

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

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Received November 3, 1995[⊗]

The dicationic Os(II) complex $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})(\text{H}_2)]^{2+}$ has been prepared as the triflate salt. The presence of a bound dihydrogen ligand is indicated by a short T_1 minimum value consistent with an H–H distance of 1.05 Å. In the partially deuterated derivative $J_{\text{HD}} = 25.5$ Hz was observed. By comparison to other structurally characterized complexes, the observed H–D coupling is most consistent with a H–H distance greater than 1 Å, which requires that the bound H_2 ligand be in the slow rotation regime. The dicationic complex is a strong acid, 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 at room temperature. A related dicationic Os(II) complex, $[\text{Os}(\text{bpy})_2(\text{CO})(\text{H}_2)]^{2+}$, has also been prepared. A short T_1 minimum value and a J_{HD} value of 29.0 Hz in the partially deuterated derivative is most consistent with a H–H distance of 0.99 Å. The bound H_2 ligand of this complex is significantly less activated toward heterolytic cleavage and is stable in solution for less than a day at room temperature.

Since the initial discovery by Kubas and co-workers of transition metal dihydrogen complexes,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 The plethora of monocationic complexes suggests that positive charge confers additional stability to the H_2 complexes. In contrast, well-characterized dications are limited to the series of osmium complexes such as $[\text{Os}(\text{NH}_3)_5(\text{H}_2)]^{2+}$ and $[\text{Os}(\text{en})_2(\text{L})(\text{H}_2)]^{2+}$ which have been reported by Taube and co-workers.^{3,4} The preparation of rhenium cationic analogs, $[\text{Re}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)]^+$, for comparison to the neutral tungsten complexes $\text{W}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2)$ by Kubas, has recently been reported.⁵ A rigorous assessment of the effect of charge on the binding of H_2 would require the preparation of complexes of the form $[\text{Os}(\text{L})_5(\text{H}_2)]^{2+}$ with ligands L comparable to those employed in the rhenium and tungsten complexes.

A search for relevant chemistry led us to the 1987 report by Sullivan, Lumpkin, and Meyer (SLM)⁶ on the protonation of $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ (bpy = 2,2'-bipyridyl). The product was characterized as the dihydride dication $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})(\text{H}_2)]^{2+}$. We now present the results of further investigations (T_1 measurements and H–D coupling) on this dication and a related complex $[\text{Os}(\text{bpy})_2(\text{CO})(\text{H}_2)]^{2+}$, which lead us to propose that they be formulated as dihydrogen complexes. During the course of these studies, Caulton, Tilset, and co-workers reported the preparation of the related dicationic complex $[\text{Os}(\text{PR}_3)_2(\text{NCCH}_3)_3(\text{H}_2)]^{2+}$ by an elegant oxidative method.⁷

Experimental Section

General Procedures. Manipulations involving the protonation of the monocation hydrides were performed under argon using standard vacuum line, Schlenk, or syringe techniques. Argon was deoxygenated and dried by passage through Schweitzerhall Inc. R3-11 CuO catalyst followed by Mallinckrodt Aquasorb containing P_2O_5 . CD_2Cl_2 and CD_3NO_2 were purchased from Cambridge Isotope Laboratories and were degassed and stored over CaH_2 . OsO_4 was acquired from Stevens Metallurgical Inc. Deuterated trifluoromethanesulfonic acid (DOTf) was prepared by reacting equimolar quantities of trifluoromethanesulfonic anhydride and D_2O which was then deoxygenated by three freeze–pump–thaw cycles and stored under Ar. All other solvents and reagents were used without further purification, except for CH_2Cl_2 which was vacuum distilled from CaH_2 .

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.

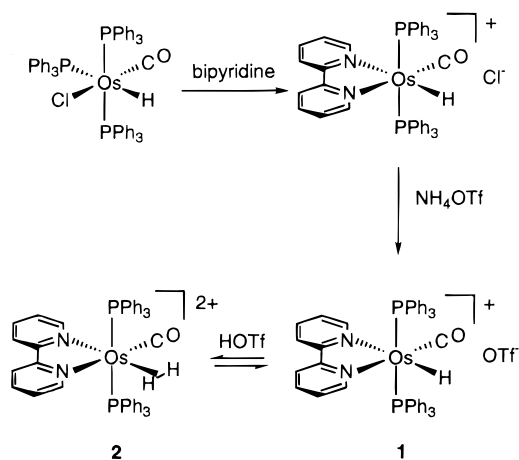
^1H NMR spectra were recorded on Bruker AC200, AF300, and WM500 spectrometers and referenced internally to the residual proton resonance of the deuterated solvent. ^{31}P $\{^1\text{H}\}$ selective NMR spectra were recorded on Bruker AC200 and WM500 spectrometers operating at frequencies of 81.02 and 202.46 MHz, respectively, with the aromatic protons selectively decoupled and referenced externally to 85% H_3PO_4 . ^1H $\{^{31}\text{P}\}$ NMR spectra were recorded on a Bruker WM500 spectrometer using a broad-band decoupling procedure to decouple the ^{31}P nuclei. Variable temperature ^1H NMR experiments were conducted using a WM500 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 $180^\circ\text{--}\tau\text{--}90^\circ$ pulse sequence method.⁸ Temperature calibration was accomplished following the Van Geet methanol calibration method.⁹ $(\text{NH}_4)_2\text{OsCl}_6$ ¹⁰ and $\text{Os}(\text{bpy})_2\text{Cl}_2$ ¹¹ were prepared following published procedures. $\text{Os}(\text{PPh}_3)_3(\text{CO})\text{HCl}$ ¹² was prepared according to published procedures with the substitution of $(\text{NH}_4)_2\text{OsCl}_6$ for Na_2OsCl_6 . $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}](\text{OTf})^6$ (**1**) (OTf = trifluoromethanesulfonate) and

[⊗] Abstract published in *Advance ACS Abstracts*, July 1, 1996.

- (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) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120–128. (b) Morris, R. H.; Jessop, P. G. *Coord. Chem. Rev.* **1992**, *121*, 155–289. (c) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913–926. (d) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95–101.
- (3) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261–2263.
- (4) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946–8947.
- (5) Heinekey, D. M.; Schomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515–4516.
- (6) Sullivan, B. P.; Lumpkin, R. S.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1247–1252.
- (7) Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473–9480.

- (8) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133.
- (9) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679–680.
- (10) Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* **1957**, *5*, 206–207.
- (11) Kober, E. M.; Caspar, J. V.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4587–4598.
- (12) Ahmad, N.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc.* **1972**, 843–847.

Scheme 1



$[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{OTf})^{13}$ were prepared using NH_4OTf to precipitate the salt instead of NH_4PF_6 . $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}](\text{OTf})^{13}$ (**3**) was prepared following published procedures using $[\text{Os}(\text{bpy})_2(\text{CO})\text{Cl}](\text{OTf})$ as the precursor.

[Os(bpy)(PPh₃)₂(CO)(H₂)](OSO₂CF₃)₂ (2**).** In a typical protonation reaction, CD_2Cl_2 (0.5 mL) was vacuum transferred to a NMR tube that had been charged with **1** (20 mg, 0.02 mmol). Trifluoromethanesulfonic acid (HOTf) (10 μL , 0.1 mmol) was added to the solution via syringe under Ar. The sample was degassed (freeze-pump-thaw, 3 cycles) and sealed under vacuum. ^1H NMR (CD_2Cl_2): δ 13.28 (s, HOTf), 8.13–6.96 (8 H, bipyridyl), 7.51–7.14 (30 H, PPh₃), –5.78 (s, 2 H, OsH₂, $T_1(\text{min}) = 15$ ms (260 K, 500 MHz)). $^{31}\text{P}\{^1\text{H}\}$ selective NMR (CD_2Cl_2): δ 8.54 (s).

[Os(bpy)(PPh₃)₂(CO)(HD)](OSO₂CF₃)₂ (2-d₁**).** Prepared as above for **2** using deuterated trifluoromethanesulfonic acid (DOTf). ^1H NMR (CD_2Cl_2): δ 11.60 (s, HOTf), 8.08–6.96 (8 H, bipyridyl), 7.72–7.10 (30 H, PPh₃), –6.00 (t, OsHD, $J_{\text{HD}} = 25.5$ Hz). $^{31}\text{P}\{^1\text{H}\}$ selective NMR (CD_2Cl_2): δ 7.92 (s).

[Os(bpy)₂(CO)(H₂)](OSO₂CF₃)₂ (4**).** In a typical protonation reaction, **3** (10 mg, 0.01 mmol) was added to a NMR tube and CD_3NO_2 or CD_2Cl_2 (0.5 mL) was vacuum transferred to the solid. HOTf (5–10 μL) was added via syringe under Ar. The sample was degassed (freeze-pump-thaw, 3 cycles) and sealed under vacuum. ^1H NMR (CD_3NO_2): δ 12.40 (s, HOTf), 9.61–7.53 (16 H, bipyridyl), –4.23 (s, 2 H, OsH₂, $T_1(\text{min}) = 12$ ms (230 K, 500 MHz)).

[Os(bpy)₂(CO)(HD)](OSO₂CF₃)₂ (4-d₁**).** Prepared as above for **4** using CD_3NO_2 as the solvent and deuterating with DOTf. ^1H NMR (CD_3NO_2): δ 13.03 (s, HOTf), 9.62–7.51 (16 H, bipyridyl), –4.23 (t, OsHD, $J_{\text{HD}} = 29.0$ Hz).

Results

Our studies began with the synthesis of $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ (**1**) as the triflate salt by the procedure outlined in Scheme 1. SLM reported UV–visible and NMR data consistent with the structural assignment of **1**.⁶ Our NMR and IR spectra for **1** are in agreement with those previously reported.^{6,13}

It was reported by SLM that protonation of **1** (PF_6 salt) with triflic acid in CH_2Cl_2 affords an insoluble oil with no gas evolution. A homogeneous system was achieved using $\text{CF}_3\text{COOH}/\text{CF}_3\text{SO}_3\text{H}$ mixtures as solvent. In this solvent system, ^1H NMR spectra were obtained which exhibit a broad resonance at –6.4 ppm. We find that the protonation can be conveniently carried out using the triflate salt of **1** and triflic acid in nitromethane or in methylene chloride. The dicationic complex **2** is soluble in these solvents and thermally robust, showing no sign of loss of H₂ or any other decomposition reaction over several months in methylene chloride at room temperature. When the protonation of **1** was attempted using protonated

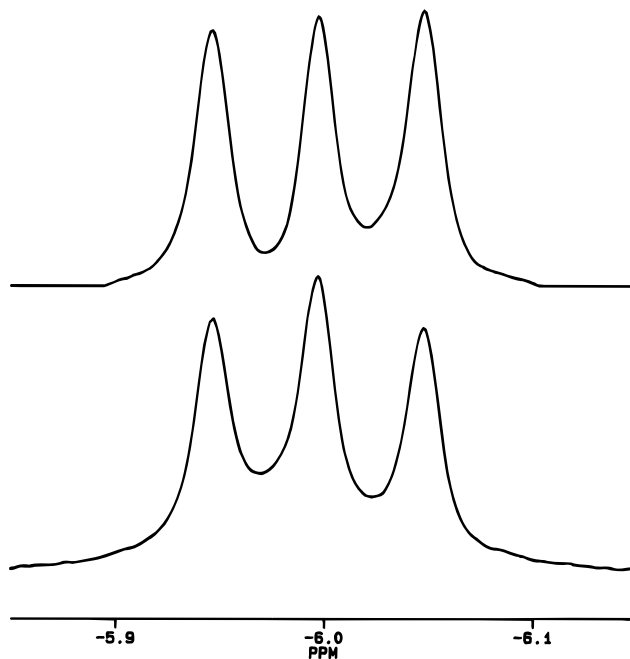


Figure 1. ^1H NMR (hydride region) of **2-d₁** at 298 K (CD_2Cl_2 , 500 MHz). The lower trace is the normal spectrum showing the increased intensity of the center resonance due to a minor amount of **2**. The upper trace is the inverted spectrum of **2-d₁** using a $180^\circ\text{-}\tau\text{-}90^\circ$ pulse sequence with $\tau = 21$ ms. Under these conditions, the signal due to **2** is nulled.

ethers, **2** was not observed. The presence of bases such as diethyl ether or water will regenerate **1** immediately without any loss to decomposition.

In the ^1H NMR spectrum of **2** recorded in CD_2Cl_2 , the hydride resonance at –5.8 ppm is fairly broad ($\Delta\nu_{1/2} = 100$ Hz). The ^{31}P NMR spectrum of **2** with the aromatic protons selectively decoupled exhibits a single resonance at +8.5 ppm ($\Delta\nu_{1/2} = 6.5$ Hz), consistent with a structure containing equivalent phosphines as postulated by SLM, and shows no evidence of H–P coupling. An investigation of the T_1 of the hydride resonance as a function of temperature shows that at 500 MHz a clear minimum value of 15 ms is reached at 260 K.

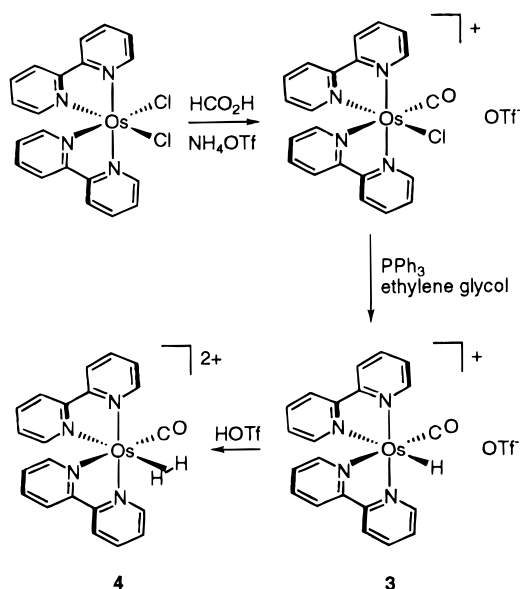
A sample of **2-d₁** was prepared by addition of deuterated triflic acid to a solution of **1** in CD_2Cl_2 . The hydride region of the ^1H NMR spectrum of **2-d₁** exhibits a sharp “triplet” resonance, as opposed to the broad singlet in **2**. The intensity ratio of the three resonances is *ca.* 1:1.2:1, with a separation of 25.5 Hz (see Figure 1). This intensity ratio is puzzling since coupling to two equivalent ^{31}P nuclei would give a 1:2:1 triplet, whereas coupling to a single deuterium would give three lines with the intensity ratio 1:1:1. The $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **2-d₁** is identical to the spectrum recorded without phosphorus decoupling, an indication that the coupling is not due to the phosphines. This result implies that the additional intensity in the central resonance of **2-d₁** is due to some contamination by **2**, arising from incomplete deuteration of the triflic acid. To confirm this hypothesis, a ^1H NMR $180^\circ\text{-}\tau\text{-}90^\circ$ inversion recovery pulse sequence experiment was performed on a sample of **2-d₁** with a delay τ designed to null the signal from the minor amount of **2** present.^{14,15} A clean 1:1:1 triplet was obtained (Figure 1) indicating H–D coupling ($J_{\text{HD}} = 25.5$ Hz). Consistent with a single structure, we find that the ^1H NMR spectra

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

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

(13) Sullivan, B. P.; Caspar, J. V.; Johnson, S. R.; Meyer, T. J. *Organometallics* **1984**, *3*, 1241–1251.

Scheme 2



of **2** and **2-d₁** are essentially independent of temperature (including J_{HD} values) down to 165 K.¹⁶

The closely related species, $[\text{Os}(\text{bpy})_2(\text{CO})\text{H}]^+$ (**3**), was also prepared as the triflate salt following the procedure outlined in Scheme 2.¹³ The NMR spectrum of **3** is consistent with the structural assignment shown, as was determined by Meyer and co-workers.¹³ The hydride resonance in the ¹H NMR spectrum of **4** in nitromethane-*d*₃ is a broad singlet at -4.2 ppm. The aromatic region in the ¹H NMR spectra for **3** and **4** shows 16 proton resonances, indicating that the two bipyridyl ligands remain inequivalent, consistent with the structures shown in Scheme 2. A T_1 study of the hydride resonance as a function of temperature shows a minimum of 12 ms at 230 K at 500 MHz. The partially deuterated analog **4-d₁** was prepared and a sharp triplet in the hydride region appears with a J_{HD} value of 29.0 Hz. The intensity of the central resonance is slightly increased due to a small contamination of **4** resulting from the incomplete deuteration of the DOTf. The small isotope shift and the H-D coupling do not appear to be temperature dependent. Complex **4** is less thermally robust than **2**. We have found that **4** is stable in methylene chloride at room temperature as a dihydrogen species for less than a day before forming the metal triflate complex as noted by Meyer and co-workers.¹³ In contrast to the highly acidic nature of **2**, complex **4** is unaffected by the presence of diethyl ether.

Discussion

Complex **2** was structurally characterized by SLM as a dihydride of Os(IV). This assignment was based on limited spectroscopic data due to the poor solubility of **2** with PF₆ as a counterion. We have prepared the triflate salt of **2**, which is soluble in methylene chloride, allowing additional NMR data to be obtained.

The ³¹P NMR spectrum of **2** shows a single sharp resonance for the equivalent phosphines as expected for a *trans* structure. No coupling to the hydride ligands was observed. A lack of coupling between bound phosphines and adjacent hydrides is often indicative of the presence of a bound dihydrogen ligand.¹⁷ More definitive NMR evidence of a bound dihydrogen is the observation of H-D coupling in the partially deuterated analog

Table 1. Structural Data for Dihydrogen Complexes

| complex | H-H (Å) | J_{HD} (Hz) | ref |
|--------------------------------------------------------------------------------------|-------------------------------------------------------|----------------------|--------|
| Mo(H ₂)(CO)(dppe) ₂ | 0.88 (ss NMR) ^a 0.85 (n) ^{b,c} | 34 | 19, 20 |
| W(CO) ₃ (P ⁱ Pr ₃) ₂ (H ₂) | 0.89 (ss NMR) 0.82 (n) | 33.5 | 19, 14 |
| [FeH(H ₂)(dppe) ₂] ⁺ | 0.82 (n) | 32 | 21 |
| [IrH(H ₂)(PPh ₃) ₂ (bq)] ⁺ | 0.94 (ss NMR) | 29.5 | 19 |
| [RuCp(H ₂)(CO)(PCy ₃) ₃] ⁺ | 0.97 (ss NMR) | 28 | 19 |
| [RuCp(H ₂)(dmpe)] ⁺ | 1.02 (ss NMR) | 22 | 19 |
| [RuCp*(H ₂)(dppm)] ⁺ | 1.10 (n) ^c | 20.9 | 22 |
| Ir(H ₂)H(Cl) ₂ (P ⁱ Pr ₃) ₂ | 1.11 (n) | 12 | 23 |
| [Os(en) ₂ (H ₂)OAc] ⁺ | 1.34 (n) | 9.1 | 24 |
| Cr(H ₂)(CO) ₃ (P ⁱ Pr ₃) ₂ | 0.85 (ss NMR) | 35 | 25 |

^a ss NMR = solid state NMR. ^b n = neutron diffraction. ^c Distance corrected by the Maverick/Trueblood method.²⁶

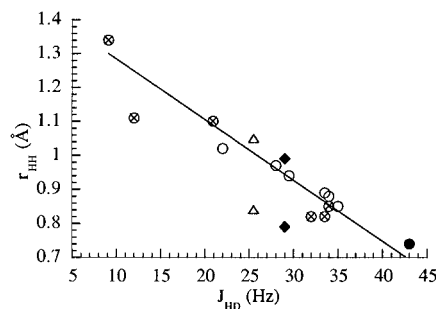


Figure 2. Plot of H-H bond length in angstroms versus J_{HD} in hertz. The symbols are as follows: (⊗) = neutron diffraction; (○) = solid state NMR; (●) = HD gas; (Δ) = from T_1 (min) of $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})(\text{H}_2)]^{2+}$, 0.84 Å (fast rotation), 1.05 Å (slow rotation); (◆) = from T_1 (min) of $[\text{Os}(\text{bpy})_2(\text{CO})(\text{H}_2)]^{2+}$, 0.79 Å (fast rotation), 0.99 Å (slow rotation).

2-d₁. The increased intensity of the center peak of the triplet is due to a small contamination of **2**, indicating that the isotope effect on the chemical shift of the proton in the dihydrogen ligand is very small and is consistent with the limited data in the literature. We find that this very 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 **2**. A rapid equilibrium between a dihydride and a dihydrogen structure would lead to temperature dependent isotope effects resulting from isotopic perturbation of equilibrium.¹⁶ The rapid relaxation shown by the hydride resonance of **2** from the T_1 study and the observed H-D coupling in the partially deuterated analog is most consistent with **2** being formulated as a dihydrogen complex.

The determination of the H-H distance in the bound dihydrogen ligand can be accomplished using solution state NMR relaxation data. Quantitative analysis by the method of Halpern and co-workers¹⁸ leads to two possible values for the H-H distance for **2**, depending upon the relative rate of H₂ ligand rotation, which are 0.84 Å (fast rotation) or 1.05 Å (slow rotation). A choice between these two rotation regimes for the determination of the H-H distance can be made based on other data as outlined below.

In reported dihydrogen complexes which have been structurally characterized by neutron diffraction or solid state NMR methods, an inverse correlation between J_{HD} and the H-H distance is observed. The available data are summarized in Table 1 and Figure 2, which show that a roughly linear relationship prevails. The line fit that is shown in Figure 2 was based on the solid state NMR and neutron diffraction data for the H-H distance and solution NMR data for the J_{HD} values

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

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

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

of the complexes shown in Table 1 with the exclusion of Ir-(H₂)H(Cl)₂(PⁱPr₃)₂ since there is some concern regarding structural differences in solution versus the solid state. On the basis of comparison to these data, the observed J_{HD} and T_1 minimum for **2** is most consistent with slow rotation of the H₂ ligand and a H–H distance of 1.05 Å. The alternative possibility of rapid rotation would require a H–H distance of 0.84 Å, which is inconsistent with the linear relationship depicted in Figure 2. Similar reasoning has been applied by Morris and co-workers²² to conclude that the H₂ ligand in [RuCp*(H₂)(dppm)]⁺ is in the slow rotation regime.

A relatively long H–H distance is also consistent with the tight binding of H₂ to the metal center observed in **2**. We find that no exchange of D₂ for H₂ occurs in complex **2** after several weeks of exposure to D₂ at room temperature in methylene chloride. This result is in contrast to the observations on the neutral tungsten complexes of Kubas²⁷ and the cationic rhenium analogs⁵ which undergo rapid D₂/H₂ exchange. The complexation of a dihydrogen ligand to a metal center is considered to result from the σ donation of the dihydrogen molecule to an empty metal orbital and π back-donation from filled metal d orbitals to the σ^* orbital of H₂. The right combination of both interactions will produce an elongated H–H bond that does not necessarily lead to oxidative addition. In these formally Os(II) d⁶ complexes, formation of the Os(IV) dihydride species is presumably disfavored by the 2+ charge on the metal center. The strong binding of the donor H₂ ligand with a dicationic Lewis acid metal center is consistent with the high acidity of **2**. Indirect evidence for the π back-donation interaction is provided by the relatively high barrier to H₂ rotation. Our data indicate that the rate of rotation of the H₂ ligand must be equal to or slower than the tumbling of the molecule in solution. The study of an osmium complex, [Os(H)₄(P-*p*-tolyl)₃]₃, by Halpern and co-workers determined the activation barrier of the tumbling of the molecule to be 2.53 kcal/mol at 277 K.¹⁸ Assuming that complex **2** has a similar barrier for tumbling in solution gives an approximation of the lower limit of the barrier to rotation of the dihydrogen ligand.

A related complex, [Os(bpy)₂(CO)(H₂)]²⁺ (**4**), was postulated by Meyer and co-workers¹³ as an intermediate in forming a

metal triflate species. The structure of **4** was considered to be either a seven coordinate Os(IV) dihydride or a six coordinate Os(II) dihydrogen species but the issue was not further investigated.

The ¹H NMR spectrum of the partially deuterated **4-d**₁ clearly shows a sharp triplet in the hydride region indicating a bound dihydrogen ligand with a J_{HD} value of 29.0 Hz. The isotope shift and the H–D coupling appear to be independent of temperature as was observed for **2**, suggesting only one structure for **4**. The H–D coupling of **4-d**₁ and the rapid relaxation of the hydride resonance of **4** is most consistent structurally as a dihydrogen complex with a H–H distance of 0.99 Å.

Complex **2** is remarkably robust in methylene chloride at room temperature. This stability is surprising in light of Morris' ligand additivity study in which it was predicted that both complexes **2** and **4**, if formulated as dihydrogen complexes, would be unstable with respect to loss of dihydrogen at 25 °C.²⁸ This prediction was based on the generalization that if the $E_{1/2}$ value of the corresponding N₂ complex was >2.0 V, the H₂ complex would be unstable at room temperature. The $E_{1/2}$ value for **2**(N₂) is slightly larger than that for **4**(N₂) (2.6 and 2.4 V, respectively),²⁸ and given that **2** is significantly more acidic than **4**, it would be expected that **2**, on the basis of this information, would be less stable than **4**. However, we have found that **4** is stable in solution at room temperature for less than a day, while **2** is stable in solution at room temperature for over 6 months.

Although ligand exchange is slow, complex **2** is a strong acid, as demonstrated by its immediate deprotonation by a variety of bases, including diethyl ether. Thus **2** represents a novel combination of high reactivity toward heterolysis combined with very tight binding of H₂. In contrast to the properties of **2**, highly acidic dihydrogen complexes such as [RuCp*(CO)₂(H₂)]⁺ are very labile with respect to loss of H₂,¹⁵ and the dicationic H₂ complexes such as [Os(NH₃)₅(H₂)]²⁺ reported by Taube and co-workers,³ which bind H₂ tightly, are not acidic. A monocationic dihydrogen complex, [Os(H₂)(CO)(pyS)(PPh₃)₂]⁺ (pyS = 2-pyridinethiolate),²⁹ which is structurally similar to **2**, has been shown to be stable with respect to loss of H₂ but is significantly less acidic since the neutral precursor is protonated with HBF₄·Et₂O, and the cation does not react with diethyl ether.

Conclusion

Complex **2** is best formulated as a dihydrogen complex, not a dihydride as originally suggested by SLM. Dications of this type, that demonstrate the combination of high acidity and low H₂ lability, provide an excellent opportunity to study subtle changes in the bonding interaction of a dihydrogen ligand with the metal center. We are continuing to investigate these interactions with related complexes.

Acknowledgment. This research was supported by the Department of Energy, Office of Basic Energy Science.

IC951427N

- (19) Zilm, K. W.; Millar, J. M. *Adv. Magn. Opt. Reson.* **1990**, *15*, 163–200.
 (20) Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569–581.
 (21) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823–8827.
 (22) Klooster, W. T.; Koetzle, T. F.; Jia, G.; Fong, T. P.; Morris, R. H.; Albinati, A. *J. Am. Chem. Soc.* **1994**, *116*, 7677–7681.
 (23) 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.
 (24) Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352–4356.
 (25) Kubas, G. J.; Nelson, J. E.; Bryan, J. C.; Eckert, J.; Wisniewski, L.; Zilm, K. *Inorg. Chem.* **1994**, *33*, 2954–2960.
 (26) Eckert, J.; Albinati, A.; White, R. P.; Bianchini, C.; Peruzzini, M. *Inorg. Chem.* **1992**, *31*, 4241–4244.
 (27) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390–3404.

(28) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471–1478.

(29) Schalf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 3808–3809.