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Electrophilic Addition vs Electron Transfer for the Interaction of Ag^+ with Molybdenum(II) Hydrides. 2. Reaction with $CpMoH(CO)_2(PMe_3)$

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The interaction of $CpMoH(CO)_2(PMe_3)$, **1**, with $AgBF_4$ in acetonitrile establishes an equilibrium ($K = 9 \pm 1$) with the hydride-bridged adduct $[Cp(CO)_2(PMe_3)Mo(\mu\text{-}H)Ag(MeCN)_x]BF_4$, **4**, which is in a fast chemical exchange on the NMR time scale with compound **1**. The interaction of **1** and $AgBF_4$ in THF leads to the formation of the trinuclear complex $\{[CpMoH(CO)_2(PMe_3)]_2Ag\}BF_4$, **5**, as an insoluble white solid in 73% yield when the Mo/Ag ratio is 2:1. The nature of the precipitate does not depend on the relative stoichiometry of the two reagents. When redissolved in acetonitrile, compound **5** dissociates, generating a mixture of **1** and **4**. Compound **4** slowly evolves to the solvent adduct, $[CpMo(CO)_2(PMe_3)(MeCN)]BF_4$, **3**, with elimination of hydrogen gas and metallic silver. The decomposition of **4** could be interpreted as either an inner-sphere electron transfer or a substitution of unstable "AgH".

Introduction

In part 1 of this series,[1] we have examined the interaction between Ag^+ (as well as other oxidizing agents including ferrocenium and a platinum anode) and the electron-rich 18-electron Mo(II) complex $CpMoH(PMe_3)_3$. Contrary to the interaction of Ag^+ with several other hydride complexes, for which products of electrophilic addition to the hydride ligand were obtained,[2−15] the interaction of silver with $CpMoH(PMe_3)_3$ (whose electrochemically reversible oxidation occurs at $E_{1/2} = -1.46$ V vs the ferrocene standard in MeCN) proceeds directly to the products of electron transfer without detection of an electrophilic addition intermediate. This paper presents the results of our investigations of the reactivity of complex $CpMoH(CO)_2(PMe_3)$, **1**, with the silver ion. The interest of this investigation is that **1**, while analogous with $CpMoH(PMe_3)_3$, **2**, shows an irreversible oxidation process at $E_{p,a} = 0.19$ V vs ferrocene in MeCN, i.e., 1.65 V more positive relative to the tris-PMe_3 complex,[16] rendering the formation of a stable addition product competitive with the oxidation process. It is therefore possible for the first time to make a comparison of the reactivity between Ag^+ and two hydride complexes belonging to the same class, i.e., **1** and **2**, and possessing quite disparate electrochemical properties.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of dinitrogen with standard Schlenk-line techniques. Solvents were purified by conventional methods and distilled under argon prior to use (THF and Et_2O from Na/benzophenone, heptane from Na, acetone from $CaSO_4$, CH_2Cl_2 from P_4O_{10}, and MeCN form CaH_2). Deuterated solvents (C_6D_6, CD_3CN, THF-d_8, and CD_3COCD_3) were degassed by three freeze−pump−thaw cycles and then stored over 4 Å molecular sieves under dinitrogen. NMR spectra were obtained with Bruker WP200 and AF400 spectrometers. The peak positions are reported with positive shifts downfield

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of TMS as calculated from the residual solvent peaks (^1H) or downfield of external 85% H_3PO_4 (^{31}P). For each ^{31}P NMR spectrum, a sealed capillary containing H_3PO_4 was immersed in the same NMR solvent used for the measurement, and this was used as reference. FT-IR spectra were recorded on a Perkin-Elmer 1880 spectrometer with KBr cells. EPR spectra were recorded on a Brucker ER200 spectrometer upgraded to ESP 300, equipped with a cylindrical ER/4103 TM 110 cavity and an X-band microwave generator. Elemental (C, H) analyses were performed by MHW Laboratories (Phoenix, AZ) and the analytical service of LSEO, Université de Bourgogne. The Ag analyses were carried out by atomic absorption with a Perkin-Elmer 5000 flame spectrophotometer. Compound **1**[17] was prepared as previously published. $AgBF_4$ was purchased from Aldrich and used as received.

Low-Temperature ^1H NMR Studies of $CpMoH(CO)_2(PMe_3)$. In an NMR tube was prepared a solution of compound **1** (76 mg, 258 μmol) in CD_3CN (345 μL). ^1H NMR (RT, δ): 5.22 (s, 5H, Cp), 1.50 (d, $J_{HP} = 10$ Hz, 9H, PMe_3), −6.35 (d, $J_{HP} = 47$ Hz, 1H, Mo−H). At room temperature the hydride resonance appears as a highly distorted doublet, with a sharp higher field signal and a very broad lower field signal. Upon cooling the signals decoalesce and lead to distinguishable resonances for the *cis* and *trans* isomers. ^1H NMR (CD_3CN, 240 K, δ): *trans* isomer, 5.13 (s, 5H, Cp), 1.49 (d, $J_{HP} = 9$ Hz, 9H, PMe_3), −6.4 (br, 1H, Mo−H); *cis* isomer, 5.28 (s, 5H, Cp), 1.45 (d, $J_{HP} = 9$ Hz, 9H, PMe_3), −6.5 (d, $J_{HP} = 66$ Hz, 1H, Mo−H). The approximate *trans*/*cis* ratio given by integration is 1:1. The assignment of the resonances to the different isomers is based on the comparison with the previously published study in toluene-d_8.[17]

A similar solution in acetone-d_6 cooled at 204 K shows better resolved resonances for the two geometric isomers. ^1H NMR (δ): *trans* isomer, 5.62 (s, 5H, Cp), 1.77 (d, $J_{HP} = 9$ Hz, 9H, PMe_3), −6.07 (d, $J_{HP} = 23$ Hz, 1H, Mo−H); *cis* isomer, 5.45 (s, 5H, Cp), 1.72 (d, $J_{HP} = 9$ Hz, 9H, PMe_3), −6.31 (d, $J_{HP} = 66$ Hz, 1H, Mo−H). ^{31}P NMR: 30.6 (s) and 25.2 (s).

Reaction between $CpMoH(CO)_2(PMe_3)$ and Ag^+ in MeCN. (a) NMR Monitoring in CD_3CN. A solution of $AgBF_4$ (286 mg; 1.47 mmol) in CD_3CN (855 μL) was prepared. Fifteen aliquots of 50 μL each of this solution (86 μmol of Ag^+ each) were added stepwise at room temperature to the solution of **1** in CD_3CN described in the previous section ($\Delta[Ag^+]/[Mo] = 1/3$ for each addition). A ^1H NMR spectrum was recorded after each addition. While the number of resonances remained constant during the experiment, their chemical shifts changed after each addition (see Results). Toward the end of the experiment ($[Ag^+]/[Mo] > 2$), some gray precipitate started to form and minor amounts of $[CpMo(CO)_2(PMe_3)(MeCN)]^+$, **3**, appeared in the ^1H NMR spectrum (<5%): *cis*-**3**, δ 5.62 (s, 5H, Cp), 1.63 (d, $J_{HP} = 5$ Hz, 9H, PMe_3); *trans*-**3**, 5.43 (s, 5H, Cp), 1.62 (d, $J_{HP} = 10$ Hz, 9H, PMe_3). These resonances match those previously reported[16] for complex **3**. The *cis*-**3**/*trans*-**3** ratio is ca. 10 and does not change with time.

(b) IR Study. Compound **1** (268 mg, 0.91 mmol) was dissolved in CH_3CN (15 mL). IR: 1927 and 1841 cm^{-1}. $AgPF_6$ (210 mg, 0.83 mmol) was added, immediately, turning the solution darker orange. An aliquot was taken for an IR spectrum. New bands at 1943 and 1855 cm^{-1}, attributed to the silver adduct $[Cp(CO)_2(PMe_3)Mo(\mu\text{-}H)Ag(MeCN)_x]^+$, **4**, alongside less intense absorbances corresponding to those of the unreacted starting material, were observed. After 1 h, new carbonyl bands at 1985 and 1897 cm^{-1}, attributed to *cis*-$[CpMo(CO)_2(PMe_3)(MeCN)]PF_6$, **3** (cf. lit. 1987 and 1898 cm^{-1}),[16] were also present (ca. 20% transformation). Attempts to recover a stable solid were unsuccessful. Cooling the acetonitrile solutions yielded white solids that proved too light- and heat-sensitive to be handled.

Interaction between $CpMoH(CO)_2(PMe_3)$ and Ag^+ in THF. (a) In a 2:1 Ratio. Synthesis of $\{[CpMoH(CO)_2(PMe_3)]_2Ag\}BF_4$, 5. To a cooled (−80 °C) THF solution (10 mL) of compound **1** (324 mg, 1.2 mmol) was added dropwise a similarly cooled solution of $AgBF_4$ (107 mg, 0.55 mmol) in THF (5 mL). The immediate precipitation of the product **5** as a white solid ensued. The colorless supernatant was removed by filter-cannula, and the white powder was dried under vacuum in the dark (302 mg, 72% yield). Anal. Found (calcd for $C_{20}H_{30}AgBF_4Mo_2O_4P_2$) %: C, 30.4 (30.7); H, 4.08 (3.86); Ag, 15 (14). IR (Nujol mull, cm^{-1}): 2920 (vs), 2725 (m), 1945 (s), 1835 (s) 1295 (m), 1154 (w), 1056 (m), 962 (s). The powder is light- and heat-sensitive and turns yellow upon decomposition. ^1H NMR (CD_3CN, δ): 5.33 (s, 5H, Cp), 1.61 (d, $J_{HP} = 10$ Hz, 9H, PMe_3), −7.01 (d, $J_{HP} = 28$ Hz, 1H, Mo−H). $^{31}P\{^1H\}$ NMR (CD_3CN, δ): 20 (s, PMe_3). $^{31}P\{^1H\text{-selec}\}$ NMR (CD_3CN, δ): 20 (d, $J_{HP} = 28$ Hz, PMe_3). IR (CD_3CN, cm^{-1}): 1947, 1926, 1860 (sh), 1841. The first and third bands are due to compound **4**, while the second and fourth bands are due to compound **1**. The yellow solutions of **5** slowly turn darker, and a dark precipitate forms. The formation of new resonances attribuable to H_2 (at 4.5 ppm) and $[CpMo(CO)_2(PMe_3)(MeCN)]BF_4$, **3** (see previous section), is observed by ^1H NMR. During this decomposition, the original resonances attributed to **5** do not disappear but rather continuously shift toward the position of the resonances of **1**. At the end of the transformation, the solution contains a 1:1 mixture of **1** and **3**, traces of H_2, and a gray precipitate.

(b) In a 1:1 Ratio. Compound **1** was generated in situ by the addition of 1 equiv of PMe_3 (102 μL) to a solution of $CpMoH(CO)_3$ (242 mg, 0.93 mmol) in THF (5 mL) according to the literature.[17] After cooling to −20 °C $AgBF_4$ (189 mg, 0.97 mmol) was added, inducing the precipitation of a light yellow solid. The orange superantant was filtered off, and the solid was dried under vacuum (237 mg, 65% yield relative to Ag^+). The ^1H NMR and IR properties of this solid correspond with those reported above for compound **5**.

(c) NMR Investigation in THF-d_8. A solution of $AgBF_4$ (132 mg, 677 μmol) in THF-d_8 (390 μL) was prepared. A 10 μL aliquot of this solution (17 μmol of Ag^+) was added to an NMR tube containing compound **1** (20.0 mg, 68 μmol) in THF-d_8 (425 μL). No change in the chemical shifts of the resonances of **1** was observed, while a yellow solid immediately precipitated. ^1H NMR: δ 5.19 (s, 5H, Cp), 1.50 (d, $J_{HP} = 9$ Hz, 9H, PMe_3), −6.12 (br d, 1H, Mo−H). The intensity change that occurred upon the addition of silver was quantitatively measured through the comparison of the integrals of the Cp vs THF-d_8 before and after the addition. The hydride resonances decreased by a factor of 54% upon reaction with silver, implying that 37 μmol of **1** (i.e., half-equivalent of silver salt per molybdenum center) has been sequestered in the precipitate.

Results

(a) Interaction of $CpMoH(CO)_2(PMe_3)$ with Ag^+ in Acetonitrile: Formation of $[CpMo(CO)_2(PMe_3)(\mu\text{-}H)Ag(MeCN)_x]^+BF_4^-$ (4). The addition of silver ions to an acetonitrile solution of **1** induces a slight color deepening and the appereance of new CO stretching bands at 1944 and 1856 cm^{-1} in the IR solution spectrum. These frequencies are red-shifted with respect to those of **1** (at 1926 and 1841 cm^{-1}), consistent with removal of electron density from the complex as could be expected from the addition of the Lewis acidic silver center. Addition of 0.9 equiv of Ag^+ induced the nearly complete disappereance of **1**, consistent with a 1:1 stoichiometry for the reaction.

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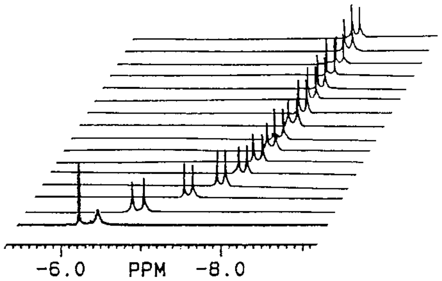

Figure 1. Stack plot of the ^1H NMR spectra of the mixture of **1** and $AgBF_4$ at different $[Ag^+]/[Mo]$ ratios. Each plot represents an addition of 1/3 units in the ratio, starting from a silver-free solution.

Additional information on this interaction is provided by the NMR study. Addition of silver ions to a solution of **1** has an indirect effect on the ^1H NMR resonances of the species: instead of creating new resonances, it induces a shift of the already existing ones. The most dramatic change is experienced by the hydridic resonance, which varies from $\delta = -6.5$ (d, $J_{HP} = 47$ Hz) at Ag/Mo = 0 to -8.1 (d, $J_{HP} = 20$ Hz) at Ag/Mo = 5 (see Figure 1). The drifts of the Cp and PMe_3 resonances are similar in trend but smaller in magnitude ($\Delta < 0.15$ ppm along the titration curve). It might seem surprising that the hydridic resonance in the solution ^1H NMR spectrum of **1** is a very asymmetric doublet. This is due to the fast dynamic exchange at room temperature of the two geometric isomers, *cis*- and *trans*-**1**, on the NMR time scale, resulting in a single set of resonances, as already reported.[17] The distinctive room-temperature asymmetry of the coalesced resonance can be attributed to the large difference of the J_{HP} in the two rapidly exchanging isomers (23 Hz for *trans*, 66 Hz for *cis*). This asymmetry is lost when silver cations are introduced in the solution.

Plots of the hydridic chemical shift and of the J_{HP} vs the $[Ag^+]/[Mo]$ ratio are reported in Figure 2a,b, respectively. The dependence of these two parameters on the relative ratio is qualitatively similar. A more detailed analysis was carried out only on the chemical shift data. Three main regions can be defined as the $[Ag^+]/[Mo]$ ratio increases: a first linear region for $[Ag^+]/[Mo] < 1$, a transition region, and a second linear region for $[Ag^+]/[Mo] > 3$, where changes are very small. The two straight lines that fit the linear regions intersect at $[Ag^+]/[Mo] \approx 1$, in agreement with a 1:1 stoichiometry, as also suggested by the IR study (see above). Given the results of the interaction between **1** and $AuPPh_3^+$,[18] the literature precedents mentioned in the Introduction, and the lowering of J_{HP} for the hydride resonance in the ^1H NMR, the product of this interaction is formulated as $[Cp(CO)_2(PMe_3)Mo(\mu\text{-}H)Ag(MeCN)_x]BF_4$, **4**; see eq 1. This formulation is in accord with the large drift of the chemical shift and with the reduction of the J_{HP} for the hydridic signal as the concentration of silver increases. The latter, in particular, is consistent with a significant weakening of the H−Mo interaction.

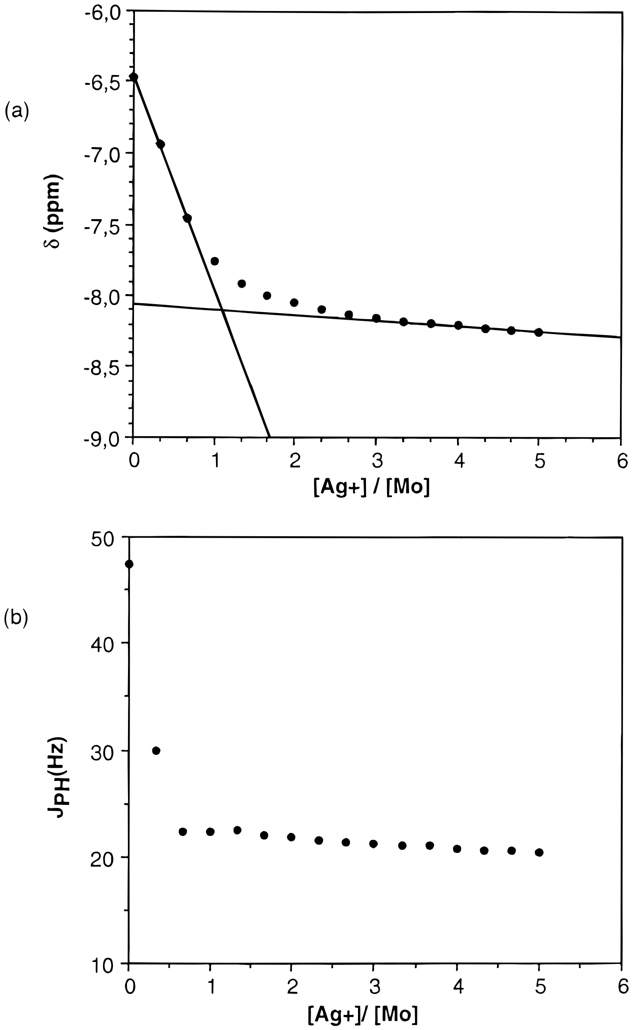

Figure 2. Plots of (a) δ (ppm) and (b) J_{HP} vs the $[Ag^+]/[Mo]$ ratio, as calculated from the spectra reported in Figure 1 (errors on $\delta < 0.1$ ppm, errors on $J < 0.2$ Hz). In (a) the solid straight lines interpolate the experimental points in the two linear regions.

$$\underset{\mathbf{1}}{CpMoH(CO)_2(PMe_3)} + AgBF_4 + x\,MeCN \rightleftarrows \underset{\mathbf{4}}{[CpMo(CO)_2(PMe_3)(\mu\text{-}H)Ag(MeCN)_x]^+BF_4^-} \quad (1)$$

The chemical shift trend in Figure 2a can thus be rationalized as the result of a rapid exchange between the 1:1 adduct, **4**, and residual **1**. This exchange could in principle take place either via dissociation of the Ag^+ ion or by an associative mechanism (see Scheme 1a). Either way, this chemical exchange prevents the direct observation of the chemical shifts of complex **4** and the H−Ag coupling for the hydride resonance, even at −80 °C. The deviation between the observed chemical shifts and the two straight lines in the transition region shows that eq 1 is not quantitative but rather an equilibrium. Fitting the NMR data to the simultaneous eqs 2a and 2b, where δ_1 and δ_4 are respectively the hydride chemical shifts for the pure compounds **1** and **4**, C_{Mo} is the analytical concentration of Mo complexes ($C_{Mo} = [\mathbf{1}] + [\mathbf{4}]$), C_{Ag} is the analytical concentration of added silver ($C_{Ag} = [Ag^+] + [\mathbf{4}]$), and K is the equilibrium constant of eq 1, gives $K = 9 \pm 1$ and $\delta_4 = -8.4 \pm 0.8$ ppm.

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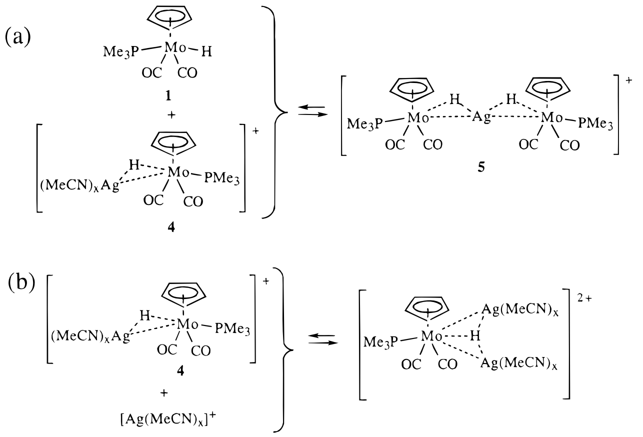
Scheme 1



$$\delta = \frac{C_{\mathrm{Mo}} - [\mathbf{4}]}{C_{\mathrm{Mo}}}\delta_1 + \frac{[\mathbf{4}]}{C_{\mathrm{Mo}}}\delta_4 \tag{2a}$$

$$K = \frac{[\mathbf{4}]}{(C_{\mathrm{Mo}} - [\mathbf{4}])(C_{\mathrm{Ag}} - [\mathbf{4}])} \tag{2b}$$

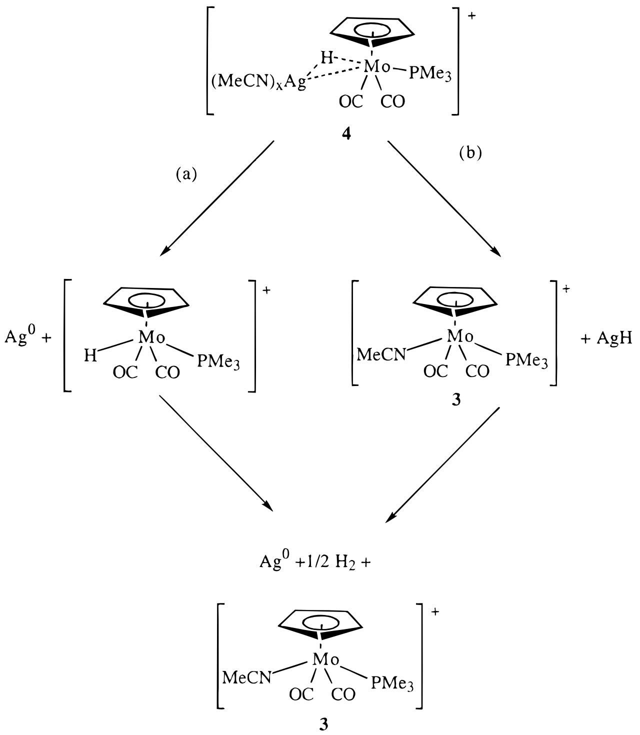
The coupling between the hydride and the silver nucleus is not observed even when a large excess of Ag^+ is administered in order to force equilibrium 1 to the right and slow the exchange between **1** and **4**. From the value of K, it can be calculated that 10.5% of **1** remains free in the presence of a 5-fold excess of Ag^+ under the conditions described in the Experimental Section. A second chemical exchange, namely, beween compound **4** and the excess Ag^+, could also take place under these circumstances (see Scheme 1b). Stable complexes of stoichiometry M_2Ag[6,10,12−15] and MAg_2,[7] analogous to the proposed intermediates in Scheme 1, have previously been described. In view of the incomplete formation reaction and the extreme light sensitivity, compound **4** could not be isolated in the solid state.

(b) Decomposition of Complex 4. Acetonitrile solutions of **4** slowly decompose with the formation of solid silver, gaseous hydrogen, and $[CpMo(CO)_2(PMe_3)(MeCN)]^+$, **3**, as confirmed by IR and NMR spectroscopy (see eq 3). Both the *cis* and the *trans* isomers are formed in the equilibrium ratio of 10:1,[16] as confirmed by the NMR spectrum. The bands of the *trans* isomer in the IR spectrum, expected at 1992 and 1904 cm^{-1},[16] are not discernible because they are overshadowed by the more intense bands of the major isomer, at 1987 and 1898 cm^{-1}.

$$\underset{\mathbf{4}}{[\mathrm{CpMo(CO)_2(PMe_3)(\mu\text{-}H)Ag(MeCN)}_x]^+} \rightarrow \underset{\mathbf{3}}{[\mathrm{CpMo(MeCN)(CO)_2(PMe_3)}]^+} + {}^1\!/_2\mathrm{H_2} + \mathrm{Ag} + (x-1)\mathrm{MeCN} \tag{3}$$

Reaction 3 may take place via an electron-transfer pathway, to generate silver and a 17-electron $[CpMo(CO)_2(PMe_3)H]^+$ intermediate. This compound was previously shown to rapidly decompose in MeCN to afford **3** and H_2,[16] i.e., the observed products of eq 3. Another possibility, however, could involve the substitution of “AgH” by MeCN. Silver hydride[19,20] is unstable and thermodynamically disfavored relative to the elements.[21−23] In this respect, reaction 3 would be analogous to the elimination of H_2 upon protonation of **1** in MeCN, to form the same final product **3**.[16] The two possibilities are highlighted in Scheme 2.

Scheme 2



The available data do not distinguish these two possibilities. The potential for the reduction of Ag^+ in MeCN ($E_{p,c} = -0.24$ V vs Fc/Fc^+) would appear insufficient to carry out the oxidation of compound **1** acetonitrile ($E_{p,a} = +0.19$ V vs Fc/Fc^+).[16] However, the irreversibility of both these electrochemical processes does not allow the feasibility of the electron transfer to be assessed from the electrochemical data. In addition, the redox properties of both the Mo and Ag center could be substantially modified by the hydride-bridging interaction in complex **4**. Finally, a slightly uphill electrochemical step could still occur if followed by an irreversible chemical process, as would be the case here.

The absence of a stereochemical control on product **3** also does not permit a distinction between the two mechanisms discussed above. Complex **3** is observed by ^1H NMR as a mixture of the *cis* and *trans* isomers at thermodynamic equilibrium (*cis*:*trans* = 10). An equilibrium mixture has also been obtained by outer-sphere one-electron oxidation of **1** and by protonation with HBF_4,[16] while the reaction with Ph_3C^+ generates only the less stable *trans* isomer, presumably because of the steric control on the Ph_3C^+ attack.[16,24] Thus, the

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isomeric ratio obtained for the Ag^+ is consistent with either an electron transfer as in the ferrocenium reaction or the elimination of a "AgH" unit, in which case Ag^+ would be sterically nondiscriminating like the proton and unlike the Ph_3C^+ reagent.

(c) Interaction of $CpMoH(CO)_2(PMe_3)$ with Ag^+ in THF: Synthesis of $\{[CpMo(CO)_2(PMe_3)(\mu\text{-}H)]_2Ag\}^+BF_4^-$, 5. In an attempt to isolate a silver adduct such as **4**, we have carried out the interaction between **1** and Ag^+ in the less coordinating and less dielectric solvent THF. The reaction leads to the precipitation of a 2:1 adduct, $\{[CpMo(CO)_2(PMe_3)(\mu\text{-}H)]_2Ag\}^+BF_4^-$, **5**, even when it is conducted in a different stoichiometric ratio (see eq 4). The reason for the formation of a 2:1 adduct, rather than a 1:1 adduct such as the product formed in MeCN (vide supra), may be attributed to the relative solubility of the different adducts and/or to the relative coordinating properties of the solvents and the [Mo]−H moiety toward the silver ion. In other words, while the Mo−H moiety in **1** coordinates Ag^+ better than THF, affording the $\{Ag(H{-}[Mo])_2\}^+$ product, the MeCN solvent coordinates even better, giving at the most a $\{Ag(H{-}[Mo])(MeCN)_x\}^+$ product, in equilibrium with $[Ag(MeCN)_y]^+$. The product **5** can be recovered in a 73% yield as a white microcrystalline solid, which darkens upon exposure to air and/or light. Its solubility is very slight in THF, but it dissolves well in acetonitrile and acetone.

$$\underset{\mathbf{1}}{2CpMoH(CO)_2(PMe_3)} + AgBF_4 \rightarrow \underset{\mathbf{5}}{\{[CpMo(CO)_2(PMe_3)(\mu\text{-}H)]_2Ag\}^+BF_4^-} \quad (5)$$

A Nujol IR spectrum of the solid displays two carbonyl stretching vibrations at 1945 and 1835 cm^{-1}. These two bands are blue- and red-shifted, respectively, from those of the starting material (*cis*-**1**, 1947 and 1864 cm^{-1}; *trans*-**1**, 1938 and 1864 cm^{-1}),[17] suggesting that the interaction between **1** and the silver center is not a simple electrostatic $Mo{-}H\cdots Ag^+$ interaction. The same phenomenon was observed for the related trimetallic heteronuclear cluster $[CpMo(CO)_2(PMe_3)(AuPPh_3)_2]^+$.[18]

Dissolution of **5** in acetonitrile produces solutions that have the same NMR and IR properties of solutions obtained by adding 0.5 equiv of Ag^+ to compound **1**, namely, equilibrium solutions of compounds **1** and **4** and residual Ag^+ (eq 1). The IR spectrum, in particular (see Experimental Section), shows that the main components of the solution are complexes **1** and **4**, rather than the intact unit **5**; see eq 6. Further addition of Ag^+ to this solution induces the conversion of **1** into **4**, as expected. This result indicates, once again, that the MeCN solvent is a better ligand than THF for the silver ion and competes more effectively against coordination of a second unit of compound **1** to the Ag center. This result further indicates that the proposed associative mechanism of silver scrambling (Scheme 1a) is plausible.

$$\underset{\mathbf{5}}{\{[CpMo(CO)_2(PMe_3)(\mu\text{-}H)]_2Ag\}^+} \xrightarrow{MeCN} \underset{\mathbf{1}}{CpMoH(CO)_2(PMe_3)} + \underset{\mathbf{4}}{[CpMo(CO)_2(PMe_3)(\mu\text{-}H)Ag(MeCN)_x]^+} \quad (6)$$

A CD_3CN solution of **5** evolved over time as expected, given the above-described behavior of complex **4** (eq 3). A 1:1 mixture of compounds **1** and **3**, plus H_2 and metallic silver, was eventually obtained.

Discussion

Three pathways could be followed in principle for the reaction between a transition metal hydride complex and an electrophilic reagent (Scheme 3): addition to the metal (path *a*), addition to the hydride ligand (path *b*), and electron transfer (path *c*). However, all pathways could potentially derive from the same electrophilic addition to the hydride ligand, subsequently evolving along different directions (paths *b*.i−iii). There are precedents for all these mechanisms. For certain protonation reactions, it has been shown that the kinetic position of attack is the hydride ligand to afford a nonclassical dihydride intermediate,[25] which evolves either to a classical dihydride product (path *b*.i)[25] or to a solvent adduct with elimination of H_2 (path *b*.ii).[16,18] A rare example of path *b*.iii is the silver oxidation of Cp_2WH_2, which allows the identification of the electrophilic addition intermediate $\{[Cp_2WH_2]_2Ag\}^+$.[12]

We were considering that complexes $CpMoH(CO)_n(PMe_3)_{3-n}$ ($n = 2$, **1**; $n = 0$, **2**) could allow us to witness a change of reactivity, because the electronic properties are profoundly influenced by the CO/PMe_3 substitution. This is suggested by previous protonation studies. While the addition of H^+ to compound **1** affords an unstable $[CpMo(H_2)(CO)_2(PMe_3)]^+$ complex which immediately expels H_2,[16] the protonation of the electron richer **2** affords the stable classical dihydride complex $[CpMoH_2(PMe_3)_3]^+$.[1,26] The latter may be occurring via an (unobserved) nonclassical intermediate according to path *b*.

Concerning the interaction with the silver electrophile, the more easily oxidizable **2** (examined in part 1 of this series) leads directly to the electron-transfer products $[\mathbf{2}]^+$ and Ag^0 without detection of an electrophilic addition intermediate.[1] The reaction between Ag^+ and the less easily oxidizable **1** reported in this contribution, on the other hand, permits the observation and

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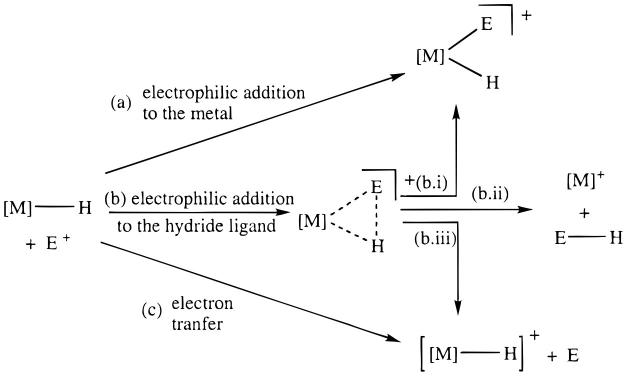
Scheme 3



isolation of electrophilic addition products, making a case in favor of the intermediacy of a hydride-bridged MoAg complex during the oxidation of **2**. The Ag^+ adduct obtained from **1** in MeCN (complex **4**) slowly decomposes to the expected products of electron transfer and thus qualifies as an intermediate of an inner-sphere electron-transfer process.

Unfortunately, the electron-transfer product $[\mathbf{1}]^+$ is too unstable and could not be observed during the decomposition of **4**. Rather, in addition to Ag, the final products are H_2 and complex **3**. These are indeed the *same products* obtained when $[\mathbf{1}]^+$ is generated by other methods (e.g., anodic oxidation of **1**). However, another pathway (elimination of the unstable silver hydride, followed by its decomposition) would in principle lead to the same observed products (see Results section and Scheme 2).

Conclusions

The reaction between the electrophilic/oxidizing agent Ag^+ with complex **1** follows the same pattern already reported for the interaction of **1** with a series of electrophiles (H^+, Ph_3C^+, $AuPPh_3^+$).[16,18] Specifically, the first stage of the interaction leads to an adduct between the substrate and the electrophile through a bridging hydride bond (Scheme 3, path *b*). However, the stability of the addition product varies in the order $E^+ = H^+, Ph_3C^+ \ll Ag(MeCN)_x^+ < AuPPh_3^+$. The decomposition of the silver addition product (complex **4**) could involve either a slow intramolecular electron transfer or the elimination of "AgH". The nature of the addition product under different conditions indicates a coordinating ability toward Ag^+ in the order THF < **1** < MeCN.

The comparison between the results reported in this contribution and those described in part 1 confirms the expected correlation between metal electron density and reactivity toward Ag^+. With the electron poorer complex **1**, the silver ion can form an electrophilic addition product, whereas the electron richer complex **2** leads directly to the oxidation product. While falling short of representing a new clear-cut example of an inner-sphere electron transfer, the results suggest that an inner-sphere pathway for electron transfer by Ag^+ is probably occurring. In other words, the silver oxidation of **2** described in part 1 would occur via the formation of an (unobserved) electrophilic addition intermediate, while the decomposition of the addition of Ag^+ to **1**, namely, complex **4**, would take place via electron transfer rather than via hydride abstraction.

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