Oxidation and Protonation of Transition Metal Hydrides: Role of an Added Base as Proton Shuttle and Nature of Protonated Water in Acetonitrile

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The Cp_2Fe^+ oxidation and the protonation of $CpMoH(CO)_2L$ (L: PPh_3, **1**; PMe_3, **2**) in MeCN have been investigated. In the dry solvent, the oxidation of both compounds consumes 1 mol of oxidant/mol of hydride with production of $[CpMo(CO)_2L(MeCN)]^+$ (L: PPh_3, [**3**]$^+$; PMe_3, [**4**]$^+$) and H_2. The stoichiometry changes toward the consumption of 2 mol of oxidant in the presence of excess water when the oxidizing equivalents are added rapidly, either chemically or electrochemically. However, 1 oxidizing equiv is again sufficient to consume the hydride material completely under conditions of slow oxidation. Under comparable conditions, the more basic **2** leads to a lower [ox]/M−H stoichiometry. Protonation of **1** and **2** with $HBF_4{\cdot}Et_2O$ in dry MeCN results in rapid H_2 evolution and formation of [**3**]$^+$ and [**4**]$^+$, respectively, whereas the presence of excess water suppresses the H_2 evolution and gives rise to protonated water. However, this process is followed by slow and irreversible delivery of the proton back to **1** or **2** to afford $[CpMoH_2(CO)_2L]^+$, which ultimately decomposes to [**3**]$^+$ or [**4**]$^+$ and H_2. The dihydride complex is too unstable to be isolated, even when the protonation of **1** or **2** is carried out in a noncoordinating solvent. The proton delivery is faster for the more basic **2** and slower for the less basic **1**. Thus, water operates as a "proton shuttle", whose speed depends on the basicity difference between the hydride complex and water. The identity of the protonated water in MeCN as $[H(H_2O)_3]^+$ is suggested by an independent ^{1}H-NMR experiment in CD_3CN.

Introduction

The oxidation of transition metal hydrides has received a great deal of attention because of the fundamental role that the metal−hydrogen bond plays in organometallic synthesis and catalysis[1] and because of the higher reactivity that odd-electron systems, e.g. 17-electron radicals obtained by oxidative processes, display with respect to their 18-electron counterparts.[2,3] It has been established that, following one-electron oxidation, the acidity of a metal hydride species is enhanced by some 20 orders of magnitudes; e.g., the pK_a decreases by a factor of ca. 20.[4] Therefore, provided a sufficiently good base is present, oxidation is usually followed by deprotonation to initiate the process of decomposition of the 17-electron product. In certain instances, the starting metal hydride complex is itself a sufficiently good base to deprotonate the oxidized hydride. The various possibilities for the first steps of the oxidation process are summarized in eqs 1−4 (ancillary ligands around the metal are

$$\text{M−H} - e^- \rightarrow [\text{M−H}]^{\bullet +} \qquad (1)$$

$$[\text{M−H}]^{\bullet +} + \text{B} \rightarrow \text{M}^\bullet + \text{BH}^+ \qquad (2a)$$

$$[\text{M−H}]^{\bullet +} + \text{M−H} \rightarrow \text{M}^\bullet + [\text{MH}_2]^+ \qquad (2b)$$

$$\text{M}^\bullet + \text{S} \rightarrow \text{M(S)}^\bullet \qquad (3)$$

$$\text{M(S)}^\bullet - e^- \rightarrow [\text{M(S)}]^+ \qquad (4)$$

omitted for generality). Following deprotonation, the resulting 17-electron M$^\bullet$ radical is trapped by a donor solvent molecule S and further oxidized to afford an 18-electron $[M(S)]^+$ species.[4] The products of this decomposition process, e.g. $[M(S)]^+$ and $[MH_2]^+$, can either be stable or further decompose to other products.

The main difference caused by the nature of the deprotonating agent (external base, eq 2a, or unreacted metal hydride, eq 2b) affects the number of moles of oxidizing agent consumed in the process: 1 faraday/mol of hydride if M−H is the proton trap (eq 5) or 2 faradays/mol of M−H if the proton is captured by an external base (eq 6).

$$2\text{M−H} + \text{S} - 2e^- \rightarrow [\text{M(S)}]^+ + [\text{MH}_2]^+ \qquad (5)$$

$$\text{M−H} + \text{S} + \text{B} - 2e^- \rightarrow [\text{M(S)}]^+ + \text{BH}^+ \qquad (6)$$

The nature of the reaction products differs in the two cases. However, the dihydride product of eq 5 may or may not be stable toward reductive elimination of H_2 (eq 7) and production of more $[M(S)]^+$, resulting in the oxidation stoichiometry of eq 8. This possibility has precedent, for instance, for the oxidation

$$[\text{MH}_2]^+ + \text{S} \rightarrow [\text{M(S)}]^+ + \text{H}_2 \qquad (7)$$

$$2\text{M−H} + 2\text{S} - 2e^- \rightarrow 2[\text{M(S)}]^+ + \text{H}_2 \qquad (8)$$

of $RhH(dppe)_2$, giving $[Rh(dppe)_2]^+$ and H_2, whereas the corresponding iridium derivative gives a 1:1 mixture of $[Ir(dppe)_2]^+$ and $[IrH_2(dppe)_2]^+$.[5] Therefore, when H_2 is reductively eliminated, the metal-containing product for both the 2 faraday/mol process (deprotonation by external base, eq 6) and the 1 faraday/mol process (deprotonation by M−H starting material, eq 8) is the same; the only difference between the

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two pathways is the final oxidation state of the hydrogen atom: H^+ in one case and H_2 in the other.

There are various reports on the oxidative chemistry of four-legged piano stool Mo(II) and analogous W(II) hydrides under a variety of experimental conditions (e.g. chemical vs electrochemical oxidation; with or without a strong base as proton acceptor), but the observed results and especially their interpretations are not always completely convincing. Kochi *et al.* reported that $CpMoH(CO)_3$ is oxidized in MeCN at a Pt electrode to consume 1.08 ± 0.05 electrons per molybdenum atom, producing $[CpMo(CO)_3]_2$.[6] However, Tilset *et al.* reported later that, under apparently identical conditions, electrolysis of $CpMoH(CO)_3$ required 2.1 ± 0.1 faradays/mol to produce a solution of $[CpMo(CO)_3(MeCN)]^+$ (*cf.* the stoichiometry of eq 6).[4] Since this experiment was carried out without added strong base, the proton is believed to be captured by the "medium", this being the solvent, or PF_6^- from the supporting electrolyte, or residual traces of water. Chemical oxidation with $Fe(phen)_3^{3+}$ (2 equiv) also produced $[CpMo(CO)_3(MeCN)]^+$ and gave evidence (^{1}H-NMR) for production of a strong acid, characterized by a broad resonance at δ 10.5.[4] The compound $CpWH(CO)_3$ behaves identically to its Mo counterpart, whereas the oxidation of $CpWH(CO)_2(PMe_3)$ gave different results depending on conditions: with Fc^+ salts ($Fc^+ = Cp_2Fe^+$, ferrocenium) as the oxidant in MeCN, a 1:1 mixture of $[CpW(CO)_2(PMe_3)(MeCN)]^+$ and $[CpW(CO)_2(PMe_3)H_2]^+$ was obtained (*cf.* eq 5), whereas in the presence of excess 2,6-lutidine, the MeCN complex was the sole W product with consumption of 2 mol of oxidant (*cf.* eq 6). At a Pt anode and in the absence of added base, however, 2 faradays/mol was consumed to produce once again the MeCN complex. This unexpected change of stoichiometry from chemical to electrochemical oxidation (both carried out without strong base) was tentatively attributed to the greater basicity of the "medium" in the electrochemical experiment; i.e., the tungsten starting complex is the only available proton acceptor in the dry MeCN used for the chemical oxidation, whereas traces of another base, presumably water, unavoidably introduced with the supporting electrolyte, would serve as the proton scavenger during the electrochemical experiment. The oxidation of $CpMoH(CO)_2(PPh_3)$, **1**, was also investigated chemically and electrochemically.[7] The stoichiometry is that of eq 6 when Fc^+ in MeCN is used as the oxidant in the presence of 2,6-lutidine, to produce $[CpMo(CO)_2(PPh_3)(MeCN)]^+$, and the same stoichiometry is found for the anodic oxidation at a Pt electrode in MeCN (1.94 ± 0.08 faraday/mol). A chemical oxidation in a *dry* medium and without added strong base has not been reported for this compound.

There are questions that still do not have an answer from the above studies: although the basicity of the "medium" has been invoked to explain a host of different observations, especially the coulometric results, and it has been hinted that water may be the responsible player,[4] more detailed studies of the "medium" basicity, specifically concerning the product distribution and oxidation stoichiometry as a function of the water concentration, have not been reported. This contribution addresses just this question on the basis of a comparative study of the chemical and electrochemical oxidation of the compounds $CpMoH(CO)_2L$ (L: PPh_3, **1**; PMe_3, **2**) and their protonation by $HBF_4 \cdot Et_2O$ with or without added water. It will be shown that water is indeed the important player for the above systems and for many of those previously reported in the literature. The results that we have obtained show how water (or any other base for that matter) can be expected to regulate the stoichiometric outcome of a metal hydride oxidation process under a general set of conditions.

Experimental Section

Materials. All operations were carried out under an atmosphere of argon using standard glovebox and Schlenk-line techniques. Solvents were dehydrated by standard methods (toluene and *n*-heptane from Na; THF and Et_2O from Na/K/benzophenone; MeCN from CaH_2), deoxygenated, and distilled directly from the dehydrating agent under dinitrogen prior to use. The amount of residual water in the solvents was assessed by titration with a coulomatic Karl Fischer titrimeter (Fisher Scientific). $CpMoH(CO)_3$,[8] $CpMoH(CO)_2(PPh_3)$ (**1**),[9] and $CpMoH(CO)_2(PMe_3)$ (**2**)[10] were prepared as previously described.

Spectroscopic and Electrochemical Analyses. Samples for ^{1}H-, $^{31}P\{^1H\}$-, and $^{19}F\{^1H\}$-NMR in thin-walled 5 mm glass tubes were measured on Bruker WP200 and XL400 spectrometers. The ^{1}H-NMR spectra were calibrated against the residual proton signal of the deuterated solvents. The ^{31}P- and ^{19}F-NMR spectra were calibrated against 85% H_3PO_4 and trifluoroacetic acid, respectively, in capillary tubes which were placed in a different 5 mm glass tube, containing the same deuterated solvent used for the measurement. Cyclic voltammograms were recorded with an EG&G 362 potentiostat connected to a Macintosh computer through MacLab hardware/software; the electrochemical cell was a locally modified Schlenk tube with a Pt counter electrode sealed through uranium glass/Pyrex glass seals. The cell was fitted with a Ag/AgCl reference electrode and a Pt (2 mm^2) working electrode. All potentials are reported vs the Fc/Fc^+ couple. Bulk electrolyses with coulometric analyses were carried out in a locally designed double Schlenk cell with the two compartments being connected by a medium frit at the lower end and a pressure-equalizing open tube at the upper end. One compartment of the cell was fitted with a Pt or Au gauze working electrode and a Ag/AgCl reference electrode, while the other compartment was fitted with a Pt counter electrode. For the coulometric experiments carried out on a thiol-coated Au electrode, the electrode was first cleaned by exposure to chromic acid and then to HF, followed by rinsing with water and immediate immersion into an ethanolic solution of $HO(CH_2)_nSH$ ($n = 2$ or 4) for ca. 3 h, according to the published procedure.[11] n-Bu_4NPF_6 (Aldrich) was used directly as received as the supporting electrolyte for all electrochemical experiments. Elemental analyses were performed by MHW Laboratories (Phoenix, AZ). The EPR spectroelectrochemical cell was a modified version of a cell described in the literature.[12] The modification consists of replacing the aqueous reference electrode with a silver wire pseudoreference electrode, in order to allow measurements at subfreezing temperatures. Measurements were carried out at the X-band microwave frequency on a Bruker ER 200 D spectrometer upgraded to ESP 300, equipped with a cylindrical ER/4103 TM 110 cavity. Solutions of the analyte (0.1−0.2 M) were electrolyzed by application of a constant current of 1 mA with an EG&G 362 galvanostat.

Preparation of $[CpMo(CO)_2(PMe_3)(MeCN)]^+PF_6^-$ ($[4]^+PF_6^-$) by Oxidation of 2 with $Fc^+PF_6^-$ in MeCN. To a yellow solution of **2** (90 mg; 0.31 mmol) in CD_3CN (3 mL) was added solid $Fc^+PF_6^-$ (104 mg; 0.306 mmol) in four portions (25, 25, 35, and 19 mg) over a period of 20 min, causing an effervescence after each addition and a deepening in color (total $Fc^+PF_6^-$ added: 104 mg, 0.306 mmol). The solution was examined by NMR and IR spectroscopy after each addition of $Fc^+PF_6^-$, showing the clean formation of Fc (^{1}H NMR δ 4.14) and a single product [^{1}H-NMR δ 5.62 (d, 5H, $J_{HP} = 0.6$ Hz, Cp), 1.59 (d, $J_{HP} = 10.4$ Hz, 9H, PMe_3); $^{31}P\{^1H\}$-NMR δ 13.6 (s, PMe_3), −140.5

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(septet, J_{PF} = 707 Hz, PF_6^-); IR 1987, 1898 cm^{-1}], assigned to $[CpMo(CO)_2(PMe_3)(CD_3CN)]PF_6$ (*cis* isomer). The clear yellow-brown solution was evaporated to dryness, and the ferrocene was extracted with heptane (4 × 10 mL), leaving an ochre microcrystalline powder. Yield: 0.07 g (80%). Anal. Calcd for $C_{12}H_{14}D_3F_6MoNO_2P_2$: C, 29.89; H, 2.93; D, 1.24; N, 2.90. Found: C, 30.0; H, 4.0; N, 2.8.

An analogous reaction was carried out in regular acetonitrile: **2** (155 mg, 0.53 mmol) and $Fc^+PF_6^-$ (178 mg, 0.53 mmol) were added to 10 mL of CH_3CN. After 5 min of stirring at room temperature, the solution was evaporated to dryness and the residue washed with Et_2O. ^1H-NMR (CD_3CN, δ): 5.62 (d, 5H, J_{HP} = 0.5 Hz, Cp), 2.38 (d, 3H, J_{HP} = 2.6 Hz, MeCN), 1.59 (d, 9H, J_{HP} = 10.3 Hz, PMe_3). ^1H-NMR (CD_2Cl_2, δ): 5.57 (s, 5H, Cp), 2.48 (d, 3H, J_{HP} = 2.4 Hz, MeCN), 1.62 (d, 9H, J_{HP} = 10.0 Hz, PMe_3). $^{31}P\{^1H\}$-NMR (CD_2Cl_2, δ): 9.7. In CD_3CN, the resonance of coordinated MeCN decreased to ca. 10% of its intensity after 8 h at room temperature, and the resonance of free MeCN at δ 1.95 increased in intensity during the same time. Minor bands in both ^1H- and ^{31}P-NMR spectra are assigned to the *trans* isomer (< 10% with respect to the main isomer): ^1H-NMR (CD_2Cl_2, δ): 5.39 (d, J_{HP} = 2.4 Hz, Cp), 2.45 (s, MeCN), 1.65 (d, J_{PH} = 10.0 Hz, PMe_3). ^{31}P-NMR (CD_2Cl_2, δ): 17.3.

Generation of *trans*-[4]$^+$ and Its Transformation to the *cis* Isomer. To a yellow solution of **2** (12 mg; 0.041 mmol) in CD_3CN (3 mL), solid $Ph_3C^+BF_4^-$ (20 mg; 0.060 mmol) is added. The reaction immediately showed the formation of Ph_3CH [^1H NMR δ 7.2] and a single product [^1H-NMR δ 5.59 (s, 5H, Cp), 1.62 (d, J_{HP} = 10.3 Hz, 9H, PMe_3); IR 1992, 1905 cm^{-1}], assigned to *trans*-$[CpMo(CO)_2(PMe_3)(CD_3CN)]BF_4$; a second product accumulated with time [^1H-NMR δ 5.63 (d, J_{HP} = 0.5 Hz, 5H, Cp), 1.61 (d, J_{HP} = 10.4 Hz, 9H, PMe_3); IR 1988, 1900 cm^{-1}] assigned to *cis*-$[CpMo(CO)_2(PMe_3)(CD_3CN)]BF_4$.

^1H-NMR Study of the Reaction between $CpMoH(CO)_2(PMe_3)$ and Fc^+. (a) In CD_3CN with *n*-Bu_4NPF_6. Compound **2** (24 mg, 0.082 mmol) and *n*-Bu_4NPF_6 (69 mg, 0.18 mmol) were introduced into a Schlenk tube and dissolved in CD_3CN (1 mL), and the resulting mixture was transferred to the NMR tube. In a separate Schlenk tube, a solution of $FcPF_6$ (63 mg, 0.19 mmol) in 0.38 mL of CD_3CN was prepared. Aliquots of the $FcPF_6$ solution (50, 50, 20, and 30 μL; total 0.077 mmol) were added to the solution of **1**. The reaction was monitored by ^1H-NMR. After each addition, the characteristic blue color of Fc^+ immediately disappeared, producing vigorous gas evolution. At this point, ^1H-NMR showed the almost complete disappearance (<5% left) of the resonance at δ 5.2 (Cp resonance of starting compound **2**). The spectrum of the resulting orange solution showed resonances corresponding to those described above for [**4**]$^+$ (*vide supra*), the ferrocene resonance at δ 4.1, and an additional resonance at δ 4.5 due to H_2.

(b) In the Presence of 2,6-Lutidine. The same experiment as described above was repeated with the only difference that 2,6-lutidine (0.072 mmol vs 0.061 mmol of **2** and 0.12 mmol of *n*-Bu_4NPF_6) was also present in the initial solution (1 mL). In this case, no gas evolution was observed. After the addition of 1.7 oxidizing equiv of Fc^+, the ^1H-NMR spectrum showed the almost complete replacement of the resonance at δ 5.2 (due to **2**) with a resonance at δ 5.6 (due to [**4**]$^+$). The amount of residual **2** at this point, by integration of the Cp ^1H-NMR resonances) is estimated as 10 ± 5% of the initial amount. The growth of an additional broad resonance was also observed, whose chemical shift changed as a function of the amount of added Fc^+ solution: δ 3.65, 4.45, 5.10, and 5.60 after the addition of 0.40, 0.80, 1.25, and 1.70 mol of Fc^+/mol of **2**, respectively.

(c) In the Presence of Water: Slow Addition. A stock solution was prepared in a Schlenk tube by dissolving compound **2** (31 mg, 0.10 mmol) in CD_3CN (3.8 mL). A 0.4 mL aliquot (0.011 mol of **2**) was transferred to an NMR tube, and water (1.6 μL, 0.077 mmol) was added. In a separate NMR tube, a solution of $FcPF_6$ (4.2 mg, 0.013 mmol) in 0.12 mL of CD_3CN was prepared. Aliquots of the $FcPF_6$ solution (24, 25, 25, 25, and 6 μL; total 0.0114 mmol) were added to the solution of **1** at 20 min intervals, and the reaction was monitored by ^1H-NMR on aliquots of the solution. After each addition, the characteristic blue color of Fc^+ immediately disappeared and no gas evolution was observed. After the addition of 0.0114 mmol of Fc^+ (1.7 oxidizing equiv), the resonance at δ 5.2 of **2** had been completely replaced by the resonance at δ 5.6 of [**4**]$^+$.

(d) In the Presence of Water: Fast Titration. Compound **2** (7.5 mg, 0.026 mmol) was dissolved in MeCN (330 μL), and water (5.5 μL, 0.31 mmol) was added. In a separate Schlenk tube, $FcPF_6$ (33.3 mg, 0.101 mmol) was dissolved in MeCN (0.90 mL). Aliquots of the ferrocenium solution were added to the solution of **2** via microsyringe. A first addition of 0.43 mL (1.9 equiv) resulted in the complete bleaching of the ferrocenium blue color within 30 s, without any noticeable gas evolution, while the yellow color of the initial solution of **2** was now orange. An additional 40 μL addition (total 2.1 equiv) did not lead to discoloration of the ferrocenium solution. The overall addition was complete in less than 5 min.

^1H-NMR Study of the Reaction between $CpMoH(CO)_2(PPh_3)$ and Fc^+. Compound **1** (9.2 mg, 0.019 mmol) and *n*-Bu_4NPF_6 (78 mg, 0.20 mmol) were introduced into a Schlenk tube and dissolved in CD_3CN (0.4 mL). To this solution was added H_2O (1 μL, 0.06 mmol), and the resulting mixture was transferred to the NMR tube. In a separate Schlenk tube, a solution of $FcPF_6$ (24 mg, 0.072 mmol) in 0.38 mL of CD_3CN was prepared. Aliquots of the $FcPF_6$ solution (50, 50, and 20 μL; total 0.023 mmol) were added to the NMR tube at 30 min intervals. The reaction was monitored by ^1H-NMR. After each addition, the characteristic blue color of Fc^+ slowly disappeared ($t_{1/2}$ ca. 5 min) and the ^1H-NMR spectrum showed a broad ferrocene resonance, which sharpened as the blue color disappeared. After 30 min from each addition, a sharp Fc resonance at δ 4.1 was again observed. At this point, ^1H-NMR showed the presence of residual resonances of compound **1** (<20%) and the resonances corresponding to those already described[7] for [**3**]$^+$ (>80%).

Protonation of 2 with HBF_4. (a) In Acetonitrile by HBF_4/H_2O. **2** (35 mg, 0.11 mmol) was dissolved in MeCN (3 mL). To the resulting pale yellow solution was added HBF_4 (48% in H_2O, 25 μL, 0.19 mmol). A smooth change of color to darker orange and gas evolution were observed. After 1 h of stirring at room temperature, the IR of the solution in the CO stretching region showed the complete conversion to *cis*-[**4**]$^+$ (1987 and 1897 cm^{-1}).

(b) In Acetonitrile by HBF_4/Et_2O. This reaction was carried out as described above in part a, except that $HBF_4 \cdot Et_2O$ was used in place of aqueous HBF_4. The final result was identical, but the gas evolution and the conversion to *cis*-[**4**]$^+$ were instantaneous. This reaction was also monitored by ^1H-NMR in CD_3CN under a variety of conditions (see Results and Discussion).

(c) In Diethyl Ether. Addition of $HBF_4 \cdot Et_2O$ (48 μL, 0.36 mmol of HBF_4) to a stirring solution of **2** (105 mg, 0.357 mmol) in Et_2O (15 mL) that had been precooled to −78 °C resulted in vigorous gas evolution and formation of a brick-red precipitate. After $^1/_2$ h of stirring at −78 °C, the solution was decanted and the solid was washed with ether and dried under vacuum. Yield: 98 mg. The ^1H- and ^{31}P-NMR spectra of this solid indicate the presence of three major products, none of which correspond to the species generated in situ in acetonitrile. ^1H NMR (δ, CD_3CN): 5.45 (s, Cp), 5.31 (d, J_{HP} = 1.8 Hz, Cp), 5.29 (d, J_{HP} = 2.0 Hz, Cp), 1.69 (d, J_{HP} = 10.2 Hz, PMe_3), 1.66 (d, J_{HP} = 10.2 Hz, PMe_3), 1.64 (d, J_{HP} = 10.2 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (δ, CD_3CN): 42.0, 24.4, 13.6. ^{19}F-NMR (δ, CD_3COCD_3): 72.8 ($w_{1/2}$ = 12 Hz, weak), 73.9 ($w_{1/2}$ = 72 Hz, strong). Recrystallization of the red solid from CH_2Cl_2/heptane produced X-ray-quality crystals of $[CpMo(CO)_3(PMe_3)][BF_4]$.

A brick-red precipitate with similar spectroscopic properties was also obtained by carrying out a similar procedure in heptane solvent.

Protonation of 1 with $HBF_4 \cdot Et_2O$ in *n*-Heptane. By a procedure identical with that described above for compound **2**, treatment of **1** with the stoichiometric amount of $HBF_4 \cdot Et_2O$ in *n*-heptane at −78 °C afforded a brick-red precipitate, which was not further investigated.

^1H-NMR Study of the Protonation of H_2O in CD_3CN. A 0.46 mL sample of CD_3CN was introduced in the NMR tube, and water (19 μL, 1.05 mmol) was added. To this solution was added $HBF_4 \cdot OEt_2$ in small aliquots via a microsirynge, and the protonation process was monitored by ^1H-NMR.

Results and Discussion

(a) Electrochemical Studies. The cyclic voltammetric behavior of $CpMoH(CO)_3$ and **1** has already been reported in the literature, both compounds being oxidized irreversibly in

MeCN. The peak potential for the anodic oxidation wave of $CpMoH(CO)_3$ has been reported by two different groups as +0.05 V[6] and +0.800 V[4] vs Fc/Fc^+. Our own measurements of this process seem closer to the pattern reported by Tilset and co-workers,[4] with an irreversible oxidation wave with $E_{p,a}$ = 0.54 V and a second irreversible oxidation wave (assigned[4] to the oxidation of the $[CpMo(CO)_3(MeCN)]^+$ product), with $E_{p,a}$ = 1.11 V. However, we could not obtain reproducible results from the coulometric experiments. We attribute this behavior to the known process[13] of reductive elimination of CpH from $CpMoH(CO)_3$ in MeCN to produce $Mo(CO)_3(MeCN)_3$ and CpH and to the subsequent oxidation of these and possibly also other intermediate products. The half-life of $CpMoH(CO)_3$ in MeCN at 37.5 °C is reported as less than 30 min.[13] Although this decomposition process is not necessarily the reason for the discrepancy between the two earlier reports,[4,6] it was a sufficient deterrent for us to continue the investigation of the oxidative process of $CpMoH(CO)_3$ in acetonitrile and we subsequently focused uniquely on the phosphine-substituted materials.

Control experiments revealed that both **1** and **2** are stable in MeCN with no observable decomposition within 3 days at room temperature. The irreversible oxidation of compound **1** on the Pt electrode has an anodic peak potential of +0.23 V by direct calibration against the oxidation of ferrocene, in good agreement with the potential of +0.26 V reported earlier and calculated on the basis of the measured potential of +0.35 V with respect to the Ag/Ag^+ reference electrode.[7] The decrease in potential upon going from $CpMoH(CO)_3$ to **1** is as expected, given the greater donor and/or lower acceptor ability of the phosphine ligand with respect to CO. The cyclic voltammogram of **2** on Pt also shows an irreversible oxidation, even at −20 °C, the anodic peak potential being found at +0.19 V with respect to ferrocene. The first oxidation wave of **2** is followed, at more positive potentials in the anodic scan, by a second irreversible oxidation wave with $E_{p,a}$ = 0.62 V, which is assigned to the oxidation of $[CpMo(CO)_2(PMe_3)(MeCN)]^+$ ([**4**]$^+$) produced by the first oxidation process (*vide infra*) and compares with the analogous process observed at $E_{p,a}$ = 0.72 V for the cyclic voltammogram of **1**.[7] Therefore, the better donor ligand PMe_3 further increases the susceptibility of the system toward oxidation. Similar trends have been observed before for other systems, for instance CpRuHLL′ (L, L′ = CO, tertiary phosphine)[14−17] and Cp* analogues[18] and for a variety of octahedral d^6 dinitrogen and η^2-dihydrogen complexes.[19]

Constant-current bulk oxidation in THF at −80 °C in an EPR spectroelectrochemical cell did not lead to the detection of any transient EPR-active species for either **1** or **2**. Given our instrument sensitivity and our experimental conditions (see Experimental Section), assuming that the one-electron oxidation products [**1**]$^+$ and [**2**]$^+$ are produced at the electrode, an upper limit of 10^{-2} s is estimated for their half-life at −80 °C.

A bulk electrochemical oxidation of **2** in MeCN was carried out at a Pt anode at a constant potential of +0.11 V with respect to the anodic peak potential of the hydride complex (+0.30 V with respect to Fc/Fc^+). The electrolysis was considered complete when the average current during the last data storage time interval dropped to less than 1% of the first time interval average current (<1/2 h). Integration of the current vs time curve gave a consumption of 1.9 ± 0.2 faradays/mol. At the end of the coulometric experiment, a Karl Fischer titration of the solution water content revealed $[H_2O]$ = 47 mM, which is a large excess with respect to the molybdenum hydride complex ([**2**] = ca. 4.2 mM), but still a small amount with respect to the concentration of supporting electrolyte (>0.1 M). The same experiment carried out on a known amount of ferrocene under identical experimental conditions gave a consumption of 1.03 ± 0.03 faradays/mol. The greater uncertainty on the coulometric result for the oxidation of **2** is related to the greater difficulty in weighing the air-sensitive hydride complex. An analogous coulometric experiment on **1** under identical conditions was reported by Smith and Tilset to afford a similar result (1.94 ± 0.08 faradays/mol of charge consumption).[7]

(b) Chemical Oxidation Studies of $CpMoH(CO)_2(PPh_3)$ in the Presence and Absence of Water and *n*-Bu_4NPF_6. As mentioned in the Introduction, the oxidation of **1** by the ferrocenium ion had been previously investigated only in the presence of a strong base (2,6-lutidine), which acts as the proton acceptor and forces the system to require 2 mol of oxidizing agent/mol of **1** according to the stoichiometry of eq 6.[7] Two faradays per mole was also required for the electrochemical oxidation in MeCN at a Pt electrode, and this was attributed to a proton transfer to the medium. We have repeated the ferrocenium oxidation experiment without strong base *but with the deliberate addition of n-Bu_4NPF_6 and water*, conditions that are meant to mimic those of the previously reported[7] electrochemical oxidation experiment. The reaction was carried out directly in MeCN-d_3 by stepwise additions of substoichiometric amounts of a solution of $FcPF_6$ in MeCN-d_3 and was monitored by ^{1}H-NMR spectroscopy. A slow reaction took place after the addition of each aliquot of $FcPF_6$, as visually indicated by the slow bleaching ($t_{1/2} \approx$ 5 min) of the characteristic deep blue color of the ferrocenium salt. The slow rate of this electron transfer process is due to the substantially positive potential necessary for the oxidation of **1** (+0.23 V with respect to the reversible wave of the Fc/Fc^+ couple). However, the start of the anodic wave upswing occurs at a potential slightly negative of the ferrocene standard and the oxidation wave is irreversible because complex [**1**]$^+$ decomposes immediately after its generation (*vide supra*); therefore an oxidation reaction eventually does take place. This experiment showed that less than 20% of starting material was left in solution after addition of 1.2 mol of Fc^+/mol of **1** (thus the complete oxidation of **1** would require between 1.4 and 1.6 equiv of Fc^+, i.e. significantly less than 2 equiv). The only Mo product observed at the end of the reaction is the acetonitrile adduct $[CpMo(CO)_2(PPh_3)(MeCN\text{-}d_3)]^+$, [**3**-$d_3$]$^+$. It therefore seems that, under these conditions, the reaction has a mixed stoichiometry, part of oxidation proceeding as in eq 6 and part as in eq 8, implying the involvement of H_2 evolution. Because of the exceedingly slow oxidation rate (see above), a noticeable gas evolution was not observed for this reaction.[20]

In conclusion, as for the oxidation of $CpWH(CO)_2(PMe_3)$ reported earlier,[4] we find that the oxidation stoichiometry for **1** changes from the electrochemical experiment (2 faradays/mol)[7] to the chemical experiment. However, our result appears puzzling because our chemical oxidation was carried out under "wet" and "ionic strength" conditions that simulated the

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(20) Professor M. Tilset has informed us that the consumption of 1 mol of oxidant/mol of **1** in MeCN was also measured in his laboratory, with observation of H_2 by ^{1}H-NMR.

conditions of the electrochemical experiment. Thus, *it may seem* that the basicity of the "medium" is comparable with that of the neutral hydride **1** under our chemical oxidation conditions, whereas the "medium" appears more basic under the electrochemical conditions previously described.[7,21] These apparently contrasting observations are reconciled and fully rationalized on the basis of the protonation experiments that will be described in section d.

(c) Chemical Oxidation Studies of $CpMoH(CO)_2(PMe_3)$ in the Presence and Absence of Water and *n*-Bu_4NPF_6 or 2,6-Lutidine. The oxidation of **2** by $FcPF_6$ proceeds at a faster rate (essentially instantaneous upon mixing the reagents) with respect to the oxidation of the corresponding PPh_3 complex, in agreement with the measured lower potential for the oxidation of this compound. The oxidation product, the salt $[\mathbf{4}]^+PF_6^-$, was isolated and characterized by ^{1}H- and ^{31}H-NMR and by elemental analysis. By analogy with the similar, previously reported $[\mathbf{3}]^+$ and $[CpW(CO)_2(PMe_3)(MeCN)]^+$ complexes,[4,7] complex $[\mathbf{4}]^+$ exists in solution as an equilibrium mixture of *cis* and *trans* isomers, with the *cis* isomer being the prevalent one. The oxidation of **2** leads directly to the equilibrium mixture of *cis*- and *trans*-$[\mathbf{4}]^+$, while generation of this system by hydride abstraction from **2** (reaction with $Ph_3C^+BF_4^-$ in MeCN) leads selectively to the *trans* isomer as the kinetically controlled product. A kinetic study of this hydride abstraction reaction was recently reported.[22] Once formed, the *trans* complex slowly isomerizes ($t_{1/2} \approx 2$ days) to the thermodynamically preferred *cis* isomer. This behavior is identical to that previously reported for $[\mathbf{3}]^+$ and for $[CpW(CO)_2(PMe_3)(MeCN)]^+$, and a rationalization for such behavior has previously been given.[4,7] Monitoring of a CD_3CN solution of $[\mathbf{4}]^+$ at room temperature shows a smooth MeCN exchange reaction ($t_{1/2} \approx 2.5$ h) forming $[\mathbf{4}\text{-}d_3]^+$ and free MeCN.

The stepwise oxidation of **2** was carried out and monitored by ^{1}H-NMR spectroscopy in MeCN-d_3 as described above for the PPh_3 analogue. In dry CD_3CN, each subsequent addition of the oxidizing agent produced an immediate quenching of the blue ferrocenium color and caused a *vigorous gas evolution*, up to the addition of *1 mol* of oxidant/mol of **2**. Correspondingly, the resonances of the starting material decreased while the resonances of *cis*-$[\mathbf{4}]^+$ and ferrocene increased. After the addition of 1 mol/mol of oxidant, the starting material was completely consumed. This shows that **2** acts as the proton acceptor for the intermediate, proton donor $[\mathbf{2}]^+$, in the dry CD_3CN solvent (eq 8). The consumption of only 1 equiv of oxidant has precedent in the literature for the ferrocenium oxidation of $CpWH(CO)_2(PMe_3)$,[4] $CpRuH(PPh_3)_2$,[16] and $Cp^*RuH_3(PPh_3)$[23] and for the acetylferrocenium oxidation of $OsH_6(PPr^i_3)_2$.[24] The 1:1 stoichiometry does not change when the experiment is repeated in the presence of *n*-Bu_4NPF_6 *but without the deliberate addition of water*. In this experiment, ca. 2 mol of the salt/mol of the hydride was used; thus the amount of any adventitious water introduced by the salt must be negligibly small (see section a above). A sharp resonance at δ 4.5 is also observed in the ^{1}H-NMR spectrum and is assigned to H_2, on the basis of a control ^{1}H-NMR spectrum of a CD_3CN solution recorded before and after an H_2 purge.

When the oxidation of **2** with Fc^+ in CD_3CN is carried out in the presence of a slight excess of 2,6-lutidine, however, there is no gas evolution, and a stoichiometry of 2 mol of Fc^+/mol of **2** is indicated by the ^{1}H-NMR experiment. A broad resonance also builds up as the reaction progresses, this being attributed to the 2,6-lutidinium acidic proton. Its position (see Experimental Section) changes with amount of lutidinium formed, presumably because of rapid self-exchange with the excess of unprotonated 2,6-lutidine.

The oxidation−titration with ^{1}H-NMR monitoring was also carried out in the presence of a large excess (ca. 10-fold) of water, the stepwise addition of aliquots of oxidant being carried out over a time span of 1.5 h. Gas evolution after the addition of each aliquot of ferrocenium solution was hardly noticeable in this case, and ca. 1.7 mol of Fc^+/mol of **2** was required to consume **2** completely. Finally, 1.9 mol of the ferrocenium oxidant was added *at one time* to 1 mol of **2** and in the presence of 10 mol of water, resulting in the *complete consumption of the oxidant* and no noticeable gas evolution.

In conclusion, the electrolyte *n*-Bu_4PF_6 is shown to have no effect in the chemical oxidation of **2** in MeCN, whereas water has a marked effect, but the number of oxidizing equivalents needed to consume the starting material depends not only on the presence or absence of water but also on the rate at which the oxidant is added to the hydride solution. For the stronger base lutidine, however, 2 mol of oxidant/mol of hydride is needed even under the same slow-addition conditions where the presence of water requires a smaller amount of oxidizing agent. Since the problem appears to lie in the competition between hydride **1** or **2** and water as bases, we next sought a deeper insight into these proton transfer processes by studying the protonation of the $\mathbf{1}/H_2O/CD_3CN$ and $\mathbf{2}/H_2O/CD_3CN$ systems by the strong acid $HBF_4{\cdot}Et_2O$ (see section d).

Before we proceed to illustrate and discuss the results of the protonation experiments, however, it is interesting to consider the susceptibility of the oxidized hydride complexes $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ to deprotonation. It has been shown that the pK_a of transition metal hydrides decreases by ca. 20 units upon oxidation, and the pK_a of $[CpMoH(CO)_3]^+$ has been estimated as ca. −6.0 in MeCN.[4] The pK_a of $[\mathbf{2}]^+$ has not been reported to the best of our knowledge, but it has been shown that a pK_a increase of 8.1 units occurs on going from $[CpWH(CO)_3]^+$ to $[CpWH(CO)_2(PMe_3)]^+$.[4] Assuming no dependence of this difference on the nature of the metal, a pK_a value of ca. +2 is estimated for $[\mathbf{2}]^+$. The pK_a of $[\mathbf{1}]^+$ is probably lower, given the lower donor/higher acceptor strength of PPh_3 with respect to PMe_3. These values are slightly lower than the pK_a reported for the hydrated proton, H_3O^+, in MeCN (2.2−2.5),[25] i.e., water has sufficient basic strength to deprotonate $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$. In addition, the high formation constants of $[H(H_2O)_n]^+$ ($n = 2-4$; $\log K_f = 3.9-5.3$)[25] effectively make water an even stronger base.

(d) Protonation Studies of $CpMoH(CO)_2L$ ($L = PPh_3$, PMe_3). When either **1** or **2** was protonated in dry MeCN with the stoichiometric amount of $HBF_4{\cdot}Et_2O$, immediate and vigorous gas evolution was observed and the color of the solution changed distinctly from yellow to orange. The only reaction product observed by IR and ^{1}H-NMR spectroscopies was $[\mathbf{3}]^+$ or $[\mathbf{4}]^+$, respectively. This result confirms that a proton transfer from the strong acid $[\mathbf{1}]^+$ to **1** (or $[\mathbf{2}]^+$ to **2**) would result in H_2

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[21] A more recent remeasurement of the coulometric oxidation of **1** in Professor Tilset's laboratory gives 1.67 ± 0.09 faradays/mol (average of five experiments). The electrolyte was dried by passing it through active alumina, i.e. the same treatment described in the previous work where the consumption of 1.94 ± 0.08 faradays/mol was reported.[7] Also, under the same conditions, a coulometric measurement of the oxidation of **2** gives the consumption of 1.25 ± 0.05 faradays/mol (average of four experiments). We are grateful to Professor Tilset for sharing these results with us.

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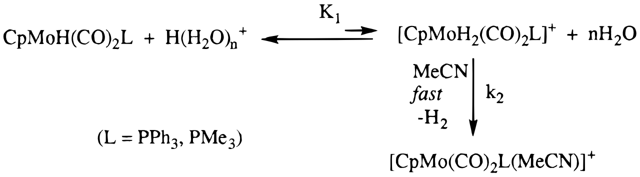
evolution, as observed in the oxidation experiment described above. Thus, the product of protonation, $[CpMoH_2(CO)_2L]^+$ (L = PPh_3, PMe_3), is unstable in MeCN and decomposes immediately via replacement of H_2 by a solvent molecule. This behavior prevents us from obtaining quantitative information on the thermodynamic basicity of **1** and **2** in MeCN relative to that of water. We have attempted to obtain such information in other, less coordinating solvents. Jia and Morris have shown that the thermodynamics of protonation of the compounds Cp*RuH(L-L) (L-L = chelating diphosphine) can conveniently be studied in CH_2Cl_2 or THF, whereas H_2 evolution occurs in MeCN.[26] However, we find that treatment of **1** or **2** with $HBF_4{\cdot}Et_2O$ in either ether, toluene, or even heptane at −78 °C always results in vigorous gas evolution and formation of a red precipitate. For the reaction of **2**, the red solid has been identified as a mixture of $[CpMo(CO)_3(PMe_3)][BF_4]$, $CpMo(CO)_2(PMe_3)FBF_3$, and other unknown species. The tricarbonyl complex was isolated in the form of single crystals from CH_2Cl_2/heptane and was characterized by an X-ray analysis.[27] The presence of $CpMo(CO)_2(PMe_3)FBF_3$ is suggested by the presence of two ^{19}F-NMR resonances at δ −72.8 and −73.9 in acetone-d_6 (the resonance of free BF_4^- is observed at δ −74.5 under the same conditions). Similar compounds, e.g. $CpMo(CO)_2(PR_3)FBF_3$ (R = Ph, OPh, Et), were described by Beck *et al.* as the products of the reaction between $CpMoH(CO)_2(PR_3)$ and $Ph_3C^+BF_4^-$, and their thermal decomposition to $[CpMo(CO)_3(PR_3)]^+$ was described.[28] It is to be remarked that, mechanistically, the interactions of H^+ and Ph_3C^+ with the hydride complex are expected to be identical, involving attack of the electrophilic reagent on the hydride ligand, formation of a presumed σ-complex intermediate, and elimination of the formal product of hydride abstraction, H_2 in one case and Ph_3CH in the other. In conclusion, complexes $[CpMoH_2(CO)_2(PR_3)]^+$ are too unstable and lose H_2 even upon the action of a nucleophile as weak as the BF_4^- counterion in noncoordinating solvents.

The instability of $[CpMoH_2(CO)_2L]^+$ contrasts with the stability of the corresponding tungsten−PMe_3 derivative, obtained as a coproduct from the corresponding oxidation of $CpWH(CO)_2(PMe_3)$ according to the stoichiometry of eq 5.[4] The stability of dihydride complexes versus reductive elimination and substitution of H_2 by MeCN recently attracted considerable attention. The susceptibility to this reaction is greatly increased by protonation; for instance, treatment of $MoH_4(PMe_2Ph)_4$, $ReH_7(PPh_3)_2$, $OsH_4(PMe_2Ph)_3$, $Cp^*RuH_3(PPh_3)$, and $OsH_6(PPr^i_3)_2$ with strong acids in MeCN affords $[MoH_2(PMe_2Ph)_4(MeCN)_2]^{2+}$,[29] $[ReH(PPh_3)_2(MeCN)_4]^{2+}$,[30] $[Os(PMe_2Ph)_3(MeCN)_3]^{2+}$,[31] $[Cp^*Ru(PPh_3)(MeCN)_2]^+$,[23] and $[OsH_3(MeCN)_2(PPr^i_3)_2]^+$,[24] respectively. It is has been shown that the process of dihydrogen reductive elimination from a classical dihydride complex proceeds through an intermediate nonclassical dihydrogen complex[32] and that the relative stability of classical vs nonclassical dihydrides depends on the metal electron density. Complexes with stronger π-acidic ligands have a greater tendency to adopt nonclassical structures with respect to analogous complexes with stronger donor ligands, and cationic complexes have a greater tendency to adopt nonclassical structure with respect to neutral ones.[33] It seems likely, therefore, that the $[CpMoH_2(CO)_2L]^+$ (L = PPh_3, PMe_3) complexes adopt a nonclassical structure which could be unstable toward H_2 substitution in the strongly coordinating MeCN solvent. Molybdenum complexes of this stoichiometry have not been isolated, to the best of our knowledge, whereas the tungsten analogue $[CpWH_2(CO)_2(PMe_3)]^+$ has been described and shown to have a classical structure.[4] The stability and structure of this complex are consistent with the greater π basicity of tungsten with respect to molybdenum.

Scheme 1



Coming back to the protonation studies in MeCN, when a large (25-fold) excess of water was introduced, protonation of the **1**/H_2O mixture resulted in *no gas evolution* and no change of color, whereas protonation of a **2**/H_2O mixture *did produce some effervescence, but at a much less vigorous rate*. Correspondingly, a dampened gas evolution resulted from the protonation of **2** in MeCN by aqueous HBF_4.

For the protonation of **1**/H_2O by $HBF_4{\cdot}Et_2O$, continued addition of small amounts of the acid to the solution of **1**/H_2O still failed to induce gas evolution initially, but the subsequent addition of a large amount of acid finally resulted in vigorous gas evolution and a color change from yellow to orange. Repeated experiments with different excess amounts of water showed that the amount of acid necessary to produce effervescence increased with the amount of water present in solution. Thus, only when water is fully protonated, does further addition of acid result in the direct protonation of **1**.

These results suggested to us a possible solution to the puzzling results of the chemical oxidations discussed in sections b and c. Water indeed competes effectively as a base with either **1** or **2** and will be protonated preferentially under the conditions utilized in our chemical and electrochemical experiments, but the basicity of **1** and **2** (especially the latter) is sufficiently high to allow an equilibrium formation of $[CpMoH_2(CO)_2L]^+$. Since formation of the latter species is followed by the *irreversible* loss of H_2, the reaction ultimately proceeds, under thermodynamic control, to the products that would be obtained by direct protonation of **1** or **2** (see Scheme 1). We can describe the function of water in this system as a “proton shuttle” between the strong acid ($HBF_4{\cdot}Et_2O$ in the protonation studies; $[\mathbf{1}]^+$ or $[\mathbf{2}]^+$ in the oxidation studies) and the hydride complex **1** or **2**.

To seek further evidence in support of this proposal, we monitored by ^{1}H-NMR the protonation of both **1**/H_2O and **2**/H_2O by $HBF_4{\cdot}Et_2O$ in CD_3CN. The results of the latter experiment are shown in Figure 1. The first spectrum (before addition of the acid) shows the resonance of water at ca. δ 2.15 and the relatively broad Cp resonance of **2** at ca. δ 5.2. The weak and broad resonance at ca. δ 3.6 is due to a THF impurity that was present in the starting complex **2**. Following the addition of the stoichiometric amount (with respect to **2**) of $HBF_4{\cdot}Et_2O$, we observe that, after 2 min, the water resonance is shifted to ca. δ 3.6, whereas the resonance of **2** is essentially unchanged. This demonstrates that water, not **2**, has been protonated. If **2**

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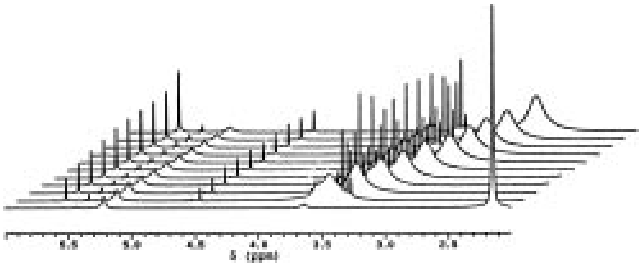


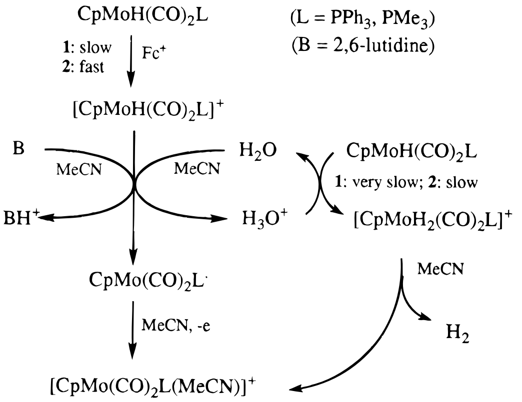
Figure 1. ^{1}H-NMR monitoring of the reaction of $HBF_4 \cdot Et_2O$ (12 μmol) with compound **2** (13 μmol) and H_2O (111 μmol) in CD_3CN (0.48 mL) at room temperature. The first spectrum was taken before the addition of $HBF_4 \cdot Et_2O$. Subsequent spectra were taken after 2, 4, 8, 13, 18, 23, 31, 38, 45, and 84 min.

were protonated, the resonance of **2** would disappear immediately, as demonstrated by the protonation experiment in dry MeCN discussed above. The shift of the water resonance is due to the rapid equilibrium, on the NMR time scale, between the protonated water, $[H(H_2O)_n]^+$, and residual H_2O (proton exchange reactions can approach the diffusion limit of reaction rates). The spectrum also shows the quartet resonance due to the methylene protons of Et_2O at δ 3.4. As the reaction progresses, the following features are observed: (a) the $[H(H_2O)_n]^+/H_2O$ resonance shifts progressively back toward the position of unprotonated H_2O; (b) the Cp resonance of **2** at δ 5.2 slowly decreases in intensity; (c) the Cp resonance of $[\mathbf{4}]^+$ at ca. δ 5.6 correspondingly increases in intensity (the sum of the intensities for the Cp resonances of **2** and $[\mathbf{4}]^+$ is constant); (d) a resonance at δ 4.5 due to dissolved H_2 progressively increases. The escape of H_2 into the head space after the initial phases of the reaction is the probable cause of the reduced rate of increase of the H_2 resonance with respect to the resonances of the other products after ca. 30 min. The variations of other resonances not shown in Figure 1 (e.g. the hydride resonance of **2**) are consistent with the above described trends. It is self-evident that all the above observations are consistent with, and further support, our proposed Scheme 1.

Given this proposed mechanism, the rate of disappearance of **2** should follow the rate law rate $= k_{\text{obs}}[\mathbf{2}][H(H_2O)_n]^+$, and from the initial rate of disappearance of **2** under the conditions utilized (see Figure 1), we calculate $k_{\text{obs}} = 0.02\ \text{s}^{-1}\ \text{M}^{-1}$. The same basic features shown in Figure 1 are also observed for the reaction of $HBF_4 \cdot Et_2O$ with a **1**/H_2O mixture in CD_3CN. The main difference between the two reactions is that the decay of **1**, formation of $[\mathbf{3}]^+$, formation of H_2, and shift of the water resonance are ca. 15 times *slower* than those for the corresponding reaction involving **2**. This phenomenon can be attributed to the expected lower basicity of **1** relative to **2**, again consistent with our proposed mechanism of Scheme 1. Independent studies on the nature of $[H(H_2O)_n]^+$ will be illustrated later in section h.

(e) Coulometric Oxidation of 2 at Thiol-Covered Au Anodes. Compound **2** was also electrolyzed at thiol-coated Au electrodes, with two different thicknesses for the self-assembled monolayer of $S(CH_2)_nOH$ groups (e.g. $n = 2$ and 4). The end-chain hydroxyl groups help establish a compact and crystalline monolayer. The effect of the electrode coating is to slow the kinetics of electron transfer, its rate dramatically decreasing with the number of methylene groups in the linear alkyl chain.[11] Consequently, the time necessary to carry out the electrolysis becomes longer. The rate of oxidation depends on several factors besides the thickness of the insulating hydroxy thiol monolayer, such as the electrode overpotential, the solution resistance, the rate of stirring, the electrode surface area, the concentration of residual, unoxidized hydride material, etc. All variables were kept identical in the two experiments, except the thickness of the monolayer.

Scheme 2



Whereas less than 30 min was usually sufficient to complete the electrolysis on the bare Pt electrode surface, ca. 1 h was required on the thiol ($n = 2$) coated electrode, and the process was not yet complete after 3 h of operation on the thiol ($n = 4$) coated electrode under otherwise identical experimental conditions. The measured charge consumptions were 1.7 ± 0.2 and 1.3 ± 0.2 farday/mol for the electrode covered with the $n = 2$ and $n = 4$ thiol, respectively (*cf.* with 1.9 ± 0.2 faradays/mol on the bare Pt electrode). When the experiment on the $n = 4$ thiol-coated Au electrode was interrupted (after 3 h of electrolysis), the resulting solution still had ca. 20% of unreacted **2** (by cyclic voltammetry). The accumulation of a gas bubble next to the septum which separates the two electrolytic compartments was noticed during the slow electrolysis on the $S(CH_2)_4OH$-coated Au electrode, which is believed to arise from H_2 evolved in the bulk. The results observed for these coulometric experiments are in perfect agreement with the proposed proton shuttle process of Scheme 1: the stoichiometry (amount of H_2 that evolves and number of faradays per mole of M−H) depends on the competition between the rates of consumption of the hydride material by the oxidation at the electrode and by the acidolysis in the bulk. As a matter of fact, the terminal OH groups of the ω-hydroxy thiols should in principle be more basic than water and could capture the protons of $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$. If this happens to a significant extent, however, the results of the experiments show that these basic centers can function as proton shuttles as water does.

(f) Mechanistic Considerations. The results of our oxidation studies are summarized and interpreted by the mechanism in Scheme 2, which is based on that proposed previously by Ryan, Tilset, and Parker,[4] with the addition of the proton shuttle action of an external base. Following the oxidation of **1** or **2** by $Fc^+PF_6^-$ in *dry* MeCN, the strongest available bases to deprotonate $[\mathbf{1}]^+$ or $[\mathbf{2}]^+$ are the starting materials themselves, ultimately affording $[\mathbf{3}]^+$ or $[\mathbf{4}]^+$ with evolution of H_2 according to the stoichiometry of eq 8. The proton transfer step affords the 17-electron $CpMo(CO)_2L^\bullet$ and the 18-electron $[CpMoH_2(CO)_2L]^+$ (L = PPh_3, PMe_3) intermediates, neither of which is stable. According to the previously established mechanism,[4] the 17-electron species coordinates MeCN and is further oxidized to the observed product (eqs 3 and 4), while the 18-electron dihydride complex evolves dihydrogen and coordinates MeCN to afford more of the observed $[\mathbf{3}]^+$ or $[\mathbf{4}]^+$ final product (eq 7).

For compound **1** or **2**, we have clearly demonstrated that neither MeCN nor the PF_6^- anion of n-Bu_4PF_6 competes with **2** as a base; thus the basicity of the "medium" in changing the oxidation stoichiometry can be solely attributed to the presence of water. Water is always introduced with the supporting electrolyte, and its concentration may be relatively large with respect to the analyte, given the large excess of electrolyte used in the typical experiments (see section a above). A reported method for the dehydration of electrolytic solutions is the passage through a column of activated neutral alumina,[7] but the results reported indicate that a certain amount of water must still be present.[21] From Scheme 1, the rate of formation of the product ($[\mathbf{3}]^+$ or $[\mathbf{4}]^+$) from **1** or **2** and the hydrated proton should be given by $k_{obs}[CpMoH(CO)_2L][H(H_2O)_n]^+$, with the second-order observed rate constant k_{obs} equal to $k_1k_2/(k_{-1}[H_2O]^n + k_2)$. This expression simplifies in the following two limiting cases: (a) rapid proton transfer pre-equilibrium followed by rate-determining H_2 elimination ($k_{-1}[H_2O]^n \gg k_2$), $k_{obs} = K_1k_2/[H_2O]^n$; (b) rate-determining proton transfer ($k_{-1}[H_2O]^n \ll k_2$), $k_{obs} = k_1$. A complete analysis of this rate law would require the determination of k_{obs} at different $[H_2O]$, which is beyond the scope of this study. On the basis of our inability to produce $[CpMoH_2(CO)_2L]^+$ (L = PMe_3, PPh_3) even in inert solvents at low temperatures (see Results and Discussions), we know that the rate of H_2 elimination (k_2) must be very high, thus suggesting that the process may be limited by the rate of proton transfer for compounds **1** and **2**. It is pertinent to observe here that any base can operate as a proton shuttle, provided the basicity of the transition metal hydride is lower than, but not too distant from, that of the base and provided the $[MH_2]^+$ product irreversibly decomposes. Thus, 2,6-lutidine does not operate as a proton shuttle for the oxidation of **1** or **2** but may do so, for instance, for the oxidation of a more basic hydride.

(g) Survey of Previously Reported Oxidations of M−H Complexes. The generic scheme of a proton shuttle during the chemical or electrochemical oxidation of a metal hydride that we have demonstrated for the oxidation of **1** and **2** (Scheme 1) brings clarity to a variety of apparently contrasting results reported in the literature.

For what concerns chemical oxidation processes, the situation had never been confused because the reported processes either were carried out in dry MeCN in the absence of an external base, always requiring 1 equiv of oxidant (ferrocenium oxidation of $CpWH(CO)_2(PMe_3)$,[4] $CpRuH(PPh_3)_2$,[16] and $Cp^*RuH_3(PPh_3)$[23] and acetylferrocenium oxidation of $OsH_6(PPr^i_3)_2$[24]), or were carried out in the presence of a strong external base with which the starting hydride complex could not compete, always requiring 2 oxidizing equiv (ferrocenium/2,6-lutidine oxidation of $CpWH(CO)_2(PMe_3)$,[4] **1**,[7] and $CpRuH(CO)(PPh_3)$,[14] and ferrocenium/pyrrolidine oxidation of $CpRuH(CO)(PMe_3)$[15]). More interesting situations derive from previously reported bulk electrolytic experiments. These are all rationalized on basis of Scheme 1 and the assumption that adventitious water was present. The reported[14] consumption of 1.70 ± 0.11 faradays/mol for the oxidation of $CpRuH(CO)(PPh_3)$ (whereas 1.93 ± 0.15 faradays/mol is consumed in the presence of 2,6-lutidine) can be attributed to a partial delivery of the proton from $[H(H_2O)_n]^+$ back to the hydride complex in the bulk within the time scale of the bulk electrolytic experiment. In agreement with the expected trends of metal basicity, the oxidation of $CpRuH(CO)(PMe_3)$ consumes 1.0 ± 0.1 faradays/mol (in the presence of a 10-fold excess of 2,6-lutidine or a 2-fold excess of pyrrolidine, this changes to 2.0 ± 0.1 faradays/mol)[15] and the oxidation of $CpRuH(PPh_3)_2$ also requires only 1 faraday/mol.[16] In fact, given the partial reversibility of the $CpRuH(PPh_3)_2$ oxidation,[16] it is likely that this oxidation process involves diffusion of the rather stable 17-electron $[CpRuH(PPh_3)_2]^+$ complex away from the electrode and direct proton delivery and consequent acidolysis of the starting material in the bulk. The consumption of 1.94 ± 0.08 faradays/mol for the oxidation of **1**,[7] on the other hand, is consistent with our findings of a very slow proton shuttle process in this case (see Results and Discussion). A slow proton shuttle would also be expected for the less basic complexes $CpMH(CO)_3$ (M = Cr, Mo, W), consistent with the consumption of 2.1 ± 0.1, 1.9 ± 0.1, and 2.2 ± 0.3 faradays/mol, respectively, in those cases.[4] $CpWH(CO)_2(PMe_3)$ should be more basic than **2**, as shown by the higher stability of its protonation product (the stoichiometry of the ferrocenium oxidation is that of eq 5). The time required to complete the electrolysis was not specified for this experiment.[4] However, the result of 1.9 ± 0.1 faradays/mol indicates that this compound is still not sufficiently basic to engage in a significant proton transfer with $[H(H_2O)_n]^+$ within the time scale of the electrolytic experiment.

The qualitative order of relative basicity in MeCN for a selected class of metal hydrides appears to be, on the basis of the collective results reviewed above, as follows: $Cp^*RuH_3(PPh_3)$, $CpRuH(PPh_3)_2$ > $CpRuH(CO)(PMe_3)$ > $CpRuH(CO)(PPh_3)$ > $CpWH(CO)_2(PMe_3)$ > $CpMoH(CO)_2(PMe_3)$ > $CpMoH(CO)_2(PPh_3)$ > $CpMH(CO)_3$ (M = Cr, Mo, W). We should emphasize again that the *thermodynamic basicity* of these hydrides cannot be determined as easily as their acidity[34−39] or as the basicity of nonhydridic compounds[40] because many of the conjugate acids spontaneously decompose by H_2 elimination,[18] even in noncoordinating solvents. A ^{1}H-NMR study of the kinetics of the proton shuttle process utilizing a suitable standard base should provide a convenient qualitative assessment of the relative basicity of hydride compounds.

(h) Protonation of Water in MeCN and Nature of $[H(H_2O)_n]^+$. As illustrated in section d, no gas evolution occurs when a $\mathbf{1}/H_2O$ mixture is treated with small amounts (relative to H_2O) of $HBF_4 \cdot Et_2O$. The number of moles of acid that is necessary to start inducing vigorous gas evolution (diagnostic of the protonation of **1**) is much less than the number of moles of H_2O. This is also indicated by an additional protonation experiment which was carried out on a solution containing equimolar amounts of **1** and H_2O: the introduction of 1 mol of $HBF_4 \cdot Et_2O$/mol of **1** caused an immediate, vigorous, and copious evolution of gas, qualitatively indistinguishable from the analogous experiment in dry solvent. It seems, therefore, that each H^+ ion introduced into the solution engages in an interaction with more than one molecule of water to form a $[H(H_2O)_n]^+$ ion with $n > 1$. Indeed, the values of K_f for $[H(H_2O)_n]^+$ for $n = 1-4$ in MeCN (1.6×10^2, 8×10^3, 6×10^4, and 2×10^5, respectively),[41] obtained by spectrophotometric methods, show that the formation of protonated water clusters is favorable in the acetonitrile solvent.

A number of experimental and theoretical studies to gauge the stability of $[H(H_2O)_n]^+$ as a function of n have been presented,[42−45] and several crystal structures of isolated

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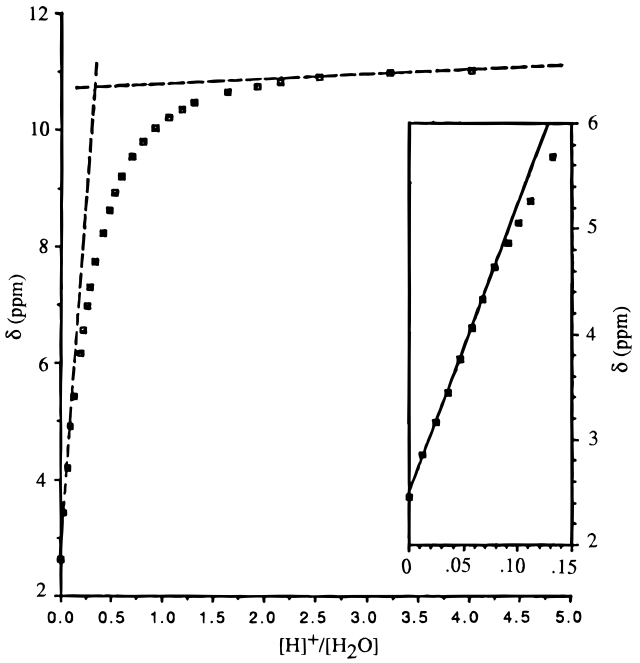

Figure 2. Position of the water resonance in MeCN-d_3 as a function of the equivalents of $HBF_4{\cdot}Et_2O$ added. $[H_2O] = 2.2$ M (inset: $[H_2O] = 1.4$ M).

$\{[H(H_2O)_n]^+\}_mX^{m-}$ acids for various values of n have been reported, e.g. $[H_9O_4][FeCl_4]$,[46] $[H_9O_4]_2[TeBr_6]$,[47] and $[H_5O_2]_2SiFe_6$,[48] but the knowledge of the nature of the hydrated proton in acetonitrile appears to be limited to the above mentioned spectrophotometric studies.[41,49] A ^{1}H-NMR study of H_2O in MeCN have been described,[50] but these have not been extended to the hydronium ions. Since we have observed that the ^{1}H-NMR resonance is rather sensitive to the state of protonation of water (see Figure 1), we have utilized this technique to probe this protonation process. Figure 2 shows the position of the ^{1}H-NMR resonance as a function of the amount of added $HBF_4{\cdot}Et_2O$. One experiment featured the addition of up to ca. 4 mol of $HBF_4{\cdot}Et_2O$/mol of H_2O, whereas a second one (shown in the inset) was carried out only up to 0.15 mol of $HBF_4{\cdot}Et_2O$/mol of H_2O with the collection of a much greater number of data at low $HBF_4{\cdot}Et_2O/H_2O$ ratios. The relative amounts of water and added acid are measured by volume (microliters of the H_2O and $HBF_4{\cdot}Et_2O$ solutions added by microsyringe to the NMR tube containing MeCN-d_3). Figure 2 can be described, to a first approximation, in terms of an initial linear increase of the chemical shift, an intermediate region where the increase of chemical shift deviates from linearity, and ultimately a new region of linearity with a much smaller slope with respect to the first linear region. The second experiment (inset of Figure 2) shows more clearly the linear relationship between the chemical shift and the amount of added acid in the region of low Et_2OH^+/H_2O ratios. The extrapolation of the two linear regions affords a breakpoint corresponding to the addition of 0.34 ± 0.01 mol of acid/mol of water. This indicates that, under the conditions of water concentration utilized (2.2 M), the *average composition* of protonated water in MeCN is $[H(H_2O)_3]^+$.

It should be noted here that nitriles are known to undergo hydrolysis to amides and carboxylic acids under acid catalysis,[51] but this process is slow at room temperature.[52] Thus, our data should not be affected by the hydrolysis process, at least at low acid concentrations. This conclusion was also reached for the spectrophotometric study of water protonation in MeCN.[49] A slow drift of chemical shift was observed only for the data at high acid/water ratios (>1:1) over several hours at room temperature.

The trend of chemical shifts in Figure 2 can be interpreted on the basis of a number of equilibria (see eq 9) with all possible values of n. The nature of the acid in a MeCN solution of

$$Et_2OH^+ + nH_2O \rightleftarrows [H(H_2O)_n]^+ + Et_2O \qquad (9)$$

$HBF_4{\cdot}Et_2O$ is likely to be Et_2OH^+ or, more rigorously, $[H(Et_2O)(MeCN)_x]^+$ (in other words, the strongest base among those available, e.g. Et_2O, BF_4^-, and MeCN, is probably the ether). The alternative formulation as the ion pair $Et_2OH^+BF_4^-$ is also unlikely, given the high dielectric constant of the solvent MeCN. In the first linear region at small H^+/H_2O ratios, the observed resonance is the result of the coalesced resonances of H_2O and $[H(H_2O)_n]^+$ in rapid exchange.

According to the previous spectrophotometric studies,[41,49] a distribution of the different $[H(H_2O)_n]^+$ species should always be present under any given set of experimental conditions. For our experimental conditions ($[H_2O] = 2.2$ M) and the K_f values given in the literature,[41] the fractions of the different water clusters should be $[H(H_2O)^+] = 6.56 \times 10^{-5}$, $[H(H_2O)_2{}^+] = 7.22 \times 10^{-3}$, $[H(H_2O)_3{}^+] = 0.12$, $[H(H_2O)_4{}^+] = 0.87$; hence the average composition of the protonated water cluster should be $[H(H_2O)_{3.84}]^+$, somewhat in disagreement with the value determined by the ^{1}H-NMR technique. The ^{1}H-NMR method provides a direct measurement of the average composition of the protonated water clusters, whereas the previously used spectrophotometric method is indirect and is based on a number of assumptions. A thorough reinvestigation of the formation constants of protonated water clusters is beyond the scope of the present work. However, the ^{1}H-NMR technique appears to have a potential greater than previously appreciated for the investigation of proton transfer equilibria and the nature of acids in a variety of different solvents.

Conclusions

The studies reported here have afforded, as the principal novel point of knowledge, the definition of the intimate role of water (and indeed any base) as a proton shuttle for regulating the stoichiometry of the oxidation, either chemical or electrochemical, of a transition metal hydride complex. A ^{1}H-NMR study of the kinetics of the proton shuttle process utilizing a suitable standard base may provide a convenient assessment of the relative basicity of hydride compounds. As a bonus, we have discovered that the ^{1}H-NMR technique can provide additional insight into the intimate nature of protonated water in acetonitrile.

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