Synthesis, Characterization, and Reactivity of Dicationic Dihydrogen Complexes of Osmium and Ruthenium

Thomas A. Luther and D. Michael Heinekey*

Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195

Received August 1, 1997[⊗]

The dicationic complexes $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ [PR_3 = PPh_3, $PMePh_2$ (**2a**,**b**)], $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**2c**), and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**) (bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline) have been prepared by the protonation of the corresponding monocationic hydrides using an excess of trifluoromethanesulfonic acid. The presence of a bound dihydrogen ligand is indicated by short T_1 minimum values consistent with H−H distances of 0.92−1.04 Å. For the partially deuterated derivatives, J_{HD} values of 25.1−31.0 Hz were observed. The dicationic complexes are strong acids, indicating that the bound H_2 is substantially activated toward heterolytic cleavage. The H_2 ligand is tightly bound to the metal center and does not undergo exchange with D_2 over the course of several weeks. The complex $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**2a**) has been shown to be very stable in solution at room temperature. In contrast, the ruthenium analogue, $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**), decomposes in solution at room temperature but is relatively stable at temperatures less than 245 K.

Introduction

Since the initial discovery by Kubas and co-workers of the transition metal dihydrogen complex $W(H_2)(P^iPr_3)_2(CO)_3$,[1] a large number of isolable H_2 complexes have been prepared, the majority of which have been found to be singly charged cationic species.[2] While the plethora of monocationic complexes may be due to the common synthetic route of protonating a neutral metal hydride, an underlying aspect may be that the positive charge confers additional stability on the H_2 complexes.[3] An assessment of the effect of charge on the binding of H_2 requires the preparation of charged complexes of the form $[M(H_2)(L)_5]^{n+}$ with ligands L comparable to those employed in the tungsten complexes. Recently, the preparation of cationic rhenium analogues, $[Re(H_2)(PR_3)_2(CO)_3]^+$ and $[Re(H_2)(PR_3)_2(CN^tBu)_3]^+$, and comparative studies with the neutral tungsten complexes were reported.[3−5]

At the outset of this study the only well-characterized dicationic complexes belonged to the osmium series $[Os(H_2)(NH_3)_4(L)]^{2+}$ and $[Os(H_2)(en)_2(L)]^{2+}$ (en = ethylenediamine).[6−8] The preparation and properties of these osmium dihydrogen dications (and monocations when L is anionic) differ greatly from those of other known dihydrogen complexes. The complexes are prepared by the reduction of osmium(III) and osmium(VI) dications under acidic conditions. The dihydrogen complexes are surprisingly nonacidic in spite of the 2+ charge, and the monohydride analogues are unknown. The complexes exhibit very strong M−H_2 interactions and quite long H−H bond lengths in the H_2 ligand (1.09−1.34 Å).

The preparation of dicationic dihydrogen complexes by the protonation of monocationic hydrides was only recently reported: $[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$ by Caulton, Tilset, and co-workers,[9] $[Os(H_2)(dppe)_2(NCMe)]^{2+}$ (dppe = 1,2-bis(diphenylphosphino)ethane) by Morris and co-workers,[10] $[M(H_2)(dppp)_2(CO)]^{2+}$ (M = Ru, Os; dppp = 1,3-bis(diphenylphosphino)propane) by Mezzetti and co-workers,[11] and, most recently, $[Fe(H_2)(L)(dppe)_2]^{2+}$ (L = CO, CNH) by Morris and co-workers.[12]

We recently reported the initial results of the protonation of $[OsH(PPh_3)_2(bpy)(CO)]^+$ (**1a**) to generate $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**2a**).[13] We now report the results of further investigations of **2a** and its analogues $[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$ (**2b**), $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**2c**), and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**) (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline).

Results

Synthesis and Characterization of the Monocationic Hydrides: $[MH(PR_3)_2(N\text{-}N)(CO)]^+$ [M = Os, PR_3 = PPh_3, $PMePh_2$, N-N = bpy (1a,b); M = Os, PR_3 = PPh_3, N-N = phen (1c); M = Ru, PR_3 = PPh_3, N-N = bpy (3)]. The monocationic hydrides $[OsH(PR_3)_2(bpy)(CO)](OTf)$ (PR_3 = PPh_3, $PMePh_2$ (**1a**,**b**)), $[OsH(PPh_3)_2(phen)(CO)](OTf)$ (**1c**), and

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451−452.
(2) Review articles: (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913−926. (b) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155−289. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95−101. (d) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120−128.
(3) Heinekey, D. M.; Radzewich, C. E.; Voges, M. H.; Schomber, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 4172−4181.
(4) Heinekey, D. M.; Voges, M. H.; Barnhart, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 10792−10802.
(5) Heinekey, D. M.; Schomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515−4516.
(6) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506−9513.
(7) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261−2263.
(8) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946−8947.
(9) Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473−9480.
(10) Schlaf, M.; Lough, A. J.; Maltby, P. A.; Morris, R. H. *Organometallics* **1996**, *15*, 2270−2278.
(11) Rocchini, E.; Mezzetti, A.; Rüegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711−720.
(12) Forde, C. E.; Landau, S. E.; Morris, R. H. *J. Chem. Soc., Dalton Trans.* **1997**, 1663−1664.
(13) Heinekey, D. M.; Luther, T. A. *Inorg. Chem.* **1996**, *35*, 4396−4399.

S0020-1669(97)00975-0 CCC: $15.00
Published on Web 01/12/1998

Scheme 1

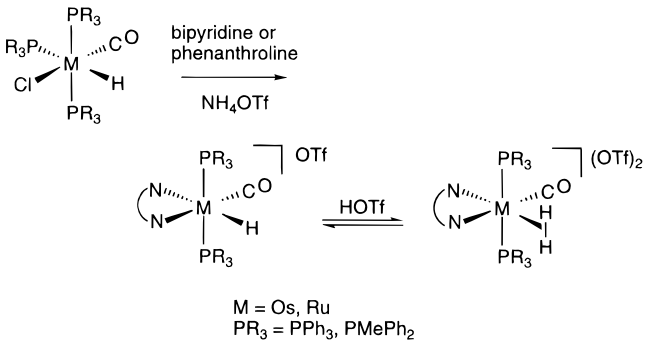

Table 1. Selected NMR Data for the Monocationic Hydride Complexes[a]

complex	^{1}H δ_H (ppm)	J_{HP} (Hz)	^{31}P δ (ppm)
$[OsH(PPh_3)_2(bpy)(CO)]^+$ (**1a**)	−12.19	18.4	+18.76
$[OsH(PMePh_2)_2(bpy)(CO)]^+$ (**1b**)	−12.22	17.6	+0.08
$[OsH(PPh_3)_2(phen)(CO)]^+$ (**1c**)	−11.98	18.1	+19.25
$[RuH(PPh_3)_2(bpy)(CO)]^+$ (**3**)	−11.31	19.6	+46.53

[a] In CD_2Cl_2.

$[RuH(PPh_3)_2(bpy)(CO)](OTf)$ (**3**) were prepared as the triflate salts as outlined in Scheme 1.

The ^{1}H NMR spectra for **1a**−**c** and **3** exhibit the expected phosphine proton resonances and separate resonances for each proton in the bipyridyl or phenanthroline ligand in the aromatic region. A triplet resonance is observed in the hydride region. The ^{31}P{selective ^{1}H} NMR spectra of these complexes consist of a single doublet resonance due to coupling to the hydride (a selective decoupling procedure was used to decouple the proton nuclei of the phosphine ligands). The NMR spectra are consistent with two equivalent *trans* phosphines and a bipyridyl or phenanthroline ligand with inequivalent protons as depicted in Scheme 1 (Table 1).

Synthesis of $[M(H_2)(PR_3)_2(N\text{-}N)(CO)]^{2+}$ [M = Os, N-N = bpy, PR_3 = PPh_3, $PMePh_2$ (2a,b); M = Os, N-N = phen, PR_3 = PPh_3 (2c); M = Ru, N-N = bpy, PR_3 = PPh_3 (4)]. We find that protonation can be conveniently carried out using the triflate salt of the monocationic hydrides and excess triflic acid (HOTf) in nitromethane or in methylene chloride (Scheme 1). The dicationic products, $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ (PR_3 = PPh_3, $PMePh_2$ (**2a**,**b**)) and $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**2c**) are soluble in these solvents and thermally robust, showing no loss of H_2 with only minor (estimated to be <10% as determined by ^{31}P NMR) decomposition occurring over a period of 18 months in CD_2Cl_2 at room temperature for **2a**. The presence of bases such as diethyl ether or water will immediately deprotonate the dicationic complexes and regenerate the monocationic hydrides without any loss to decomposition.

The ^{1}H and ^{31}P{selective ^{1}H} NMR spectra for the ruthenium analogue, **4**, are similar to those of the other dihydrogen dications (Table 2). However, **4** is much less robust than the osmium dications. In fact, **4** decomposes at room temperature but appears to be relatively stable when stored at 245 K. The ^{31}P{selective ^{1}H} NMR spectrum (in CD_2Cl_2) indicates that the decomposition of **4** leads initially to the formation of the chloride cation, $[RuCl(PPh_3)_2(bpy)(CO)]OTf$.

Preparation of $[M(HD)(PR_3)_2(N\text{-}N)(CO)]^{2+}$ [M = Os, N-N = bpy, PR_3 = PPh_3, $PMePh_2$ (2a-d_1,b-d_1); M = Os, N-N = phen, PR_3 = PPh_3 (2c-d_1); M = Ru, N-N = bpy, PR_3 = PPh_3 (4-d_1)]. The HD complexes were prepared by addition of excess deuterated triflic acid (DOTf) to a solution of the monocationic hydride in CD_2Cl_2. The hydride region of the ^{1}H NMR spectra exhibit a sharp "triplet" resonance, as opposed to the broad singlet in the H_2 complexes. The intensity ratio of the three resonances is approximately 1:1.2:1 for these complexes. The increased intensity of the center peak of the triplet of the HD resonances is due to the presence of a small amount of the H_2 species resulting from the incomplete deuteration of the triflic acid.[13] The ^{31}P{selective ^{1}H} NMR spectra exhibit a singlet resonance for the HD complex with no observable coupling. We find that the ^{1}H NMR spectra of the H_2 complexes and their corresponding HD analogues are essentially independent of temperature (including J_{HD} values) down to 165 K.

Table 2. Selected NMR Properties of the Dicationic Dihydrogen Complexes

complex	^{1}H δ[a] ($\Delta\nu_{1/2}$)[b]	J_{HD}[c] ($\Delta\delta$)[d]	T_1[e]	^{31}P δ[f] ($\Delta\nu_{1/2}$)
$[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**2a**)	−5.78 (170)	25.3 (+18)	15.2[g]	+8.54 (6.5)
$[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$ (**2b**)	−6.23 (41)	25.5 (+20)	16.5[h]	−6.02 (8.4)
$[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**2c**)	−5.63 (39)	25.5 (< +20)	6.3[i]	+8.60 (7.0)
$[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**)	−6.70[j] (110)	31.0[j] (< +20)	3.9[k]	+32.81[j] (12.6)

[a] ^{1}H NMR chemical shift of the H_2 resonance (ppm). [b] Half-height line width (Hz). [c] J_{HD} value of the HD analogue measured at 500 MHz (Hz). [d] ^{1}H NMR chemical shift difference between the H_2 and HD resonances, $\delta_{H_2} - \delta_{HD}$ (ppb). [e] T_1 minimum of the H_2 resonance (ms). [f] ^{1}P NMR chemical shift of the H_2 complex (ppm). [g] 263 K at 500 MHz. [h] 260 K at 500 MHz. [i] 200 K at 200 MHz. [j] Recorded at 253 K. [k] 240 K at 200 MHz.

A sealed NMR tube containing **2a** in CD_2Cl_2 and 1 atm of D_2 was monitored for a period of 2 weeks. A similar sample was prepared containing **4** in CD_2Cl_2 with 1 atm of D_2, stored at 245 K, and monitored by NMR for a period of 2 months. No evidence of deuterium incorporation was observed by ^{1}H and ^{31}P NMR spectroscopy in either sample.

Basicity of $[MH(PPh_3)_2(bpy)(CO)]^+$ [M = Os, Ru (1a, 3)]. Approximately 4 equiv of HOTf is required to completely generate the dication species. When a large excess (10 equiv) of $[H(Et_2O)_x]BAr'_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) is reacted with **1a**, the formation of **2a** does not occur. When $[H(Et_2O)]BF_4$ is used for protonation, the hydride monocations are only partially protonated. A direct basicity comparison was performed in an NMR tube with equimolar amounts of **1a** and **3**. Incremental amounts of HOTf were added, and the percentages of the mono- and dicationic species were determined by ^{31}P NMR spectroscopy. The data indicate that the ruthenium complex **4** is slightly more acidic than the osmium analogue **2a**.

Attempts to isolate the dication **2a** were unsuccessful. Addition of pentane to a methylene chloride solution of **2a** resulted in precipitation of a gummy residue. The NMR spectra of this residue are consistent with the presence of **2a** and HOTf. When a methylene chloride solution of **2a** is placed under dynamic vacuum, an oily film is observed upon the removal of solvent. The ^{1}H and ^{31}P NMR spectra indicate that only **2a**, **1a**, and HOTf are present. There is no evidence of any product that involves the loss of H_2.

Synthesis of $[MX(PPh_3)_2(bpy)(CO)]^+$ [M = Os, Ru; X = Cl, Br]. When *N*-chlorosuccinimide (NCS) is added to solutions of **1a** and **3**, succinimide is generated along with a single new complex that is formed cleanly and quantitatively by NMR. The aromatic region in the ^{1}H NMR spectra for these complexes

Scheme 2

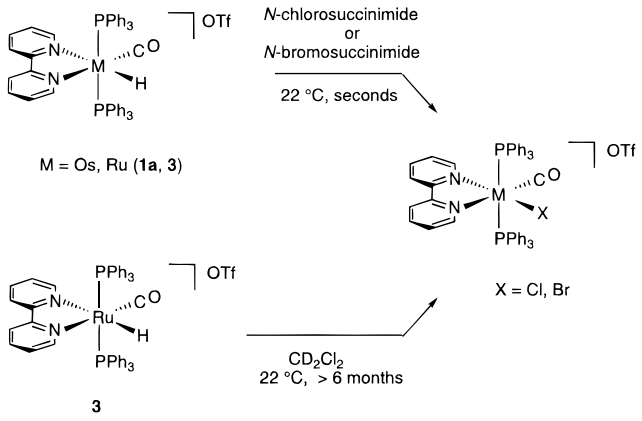

exhibit the expected eight resonances for the inequivalent bipyridyl protons and a narrow band for the triphenylphosphine protons and are now lacking observable resonances in the hydride region. The ^{31}P{selective ^{1}H} NMR spectra reveal only a singlet resonance (δ −1.17 for the osmium complex and δ +27.39 for the ruthenium analogue). The NMR spectra are consistent with the formulation of these complexes as $[OsCl(PPh_3)_2(bpy)(CO)]^+$ and $[RuCl(PPh_3)_2(bpy)(CO)]^+$ (Scheme 2). Complex **1a** was also reacted with *N*-bromosuccinimide (NBS) with similar results, the generation of succinimide and a single new complex characterized as $[OsBr(PPh_3)_2(bpy)(CO)]^+$. The ^{1}H and ^{31}P{selective ^{1}H} NMR spectra for this species are very similar to the others with a singlet resonance at δ −1.97 in the ^{31}P{selective ^{1}H} NMR spectrum. $[RuCl(PPh_3)_2(bpy)(CO)]^+$ was also formed when a CD_2Cl_2 solution of **3** was allowed to stand at room temperature for an extended period (Scheme 2). After 6 months, the concentration of the chloride cation is approximately the same as the concentration of **3**, as determined by the intensity of the resonances in the ^{31}P{selective ^{1}H} NMR spectrum.

A solution of the ruthenium chloride cation $[RuCl(PPh_3)_2(bpy)(CO)]^+$ was reacted with silver triflate (AgOTf) under an atmosphere of hydrogen. The ^{31}P{selective ^{1}H} NMR spectrum exhibits a new resonance at δ +15.7. After 24 h, this resonance decreased in intensity and several new unidentified resonances emerged. No reactions were observed between AgOTf and the corresponding osmium monocationic chloride and bromide complexes.

Discussion

The ^{31}P{selective ^{1}H} NMR spectra of the dications display a single sharp resonance for the equivalent phosphines as expected for a *trans* structure. A bound dihydrogen ligand often lacks observable coupling to adjacent bound phosphines.[14] The narrowness of the line widths ($\Delta\nu_{1/2}$) in the ^{31}P{selective ^{1}H} NMR spectra for the dications (6.5−12.6 Hz) imply that any H−P coupling must be less than 3 Hz. More definitive NMR evidence of a bound dihydrogen ligand is the observation of a large H−D coupling in the partially deuterated analogue. The preparation of the HD analogues of **2a**−**c** and **4** is accomplished by reacting the monocationic hydrides with excess DOTf. The small upfield shift of the HD resonance from the H_2 signal ($\Delta\delta$ < +20 ppb) for these complexes is typical of reported dihydrogen complexes[15] and smaller than what is observed in H_2/HD gas ($\Delta\delta$ = +36 ppb).[16] This small chemical shift difference and the magnitude of the H−D coupling are essentially independent of temperature, suggesting that there is only one structure for these dicationic complexes. A rapid equilibrium between a dihydride and a dihydrogen structure would likely lead to temperature-dependent isotope effects resulting from isotopic perturbation of equilibrium.[17]

In reported dihydrogen complexes which have been structurally characterized by neutron diffraction or solid state NMR methods, an inverse correlation between the H−H distance and J_{HD} of the HD analogue is observed.[13] The equation corresponding to the inverse relationship between r_{HH} and J_{HD} from corrected neutron diffraction and solid state NMR data[18] is

$$r_{HH} = 1.44 - 0.0168(J_{HD}) \quad (1)$$

Morris and co-workers have used a larger set of distances and J_{HD} values to develop a similar equation for the H−H bond length. They have also included the uncorrected neutron data and distances determined from X-ray diffraction data along with the more reliable distances from solid state NMR and corrected neutron data. However, with this larger data set, the equation is surprisingly similar to eq 1:[18a]

$$r_{HH} = 1.42 - 0.0167(J_{HD}) \quad (2)$$

The rapid T_1 relaxation of the H_2 resonance of the dicationic complexes provides another method for the determination of the H−H distance. Quantitative analysis by the method of Halpern and co-workers[19] leads to two possible values for the H−H distance in the dihydrogen complexes, depending upon the relative rate of the H_2 ligand rotation.[20] Gusev and co-workers[21] have analyzed the T_1 minimum and J_{HD} data of reported dihydrogen complexes that have J_{HD} values ≥25 Hz. In only a few cases, namely those with the general formula *trans*-$M(H_2)H(P\text{-}P)_2^+$ (M = Fe, Ru; P-P = chelating phosphine), is it necessary to invoke the fast rotation model to produce a reasonable H−H distance in the H_2 ligand. In general, the determination of the H−H distance in the H_2 ligand using T_1

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

(15) Reported isotope shifts in dihydrogen complexes are generally <50 ppb. Reported exceptions: (a) $\Delta\delta$ = +90 ppb for $Ru(H_2)$(OEP)(THF) (OEP = octaethylporphyrin), +130 ppb for $Os(H_2)$(OEP)(*Im) (*Im = 3-*tert*-butyl-4-phenylimidazole), and −200 ppb for $Ru_2(H_2)$(DPB)-$(*Im)_2$ (DPB = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)-porphyrinyl]biphenylene) [Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E.; Lewis, N. S.; Lopez, M. A.; Guilard, R.; L'Her, M.; Bothner-By, A. A.; Mishra, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 5654−5664]. (b) $\Delta\delta$ = +200 ppb for $[Cp_2Ta(CO)(H_2)]^+$ [Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalón, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1994**, *116*, 2635−2636]. (c) $\Delta\delta$ = +80 ppb for $[Os(H_2)(en)_2OAc]^+$ (en = ethylenediamine; OAc = acetate) [Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352−5356].

(16) Evans, D. F. *Chem. Ind.* **1961**, 1960.

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

(18) Includes structural and solution data reported in ref 13 and recently published data from: (a) Maltby, P. A.; Schlaf, M.; Steinbeck, M.; Lough, A. J.; Morris, R. H.; Klooster, W. T.; Koetzle, T. F.; Srivastava, R. C. *J. Am. Chem. Soc.* **1996**, *118*, 5396−5407. (b) King, W. A.; Luo, X-L.; Scott, B. L.; Kubas, G. J.; Zilm, K. W. *J. Am. Chem. Soc.* **1996**, *118*, 6782−6783.

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

(20) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031−7036.

(21) Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775−6783.

(22) Luther, T. A.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 6688−6689.

Table 3. Determination of the H−H Distance in the H_2 Ligand of the Dicationic Dihydrogen Complexes from T_1 Minimum (Fast-Rotation and Static Models) and J_{HD} Values of the HD Analogues

complex	r_{HH} (Å)	
$[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**2a**)	0.82/1.03[a]	1.02[b,c]
$[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$ (**2b**)	0.83/1.04	1.01
$[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**2c**)	0.82/1.03	1.02[c]
$[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**)	0.76/0.95	0.92

[a] H−H distance calculated from the T_1 minimum values for fast-rotation/static regimes of the H_2 ligand. [b] H−H distance calculated from the J_{HD} value of the HD complex and eq 1. [c] Distance calculated from the corrected J_{HD} value of 25.1 Hz.[22]

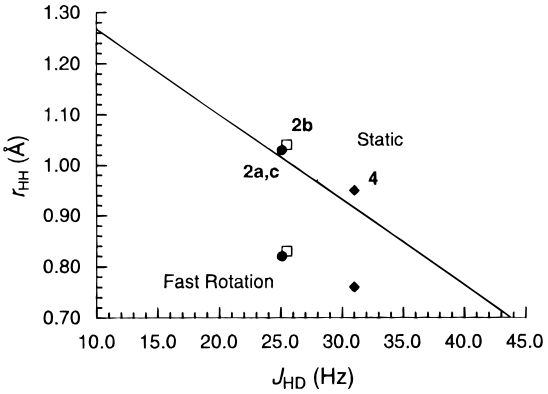

Figure 1. Plot of H−H distance versus J_{HD}. The line represents the inverse linear relationship between r_{HH} and J_{HD} values using eq 1. H−H distances for the dicationic species $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ (PR_3 = PPh_3, $PMePh_2$) (**2a**,**b**), $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**2c**), and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**) are calculated from the T_1 minimum values using static and fast-rotation models for the H_2 ligand. The J_{HD} values for **2a**-d_1 and **2c**-d_1 have been corrected for the field-dependent residual D_{HD}.[22]

minimum data should consider the rotation around the M−H_2 axis as static.

The determination of the H−H bond lengths in the H_2 ligand of the dications **2a**−**c** and **4** by the T_1 minimum method using a static rotation model is in general agreement with the distances calculated from the J_{HD} values (Table 3 and Figure 1). The slight overestimation of the bond length by the T_1 minimum method using the static model (<4% in these complexes) was also reported for $W(H_2)(P^iPr_3)_2(CO)_3$.[23]

A relatively long H−H distance is consistent with the tight binding of H_2 to the metal center. A common route for partial incorporation of deuterium into the H_2 ligand of dihydrogen complexes is to expose the complex to deuterium gas. The incorporation is proposed to occur by isotopic scrambling due to the combination of the lability and the acidity of the H_2 ligand.[24] An example of deuterium incorporation by this route is the reaction of $[Re(H_2)(PCy_3)_2(CN^tBu)_3]^+$ with D_2.[4] We have found no observable deuterium incorporation when samples of **2a** and **4** (maintaining temperatures of <245 K for **4**) were exposed to D_2 for extended periods.

It has been found that an excess of triflic acid is required to protonate the monocationic hydrides. A large excess of $[H(Et_2O)]BF_4$ will only partially generate the dications, presumably due to the presence of diethyl ether. The dication **2a** was not observed when 10 equiv of $[H(Et_2O)_x]BAr'_4$ was reacted with **1a** due to the larger amount of diethyl ether associated with the acid and the water that is inevitably present.[25] It is important to note that the protonation reactions of the monohydride cations were performed in CD_2Cl_2 and quantitation of pK_a values is difficult.[26] The dicationic complexes **2a**−**c** and **4** are extremely acidic since they will protonate diethyl ether ($[H(Et_2O)]^+$ pK_a = −2.6)[27] and are similar in acid strength to HOTf (estimated aqueous pK_a = −4.9).[28,29]

The instability of $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**) at room temperature in comparison with the osmium analogues is consistent with the observed trend in the iron triad as noted by Morris and co-workers[30] and also in the complexes $[M(H_2)(dppp)_2(CO)]^{2+}$ (M = Ru, Os) as noted by Mezzetti and co-workers.[11] The H−H distance in the H_2 ligand of **4**, as determined by T_1 minimum and J_{HD} data, is shorter than the distance in the osmium analogues, consistent with a weaker M−H_2 interaction. The loss of H_2 from **4** would generate the highly reactive 16-electron Lewis acid $[Ru(PPh_3)_2(bpy)(CO)]^{2+}$, which can presumably abstract chloride from the solvent (CD_2Cl_2), forming the chloride cation $[RuCl(PPh_3)_2(bpy)(CO)]^+$. The chloride cation can also be generated from the monohydride cation $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**3**) by the immediate and quantitative reaction with *N*-chlorosuccinimide. The chloride cation has also been observed to form via a slow reaction of **3** with the CD_2Cl_2 solvent over a 6 month period (Scheme 2). The generation of a similar chloride cation was observed by Mezzetti and co-workers[11] in the decomposition of $[Ru(H_2)(dppp)_2(CO)]^{2+}$.

The preparation of the chloride analogues of **1a** and **3**, $[OsCl(PPh_3)_2(bpy)(CO)]^+$ and $[RuCl(PPh_3)_2(bpy)(CO)]^+$, was of interest as a possible alternative route for the preparation of the dihydrogen dicationic complexes $[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**2a**) and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**). It was recently reported that AgOTf can be used to abstract chloride from $Cp^*Ir(PMe_3)Cl_2$ under an atmosphere of hydrogen to cleanly generate $[Cp^*Ir(PMe_3)H_3]^+$.[17] However, we found the reaction of $[RuCl(PPh_3)_2(bpy)(CO)]^+$ with AgOTf under H_2 at room temperature leads to a new species which was not the expected dihydrogen dication (no reaction occurred at lower temperatures). The $^{31}P\{$selective $^1H\}$ NMR spectrum exhibits a singlet at +15.7, which is consistent with the formulation $[Ru(OTf)(PPh_3)_2(bpy)(CO)]^+$. In contrast to the reaction of the ruthenium chloride complex with AgOTf, there is no reaction with the osmium chloride or bromide analogues.

The complexes $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ (PR_3 = PPh_3, $PMePh_2$) (**2a**,**b**), $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**2c**), and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**) are extremely strong acids, as demonstrated by their immediate deprotonation by diethyl ether. Thus **2a**−**c** and **4** along with the complexes recently reported by Mezzetti and co-workers,[11] $[M(H_2)(dppp)_2(CO)]^{2+}$ (M = Ru, Os), and $[Fe(H_2)(R)(dppe)_2]^{2+}$ (R = CO, CNH) reported by Morris and co-workers[12] represent an interesting combination of high reactivity toward heterolysis and very tight binding of H_2. In contrast to the properties of this group of dihydrogen

(23) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000−7009.
(24) Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632−3632.
(25) Radzewich, C. E. Ph.D. Thesis, University of Washington, 1997.
(26) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 9, pp 324−334.
(27) The pK_a of protonated diethyl ether in aqueous sulfuric acid: Perdoncin, G.; Scorrano, G. *J. Am. Chem. Soc.* **1977**, *99*, 6983−6986.
(28) Fujinaga, T.; Sakamoto, I *J. Electroanal. Chem.* **1977**, *85*, 185−201.
(29) The aqueous pK_a of HOTf has also been estimated to be <−10: Cox, R. A.; Krull, U. J.; Thompson, M.; Yates, K. *Anal. Chim. Acta* **1979**, *106*, 51−57.
(30) Cappellani, E. P.; Drouin, S. D.; Jia, G.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375−3388.

Table 4. Properties of the Acidic Dicationic Dihydrogen Complexes

complex	$E_{1/2}$[a]	J_{HD}[b]	r_{HH}[c]	stability[d]
$[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$ [e]	1.9	25.5	1.01	*f*
$[Os(H_2)(dppe)_2(NCMe)]^{2+}$ [g]	2.1	21.4	1.08	H_2/D_2[h]
$[Fe(H_2)(CNH)(dppe)_2]^{2+}$ [i]	2.3	32.5	0.89	stable
$[Os(H_2)(bpy)_2(CO)]^{2+}$ [j]	2.4	29.0	0.95	24 h[k]
$[Os(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**2a**)	2.6	25.1[l]	1.02	stable
$[Os(H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$ (**2b**)	2.6	25.5	1.01	stable
$[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**2c**)	2.6	25.1[l]	1.02	stable
$[Os(H_2)(dppp)_2(CO)]^{2+}$[m]	2.7	32.0	0.90	stable
$[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**)	2.9	31.0[n]	0.92	unstable
$[Fe(H_2)(CO)(dppe)_2]^{2+}$ [i]	3.0	33.1	0.88	stable
$[Ru(H_2)(dppp)_2(CO)]^{2+}$ [m]	3.0	34.2[o]	0.87	unstable

[a] Calculated $E_{1/2}$ of the N_2 analogue (V).[32] [b] J_{HD} of the HD analogue (Hz). [c] Calculated from the J_{HD} value of the HD analogue using eq 1 (Å). [d] Stability with respect to loss of H_2 at room temperature. [e] Reference 9. [f] Not reported. [g] Reference 10. [h] Exchanges slowly with D_2. [i] Reference 12. [j] Reference 13. [k] Loss of H_2 occurs after 24 h. [l] Corrected J_{HD} value.[22] [m] Reference 11. [n] Measured at 253 K. [o] Measured at 193 K.

dications, highly acidic dihydrogen complexes such as $[Ru(H_2)Cp^*(CO)_2]^+$ are very labile with respect to loss of H_2,[31] while the dicationic H_2 complexes such as $[Os(H_2)(NH_3)_4(L)]^{2+}$ and $[Os(H_2)(en)_2(L)]^{2+}$ reported by Taube and co-workers, which tightly bind H_2, are not acidic.[6−8] The two other dicationic complexes $[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$ reported by Tilset, Caulton, and co-workers,[9] and $[Os(H_2)(dppe)_2(NCMe)]^{2+}$, reported by Morris and co-workers,[10] represent an intermediate level of reactivity toward heterolysis and binding of the H_2 ligand. The lability of the H_2 ligand has been demonstrated in the generation of the HD complex $[Os(HD)(dppe)_2(NCMe)]^{2+}$ by slow, reversible H_2/D_2 ligand exchange. On the basis of the similarity in the calculated $E_{1/2}$ values for the corresponding N_2 analogues[32] of the two complexes, $[Os(H_2)(P^iPr_3)_2(NCMe)_3]^{2+}$ may also show reversible H_2 loss comparable with that of $[Os(H_2)(dppe)_2(NCMe)]^{2+}$ (Table 4).

The stability of the dicationic dihydrogen complexes is surprising in light of the calculated oxidation potential[33] of the corresponding dinitrogen complexes. It was predicted that if the oxidation potential of the N_2 complex was greater than 2 V, the π back-donation from the metal center to the dihydrogen ligand would not be sufficient for a stable $M-H_2$ complex.[32] The formal charge of the metal center in these dicationic complexes apparently increases the $M-H_2$ σ interaction, strengthening the binding of the H_2 ligand.

Conclusions

The complexes $[Os(H_2)(PR_3)_2(bpy)(CO)]^{2+}$ (PR_3 = PPh_3, $PMePh_2$) (**2a**,**b**), $[Os(H_2)(PPh_3)_2(phen)(CO)]^{2+}$ (**2c**), and $[Ru(H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ (**4**) are formulated as dihydrogen complexes with H−H distances of 0.92−1.02 Å. The osmium complexes are extremely acidic and exhibit very strong $M-H_2$ interactions as evidenced by long H−H distances and the nonlability of the H_2 ligand. The ruthenium complex **4** is relatively stable at temperatures less than 245 K but decomposes at room temperature and is also slightly more acidic than the osmium analogues.

Experimental Section

General Procedures. Manipulations of air-sensitive complexes were performed under argon using standard vacuum-line, Schlenk, or syringe techniques. Argon was deoxygenated and dried by passage through R3-11 CuO catalyst (BASF) followed by Mallinckrodt Aquasorb containing P_2O_5. CD_2Cl_2 and CD_3NO_2 (Cambridge Isotope Laboratories) were vacuum-distilled from CaH_2. OsO_4 was purchased from Stevens Metallurgical Inc. $RuCl_3 \cdot 3H_2O$ was purchased from Alfa Products. All other solvents and reagents were used without further purification, except for CH_2Cl_2, which was vacuum-distilled from CaH_2. Elemental analyses were performed by Canadian Microanalytical Services, Delta, British Columbia, Canada. Infrared spectra were recorded on a Perkin-Elmer model 1600 Fourier transform spectrophotometer (2.0 cm^{-1} resolution). Samples were examined on NaCl cells as Nujol mulls.

^1H NMR spectra were recorded on Bruker AC200, DPX200, AF300, and AM500 spectrometers and referenced internally to the residual proton resonance of the deuterated solvent with respect to TMS. $^{31}P\{$selective $^1H\}$ NMR spectra were recorded on Bruker AC200 (^{31}P: 81.02 MHz) and AM500 (^{31}P: 202.46 MHz) spectrometers and referenced externally to 85% H_3PO_4. $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AF300 (^{13}C: 75.47 MHz) and AM500 (^{13}C: 125.76 MHz) spectrometers and referenced internally to the carbon resonance of the solvent relative to TMS. Variable-temperature ^1H NMR experiments were conducted using a AM500 spectrometer equipped with a Bruker B-VT 1000 temperature control module with a copper−constantan thermocouple. Proton T_1 studies were performed using the standard inversion recovery 180°−τ−90° pulse sequence method.[34] Temperature calibration was accomplished by following the Van Geet methanol calibration method.[35] Deuterated trifluoromethanesulfonic acid (DOTf) was prepared by reacting equimolar quantities of trifluoromethanesulfonic anhydride and D_2O which was deoxygenated by three freeze−pump−thaw cycles and stored under Ar. ^1H NMR chemical shift differences between the H_2 and HD resonances ($\Delta\delta = \delta_{H_2} - \delta_{HD}$) were determined using 180°−τ−90° pulse sequences with delays designed to separately nullify the H_2 and HD resonances in the deuterated sample. $OsH(Cl)(PPh_3)_3(CO)$,[36] $RuH(Cl)(PPh_3)_3(CO)$,[36] $[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (**1a**),[13] $[Os(H_2)(PPh_3)_2(bpy)(CO)](OSO_2CF_3)_2$ (**2a**),[13] and $[H(Et_2O)_x](BAr'_4)$[37] were prepared by published procedures.

$[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (1a). Additional data are as follows. ^1H NMR (CD_2Cl_2): δ 8.62 (1 H, d, J_{HH} = 5.3 Hz), 7.54 (1 H, d, J_{HH} = 5.3 Hz) *6,6′*-bipyridyl, 8.13 (2 H, d, J_{HH} = 8.1 Hz) *3,3′*-bipyridyl, 7.79 (1 H, t, J_{HH} = 7.9 Hz), 7.72 (1 H, t, J_{HH} = 7.9 Hz) *4,4′*-bipyridyl, 7.05 (1 H, t, J_{HH} = 6.5 Hz), 6.38 (1 H, t, J_{HH} = 6.5 Hz) *5,5′*-bipyridyl, 7.33−7.23 (m, 30 H, $P(C_6H_5)_3$), −12.19 (t, 1 H, J_{HP} = 18.4 Hz, Os*H*, T_1 min = 500 ms (247 K, 500 MHz)). $^{31}P\{$selective $^1H\}$ NMR (CD_2Cl_2): δ 18.76 (d, J_{PH} = 17 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 186.56 (t, J_{CP} = 10.8 Hz, *C*O), 155.6, 154.9 (*2,2′*-bipyridyl), 155.2, 153.7 (*6,6′*-bipyridyl), 138.1, 137.3 (*4,4′*-bipyridyl), 127.6, 127.2 (*5,5′*-bipyridyl), 124.2, 123.8 (*3,3′*-bipyridyl), 133.4 (t, J_{CP} = 5.4 Hz, *o*-C_6H_5), 131.2 (t, J_{CP} = 25.4 Hz, *ipso*-C_6H_5), 130.7 (s, *p*-C_6H_5), 128.9 (t, J_{CP} = 4.5 Hz, *m*-C_6H_5). Anal. Calcd for $C_{48}H_{39}N_2F_3O_4P_2SOs$: C, 54.96; H, 3.75; N, 2.67. Found: C, 54.52; H, 3.80; N, 2.66. IR (Nujol): ν(OsH) = 2081 cm^{-1}, ν(CO) = 1923 cm^{-1} (s).

$OsH(Cl)(PMePh_2)_3(CO)$. This was prepared using conditions similar to those reported for $OsH(Cl)(PPh_3)_3(CO)$ with the substitution of $PMePh_2$ for PPh_3. ^1H NMR (C_6D_6): δ 7.82−6.63 (m, 30 H, $PCH_3(C_6H_5)_2$), 2.30 (s, 6 H, $PCH_3(C_6H_5)_2$), 1.90 (s, 3 H, $PCH_3(C_6H_5)_2$), −6.45 (dt, 1 H, $J_{HP_{trans}}$ = 85.3 Hz, $J_{HP_{cis}}$ = 22.2 Hz, Os*H*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −20.1 (t, J_{PP} = 13 Hz), −23.3 (d, J_{PP} = 13 Hz).

$[OsH(PMePh_2)_2(bpy)(CO)](OSO_2CF_3)$ (1b). This was prepared under conditions similar to those for **1a** using $OsH(Cl)(PMePh_2)_3(CO)$.

(31) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824−1826.
(32) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471−1478.
(33) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271−1285.
(34) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126−4133.
(35) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679−680.
(36) Ahmad, N.; Levinson, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45−64.
(37) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11* 3920−3922.

^{1}H NMR (CD_2Cl_2): δ 8.61−6.92 (m, 28 H, bipyridyl and $PCH_3(C_6H_5)_2$), 1.75 (t, 6 H, J_{HP} = 3.2 Hz, $PCH_3(C_6H_5)_2$), −12.22 (t, 1 H, J_{HP} = 17.6 Hz, Os*H*). ^{31}P {selective ^{1}H} NMR (CD_2Cl_2): δ 0.08 (d, J_{PH} = 14 Hz).

[OsH(PPh$_3$)$_2$(phen)(CO)](OSO$_2$CF$_3$) (1c). This was prepared under conditions similar to those for **1a** substituting phenanthroline for bipyridine. ^{1}H NMR (CD_2Cl_2): δ 9.02 (1 H, d, J_{HH} = 4.9 Hz), 7.95 (1 H, d, J_{HH} = 5.2 Hz) *2,9*-phenanthroline, 8.28 (1 H, d, J_{HH} = 8.1 Hz), 8.21(1 H, d, J_{HH} = 8.1 Hz) *4,7*-phenanthroline, 7.91 (2 H, s) *5,6*-phenanthroline, 6.84 (1 H, d, J_{HH} = 5.3 Hz), 6.83 (1 H, d, J_{HH} = 5.3 Hz) *3,8*-phenanthroline, 7.29−7.10 (m, 30 H, $P(C_6H_5)_3$), −11.98 (t, 1 H, J_{HP} = 18.1 Hz, Os*H*). ^{31}P{selective ^{1}H} NMR (CD_2Cl_2): δ 19.25 (d, J_{PH} = 17 Hz). IR (Nujol): ν(OsH) = 2063 cm^{-1}, ν(CO) = 1929 cm^{-1} (s).

[RuH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (3). This was prepared under conditions similar to those for **1a** using RuH(Cl)(PPh$_3$)$_3$(CO). ^{1}H NMR (CD_2Cl_2): δ 8.64 (1 H, d, J_{HH} = 4.8 Hz), 7.59 (1 H, d, J_{HH} = 5.0 Hz) *6,6′*-bipyridyl, 8.05 (1 H, d, J_{HH} = 9.1 Hz), 8.03 (1 H, d, J_{HH} = 9.7 Hz) *3,3′*-bipyridyl, 7.81 (1 H, t, J_{HH} = 7.7 Hz), 7.69 (1 H, t, J_{HH} = 7.7 Hz) *4,4′*-bipyridyl, 7.15 (1 H, t, J_{HH} = 6.2 Hz), 6.44 (1 H, t, J_{HH} = 6.4 Hz) *5,5′*-bipyridyl, 7.35−7.25 (m, 30 H, $P(C_6H_5)_3$), −11.31 (t, 1 H, J_{HP} = 19.6 Hz, Ru*H*, T_1 min = 193 ms (205 K, 200 MHz), T_1 min = 475 ms (252 K, 500 MHz)). ^{31}P{selective ^{1}H} NMR (CD_2Cl_2): δ 46.5 (d, J_{PH} = 18 Hz, T_1 min = 616 ms (202 K, 202 MHz)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 204.9 (t, J_{CP} = 14.9 Hz, *C*O), 155.0, 153.7 (*6,6′*-bipyridyl), 154.3, 153.9 (*2,2′*-bipyridyl), 138.1, 137.9 (*4,4′*-bipyridyl), 126.8, 126.6 (*5,5′*-bipyridyl), 123.5, 123.4 (*3,3′*-bipyridyl), 133.4 (t, J_{CP} = 5.7 Hz, *o*-C_6H_5), 131.7 (t, J_{CP} = 22.1 Hz, *ipso*-C_6H_5), 130.6 (s, *p*-C_6H_5), 128.9 (t, J_{CP} = 4.4 Hz, *m*-C_6H_5). Anal. Calcd for $C_{48}H_{39}N_2F_3O_4P_2SRu\cdot CH_2Cl_2$: C, 56.33; H, 3.96; N, 2.68. Found: C, 56.64; H, 3.93; N, 2.75.

[Os(H$_2$)(PMePh$_2$)$_2$(bpy)(CO)](OSO$_2$CF$_3$)$_2$ (2b). This was prepared using conditions similar to those reported for **2a** and **2a**-d_1. ^{1}H NMR (CD_2Cl_2): δ 8.46−7.03 (m, 28 H, bipyridyl and $PCH_3(C_6H_5)_2$), 1.81 (t, 6 H, J_{HP} = 3.8 Hz, $PCH_3(C_6H_5)_2$), −6.23 (s, 2 H, Os(H_2), $\Delta\nu_{1/2}$ = 41 Hz, T_1 min = 16.5 ms (260 K, 500MHz)). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −6.02 (s, $\Delta\nu_{1/2}$ = 8.4 Hz). For **2b**-d_1: J_{HD} = 25.5 Hz, $\Delta\delta$ = +20 ppb.

[Os(H$_2$)(PPh$_3$)$_2$(phen)(CO)](OSO$_2$CF$_3$)$_2$ (2c). This was prepared using conditions similar to those reported for **2a** and **2a**-d_1. ^{1}H NMR (CD_2Cl_2): δ 8.58 (d, 1 H, J_{HH} = 8.2 Hz), 8.49 (d, 1 H, J_{HH} = 8.2 Hz), 8.44 (d, 1 H, J_{HH} = 4.7 Hz), 8.28 (d, 1 H, J_{HH} = 4.8 Hz), 8.09 (m, 2 H), 7.37 (dd, 2H, J_{HH} = 5.4 Hz, J_{HH} = 5.5 Hz), 7.45 (t, 6 H, J_{HH} = 7.5 Hz, *p*-$P(C_6H_5)_3$), 7.26 (t, 12 H, J_{HH} = 7.3 Hz, *o*-$P(C_6H_5)_3$), 6.94 (dt, 12 H, J_{HH} = 6.0 Hz J_{HH} = 6.1 Hz, *m*-$P(C_6H_5)_3$), −5.63 (s, 2 H, Os(H_2), $\Delta\nu_{1/2}$ = 39 Hz, T_1 min = 6.3 ms (200 K, 200MHz)). ^{31}P{selective ^{1}H} NMR (CD_2Cl_2): δ 8.60 (s, $\Delta\nu_{1/2}$ = 7.0 Hz). For **2c**-d_1: J_{HD} = 25.5 Hz, $\Delta\delta$ < +20 ppb.

[Ru(H$_2$)(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$)$_2$ (4). This was prepared using conditions similar to those reported for **2a** and **2a**-d_1 with the added precautions that the sample was kept at 195 K until inserted into the precooled NMR probe and spectra were recorded at temperatures less than 273 K. ^{1}H NMR (CD_2Cl_2, 253 K): δ 8.02−7.01 (m, 8 H, bipyridyl), 7.50 (t, 6 H, J_{HH} = 7.4 Hz, *p*-$P(C_6H_5)_3$), 7.33 (t, 12 H, J_{HH} = 7.7 Hz, *o*-$P(C_6H_5)_3$), 7.08 (dt, 12 H, J_{HH} = 6.5 Hz, J_{HH} = 6.7 Hz, *m*-$P(C_6H_5)_3$), −6.70 (s, 2 H, Ru(H_2), $\Delta\nu_{1/2}$ = 110 Hz, T_1 min = 3.9 ms (240 K, 200 MHz)). ^{31}P{selective ^{1}H} NMR (CD_2Cl_2, 253 K): δ 32.81 (s, $\Delta\nu_{1/2}$ = 12.6 Hz). For **4**-d_1: J_{HD} = 31.0 Hz, $\Delta\delta$ < +20 ppb.

Basicity Measurements of [OsH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (1a) and [RuH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (3). The individual basicity studies were performed by adding either **1a** (20−22 mg, 0.019−0.021 mmol) or **3** (20−22 mg, 0.021−0.023 mmol) to an NMR tube equipped with a J. Young Teflon valve. CD_2Cl_2 (0.5 mL) was vacuum-transferred to the tube, and the solids were dissolved. Incremental amounts of HOTf (4−12 μL) or $[H(Et_2O)]BF_4$ (8−33 μL) were added via a gastight microsyringe under a flow of Ar, and the tube was sealed. The basicity study with $[H(Et_2O)_x]BAr'_4$ (Ar′ = 3,5-$(CF_3)_2C_6H_3$) (174 mg) and **1a** (21 mg, 0.020 mmol) was performed by adding both solids to a sealable NMR tube and vacuum-transferring CD_2Cl_2 (0.5 mL) to the solids. The tube was evacuated and flame-sealed.

Table 5. Protonation Comparison of $[OsH(PPh_3)_2(bpy)(CO)]^+$ (**1a**) and $[RuH(PPh_3)_2(bpy)(CO)]^+$ (**3**) with Triflic Acid[a]

no. of equiv of HOTf	% **1a**	% **2a**	% **3**	% **4**
1	100	0	100	0
2	58	42	79	21
3	16	84	40	60
4	0	100	0	100

[a] Samples were prepared and maintained at temperatures of 195−265 K, and relative concentrations were determined by integration of the resonances in the ^{31}P{selective ^{1}H} NMR spectra recorded at 222 K.

The comparative basicity study was carried out by adding **1a** (30 mg, 0.029 mmol) and **3** (28 mg, 0.029 mmol) to an NMR tube equipped with a J. Young Teflon valve. CD_2Cl_2 (0.5 mL) was vacuum-transferred to the solids and dissolved. Incremental amounts of HOTf (5−20 μL) were added via a gastight microsyringe under a flow of Ar, and the tube was sealed. The concentrations were obtained from integration of the ^{31}P{selective ^{1}H} NMR spectra. Due to decomposition at room temperature, the basicity measurements involving **3** were performed at 222 K (Table 5).

[RuCl(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$). [RuH(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) (**3**) (8 mg, 0.01 mmol) and *N*-chlorosuccinimide (2 mg, 0.02 mmol) were added to a sealable NMR tube. CD_2Cl_2 (0.5 mL) was vacuum-transferred to the solids. Diethyl ether (2 mL) was added to the solution via syringe under a flow of Ar. The resulting precipitate was washed with diethyl ether (2 × 2 mL) and the excess solvent removed with a pipet. The solids were dried in vacuo overnight. CD_2Cl_2 (0.5 mL) was added via vacuum transfer, and the tube was flame-sealed. ^{1}H NMR (CD_2Cl_2): δ 8.47−6.43 (bipyridyl and $P(C_6H_5)_3$). ^{31}P{selective ^{1}H} NMR (CD_2Cl_2): δ 27.38 (s).

[OsCl(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$). This was prepared as above using $[OsH(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (**1a**). ^{1}H NMR (CD_2Cl_2): δ 8.40 (1 H, d, J_{HH} = 8.0 Hz), 8.25 (1 H, d, J_{HH} = 8.0 Hz) *3,3′*-bipyridyl, 8.32 (1 H, d, J_{HH} = 5.2 Hz), 7.62 (1 H, d, J_{HH} = 5.7 Hz) *6,6′*-bipyridyl, 7.96 (1 H, t, J_{HH} = 7.5 Hz), 7.65 (1 H, t, J_{HH} = 7.7 Hz) *4,4′*-bipyridyl, 6.97 (1 H, t, J_{HH} = 6.3 Hz), 6.48 (1 H, t, J_{HH} = 6.5 Hz) *5,5′*-bipyridyl, 7.35−7.23 (m, 30 H, $P(C_6H_5)_3$). ^{31}P{selective ^{1}H} NMR (CD_2Cl_2): δ −0.33 (s).

[OsBr(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$). This was prepared as above using *N*-bromosuccinimide. ^{1}H NMR (CD_2Cl_2): δ 8.50 (1 H, d, J_{HH} = 8.0 Hz), 8.34 (1 H, d, J_{HH} = 7.9 Hz) *3,3′*-bipyridyl, 8.42 (1 H, d, J_{HH} = 5.1 Hz), 7.65 (1 H, d, J_{HH} = 6.6 Hz) *6,6′*-bipyridyl, 7.96 (1 H, t, J_{HH} = 7.6 Hz), 7.66 (1 H, t, J_{HH} = 8.0 Hz) *4,4′*-bipyridyl, 6.89 (1 H, t, J_{HH} = 6.4 Hz), 6.46 (1 H, t, J_{HH} = 6.4 Hz) *5,5′*-bipyridyl, 7.34−7.21 (m, 30 H, $P(C_6H_5)_3$). ^{31}P{selective ^{1}H} NMR (CD_2Cl_2): δ −1.97 (s).

Reaction of [RuCl(PPh$_3$)$_2$(bpy)(CO)](OSO$_2$CF$_3$) with AgOSO$_2$CF$_3$ and H$_2$. $[RuCl(PPh_3)_2(bpy)(CO)](OSO_2CF_3)$ (8 mg, 0.01 mmol) and silver triflate (2 mg, 1 mmol) were added to an NMR tube equipped with a J. Young Teflon valve. The NMR tube was evacuated, CD_3NO_2 (0.5 mL) was vacuum-transferred to the sample, and H_2 (800 Torr) was added. ^{1}H NMR (CD_3NO_2): δ 8.74−7.09 (bipyridyl and $P(C_6H_5)_3$). ^{31}P{selective ^{1}H} NMR (CD_3NO_2): δ 15.7 (s).

Acknowledgment. This research was supported by the National Science Foundation.

IC970975T