) and $[H(Et_2O)_2]^+BAr'_4{}^-$ (202 mg, 0.200 mmol), and the solution was stirred for 10 min at 22 °C, during which time it turned from yellow to colorless. Hexane (30 mL) was added, and slow evaporation of the solvent under vacuum gave a white, air-sensitive precipitate, which was collected by filtration, washed with hexane (50 mL), and dried under vacuum to give $[CpW(CO)_2(PMe_3)(H)_2]^+BAr'_4{}^-$ (228 mg, 0.183 mmol, 92%). ^1H NMR (CD_2Cl_2): δ 7.73 (br, 8H, *o*-H), 7.58 (br, 4H, *p*-H), 5.48 (s, 5H, Cp), 1.79 (d, $J = 10.5$ Hz, 9H, PMe_3), −2.42 (d, $J = 41$ Hz, 2H, $W(H)_2$). ^{13}C NMR (CD_2Cl_2, 250 K): 201.4 (br, CO), 161.5 (1:1:1:1 quartet, $J_{BC} = 50.2$ Hz, *ipso*-C), 134.5 (*o*-C), 128.4 (br, q, $^2J_{CF} = 29$ Hz, *m*-C), 124.2 (q, $^1J_{CF} = 272$ Hz, CF_3), 117.3 (*p*-C), 87.3 (Cp), 23.6 (d, $J_{PC} = 39$ Hz, PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 295 K): δ -32.4 (s, $^1J_{PW} = 208$ Hz). IR (CH_2Cl_2): $\nu(CO)_{asym}$ 2079 (rel intensity 1.0), $\nu(CO)_{sym}$ 2023 (rel intensity 1.33) cm^{-1}; calculated[6] OC−W−CO = 98°. Anal. Calcd for $C_{42}H_{28}BF_{24}O_2PW$: C, 40.47; H, 2.26. Found: C, 40.57; H, 2.37.

Preparation of $CpW(CO)_2(PCy_3)H$. A solution of $CpW(CO)_3H$ (1.0 g, 3.0 mmol) and PCy_3 (820 mg, 2.92 mmol) in toluene (50 mL) was heated under reflux for 15 h. The solvent was evaporated under vacuum, and the residue was washed with hexane (60 mL) to give a pale yellow solid (1.68 g, 2.86 mmol, 98%). ^1H NMR (CD_2Cl_2): δ 5.31 (s, 5H, Cp), 1.85−1.24 (br, m, 33H, $P(C_6H_{11})_3$), −7.65 (br d, $J_{PH} = 65$ Hz, 1H, WH). IR (CH_2Cl_2): $\nu(CO)$ 1915 (vs), 1821 (s) cm^{-1}. Anal. Calcd for $C_{25}H_{39}O_2PW$: C, 51.20; H, 6.70. Found: C, 51.19; H, 6.54.

Preparation of $[CpW(CO)_2(PCy_3)(H)_2]^+OTf^-$. HOTf (50 μL, 0.56 mmol) was added to a solution of $CpW(CO)_2(PCy_3)H$ (300 mg, 0.512 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 5 min at 22 °C, during which time the color changed from yellow to pale yellow. Hexane (30 mL) was added by vacuum transfer. The resulting air- and temperature-sensitive white precipitate was collected by filtration, washed with hexane (30 mL), and dried under vacuum to give $[CpW(CO)_2(PCy_3)(H)_2]^+OTf^-$ (340 mg, 0.462 mmol, 90%). This compound is thermally unstable. In CD_2Cl_2 solution, it decomposes with an approximate halflife of 16 h at room temperature, and it eventually turns black even when stored as a solid. ^1H NMR (CD_2Cl_2): δ 5.65 (s, 5H, Cp), 1.94−1.24 (br, m, 33H, $P(C_6H_{11})_3$), −2.78 (br, d, $J_{PH} = 38$ Hz, 2H, $W(H)_2$). ^{13}C NMR (CD_2Cl_2, 220 K): 203.0 (br, CO), 119.0 (q, $J_{CF} = 316$ Hz, CF_3), 87.3 (Cp), 38.8 (d, $^1J_{PC} = 24$ Hz, C-1 of PCy_3), 29.6 (s, C-3 of PCy_3), 26.9 (d, $^2J_{PC} = 8.5$ Hz, C-2 of PCy_3), 25.5 (s, C-4 of PCy_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.1 (s, $^1J_{PW} = 207$ Hz). IR (CH_2Cl_2): $\nu(CO)_{asym}$ 2068 (rel intensity 1.0), $\nu(CO)_{sym}$ 2011 (rel intensity 1.08) cm^{-1}; calculated[6] OC−W−CO = 92°.

Preparation of $[CpW(CO)_2(PCy_3)(H)_2]^+BAr'_4{}^-$. CH_2Cl_2 (10 mL) was vacuum-transferred into a flask containing $CpW(CO)_2(PCy_3)H$ (190 mg, 0.324 mmol) and $[H(Et_2O)_2]^+BAr'_4{}^-$ (280 mg, 0.276 mmol). The mixture was stirred for 5 min at 22 °C, during which time the it became colorless. Hexane (30 mL) was added by vacuum transfer, and slow evaporation of the solvent gave a white air-sensitive precipitate, which was collected by filtration, washed with hexane (30 mL), and dried under vacuum to give $[CpW(CO)_2(PCy_3)(H)_2]^+BAr'_4{}^-$ (397 mg, 0.273 mmol, 99%). ^1H NMR (CD_2Cl_2): δ 7.73 (br, 8H, *o*-H), 7.57 (br, 4H, *p*-H), 5.56 (s, 5H, Cp), 1.97−1.78 (m, 33H, PCy_3), −2.61 (d, $J = 38$ Hz, 2H, $W(H)_2$). ^{13}C NMR (CD_2Cl_2, 250 K): 201.4 (br, CO), 161.8 (1:1:1:1 quartet, $J_{BC} = 50$ Hz, *ipso*-C), 134.8 (s, *o*-C), 128.8 (br, q, $^2J_{CF} = 31$ Hz, *m*-C), 124.6 (q, $J_{CF} = 272$ Hz, CF_3), 117.6 (*p*-C), 87.4 (Cp), 39.6 (d, $^1J_{PC} = 24.7$ Hz, C-1 of PCy_3), 30.2 (s, C-3 of PCy_3), 27.3 (d, $^2J_{PC} = 10.6$ Hz, C-2 of PCy_3), 25.9 (s, C-4 of PCy_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 30.0 (s, $^1J_{PW} = 205$ Hz). IR (CH_2Cl_2): $\nu(CO)_{asym}$ 2069 (rel intensity 1.0), $\nu(CO)_{sym}$ 2013 (rel intensity 1.09) cm^{-1}; calculated[6] OC−W−CO = 93°. Anal. Calcd for $C_{57}H_{52}BF_{24}O_2PW$: C, 47.19; H, 3.61. Found: C, 46.89; H, 3.54.

Preparation of $[CpW(CO)_2(PPh_3)(H)_2]^+BAr'_4{}^-$. CH_2Cl_2 (5 mL) was vacuum-transferred into a flask containing $Cp(CO)_2(PPh_3)WH$ (135 mg, 0.238 mmol) and $[H(Et_2O)_2]^+BAr'_4{}^-$ (200 mg, 0.198 mmol). The solution was stirred for 5 min at 22 °C, and hexane (10 mL) was added by vacuum transfer. Slow evaporation of the solvent under vacuum gave a white precipitate, which was collected by filtration, washed with hexane (20 mL), and dried under vacuum to give $[CpW(CO)_2(PPh_3)(H)_2]^+BAr'_4{}^-$ (277 mg, 0.193 mmol, 98%). ^1H NMR (CD_2Cl_2): δ 7.74 (br, 8H, *o*-H), 7.57 (br, 4H, *p*-H), 7.56−7.31 (m, 15H, PPh_3), 5.37 (s, 5H, Cp), −1.33 (d, $J = 38$ Hz, 2H, $W(H)_2$). ^{13}C NMR (CD_2Cl_2, 250 K): 201.4 (br, CO), 161.8 (1:1:1:1 quartet, $J_{BC} = 51$ Hz, *ipso*-C), 134.8 (s, *o*-C), 132.9 (d, $^2J_{PC} = 10$ Hz, *o*-C of PPh_3), 132.4 (s, *p*-C of PPh_3), 131.8 (d, $^1J_{PC} = 57$ Hz, *ipso*-C of PPh_3), 129.6 (d, $^3J_{PC} = 11$ Hz, *m*-C of PPh_3), 128.4 (br, q, $^2J_{CF} = 32$ Hz, *m*-C), 124.6 (q, $^1J_{CF} = 273$ Hz, CF_3), 117.6 (*p*-C), 89.4 (Cp). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 17.3 (s, $^1J_{PW} = 205$ Hz). IR (CH_2Cl_2): $\nu(CO)_{asym}$ 2078 (rel intensity 1.0), $\nu(CO)_{sym}$ 2025 (rel intensity 1.08) cm^{-1}; calculated[6] OC−W−CO = 92°.

T_1 Measurement of HOTf at 25 °C. An 0.1 M solution of HOTf in CD_2Cl_2 was prepared by adding HOTf (5.5 μL, 0.062 mmol) to CD_2Cl_2 (0.61 mL). The solution was freeze−pump−thawed three times on a high-vacuum line, and a T_1 measurement at 25 °C gave a value of 9.4 s.

Concentration Dependence of the ^1H NMR Chemical Shift of HOTf in CD_2Cl_2. NMR spectra were recorded at 22 °C on a CD_2Cl_2 solution (0.62 mL) in which HOTf was added in 2 μL increments. The chemical shift of the HOTf peak as a function of concentration is shown in Figure 6; the plot is linear ($R = 0.997$) up to [HOTf] = 0.22 M. The concentration of HOTf in the plot represents the concentration of HOTf added to the solution, although the data suggest that some of it may not be dissolved in solution above [HOTf] = 0.22 M. The equation is ppm = 3.09(ppm/M)[HOTf] + 8.04 ppm, indicating a chemical shift of δ 8.04 for HOTf at infinite dilution in CD_2Cl_2. Above [HOTf] = 0.22 M, the chemical shift continued to move downfield as [HOTf] increased, but the change was nonlinear. Broad resonances at δ 11.8 and δ 11.5 were observed above this concentration. The resonance at δ 11.8 was

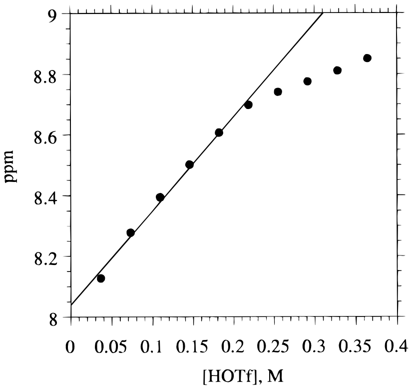

Figure 6. Plot of ^{1}H NMR chemical shift vs concentration of HOTf (CD_2Cl_2; 22 °C).

Table 8. ^{1}H NMR Chemical Shifts of HOTf in the Presence of PPN^+OTf^- (0.09 M)

μL of HOTf added	[HOTf] (M)	δ (ppm) of HOTf	μL of HOTf added	[HOTf] (M)	δ (ppm) of HOTf
6	0.10	16.19	18	0.31	13.11
12	0.20	14.11	24	0.41	12.62

initially larger, but the resonance at 11.5 increased in relative intensity as [HOTf] increased. When 18 μL HOTf had been added, the solution was cloudy and the resonances at δ 11.8 and 11.5 were of equal peak heights, with both having $\omega_{1/2} \approx 60$ Hz.

Effect of Added PPN^+OTf^- on the Chemical Shift of HOTf in CD_2Cl_2. NMR spectra were recorded on a CD_2Cl_2 solution (0.66 mL) containing PPN^+OTf^- (41 mg, 0.060 mmol, 0.09 M; PPN = bis(triphenylphosphine)nitrogen(1+), Ph_3PNPPh_3) in which HOTf was added in 6 μL increments. The resonance was observed as a broad singlet, and the chemical shifts are found in Table 8.

Effect of PPN^+OTf^- on the T_1 of HOTf in CD_2Cl_2. HOTf (5.5 μL, 0.062 mmol, 0.095 M), PPN^+OTf^- (41 mg, 0.060 mmol, 0.09 M), and 1,2-dichloroethane (3 μL, internal standard) were added to CD_2Cl_2 (0.65 mL) in an NMR tube. The solution was freeze−pump−thawed three times on a high-vacuum line, and a T_1 measurement at 25 °C for HOTf (δ 16.11) gave $T_1 = 1.5$ s ($T_1 \approx 4.5$ s for the aromatic protons of PPN^+). When the solution was cooled to −80 °C, the HOTf resonance moved to δ 17.15, but the T_1 of HOTf remained at 1.5 s ($T_1 \approx 1.0$ s for the aromatic protons of PPN^+ at −80 °C). The integration of HOTf at −80 °C dropped to 73% of the amount at 25 °C, and broad resonances were observed around δ 12 at −80 °C.

Temperature Dependence of the ^{1}H NMR Chemical Shift of HOTf in CD_2Cl_2. A singlet (δ 8.37, $\omega_{1/2} = 3$ Hz) was observed at 22 °C for a CD_2Cl_2 solution (0.59 mL) containing HOTf (5 μL, 0.1M). At −50 °C, the chemical shift of the singlet had changed to δ 9.23, and the integrated intensity of this peak (relative to 1,2-dichloroethane internal standard) dropped to 66% of the initial value. Broad resonances were observed at δ 11.4 ($\omega_{1/2} \approx 40$ Hz, 19%) and at δ 10.9 (12%), indicating a mass balance of 97% of the initial intensity of the resonance that was measured at 22 °C. At −80 °C a singlet was observed at δ 9.00 which accounted for only 8% of the initial intensity.

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Supporting Information Available: Tables giving additional experimental details of the X-ray diffraction structure, final anisotropic thermal parameters for the non-hydrogen atoms, calculated hydrogen atom positions, complete interatomic distances and angles, atomic coordinates and thermal parameters, and a table of distances and angles for the hydrogen-bonding interactions (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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