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Reactions of $(P^iPr_3)_2OsH_6$ Involving Addition of Protons and Removal of Electrons. Characterization of $(P^iPr_3)_2Os(NCMe)_xH_y^{z+}$ ($x = 0, 2, 3$; $y = 1, 2, 3, 4, 7$; $z = 1, 2$), Including Dicationic η^2-H_2 Complexes

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Abstract: The classical Os^{VI} hexahydride $(P^iPr_3)_2OsH_6$ (**1**) undergoes a chemically irreversible oxidation at a remarkably low oxidation potential $E_p = 0.77$ V vs Cp_2Fe/Cp_2Fe^+ (cyclic voltammetry, Au electrode, acetonitrile/0.1 M $Bu_4N^+PF_6^-$). Chemical oxidation with 1 equiv of acetylferrocenium tetrafluoroborate in dichloromethane generates $(P^iPr_3)_2OsH_3(H_2)_2^+$ (**4**) as a major product, presumably by proton transfer from the Brønsted acid $\mathbf{1}^{\bullet+}$ to **1**. Compound **4** is also available by treatment of **1** with HBF_4; **1** is regenerated by the addition of piperidine. In acetonitrile, **4** undergoes loss of H_2 to give $(P^iPr_3)_2Os(NCMe)_2H_3^+$ (**2**), believed to probably assume a classical trihydride structure. Further reaction with acetonitrile leads to $(P^iPr_3)_2Os(NCMe)_3H^+$ (**3**); quite remarkably, this reaction can be reversed when one acetonitrile ligand is displaced by H_2. The cationic hydrides **2** and **3** do not undergo proton transfer to amine bases; rather, both can be protonated by HBF_4 to give the dicationic complexes $(P^iPr_3)_2Os(NCMe)_2H_4^{2+}$ (**5**, with one or two η^2-H_2 ligands) and $(P^iPr_3)_2Os(NCMe)_3(H_2)^{2+}$ (**6**), respectively. These reactions are reversed when piperidine is added. The polyhydride complexes have been characterized by ^1H NMR spectroscopy by $T_{1\min}$ measurements and by measurements of J_{HD} values for partially deuterated samples. Thus, the H−H distance in **4** is estimated as 1.00 Å (0.79 Å, fast-spinning). For **2**, the $T_{1\min}$ and J_{HD} leaves it in the uncertain range between classical and nonclassical hydrides. Assuming a hydride/dihydrogen structure, a H−H distance of 1.40 Å (1.11 Å, fast-spinning) is calculated, indicating a dihydrogen ligand at or beyond the brink of cleavage. However, a trihydride classical structure is favored due to the relatively slow reaction of **2** with acetonitrile. The H−H distance in **5** is 1.09 Å (0.86 Å, fast-spinning) assuming a bis-(η^2-H_2) structure, or 0.97 Å (0.77 Å, fast-spinning) for a (η^2-H_2)$(H)_2$ structure. For **6**, the H−H distance is 1.09 Å (0.87 Å, fast-spinning).

Introduction

Reactions that involve the cleavage or formation of metal−hydrogen bonds are of crucial importance in catalytic and stoichiometric processes.[2] Knowledge of the thermodynamics and mechanisms of heterolytic (H^+ dissociation) and homolytic ($H^\bullet$ dissociation)[2a,b] M−H bond cleavage is therefore central to the understanding of organometallic reactions.

The oxidation of neutral 18-electron metal hydrides serves to activate the M−H bonds toward deprotonation[3,4] and, to a lesser extent, toward homolysis.[4] In acetonitrile solutions the homolytic activation amounts to ca. 30 kJ/mol, while the acidity enhancement is about 20−25 pK_a units, or around 150 kJ/mol, for a number of hydrides. Because of this great activation toward proton loss, reactions that involve proton transfer from metal hydride cation radicals $M{-}H^{\bullet+}$ are commonly observed.[3,5] Such a deprotonation (eq 1) formally represents a 2-electron reduction of the metal. This behavior has been noted for several monohydrides and also for some polyhydrides.

$$M{-}H \rightarrow M{-}H^{\bullet+} \rightarrow M^\bullet + H^+ \qquad (1)$$

Another reaction pathway is conceivable for complexes containing two or more hydride ligands, since such species may give a formal two-electron reduction by a coupling of two hydrides to generate a coordinated dihydrogen ligand. If the polyhydride is already in a high oxidation state prior to the oxidation, such a process is more likely to occur.[6] Dihydrogen complexes have been found to be as acidic or slightly more acidic (about 1 pK_a unit) than the isomeric dihydrides.[7] Therefore, a proton transfer from a polyhydride cation radical may occur by an intermediate formation of a transient dihy-

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[1] (a) University of Oslo. (b) Indiana University.

[2] (a) *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH Publishers: New York, 1991. (b) Bullock, R. M. *Comments Inorg. Chem.* **1991**, *12*, 1. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (d) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992.

[3] (a) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618. (b) Ryan, O. B.; Tilset, M.; Parker, V. D. *Organometallics* **1991**, *10*, 298. (c) Ryan, O. B.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 9554.

[4] (a) Tilset, M. *J. Am. Chem. Soc.* **1992**, *114*, 2740. (b) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077.

[5] (a) Klingler, R. J.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 208. (b) Detty, M. R.; Jones, W. D. *J. Am. Chem. Soc.* **1987**, *109*, 5666. (c) Castello, M. T.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2563. (d) Chen, L.; Davis, J. A. *Inorg. Chim. Acta* **1990**, *175*, 41. (e) Westerberg, D. E.; Rhodes, L. F.; Edwin, J.; Geiger, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 1107. (f) Ryan, O. B.; Smith, K.-T.; Tilset, M. *J. Organomet. Chem.* **1991**, *421*, 315. (g) Smith, K.-T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681. (h) Zlota, A.; Tilset, M.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 3816. (i) Pedersen, A.; Tilset, M. *Organometallics* **1994**, *13*, 4887. (j) Smith; K.-T.; Tilset, M.; Kristjánsdóttir, S. S.; Norton, J. R. *Inorg. Chem.* Submitted for publication.

[6] For reviews of the chemistry of dihydrogen complexes see: (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (d) Kubas, G. *Acc. Chem. Res.* **1988**, *21*, 120. (e) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

drogen complex (eq 2).

$$L_nM(H)_2 \rightarrow L_nM(H)_2^{\bullet +} \rightarrow L_nM(H_2)^{\bullet +} \rightarrow L_nM(H)^{\bullet} + H^+ \quad (2)$$

Since the first discovery of complexes containing coordinated dihydrogen as a ligand,[8] several methods have been introduced that allow the distinction between classical (hydride) and nonclassical (dihydrogen) bonding of H_2 at the metal. Short spin–lattice relaxation time constants (T_1) for the hydride resonances in ^{1}H NMR spectroscopy are diagnostic for dihydrogen complexes. Another NMR-based method that supplements the T_1 method is the evaluation of $^1J_{HD}$ coupling constants for partially deuterated species.[6a,c,e,9]

It has been proposed that electrochemical methods may be useful for making a distinction between classical and nonclassical bonding in polyhydrides.[5c,10] On the basis of the oxidation-state formalism, the oxidation potentials should be considerably lower for nonclassical hydrides than for the isomeric classical hydrides. Results from oxidation potential measurements can however be ambiguous, especially if only one of the dihydride/dihydrogen complex isomers is available. An extra complication arises if the unfavored isomer is readily available as a low-lying thermally excited state. If the classical isomer is the favored one, the oxidation process can occur at the oxidation potential of the unfavored, but most readily oxidized, nonclassical isomer if the two interconvert rapidly on the measurement time scale, and erroneous conclusions can be drawn about H_2 bonding of the complex in its ground state. Accordingly, some complexes that were investigated by electrochemistry[10] were initially characterized as dihydrogen complexes, but have later been shown to be dihydrides.

Recently, we reported that electrochemical investigations of polyhydrides can lead to H_2 liberation which, if it occurs fast enough that the H_2 is released near the electrode surface, may give rise to adsorption of H_2 at Pt electrodes.[5h] Cyclic voltammograms for such polyhydrides can show waves due to adsorbed H_2 as well as curve-crossing phenomena typical of adsorption waves, and it is possible that such behavior may be diagnostic of oxidative generation of dihydrogen complexes.

We report here results of an investigation of the oxidation chemistry of $(P^iPr_3)_2OsH_6$ (**1**). This compound is believed to exist as a classical Os^{VI} hexahydride.[11] Due to the high formal oxidation state, **1** should be a prime candidate for oxidative induction of H–H coupling and/or proton transfer accompanied by a formal two-electron reduction of the Os center.

Results and Discussion

Electrochemical Oxidation of $(P^iPr_3)_2OsH_6$ (1) in Acetonitrile. Cyclic voltammetry measurements showed the oxida-

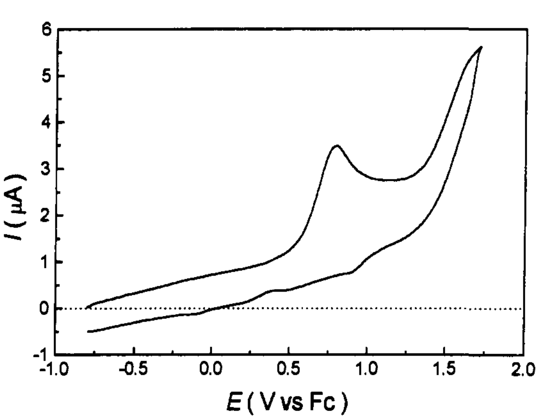

Figure 1. Cyclic voltammogram for the oxidation of **1** (1.0 mM) in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at a gold disk electrode (d = 0.6 mm) at a voltage sweep rate ν = 1.0 V/s at 20 °C.

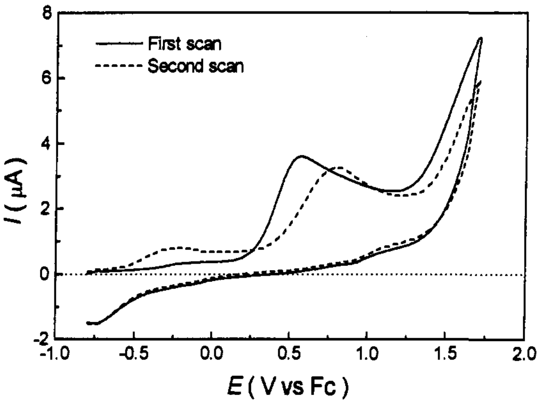

Figure 2. Cyclic voltammogram for the oxidation of **1** (1.0 mM) in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at a platinum disk electrode (d = 0.6 mm) at a voltage sweep rate ν = 1.0 V/s at 20 °C. A 15-s delay was imposed between the two scans.

tion peak potential for **1** to be 0.77 V vs the Cp_2Fe/Cp_2Fe^+ (Fc) couple in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at a gold disk electrode. Figure 1 shows the cyclic voltammogram for **1**. The signal is chemically irreversible at voltage sweep rates ν up to ca. 100 V/s, suggesting that $\mathbf{1}^{\bullet +}$ is rapidly consumed in a follow-up reaction. Higher sweep rates led to signal broadening that precluded the assessment of the degree of chemical reversibility. The oxidation wave is quite broad even at ν = 1.0 V/s, indicative of relatively slow heterogeneous charge transfer. It was furthermore established that reduction waves are absent for **1** down to −2.0 V vs Fc. Thus, the formally high-oxidation-state complex **1** is quite readily oxidized, but not reduced!

Repeated-scan cyclic voltammetry measurements performed at a platinum disk electrode, but not at gold, showed the appearance of a reduction wave at ca. −0.7 V and an oxidation wave at ca. −0.2 V during the second and subsequent scans. Cyclic voltammograms for two successive scans at Pt are shown in Figure 2. The voltammograms were recorded at a voltage sweep rate ν = 1.0 V/s, with a 15-s delay between the two scans. (This delay time is sufficient for essentially complete renewal of the diffusion layer of the electrode, resulting in identical voltammograms for the successive scans for uncomplicated electron-transfer processes.) When 3% H_2 in N_2 was purged through the solution for 3–4 min, the waves at −0.2 and −0.7 V gained intensity. A subsequent Ar purge restored the original voltammogram. This behavior is reminiscent of earlier observations for $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)H_3$.[5h] In that case, we attributed a similar peak to the oxidation of adsorbed H_2 at the Pt electrode. The effect of H_2 adsorption was less pronounced for **1** than for the Ru complex. A superposition of

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[7] (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (b) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (c) Bautista, M. T.; Capellani, E. P.; Drovin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. D. *J. Am. Chem. Soc.* **1991**, *113*, 4876. (d) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471.

[8] Kubas, G. J.; Ryan, R. R.; Vergamini, P. J.; Wasserman, H. *J. Am. Chem. Soc.* **1984**, *106*, 451.

[9] (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126. (b) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (c) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (d) Crabtree, R. H.; Habib, A. *Inorg. Chem.* **1986**, *25*, 3698.

[10] (a) Bianchini, C.; Laschi, F.; Peruzzini, M.; Ottaviani, F. M.; Vacca. A; Zanello, P. *Inorg. Chem.* **1990**, *29*, 3394. (b) Zanello, P. *Comments Inorg. Chem.* **1991**, *11*, 339.

[11] (a) Gusev, D. G.; Kuznetsov, V. F.; Eremenko, I. L.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 5831. (b) Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *29*, 2930.

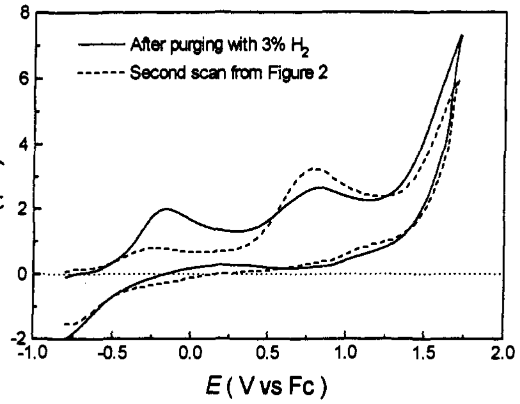

Figure 3. Cyclic voltammogram for **1** at the Pt electrode after purging the solution with 3% H_2 in N_2. Otherwise, the experimental conditions are as for Figure 2.

the cyclic voltammogram for **1** after purging with 3% H_2 and the second scan from Figure 2 is shown in Figure 3.

Coulometry Measurements of $(P^iPr_3)_2OsH_6$ (1) in Acetonitrile. Constant-current coulometry with in situ CV monitoring of the disappearance of the substrate by means of a separate 3-electrode assembly was used in order to establish the consumption of charge during the oxidation of **1**. For electrode reactions in which no new electroactive species are generated, the potential of our Pt gauze working electrode stays well below the CV peak potential for the electrode reaction for about 90–95% of the electrolysis time under the actual experimental conditions. The selectivity of the method should therefore be excellent. A multielectron oxidation (ca. 4–6 faraday/mol) was found. A constant-potential electrolysis at +0.8 V vs Fc led to the consumption of ca. 5 faraday/mol of charge at the Pt electrode before **1** was completely consumed, in agreement with the constant-current coulometry measurements. Only limited information regarding the primary electron-transfer processes is obtained from these experiments because the CV monitoring electrode showed that new electroactive species which were oxidized at the oxidation potential of **1** were generated during the electrolysis. Furthermore, the oxidation of chemisorbed H_2 at the Pt electrode also contributes to the overall current flow.

In order to avoid the complications arising from the oxidation of chemisorbed H_2, constant-potential coulometry experiments were performed at an Au gauze working electrode,[12] but otherwise under identical conditions. Now, four separate measurements reproducibly resulted in the consumption of 3.1 ± 0.1 faraday/mol of charge for the full consumption of **1**. During the constant-potential coulometry measurements at the Au electrode, the current flowing through the cell was essentially constant until almost 3 faraday/mol of charge had been consumed. After this, a constant current ca. 15% of the initial one continued to pass through the cell (Figure 4). (The background current for an acetonitrile/0.1 M $Bu_4N^+PF_6^-$ solution free of **1** was essentially zero under similar conditions.) Extrapolation of this segment back to $t = 0$ leads to a consumption of 2.6 faraday/mol of charge that is attributed to the oxidation of **1**. This result is only in reasonable agreement with that (2 faraday/mol) required for the oxidation of **1** to monocationic Os complexes and equimolar amounts of H^+. The source of the excess current has not been identified; it is possible that minor side products are able to catalyze solvent or electrolyte oxidation.[13]

A preparative electrolysis experiment was performed by passing a constant current through a solution of **1** in acetonitrile/0.05 M $Me_4N^+BF_4^-$ until 1 faraday/mol of charge had been consumed. After workup of the electrolysis mixture, the ^1H NMR spectrum of the dichloromethane-soluble part was recorded and showed the presence of **1**, $(P^iPr_3)_2Os(NCMe)_2H_3{}^+BF_4^-$ (**2**), and $(P^iPr_3)_2Os(NCMe)_3H^+BF_4^-$ (**3**) in a 37:53:10 ratio. It will later be demonstrated that **3** is formed by loss of H_2 from **2**. (Details of the spectroscopic data and identification of the products will be given later.) Partial instability of **1** to the workup procedure may attribute to the fact that the (**2**+**3**):**1** ratio is somewhat greater than 1 which is that anticipated if $\mathbf{1}^{\bullet+}$ undergoes proton transfer to **1** (vide infra).

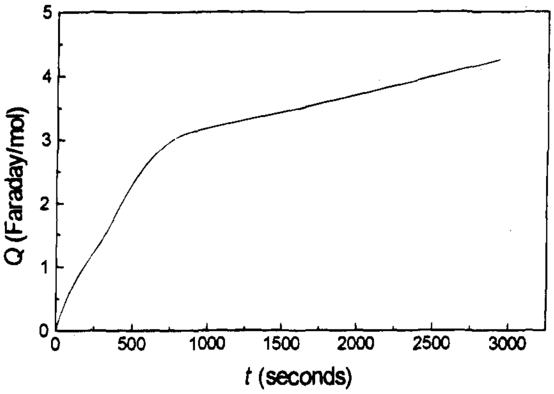

Figure 4. Charge passed (faraday/mol) vs time for a constant-potential electrolysis (E = +0.8 V vs Fc) of **1** in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ at a gold gauze electrode.

In summary, the electrochemical oxidation in acetonitrile was seen to be a multielectron process (4–6 faraday/mol by coulometry at the Pt electrode, ca. 3 faraday/mol at the Au electrode). A maximum of 4 faraday/mol would result from complete oxidation of three hydrides to H^+ and quantitative generation of **2**; oxidation of five hydrides to H^+ and generation of **3** requires 6 faraday/mol. These values are in reasonable agreement with the coulometry data for the oxidation of **1** at Pt. On the other hand, generation of equimolar amounts of **2**, H^+, and H_2 would require only 2 faraday/mol. The coulometry results suggest that the H_2 that is generated undergoes oxidation at the Pt electrode but not at Au. It is not known whether H_2 is oxidized as a consequence of stepwise liberation from the metal and adsorption at the Pt electrode, or if the Pt electrode actively assists in the liberation of H_2.

Chemical Oxidation of $(P^iPr_3)_2OsH_6$ (1) in Acetonitrile. In order to obtain more precise information regarding the consequences of the primary electron-transfer process, we focused on the use of a homogeneous oxidizing agent. The homogeneous oxidation of **1** was effected by the use of $AcFc^+BF_4^-$ (AcFc = acetylferrocene, $CpFe(\eta^5\text{-}C_5H_4COMe)$; E_{ox} = +0.25 V vs Fc) as the oxidizing agent. By ^1H NMR spectroscopy, it was established that 1 equiv of $AcFc^+BF_4^-$ in acetonitrile-d_3 led to complete consumption of **1**. Only one oxidation product was observed by ^1H NMR spectroscopy immediately after the oxidation, and this has been identified as $(P^iPr_3)_2Os(NCCD_3)_2H_3{}^+BF_4^-$. The synthesis and characterization of $(P^iPr_3)_2Os(NCMe)_2H_3{}^+BF_4$ (**2**) will be described later. Charge balance dictates that because this singly charged product was formed after the consumption of only 1 equiv of oxidant, all the hydride ligands that are not retained in the product must have been eliminated as a neutral molecule, most likely as H_2. The product $(P^iPr_3)_2Os(NCCD_3)_2H_3{}^+$ reacted further by H_2 dissociation at ambient temperature in acetonitrile to give (P^i-

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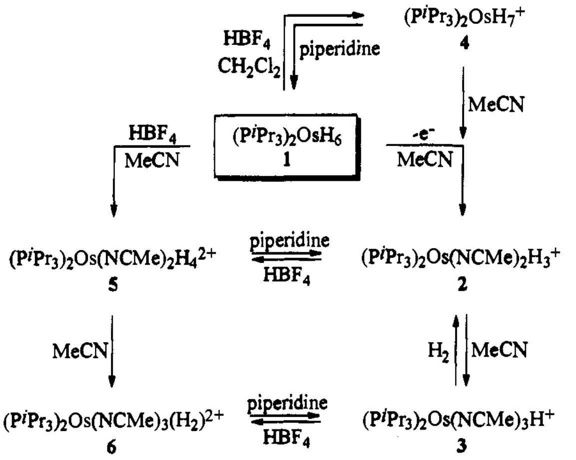
[12] The nature of the electrode material (Pt vs Au) can have a profound effect on the results of coulometric measurements for the oxidation of transition-metal hydrides: Poli, R. Personal communication.

[13] Multielectron processes were found for the oxidation of $CpRe(PPh_3)(NO)R$ in dichloromethane and DMSO and it was suggested that solvent oxidation might be responsible: Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *Organometallics* **1987**, *6*, 1628.

Scheme 1



$Pr_3)_2Os(NCCD_3)_3H^+$; we therefore assume that the presence of $(P^iPr_3)_2Os(NCMe)_3H^+BF_4^-$ (**3**) in the mixture isolated from preparative electrolysis of **1** is due to a secondary reaction of **2** during the electrolysis and workup (eq 3).

$$\underset{\mathbf{1}}{(P^iPr_3)_2OsH_6} \xrightarrow[\text{MeCN}]{-e^-} \underset{\mathbf{2}}{(P^iPr_3)_2Os(NCMe)_2H_3^+} \xrightarrow{\text{MeCN}} (P^iPr_3)_2Os(NCMe)_3H^+ \quad (3)$$

Protonation of 1. Keeping in mind the arguments presented in the introduction, we suspected that a proton transfer from $\mathbf{1}^{\bullet +}$ to **1** could occur, initiating secondary reactions that lead to the observed product **2**. An investigation of the protonation of **1** in dichloromethane and acetonitrile was therefore carried out.

When excess $HBF_4{\cdot}Et_2O$ was added to a solution of **1** in dichloromethane-d_2 in an NMR tube, a species which has been assigned the formula $(P^iPr_3)_2OsH_7^+BF_4^-$ (**4**) was the only product. Scheme 1 summarizes this reaction and others that will be described in the following. The ^1H NMR spectrum shows a characteristic hydride signal at δ −7.02 (t, J = 4.0 Hz, 7 H), and a singlet is seen at δ 43.8 in the $^{31}P\{^1H\}$ NMR spectrum. Additional support for the proposed chemical formula of **4** is provided through its reaction with piperidine, which quantitatively regenerates **1**.

From $T_{1\min}$ (12.2 ms, 300 MHz, −104 °C) of **4**, it is certain that there is at least one H_2 ligand bound to Os, and we have considered the possibility of more than one. No decoalescence of the hydride signal is observed ($\Delta\nu_{1/2}$ = 70 Hz at −120 °C in dichloromethane-d_2/toluene-d_8 (9:1)). The hydrides of compound **4** were found to exchange with D_2 after several minutes at room temperature. There is very little isotope effect on the chemical shift ($\Delta\delta$ = 12 ppb in **4**-d_6; the temperature dependence has not been investigated). At 93% deuteration,[14] the only significant isotopomer observed in the ^1H NMR spectrum is **4**-d_6, and Figure 5 shows this spectrum in detail. Some line-splitting due to HD (3.1 ± 0.1 Hz) and HP (4.0 Hz) coupling is observed in this signal, with some of the outer lines too small to be observed. Making the "usual" assumptions of statistical isotopic populations and of HD coupling *only* in η^2-HD, the $^1J_{HD}$ value obtained (65.1 Hz) is too large to be consistent with the formulation $(P^iPr_3)_2OsH_5(H_2)^+$.[15] Using the formulation $(P^iPr_3)_2OsH_3(H_2)_2^+$, the corresponding $^1J_{HD}$ value of 32.6 Hz is entirely reasonable. Recently, Moreno et al. assigned the structure of Tp^*RuH_5 (Tp^* = hydridotris(3,5-dimethylpyrazolyl)borate) as $Tp^*RuH(H_2)_2$, based on this argument.[16]

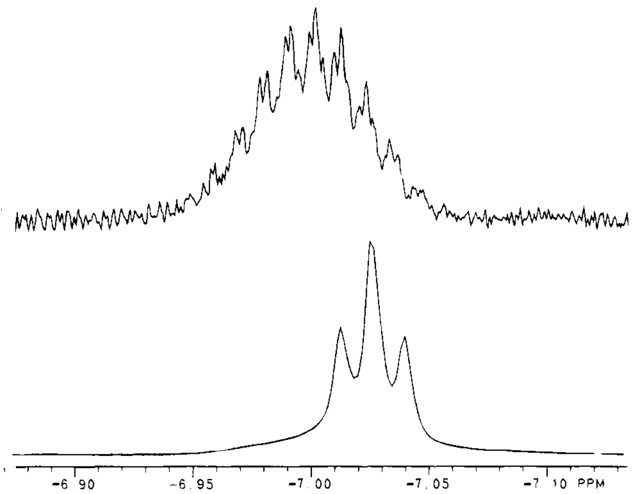


Figure 5. 500-MHz ^1H NMR spectrum (hydride region) of **4** (bottom) and **4**-d_6 (top) at ambient temperature.

While we do favor the bis-(η^2-H_2) structure, we wish to point out some of the possible pitfalls in the assumptions made here. First, we must assume a statistical population of isotopomers (i.e., the hydrogen atom in **4**-d_6 is equally populating all sites). This may not be true. That is, there may be a significant thermodynamic isotope effect.[17] Second, this calculation assumes no HD coupling when not in η^2-HD. Very good evidence to the contrary has been reported in some established classical hydrides.[18] Therefore, while we prefer the bis-(η^2-H_2) formulation, the mono-(η^2-H_2) formulation cannot be rigorously ruled out. The HH distance in **4** can be estimated as 1.00 Å (0.79 Å, fast-spinning[19]) from its $T_{1\min}$ value, based on the formulation $(P^iPr_3)_2OsH_3(H_2)_2^+$.[20]

An interesting comparison can be made to the isoelectronic compounds L_2ReH_7, which have *one* short HH distance (1.36 Å when L = P(p-tolyl)$_3$, according to neutron diffraction[21]). We attribute the greater nonclassical bonding character in **4** to decreased back-bonding from the cationic metal center.

Cationic Acetonitrile Osmium Complexes. When **4** is dissolved in acetonitrile, it undergoes a reaction within 10 min

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[14] Extent of deuteration was determined by the integral ratio of the hydride resonance to the methine resonance of the phosphine (the methyl signal overlaps with the methyl signal of ether), acquired using long (10 s) acquisition delays.

[15] The observed splitting of 3.1 Hz is $^2/_7 \times {}^1/_6$ of $^2J_{HD}$, since in $(P^iPr_3)_2OsH_5(H_2)^+$ only 2 of 7 sites have coupling, and this is averaged over 6 D atoms. Therefore, $J_{HD,avg}$ = 3.1 Hz = $(^2/_7)(^1/_6)^1J_{HD}$, so $^1J_{HD}$ = 65.1 Hz, which is much larger than in free HD (43.2 Hz).

[16] Moreno, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **1994**, *116*, 2635.

[17] Heinekey, O. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137.

[18] Tp^*IrH_4: Paneque, M.; Poveda, M. L.; Taboada, S. *J. Am. Chem. Soc.* **1994**, *116*, 4519 and references therein. See also ref 6a.

[19] A correction is often made for these calculations (0.794) when the assumption is made that the rate of molecular tumbling is negligible compared to H_2 rotation. While we do not necessarily believe this to be the case, these values will also be reported throughout, for easy reference.

[20] Using the $T_{1\min}$ of $(P^iPr_3)_2OsH_6$ (119 ms, 300 MHz) as a normalization factor, we have the following relaxation model:

$$R^* = \frac{1}{0.119s} = 8.40s^{-1}$$

$$R_{obs} = \frac{1}{0.0122s} = \frac{1}{7}(7R^* + 4R_{HH})$$

$$R_{HH} = 128.7s^{-1}$$

According to $R_{max} = 38700\nu^{-1}(r_{HH})^{-6}$, r_{HH} = 1.00 Å. If the "fast-spinning" model were used, the value would be 0.79 Å.

[21] Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241.

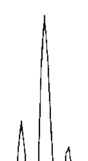

Figure 6. 500-MHz ^1H NMR spectrum (hydride region) of **2**-d_2 at ambient temperature.

to produce $(P^iPr_3)_2Os(NCMe)_2H_3^+BF_4^-$ (**2**), isolated in 80% yield. The ^1H NMR spectrum (dichloromethane-d_2) shows a hydride signal at δ −12.21 (t, $J = 11.4$ Hz, 3 H) and one singlet for the two coordinated acetonitrile ligands. A $^{31}P\{^1H\}$ NMR singlet is observed at δ 26.5. No intermediates, such as $(P^iPr_3)_2Os(NCMe)H_5^+$, were detected when **4** reacted with acetonitrile in dichloromethane.

Compound **2** falls into the general category $L_4MH_3^+$ (M = Fe, Ru, Os), which has been extensively studied with several different phosphines.[22] Most of these complexes have been formulated as $L_4MH(H_2)^+$, with either trihydride[23] or trihydrogen[24] ligation proposed to mediate hydride site exchange. To our knowledge, this is the first example in this class containing nitrile ligands.

We assign the bulky phosphine ligands to *trans* positions, based on the observation of an apparent quartet at δ 1.15 ppm. In complexes with smaller (110−112°) P−Os−P angles,[25] this signal appears as a doublet of doublets. The observation of two IR stretches in the CN region allows us to assign *cis* positions to the nitrile ligands. At −142 °C, the hydride signal in the ^1H NMR spectrum only broadens ($\Delta\nu_{1/2} = 53$ Hz) while retaining a symmetrical shape, but shows no sign of decoalescence. No temperature dependence of the chemical shift was observed. This facile fluxionality of the three hydride ligands is also consistent with the above assignments, which leave two *cis* positions in an octahedron for the three hydrides. The only structural variable which remains is the classical/nonclassical nature of the hydrides.

The $T_{1\min}$ value of 65.5 ms (−99 °C, $CDFCl_2/CDF_2Cl$, 300 MHz) is in the "fuzzy" range between classical and nonclassical hydrides. Assuming a hydride−dihydrogen structure, a lower limit for the H−H distance in the H_2 ligand is estimated to be 1.40 Å (1.11 Å if fast-spinning), which is quite long. In the pentagonal bipyramidal structure, we estimate an H••H distance of 1.57 Å.[26] Partially deuterated **2** can be generated by dissolving **4**-d_6 in acetonitrile-d_3. A very small coupling ($J_{HD} = 2.8$ Hz) was observed in **2**-d_2[27] at 25 °C (Figure 6). While the assumption is often made that *no* HD coupling should be present between hydrides, recent examples of well-characterized classical hydrides have displayed HD couplings as large as 3.3 Hz.[18] Only a very small isotopic shift ($\Delta\delta < 10$ ppb), and no hydride decoalescence (−90 °C, 300 MHz), was observed in **2**-d_2.

The $T_{1\min}$ and J_{HD} data are somewhat similar to "hydrogen on the brink of heterolytic cleavage" observed for $(depe)_2OsH(H{\cdot\cdot}H)^+$ ($T_{1\min} = 80$ ms,[28] $J_{HD,avg} = 3.8$ Hz). The authors tentatively favored assignment of this compound as a *trans*-$H(H_2)$ complex, rapidly interconverting with a trihydride, even at −93 °C. Recently, *neutral* $(P^iPr_3)_2OsH_3Cl$ ($T_{1\min} = 72$ ms) was reported as a classical trihydride with H−Os−H angles of 60° in a C_{2v} structure, exhibiting quantum mechanical exchange coupling.[29] Since values for **2** are similar to both of these cases, and no hydride decoalescence (^1H NMR) or OsH stretches (IR) are observed, we turn to chemical evidence. Thus, the very slow reaction with acetonitrile leads us to favor the trihydride structure for **2**. Also, the only reasonable driving force for the reaction **3** + H_2 → **2** + MeCN (*vide infra*) is the oxidation of Os^{II} to Os^{IV}.

When **2** is stirred in acetonitrile for 12 h at ambient temperature, a further reaction occurs (Scheme 1) to give $(P^iPr_3)_2Os(NCMe)_3H^+BF_4^-$ (**3**) in good yield. The ^1H NMR spectrum of **3** (dichloromethane-d_2) shows a hydride triplet at δ −16.01 ($J = 19.1$ Hz, 1 H) and two singlets (2:1 relative intensities) due to the coordinated acetonitriles. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 21.2. The spectroscopic data are consistent with an octahedral structure in which the acetonitrile ligands are *mer* oriented and the phosphines *trans*. Remarkably, the reaction with acetonitrile is *reversible*. When **3** is dissolved in dichloromethane-d_2 and exposed to an atmosphere of H_2, conversion back to **2** and free acetonitrile is observed within 1 h (Scheme 1). When **3**(BF_4^-) is dissolved in acetonitrile-d_3, the acetonitrile ligand trans to hydride exchanges with the solvent. Within 20 min or less, the exchange is complete. The other two acetonitrile ligands also exchange with solvent, but only very slowly (virtually complete after 3 days).

Dicationic Osmium Complexes. The treatment of **1** with excess $HBF_4{\cdot}Et_2O$ in acetonitrile-d_3 led to products different from that formed (**4**) in dichloromethane. The spectroscopic data (^1H NMR δ −11.75 (br s, 4 H); ^{31}P NMR δ 26.9 (s); see Experimental Section for further details) suggest the formula $(P^iPr_3)_2Os(NCCD_3)_2H_4^{2+}$. The product formula is supported by its reaction with piperidine, which produces **2**. Conversely, treatment of $(P^iPr_3)_2Os(NCCD_3)_2H_3^+$ with $HBF_4{\cdot}Et_2O$ in acetonitrile-d_3 produces $(P^iPr_3)_2Os(NCCD_3)_2H_4^{2+}$ (Scheme 1). It is quite surprising to us that the cationic hydride **2** can be readily protonated, whereas it has shown no tendency to undergo deprotonation by triethylamine ($pK_a(Et_3NH^+) = 18.5$ in acetonitrile[30]) or piperidine (pK_a(piperidineH$^+$) = 18.9[30]). It is likely that the formation of $(P^iPr_3)_2Os(NCMe)_2H_4^{2+}$ (**5**) from **1** and excess acid proceeds through **4** and **2** as intermediates.

The extremely fast relaxation of the hydrides ($T_{1\min} = 12.2$ ms, −67 °C, $CDFCl_2/CDF_2Cl$) of **5** suggests one or two dihydrogen ligands. Assuming a bis-(η^2-H_2) structure, the H−H distance would be 1.09 Å (0.86 Å, fast-spinning); with a (η^2-H_2)$(H)_2$ model, the H−H distance is 0.97 Å (0.77 Å, fast-spinning).[31] Again, only line broadening is observed down to

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[22] In Heinekey's review (ref 6a), nearly one-quarter of the dihydrogen complexes listed were of this general formula.

[23] Maseras, F.; Duran, M.; Lledós, A.; Bertrán, J. *J. Am. Chem. Soc.* **1992**, *114*, 2922.

[24] See for example: (a) Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19. (b) Jia, G.; Drouin, S. D.; Jessop, P. G.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 906.

[25] (a) $(P^iPr_3)_2OsH_2X_2$: Gusev, D. G.; Kuhlman, R.; Rambo, J. R.; Berke, H.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 281. (b) $[\{(P^iPr_3)_2OsH_2\}_2(\mu\text{-}Cl)_3]^+$: Kuhlman, R.; Streib, W.; Caulton, K. G. *Inorg. Chem.* **1995**, *34*, 1788. (c) Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *Chem. Ber.* **1994**, *127*, 27.

[26] r_{HH} is calculated in a similar way to that in ref 20, using $R^* = 3.85s^{-1}$, from $T_{1\min}$ of the classical hydride of $(P^iPr_3)_2OsClH(H_2)$ (260 ms).

[27] By integration there is 83% D-incorporation, so the HD_2 isotopomer should be the one primarily observed by ^1H NMR.

[28] This value has been averaged among the H and H••H sites, and "corrected" to 300 MHz for direct comparison.

[29] Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685.

[30] Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45.

[31] r_{HH} calculated in a similar way to that described in ref 26, using $R^* = 3.85s^{-1}$.

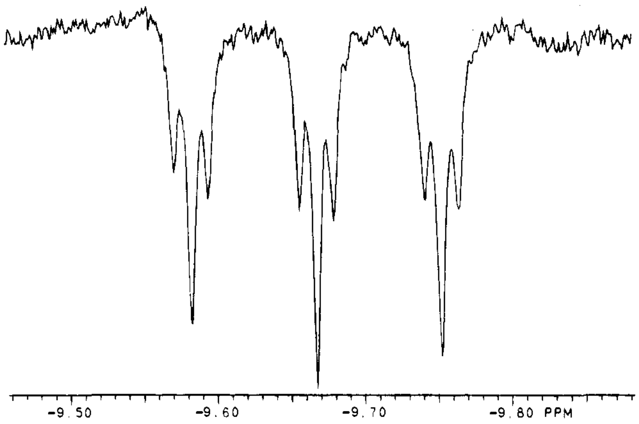

Figure 7. 500-MHz ^{1}H NMR spectrum (hydride region) of **6**-d_1. A $\pi-\tau-\pi/2$ pulse sequence was used to suppress the signal from **6**-d_6 at ambient temperature.

-100 °C (dichloromethane-d_2/toluene-d_8), where the hydride resonance broadens into the baseline. In $CDFCl_2/CDF_2Cl$, the signal broadens into the baseline only at about −145 °C. We attribute the broadening to fast spin−spin relaxation, rather than decoalescence. We have been unable to achieve sufficient deuterium incorporation into **5** to observe J_{HD}.

It was noted that after 24 h at ambient temperature, $(P^iPr_3)_2Os(NCCD_3)_2H_4^{2+}$ underwent another reaction to give $(P^iPr_3)_2Os(NCCD_3)_3(H_2)^{2+}$ (^{1}H NMR δ −9.63 (br, 2 H); $^{31}P\{^1H\}$ NMR δ 11.2 (s); further details are found in the Experimental Section). The reaction of $(P^iPr_3)_2Os(NCCD_3)_3(H_2)^{2+}$ with piperidine yields $(P^iPr_3)_2Os(NCCD_3)_3H^+$, and treatment of **3** with $HBF_4{\cdot}Et_2O$ yields $(P^iPr_3)_2Os(NCMe)_3(H_2)^{2+}(BF_4^-)_2$ (**6**) (Scheme 1). These observations support the structure assigned for **6**. Again, it is noteworthy that a cationic hydride **3** can be readily protonated, but shows no tendency to undergo deprotonation when treated with triethylamine or piperidine.

Like **3**, this complex is octahedral, with *trans* phosphines. Two signals are observed (^{1}H NMR) for the acetonitrile ligands in a 2:1 ratio, consistent with a *mer* arrangement of these ligands. The sixth site is occupied by a dihydrogen ligand as suggested by the fast hydride relaxation ($T_{1\min}$ = 12.4 ms, −50 °C, CD_2Cl_2, 300 MHz). In this case, the H−H distance can be determined very accurately, since the relaxation of the hydride in **3** ($T_{1\min}$ = 200 ms, −55 °C, CD_2Cl_2, 300 MHz) serves as an excellent "normalization factor" for finding the spin−lattice relaxation due to H−H interaction in the H_2 ligand. The distance is 1.09 Å (0.87 Å, fast-spinning). Addition of acetonitrile and $HBF_4{\cdot}Et_2O$ to **4**-d_6 allowed spectroscopic detection of **6**-d_1 (Figure 7). The spectrum showed J_{HD} = 25.5 Hz. In this case, the HD resonance appeared at 30 ppb higher field than the H_2 resonance. This signal was also narrow enough to allow observation of J_{HP} = 3.5 Hz.

Oxidation of $(P^iPr_3)_2OsH_6$ (1) in Dichloromethane-d_2. Equimolar amounts of **1** and $AcFc^+BF_4^-$ were dissolved in dichloromethane-d_2. The solution turned from the dark blue color of the oxidant to dark red after the oxidation. One equivalent of the oxidizing agent was needed for **1** to be fully consumed. The ^{1}H NMR spectrum showed two major products. One product was identified as $(P^iPr_3)_2OsH_7^+$ (**4**) by comparison with an authentic sample. The other major product (**7**) showed ^{1}H NMR resonances at δ 2.00 (6 H), 1.2 (overlapping with another product signal, estimated 36 H), and −7.25 (br). Due to partially overlapping signals for the P^iPr_3 ligands of **4** and **7**, the hydride signals are the ones which most reliably give relative signal intensities. However, the relative amount of each compound cannot be unambiguously determined since the number of hydrides in **7** is as yet unknown. The relative intensities of the hydride signals for **4** and **7** varied somewhat from one experiment to the next.

A low-temperature ^{1}H NMR spectroscopy study was undertaken of one such reaction. At −100 °C, the spectrum showed a splitting of the hydride signal for **7** to give new resonances (1:2:2 ratio) at δ −0.1 (br, 1 H), −3.7 (br, 2 H), and −15.6 (br, 2 H). The hydride resonance for **4** remained sharp. The $^{31}P\{^1H\}$ signal for **7** appeared at δ 45.9. At −80 °C, the hydride signal for **7** had a T_1 value of 47(3) ms.

Addition of Acetonitrile to the Oxidation Products of $(P^iPr_3)_2OsH_6$ (1) in Dichloromethane-d_2. When acetonitrile was added to the dark red solution containing the oxidation products **4** and **7**, the solution turned immediately to an orange color. All oxidation products reacted with acetonitrile to give $(P^iPr_3)_2Os(NCMe)_2H_3^+$ (**2**). The reaction appeared to be quantitative (comparison of phosphine methine signals with the solvent peak as internal standard). Thus, compound **7** must contain at least three hydride ligands and a positive charge per Os center.

Summary: Proton-Transfer Mechanism for the Reactions of $1^{\bullet+}$. The accumulated experimental evidence suggests that the primary reaction of $1^{\bullet+}$ is the transfer of a proton to **1**. The ability of **1** to act as a Brønsted base is demonstrated by its reaction with $HBF_4{\cdot}Et_2O$ to give **4**. We had initially considered it less likely that the Os^{VI} complex would undergo protonation to give a very high oxidation state Os^{VIII} cationic heptahydride $(P^iPr_3)_2Os(H)_7^+$. Accordingly, this is avoided by the generation of the Os^{VI} or Os^{IV} dihydrogen complexes $(P^iPr_3)_2Os(H)_5(H_2)^+$ or $(P^iPr_3)_2Os(H)_3(H_2)_2^+$ (**4**). The immediately formed products of the proton-transfer reaction are then $(P^iPr_3)_2OsH_5^{\bullet}$ and **4**.

In dichloromethane, **4** was directly observed as an oxidation product. The exact fate of $(P^iPr_3)_2OsH_5^{\bullet}$ is not known, but the radical is likely to be a precursor for the unidentified products (e.g. **7**). We propose as possible reaction pathways Cl atom abstraction from the solvent and perhaps radical/radical or radical/cation radical recombination reactions to give dinuclear complexes.

In acetonitrile, all products have been identified so the situation is more clear. The initial proton-transfer product **4** has been shown to readily undergo loss of four H (as two H_2) to give the observed product $(P^iPr_3)_2Os(NCMe)_2H_3^+$ (**2**). It is also readily understood how the radical $(P^iPr_3)_2OsH_5^{\bullet}$ can undergo a further oxidation (presumably aided by prior acetonitrile coordination to give a readily oxidized 19-electron radical[32]) to give $(P^iPr_3)_2OsH_5^+$ which is a likely precursor to **2**. Thus, the quantitative, one-electron chemical oxidation is rationalized by the mechanism which is summarized in Scheme 2.

Conclusions

This work confirms the reaction types which occur on outer-sphere oxidation of transition-metal polyhydrides: (1) greatly enhanced Brønsted acidity (bimolecular proton transfer), (2) intramolecular redox reaction, leading to conversion of two hydride ligands to H_2, (3) reaction with solvent: evolution of H_2 and coordination of acetonitrile.

This chemistry begins with Os^{VI} in the hexahydride (d^2), but protonation yields d^4 Os^{IV}. Acetonitrile enables loss of two molecules of H_2, to give a trihydride of Os^{IV} in **2**. The absence of an H_2 ligand in **2** is supported by its *slow* (12 h) reaction in which acetonitrile replaces two hydride ligands (loss of H_2,

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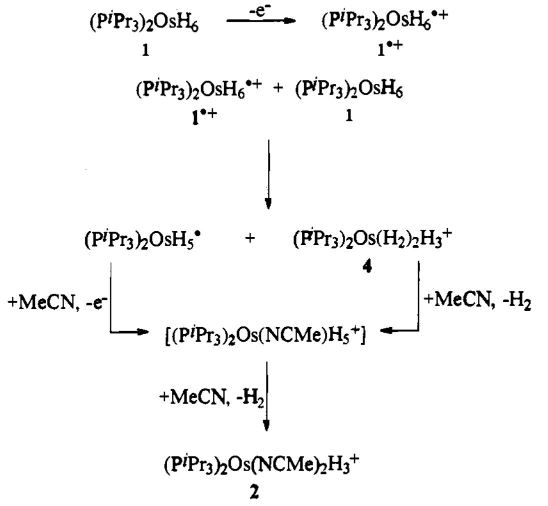
[32] For a quantitative consideration of the effect of acetonitrile coordination at some 17-electron metal centers, see: Tilset, M. *Inorg. Chem.* **1994**, *33*, 3121.

Scheme 2



giving Os^{II} in **3**). The absence of an H_2 ligand (often Brønsted acidic) is also consistent with the fact that $(P^iPr_3)_2Os(NCMe)_2H_3^+$ is not deprotonated by piperidine. Piperidine also is incapable of deprotonating the monocation monohydride $(P^iPr_3)_2Os(NCMe)_3H^+$ because this is a reduction to Os^0, an oxidation state which would be too unstable in the absence of strong π-acid ligands. Said differently, $(P^iPr_3)_2Os(NCMe)_3$ would be so electron rich at Os that it would be more Brønsted basic than piperidine.

Both **2** and **3** retain Brønsted basicity in spite of their cationic character, but this is by virtue of protonation at their hydride ligands, not at the metal, to give H_2 ligands. Species **5** and **6** are Brønsted acidic (towards piperidine) *because* they both are dihydrogen complexes and *di*cations. It is perhaps surprising that $(P^iPr_3)_2Os(NCMe)_2H_4^{2+}$, which contains at least one H_2 ligand (Os^{IV}), and maybe even two (Os^{II}), reacts only slowly in acetonitrile to replace one H_2. This reaction may be slow because it involves reduction of osmium.

The reversibility of the interconversion of **2** and **3**, in particular the conversion of **3** to **2**, relies on the strong *trans* effect of the hydride ligand in octahedral **3**, and also (see above) the thermodynamic assistance from the oxidation to Os^{IV} by the added H_2. Except for this example, it is unusual[33] for H_2 to replace a neutral ligand in a reaction. This oxidation by an oxidant as weak as H_2 is assisted because the Os^{II} in **3** contains no strong π-acid ligands.

Taube's group has studied the complexes $Os(H_2)(H_2NC_2H_4NH_2)_2L^{n+}$, which exist with H_2 either *cis* or *trans* to L (L = halide, pseudohalide ($n = 1$), and neutral Lewis base ($n = 2$)). Their J_{HD} and T_{1min} values[34] and the H−H distance[35] (1.34 Å from neutron diffraction when L = CH_3COO^-; J_{HD} = 9.0 Hz) are consistent with all of these complexes having "long" H−H separations (>1.3 Å). Thus, Os^{II} in a ligand environment devoid of π-acids (but dicationic!) is sufficiently reducing to strongly lengthen the H−H bond. The octahedral d^6 structure is preferred. For comparison, uncharged $OsH_4(PMe_2Ph)_3$[36] is *not* the d^6 octahedral $Os^{II}(H)_2(H_2)(PMe_2Ph)_3$, but rather d^4 $Os^{IV}(H)_4(PMe_2Ph)_3$, and the charged $OsH_5(PMe_2Ph)_3^+$[37] is a pentahydride of Os^{VI}, with a shortest H/H distance of 1.49 Å (i.e., over twice the bond length in free H_2).

It has been demonstrated that 5d metals have a greater tendency to be classical hydrides than their 4d congeners.[38] In the presence of attendant π-acid ligands, even 5d metals will have η^2-H_2 ligands. For example, $L_4ReH_4^+$ is a tetrahydride,[39] while $L_3Re(CO)(H)_4^+$ is in rapid equilibrium with $L_3Re(CO)(H)_2(H_2)^+$.[40] We have demonstrated here that increasing the charge on a 5d metal center has a similar effect. While $L_4Re(H)_4^+$ is classical, $(P^iPr_3)_2Os(NCMe)_2H_4^{2+}$ is nonclassical. It should also be noted that $(P^iPr_3)_2Os(NCMe)_3(H_2)^{2+}$ is isoelectronic with the Kubas[8] complex $(PCy_3)_2W(CO)_3(H_2)$ and with Heinekey's cationic[41] compounds $(PR_3)_2Re(CO)_3(H_2)^+$; the Os complex contains an η^2-H_2 ligand, despite the lack of π-acidic ligands, due to its dicationic metal center.

Experimental Section

General Procedures. All manipulations involving inorganic and organometallic compounds were carried out with use of vacuum line, Schlenk, syringe, or drybox techniques. Acetonitrile was distilled from P_2O_5, acetonitrile-d_3 and dichloromethane-d_2 were vacuum transfered from CaH_2, and THF and ether were distilled from sodium benzophenone ketyl. Acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$ was used as solvent for electrochemical experiments and was passed through a column of active neutral alumina before use to remove water and protic impurities. The electrolyte was freed of air by purging with solvent-saturated, purified argon, and all measurements and electrolyses were carried out under a blanket of solvent-saturated argon.

Electrochemical measurements were performed with an EG&G-PAR Model 273 Potentiostat/Galvanostat driven by an external HP 3314A sweep generator. The signals were fed to a Nicolet 310 digital oscilloscope and processed by an on-line personal computer. The working electrode was a Pt or Au disk electrode (d = 0.6 mm), the counter electrode was a Pt wire, and the Ag wire reference electrode assembly was filled with acetonitrile/0.01 M $AgNO_3$/0.1 M $Bu_4N^+PF_6^-$. The reference electrode was calibrated against Cp_2Fe which is also used as the reference in this work. The positive-feedback *iR* compensation circuitry of the potentiostat was employed; the separation of anodic and cathodic peak for the Cp_2Fe oxidation was 59−61 mV in acetonitrile at a voltage scan rate ν = 1.0 V/s.

^1H NMR spectra were recorded on Varian-Gemini 200, Varian XL 300, and Bruker AM 500 instruments. Chemical shifts are reported in ppm relative to tetramethylsilane, with the residual solvent proton resonance as internal standard (δ 1.93 for acetonitrile-d_3, 5.32 for dichloromethane-d_2, 7.47 for $CDFCl_2$). ^1H NMR specra were obtained using a 45° pulse and a 10 s pulse delay for integration of signals. The precision of measured T_{1min} data was usually better than 1 ms and therefore these data are reported with three significant figures. $^{31}P\{^1H\}$ NMR spectra were recorded on a Nicolet 360 instrument operating at 146 MHz. Chemical shifts are reported in ppm relative to 85% H_3PO_4. Temperatures reported in NMR experiments were calculated from the peak separation of the signals of methanol.

$(P^iPr_3)_2OsH_6$ (**1**),[42a] $AcFc^+BF_4^-$,[42b] and the mixture of $CDFCl_2/CDF_2Cl$[43] were prepared according to published procedures. Other chemicals were used as received from commercial suppliers. Elemental analyses were performed by Desert Analytics in Tucson, AZ.

Preparation of $(P^iPr_3)_2OsH_7^+BF_4^-$ (4). Compound **1** (263 mg, 0.51 mmol) was dissolved in ether (10 mL) and $HBF_4{\cdot}Et_2O$ (200 μL,

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(33) For replacement of H_2O, see: (a) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032. (b) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390.

(34) Li, Z.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 9506.

(35) Hasegawa, T.; Li, Z.; Parkin, G.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352.

(36) Hart, D. W.; Bau, R.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 7557.

(37) Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966.

(38) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1994**, *136*, 845 and references therein.

(39) Lunder, D. M.; Green, M. A.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 4527.

(40) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912.

(41) Heinekey, D. M.; Schlomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515.

(42) (a) Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288. (b) Carty, P.; Dove, M. F. A. *J. Organomet. Chem.* **1971**, *28*, 125.

(43) Siegel, J. S.; Anet, F. A. L. *J. Org. Chem.* **1988**, *53*, 2629.

1.46 mmol) was added. This caused the instant precipitation of $(P^iPr_3)_2OsH_7{}^+BF_4{}^-$ as a white powder. Compound **4** *cannot* be washed with ether (**1** is reformed), so we have only used **4** as an in situ precursor to compounds **2** and **3**. ^{1}H NMR (dichloromethane-d_2, 200 MHz) δ −7.02 (t, J = 4.0 Hz, 7 H), 1.15 (apparent q, 36 H), 2.16 (m, 6 H); $T_{1\min}$ (300 MHz, −104 °C, $CDFCl_2/CDF_2Cl$) 12.2 ms; $^{31}P\{^1H\}$ NMR (dichloromethane-d_2) δ 43.8 (s). The addition of 1.5 equiv of piperidine to a solution of **4** in dichloromethane-d_2 quantitatively regenerated **1**.

In the absence of excess HBF_4 *or* in the presence of H_2, compound **4** is stable indefinitely in dichloromethane-d_2 solution. With excess acid, decomposition is observed over a period of several hours to several uncharacterized products.

Preparation of $(P^iPr_3)_2Os(NCMe)_2H_3{}^+BF_4{}^-$ (2). Solid **4** was prepared from **1** (263 mg, 0.509 mmol) and dissolved in acetonitrile (5 mL). After the solution was stirred for 10 min, it was filtered through a cannula into a Schlenk flask. The solution was then concentrated to ca. 0.5 mL by vacuum transfer, and addition of ether caused the product **2** to precipitate as a white powder. The solvent was decanted, and the product (278 mg, 80%) was washed with ether and dried under vacuum. ^{1}H NMR (dichloromethane-d_2, 200 MHz) δ −12.21 (t, J = 11.4 Hz, 3 H), 1.17 (apparent q, 36 H), 2.10 (m, 6 H), 2.50 (s, 6 H); $T_{1\min}$ (300 MHz, −99 °C, $CDFCl_2/CDF_2Cl$) 65.5 ms; $^{31}P\{^1H\}$ NMR δ 26.5 (s); IR (KBr) ν_{CN} = 2154 (br, s), 2127 (shoulder). Anal. Calcd for $C_{22}H_{51}BF_4N_2OsP_2$: C, 38.71; H, 7.53; N, 4.10. Found: C, 38.58; H, 7.70; N, 4.16.

Preparation of $(P^iPr_3)_2Os(NCMe)_3H^+BF_4{}^-$ (3). Solid **2** (60 mg, 0.088 mmol) was dissolved in acetonitrile (5 mL), and the solution was stirred for 12 h and then concentrated to ca. 0.5 mL. The white product was precipitated by the addition of ether. The solvent was decanted, and the product (58 mg, 91%) was washed with ether. ^{1}H NMR (dichloromethane-d_2, 200 MHz) δ −16.01 (t, J = 19.1 Hz, 1 H), 1.30 (apparent q, 36 H), 2.30 (m, 6 H), 2.36 (s, 6 H), 2.48 (s, 3 H); $T_{1\min}$ (300 MHz, −55 °C, dichloromethane-d_2) 200 ms; $^{31}P\{^1H\}$ NMR δ 21.2 (s); IR (KBr) ν_{CN} = 2242 (vs), 2091 (s). Anal. Calcd for $C_{24}H_{52}BF_4N_3OsP_2$: C, 39.95; H, 7.26; N, 5.82. Found: C, 39.60; H, 7.07; N, 5.97.

Preparation of $(P^iPr_3)_2Os(NCMe)_2H_4{}^{2+}$ (5) by Protonation of 2. An NMR tube was loaded with **2** (10 mg, 0.015 mmol) and acetonitrile-d_3 (0.6 mL). The solution was immediately treated with $HBF_4{\cdot}Et_2O$ (5 μL, 0.036 mmol). The ^{1}H NMR spectrum showed **2** (15%) and $(P^iPr_3)_2Os(NCMe)_2H_4{}^{2+}$ (**5**, 85%) as the only detectable Os species. The protonation can also be done in dichloromethane-d_2. ^{1}H NMR (dichloromethane-d_2) δ −11.75 (br s, 4 H), 1.26 (apparent q, 36 H), 2.63 (m, 6 H), 2.72 (s, 6 H); $T_{1\min}$ (300 MHz, −67 °C, $CDFCl_2/CDF_2Cl$) 12.2 ms; $^{31}P\{^1H\}$ NMR δ 26.9 (s). Attempts to isolate **5** by precipitation with ether or toluene only led to the isolation of **2**. When the acetonitrile-d_3 solution of **5** was treated with piperidine (5 μL, 0.051 mmol), the ^{1}H NMR spectrum revealed that **5** quantitatively was deprotonated to reform **2**.

Preparation of $(P^iPr_3)_2Os(NCMe)_3(H_2)^+$ (6) by Protonation of 3. An NMR tube was loaded with **3** (10 mg, 0.014 mmol) and acetonitrile-d_3 (0.6 mL). The solution was treated with $HBF_4{\cdot}Et_2O$ (5 μL, 0.036 mmol). The ^{1}H NMR spectrum showed **6** to be the only product. ^{1}H NMR (dichloromethane-d_2) δ −9.60 (br, 2 H), 1.38 (apparent q, 36 H), 2.57 (m, 6 H), 2.68 (s, 6 H), 2.85 (s, 3 H); $T_{1\min}$ (300 MHz, −50 °C, dichloromethane-d_2) 12.4 ms; $^{31}P\{^1H\}$ NMR δ 11.2 (s). Attempts to isolate **6** by precipitation with ether only led to the isolation of **3**. When the acetonitrile-d_3 solution of **6** was treated with piperidine (5 μL, 0.051 mmol), the ^{1}H NMR spectrum showed that the starting material **3** was quantitatively regenerated.

Oxidation of $(P^iPr_3)_2OsH_6$ (1) with $AcFc^+BF_4{}^-$ in Acetonitrile-d_3. An NMR tube was loaded with **1** (10.0 mg, 0.019 mmol) and $AcFc^+BF_4{}^-$ (5.7 mg, 0.018 mmol) in acetonitrile-d_3 (0.5 mL). The ^{1}H NMR spectrum showed the presence of $(P^iPr_3)_2Os(NCCD_3)_2H_3{}^+BF_4{}^-$, identified by comparison with an authentic sample of **2**. The solution was stored at ambient temperature for 20 h, after which the ^{1}H NMR spectrum revealed the clean transformation of $(P^iPr_3)_2Os(NCCD_3)_2H_3{}^+$ to $(P^iPr_3)_2Os(NCCD_3)_3H^+$.

Constant-Current and Constant-Potential Coulometry. Preparative Electrolysis of $(P^iPr_3)_2OsH_6$ (1). All electrolysis experiments were performed in an H-shaped cell, the compartments of which were separated by a medium-frit glass junction. A platinum-gauze or gold-gauze working electrode was used. In a typical experiment, **1** (20 mg, 0.039 mmol) was dissolved in acetonitrile/0.05 M $Me_4N^+BF_4{}^-$ (20 mL) in the electrolysis cell. The solution was electrolyzed for 360 s (373 s are required for a one-electron oxidation) at a current of 10 mA. The electrolyzed solution was transferred to a Schlenk flask and the solvent was removed by vacuum transfer. The residue was extracted with dichloromethane (5 mL) and the extract was filtered. Dichloromethane was removed by vacuum transfer, and the residue was dissolved in acetonitrile-d_3. ^{1}H NMR (acetonitrile-d_3, 200 MHz) showed **1** (37%), **2** (53%), and **3** (10%).

Protonation of $(P^iPr_3)_2OsH_6$ (1) with $HBF_4{\cdot}Et_2O$ in Acetonitrile-d_3. An NMR tube was loaded with **1** (10 mg, 0.019 mmol) dissolved in acetonitrile-d_3 (0.5 mL). Excess $HBF_4{\cdot}Et_2O$ (15 μL, 0.110 mmol) was added. The ^{1}H NMR spectrum showed $(P^iPr_3)_2Os(NCCD_3)_2H_4{}^{2+}$. ^{1}H NMR (acetonitrile-d_3, 200 MHz) δ 2.63 (m, 6 H), 1.26 (apparent q, 36 H), −11.75 (br, 4 H). After the solution was stored at ambient temperature for 24 h, the ^{1}H NMR spectrum showed $(P^iPr_3)_2Os(NCCD_3)_3(H_2)^{2+}$. This product was stable for days in the acid-containing acetonitrile solution. ^{1}H NMR (acetonitrile-d_3, 200 MHz) δ 2.56 (m, 6 H), 1.31 (apparent q, 36 H), −9.63 (br, 2 H).

Oxidation of $(P^iPr_3)_2OsH_6$ (1) in Dichloromethane-d_2. $AcFc^+BF_4{}^-$ (5.7 mg, 0.018 mmol) was dissolved in dichloromethane-d_2 (0.5 mL) and added to solid **1** (10 mg, 0.019 mmol). The solution turned from dark blue to dark red immediately. The ^{1}H NMR (200 MHz) spectrum revealed $(P^iPr_3)_2OsH_7{}^+$ (**4**), **7**, and other trace products. ^{1}H NMR (**7**) δ −7.25 (br), 1.24 (app q, J = 7.5 Hz), 2.00 (m).

Reversible Protonation of $(P^iPr_3)_2OsH_6$ (1) in Dichloromethane-d_2. Compound **1** (10 mg, 0.019 mmol) was dissolved in dichloromethane-d_2 (0.5 mL) in an NMR tube. The solution was acidified with $HBF_4{\cdot}Et_2O$ (5.5 μL, 0.040 mmol). The ^{1}H NMR spectrum (200 MHz) revealed **4** as the only product. After addition of piperidine (6 μL, 0.060 mmol), the ^{1}H NMR spectrum showed 1 as the only Os-containing species.

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