

Electrochemical Oxidation and Reduction of Cationic Carbonyl Hydride Complexes of Group VI Transition Metals

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Voltammetric experiments are reported which establish kinetic and thermodynamic properties associated with the redox chemistry of carbonyl hydride complexes $[M(\text{CO})_2(\text{P-P})_2\text{H}](\text{SO}_3\text{CF}_3)$ ($M = \text{Cr}, \text{Mo}, \text{W}$; $\text{P-P} = \text{Ph}_2\text{-PCH}_2\text{PPh}_2$ (dpm), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dpe)). A systematic relationship is shown between redox data obtained for the hydride complexes and those for the $M(\text{CO})_2(\text{P-P})_2$ complexes. Isomerization reactions of the seven-coordinate hydride complexes give rise to interesting mechanistic features which accompany the oxidation as well as the reduction, and both are found to proceed *via* metal–hydrogen bond cleavage. The oxidation process corresponds to an ECEC reaction pathway $\{(E) [\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}]^+ \rightleftharpoons [\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}]^{2+} + e^-; (C) [\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}]^{2+} \rightarrow \text{trans-}[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+ + \text{H}^+; (E) \text{trans-}[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+ \rightleftharpoons \text{trans-}[\text{Mo}(\text{CO})_2(\text{dpe})_2]^{2+} + e^-; (C) \text{trans-}[\text{Mo}(\text{CO})_2(\text{dpe})_2]^{2+} \rightarrow \text{products}\}$ or a related mechanism while the reduction process involves the formation of hydrogen: $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}]^+ + e^- \rightleftharpoons \text{cis-Mo}(\text{CO})_2(\text{dpe})_2 + \frac{1}{2}\text{H}_2$. In the case of the oxidation of the tungsten and the $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}]^+$ complexes, a chemically reversible one-electron oxidation process is detected at low temperature in butyronitrile. The investigation of the deuterated complex $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{D}]^+$ allows the detection of a normal isotope effect on the metal–hydrogen bond cleavage reaction. The oxidized species $[\text{M}(\text{CO})_2(\text{P-P})_2\text{H}]^{2+}$ can be viewed as extremely strong acids.

Introduction

Considerable interest in organometallic acids and their kinetic and thermodynamic properties has existed since their discovery in 1931 by Hieber et al.¹ Research on this class of complexes, which contain one or more hydride ligands, has tended to focus on their role as intermediates in catalytic reactions.² A survey which includes an overview of theoretical and experimental progress in this field was published recently by Dedieu.³

Electrochemical methods often have proved to be valuable in establishing thermodynamic as well as kinetic properties of organometallic complexes in the solution phase. For example, the correlation between thermodynamic properties of compounds containing acidic protons and data obtained from electrochemical and spectroscopic measurements has been exploited to establish approximate acidity constants for a range of C–H acids⁴ and organometallic complexes.⁵ Additionally, redox potentials have been combined with calorimetric and other data⁶ to establish important thermodynamic cycles.

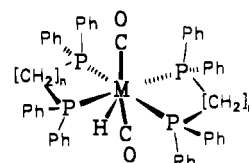
The hydride complexes, which have been subjected to investigation by voltammetric techniques in this work are

obtained (eq 1) by protonation of a well-studied group of



carbonyl complexes of the type *cis*- or *trans*- $\text{M}(\text{CO})_2(\text{P-P})_2$ ($M = \text{Cr}, \text{Mo}, \text{W}$; $\text{P-P} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dpm), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dpe)).

Mechanistic studies⁷ on the formation of complexes **1** and **3–6** and calorimetric data determined by Angelici et al.⁸ have been reported. However, no redox data on these compounds are



M =	Cr	Cr	Mo	Mo	W	W
n =	1	2	1	2	1	2
	1	2	3	4	5	6

available, in contrast to the case of the zerovalent *cis*- or *trans*- $\text{M}(\text{CO})_2(\text{P-P})_2$ compounds, which are known to be easily oxidized.⁹ The hydride complexes $[\text{M}(\text{CO})_2(\text{P-P})_2\text{H}]^+$ could in fact be regarded as $\text{M}(\text{II})$ compounds when compared to $[\text{M}(\text{CO})_2(\text{P-P})_2\text{X}]^+$ compounds¹⁰ with $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$. Hence, redox as well as acid–base relationships between $\text{M}(\text{CO})_2(\text{P-P})_2$ and $[\text{M}(\text{CO})_2(\text{P-P})_2\text{H}]^+$ could be anticipated.

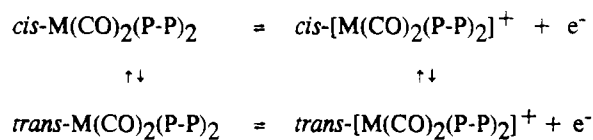
The complexes $\text{M}(\text{CO})_2(\text{dpm})_2$ and $\text{M}(\text{CO})_2(\text{dpe})_2$ exist in two isomeric forms (*cis* and *trans*) which are electrochemically

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oxidized at well-separated potentials. Consequently, their voltammetric behavior has been summarized in a square reaction scheme:^{9c,11}



In most solvents the neutral species prefers the *cis* conformation, but after oxidation the *trans*⁺ form is heavily favored.^{9c} A second one electron oxidation step has also been reported,¹² although less information regarding the mechanism of this process is available.

In principle, the protonation reaction in eq 1 leads to the possibility of an additional dimension being present in the mechanistic scheme of redox and isomerization processes. In this work an attempt has been made to establish whether redox reactions in the square scheme and protonation reactions in eq 1 are in fact coupled in a systematic manner. An obvious aid in these mechanistic studies is the use of deuterated complexes $[\text{M}(\text{CO})_2(\text{P-P})_2\text{D}]^+$. The deuterated form of one of the compounds therefore has been synthesized and its voltammetry compared with that of $[\text{M}(\text{CO})_2(\text{P-P})_2\text{H}]^+$ in order to establish isotope effects that confirm the coupling of acid–base reactions with the redox chemistry.

Experimental Section

Synthesis. The preparation of the hydride complexes **1–6** as well as the deuterated complexes **4b** was based on literature procedures.⁸ Protonation (deuteration) of the metal carbonyl complexes $\text{M}(\text{CO})_2(\text{dpm})_2$ ⁹ and $\text{M}(\text{CO})_2(\text{dpe})_2$ ¹³ was undertaken using a standard Schlenk line technique under an atmosphere of dry dinitrogen. Solvents such as dichloromethane and hexane were dried using standard procedures.¹⁴ A general procedure for synthesis was as follows:

The metal complex *cis*- $\text{M}(\text{CO})_2(\text{dpm})_2$ or *cis*- $\text{M}(\text{CO})_2(\text{dpe})_2$ (0.2 mmol) was suspended or dissolved in dichloromethane (10 mL) and trifluoromethanesulfonic acid (approximately 0.22 mmol in dichloromethane) was added slowly under stirring to the reaction mixture. Upon completion of the addition of the acid, a pale colored solution was obtained, and adding hexane (20 mL) led to a pale precipitate of the hydride complex. After decanting and drying *in vacuo*, the compound was reprecipitated from dichloromethane/hexane and finally dried for several hours *in vacuo*. The hydride complexes $[\text{M}(\text{CO})_2(\text{dpm})_2\text{H}]\text{SO}_3\text{CF}_3$ and $[\text{M}(\text{CO})_2(\text{dpe})_2\text{H}]\text{SO}_3\text{CF}_3$ were stored in the dark under dinitrogen. Due to the high sensitivity of *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ toward photooxidation in the presence of halogenated hydrocarbons, the synthesis of compound **2** was carried out in the dark. Yields were typically 80%. Deuterated complexes were obtained using deuteriotrifluoromethanesulfonic acid.

A sample of $[\text{trans-Mo}(\text{CO})_2(\text{dpe})_2](\text{SO}_3\text{CF}_3)$ was prepared by oxidation of *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ in acetonitrile using 1 equiv of AgSO_3CF_3 . After filtration and removal of the solvent *in vacuo*, a red glassy product was obtained (IR absorption in dichloromethane solution $\nu(\text{CO})$ 1873 cm^{-1}).

For spectroscopic characterization, a Bruker AM 300 NMR was used (¹H-NMR and ¹³C-NMR referenced against internal TMS, ³¹P-NMR referenced against external 85% H_3PO_4 , ²D-NMR referenced against $\text{CDCl}_3 = 7.24$ ppm) and FTIR spectra were recorded on a Perkin-Elmer 1720 X instrument. Electro-spray mass spectra were obtained with a VG Bio-Q triple quadrupole mass spectrometer (Bio-Q, V.G. Bio Tech., Altrincham, Cheshire, England) using a water/methanol/acetic acid mobile phase. The compound was dissolved in dichloromethane (2 mM), and this solution was then diluted 1:10 with methanol. Details concerning experimental parameters have been published.¹⁵

Reagents and Voltammetric Instrumentation. Unless otherwise stated, all reagents were of analytical or electrochemical grade purity. The supporting electrolyte (NBu₄PF₆, tetrabutylammonium hexafluorophosphate) was prepared using a literature procedure.¹⁶ Purified and dried¹⁷ solvents were used in an electrochemical cell connected to a Schlenk line. Instruments used for electrochemical measurements were a BAS 100A electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) (IR compensation was used as recommended by the manufacturer) and a Cypress Systems Model SYCY-1 electroanalysis system. All potentials have been referenced to internal ferrocene ($E_{1/2} = 0.00$ V) but were measured using a Ag/AgCl reference (a AgCl-coated silver wire which was immersed and equilibrated in the electrolyte containing solvent used for the experiment).

Results and Discussion

The preparation of the cationic metal hydride complexes **1–6** involves a simple protonation reaction of the neutral metal carbonyl compounds. The synthesis of these compounds has been described⁸ previously except for $[\text{Cr}(\text{CO})_2(\text{dpe})_2\text{H}]^+$ (**2**). The complex *trans*- $\text{Cr}(\text{CO})_2(\text{dpe})_2$ undergoes photooxidation in halogenated solvents. Since the protonation step is associated with an equilibrium reaction (eq 1), it follows that, in the presence of light, photooxidation is a major side reaction. However, in absence of light, compound **2** may be readily prepared. The spectroscopic data for compounds **1–6** are collected in Table 1. These data (where comparisons are available) are consistent with published results, although some interesting new features may be extracted. The chemical shifts of the ¹H-NMR resonances of the hydride protons occur at relatively lower frequency for the chromium species **1** and **2** as well as for compounds **4** and **6** with dpe ligands. Compound **2** exhibits a high rate of structural fluctuation, as indicated by the quintet splitting of the ¹H-NMR signal for the hydride proton at room temperature which freezes into a triplet of triplets only at low temperature. On the other hand, compound **1** does exhibit a small rate of structural fluctuation as indicated by the splitting of the ¹³C-NMR signal for the carbonyl carbon into a triplet of triplets and by the splitting of the ³¹P-NMR resonance into an AA'XX' system. At room temperature this is not observed for compounds **2–6**. The IR absorptions of the carbonyl bands, which are often employed as an indicator for electron density on the metal center donated into the carbonyl π^* -orbital, consistently show lower values (higher electron donation of the metal center) for the dpe-containing species **2**, **4**, and **6** compared to the dpm-containing compounds. Unfortunately, the IR absorption for the metal–hydride bond cannot be detected. The

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Table 1

compound	¹ H-NMR in CDCl ₃ , δ in ppm vs TMS	¹³ C{ ¹ H}-NMR in CDCl ₃ , δ in ppm vs TMS	IR absorption ν(C=O) in dichloromethane, cm ⁻¹		³¹ P NMR in CDCl ₃ , δ
			[M(CO) ₂ (P-P) ₂ H] ⁺	cis-M(CO) ₂ (P-P) ₂	
[Cr(CO) ₂ (dpm) ₂ H](SO ₃ CF ₃) (1) pale yellow	-7.22 (1H, tt, JHP109/27) CrH, 4.83 (4H, br) CH ₂ , 7.11-7.46 (40H, m) Ph	221.0 (tt, JCP18/12) CO, 134.9-128.9 Ph, 48.8 (t, JCP18) CH ₂	1976 w, 1885 s	1841 s, 1780 m	9.8, 45.8
[Cr(CO) ₂ (dpe) ₂ H](SO ₃ CF ₃) (2) pale yellow	-6.88 (1H, q, br, JHP30) CrH, 2.67 (8H, m) CH ₂ , 7.14-7.40 (40H, m) Ph	221.3 (q, JCP15) CO, 131.9-133.7 Ph, 36.9 (br) CH ₂ , 32.2 (br) CH ₂ ^a	1971 w, 1866 s	1846 s, 1772 m	76.4, 95.7
[Mo(CO) ₂ (dpm) ₂ H](SO ₃ CF ₃) (3) pale yellow	-3.66 (1H, tt, JHP66/14) MoH, 4.69 (4H, t, JHP8) CH ₂ , 7.08, 7.48 (40H, m) Ph	210.7 (q, JCP7) CO, 134.7-128.8 Ph, 46.2 (q, JCP15) CH ₂	1993 w, 1899 s	1859 s, 1791 m	-12.4, 15.7
[Mo(CO) ₂ (dpe) ₂ H](SO ₃ CF ₃) (4) pale orange	-5.36 (1H, tt, JHP70/12) MoH, 2.62-2.71 (8H, m) CH ₂ , 7.07-7.67 (40H, m) Ph	210.9 (q, JCP12) CO, 135.1-128.0 Ph, 32.3 (q, JCP7) CH ₂ , 26.4 (q, JCP7) CH ₂	1986 w, 1880 s	1851 s, 1783 m	54.7, 77.4
[W(CO) ₂ (dpm) ₂ H](SO ₃ CF ₃) (5) pale green	-1.53 (1H, tt, JHP65/14, JHW13) WH, 4.90 (4H, m) CH ₂ , 7.05-7.46 (40H, m) Ph	203.7 (JCW60), 133.8-123.0 Ph, 46.4 (m) CH ₂	1979 w, 1884 s	1856 s, 1791 m	-32.6, -11.8
[W(CO) ₂ (dpe) ₂ H](SO ₃ CF ₃) (6) pale yellow	-4.94 (1H, tt, JHP73/13, JHW16) WH, 2.54-2.76 (8H, m) CH ₂ , 7.08-7.47 (40H, m) Ph	203.5 (q, JCP7) CO, 134.5-128.6 Ph, 34.4 (m) CH ₂ , 25.7 (m) CH ₂	1974 w, 1866 s	1847 s, 1780 m	36.9, 57.6

^a Measured in acetonitrile-d₃.

Table 2. Peak Potentials^a Obtained from Cyclic Voltammograms (1 mm Diameter Pt Disk Electrode, *T* = 20 °C) for Reduction and Oxidation of Complexes 1-6 (1 mM) in Acetonitrile (0.1 M NBu₄PF₆, Scan Rate 20 mV s⁻¹) and Butyronitrile (0.2 M NBu₄PF₆, Scan Rate 200 mV s⁻¹)

	acetonitrile		butyronitrile	
	<i>E</i> _p ^{red} , V ^b	<i>E</i> _p ^{ox} , V ^b	<i>E</i> _p ^{red} , V ^b	<i>E</i> _p ^{ox} , V ^b
[Cr(CO) ₂ (dpm) ₂ H] ⁺ (1)	-2.12	0.55	-2.19	0.55
[Cr(CO) ₂ (dpe) ₂ H] ⁺ (2)	-2.13	0.45	-2.18	0.57
[Mo(CO) ₂ (dpm) ₂ H] ⁺ (3)	-2.26	0.75	-2.40	0.77
[Mo(CO) ₂ (dpe) ₂ H] ⁺ (4)	-2.39	0.88	-2.50	0.89
[W(CO) ₂ (dpm) ₂ H] ⁺ (5)	-2.29	0.75	-2.41	0.77
[W(CO) ₂ (dpe) ₂ H] ⁺ (6)	-2.48	0.86	-2.60	0.87

^a *E*_p^{red} and *E*_p^{ox} are the peak potentials for the irreversible reduction and oxidation processes, respectively. Some of the oxidation processes became reversible at faster scan rates or lower temperature (see text).
^b *V*_s Fc⁺/Fc.

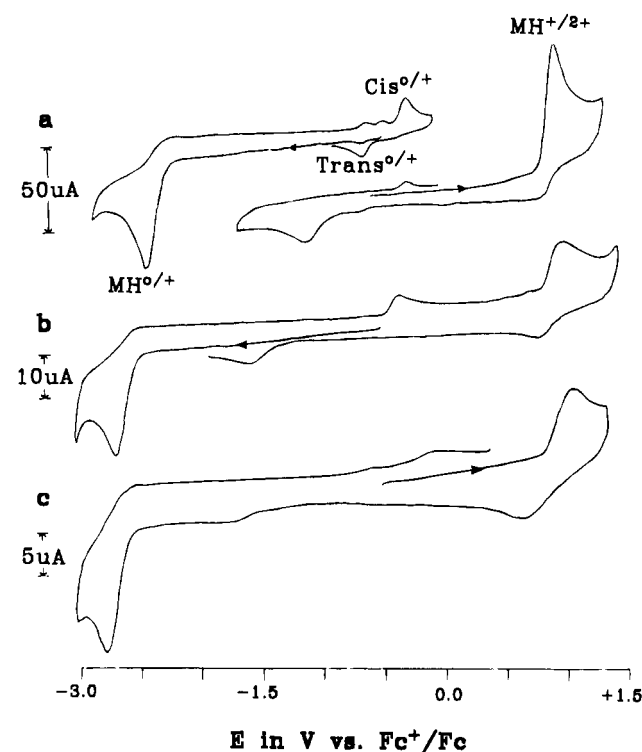


Figure 1. Cyclic voltammograms obtained for 1 mM [Mo(CO)₂(dpe)₂H](SO₃CF₃) (4) in butyronitrile (0.2 M NBu₄PF₆) at a scan rate of 200 mV s⁻¹ and with a 5 mm diameter glassy carbon disk electrode at temperatures of (a) 20 °C, (b) -30 °C, and (c) -50 °C.

molecular structure of complexes 1-6 may be assumed to be closely related to that of *trans*-[M(CO)₂(P-P)₂]⁺ as judged by the very weak IR absorption for the ν_{sym}(CO) at higher wavenumbers and confirmed in the particular case of [Mo(CO)₂(dpe)₂H]⁺ by X-ray crystallography.¹⁸

The voltammetric behavior of the metal hydride complexes 1-6 can be studied in acetonitrile (0.1 M NBu₄PF₆). The use of butyronitrile (0.2 M NBu₄PF₆) permits wider temperature and potential ranges to be used. Data obtained at 20 °C in both solvents are summarized in Table 2. While details of the processes are very scan rate and temperature dependent, all complexes exhibit related behavior in that they can be oxidized at potentials around 1 V vs Fc⁺/Fc and are reduced at about -2.7 V vs Fc⁺/Fc at a glassy carbon electrode. Figure 1 shows cyclic voltammograms of [Mo(CO)₂(dpe)₂H]SO₃CF₃ (4) ob-

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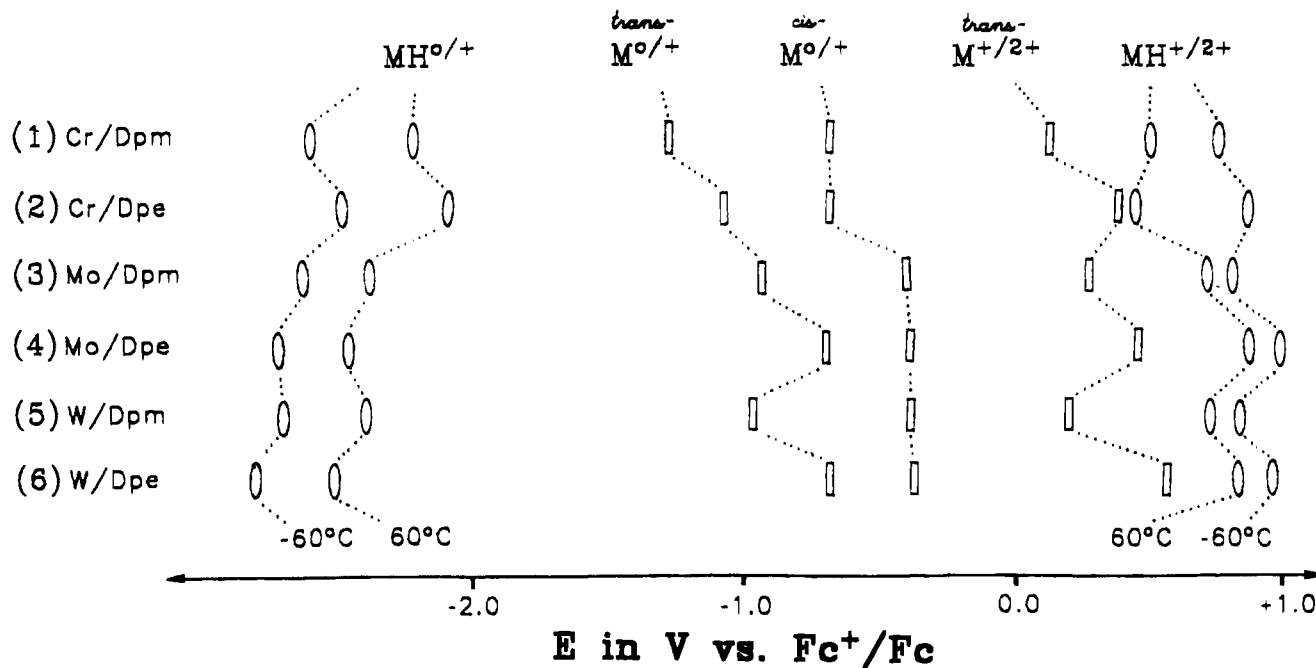
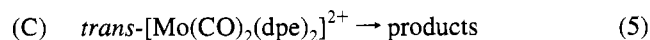
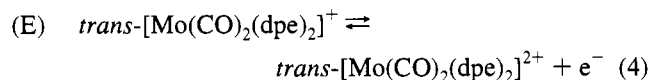
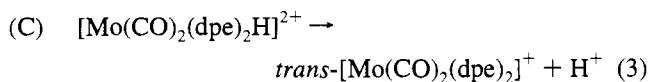
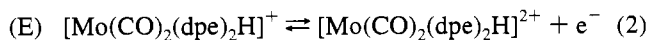


Figure 2. Summary of *trans*- $M^{0/+}$, *cis*- $M^{0/+}$, and *trans*- $M^{+/2+}$ potentials obtained from cyclic voltammograms recorded in acetone (0.1 M NBu_4ClO_4).⁹ Potentials are converted to the Fc^+/Fc reference system by assuming $E^\circ(\text{Fc}^+/\text{Fc}) = 0.32 \text{ V vs Ag/AgCl (0.1 M LiCl, acetone)}$. Data for $\text{MH}^{0/+}$ and $\text{MH}^{+/2+}$ potentials are obtained from cyclic voltammograms in butyronitrile (0.2 M NBu_4PF_6) at $T = -60$ and $+60$ °C.

tained under a range of conditions. The oxidation process at 0.92 V vs Fc^+/Fc becomes chemically reversible at low temperature (-30 °C at a scan rate of 200 mV s^{-1}), although the shape of the response is broad presumably due to irreversible heterogeneous charge transfer kinetics. In contrast, the reduction process, which has a peak potential of $-2.43 \text{ V vs Fc}^+/\text{Fc}$ at 20 °C remains irreversible at low temperature.

Potential data obtained at -60 and at $+60$ °C for oxidation and reduction of the hydride complexes are compared with data obtained for the *cis*- and *trans*- $M(\text{CO})_2(\text{P-P})_2$ complexes⁹ in Figure 2. A distinct pattern which depends on both the metal center and the phosphine ligand can be observed for the nonprotonated complexes. The small variation with phosphine ligand implies minimal influence of the ligand on the reversible potential for oxidation of the *cis* species (*cis*- $M^{0/+}$). The pattern shown in Figure 2 for the *trans*- $M^{0/+}$ process also is observed for the *trans*- $M^{+/2+}$ process and, although less pronounced, also for the oxidation of the hydride complexes ($\text{MH}^{+/2+}$). The evidence available that the structures of the hydride complexes 1–6 are closely related to the *trans* forms is therefore supported by this pattern. Interestingly, the reduction potentials for the hydride complexes exhibit a different (opposite) trend. However, since this is an irreversible process in which the potentials are determined by both kinetic and thermodynamic considerations, the significance of the observation is not clear.

The scan rate and temperature dependence, the nature of the processes on second and subsequent cycles of the voltammogram, and the fact that the potentials for the oxidation of nonprotonated compounds are less positive than those for oxidation of the hydride complexes (Figure 2) suggest that the $\text{MH}^{+/2+}$ oxidation process may be of the ECEC type. An example ECEC mechanism that is consistent with the available data is given for $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}]^+$ (4) in eqs 2–5. That is,



the oxidation process at 0.92 V vs Fc^+/Fc is followed by loss of the proton to give the monocationic complex *trans*- $[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+$. However, at this positive potential *trans*- $[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+$ must be immediately oxidized to give the dicationic product $[\text{Mo}(\text{CO})_2(\text{dpe})_2]^{2+}$, which then reacts further to give the final product of the oxidation. However, we have to point out that mechanistic pathways associated with disproportionation reactions have been proposed for oxidation of $[\text{ReCl}(\text{dpe})_2\text{H}]^+$.^{19a} The experiments used in this paper are not able to readily distinguish between a number of possible mechanisms.²⁰ Further speculation on the details of the mechanism is therefore unwarranted. The ultimate product has not been unambiguously identified. However, a new reduction process at $-1.12 \text{ V vs Fc}^+/\text{Fc}$ (Figure 1a) also observed on reverse scan after oxidation of *trans*- $[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+$ apparently generates *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$, which is identified *via* its characteristic oxidation process at $-0.30 \text{ V vs Fc}^+/\text{Fc}$ on second and subsequent cycles. The final product of the reaction can therefore in the absence of strongly coordinating anions be postulated to be a complex such as $[\text{Mo}(\text{CO})_2(\text{dpe})_2(\text{solvent})]^{2+}$ where solvent = butyronitrile or acetonitrile. Complexes of this type have been reported in other studies.¹⁰ A comparison of voltammograms obtained for complexes 1–6 at the same scan rate and temperature suggests that the short-lived formally 17-electron dications $[\text{M}(\text{CO})_2(\text{P-P})_2\text{H}]^{2+}$ are more stable in the order $\text{W} > \text{Mo} > \text{Cr}$ and are more stable when dpe is the ligand rather than dpm. That is, chemically reversible oxidation processes are obtained for

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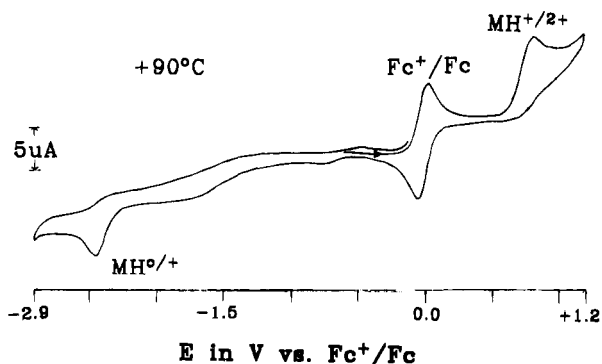


Figure 3. Cyclic voltammogram (scan rate 200 mV s^{-1} , 1 mm diameter platinum disk electrode, temperature $+90 \text{ }^\circ\text{C}$) of $1 \text{ mM } [\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}](\text{SO}_3\text{CF}_3)$ (**4**) in butyronitrile ($0.2 \text{ M NBu}_4\text{PF}_6$) in the presence of ferrocene as an internal standard.

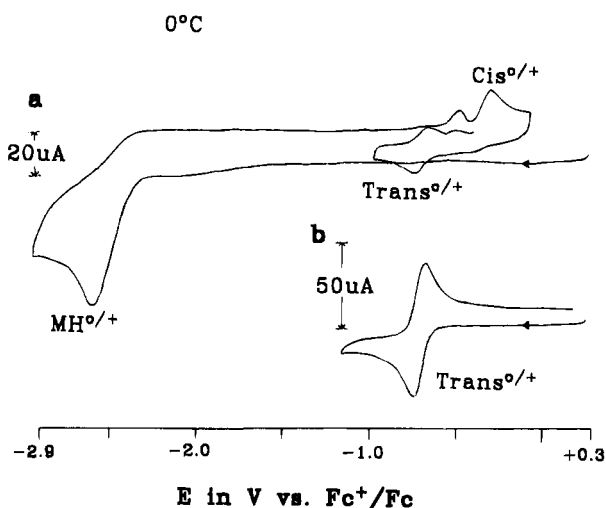
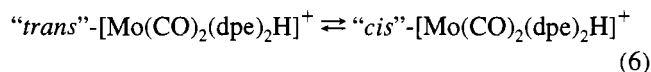


Figure 4. Cyclic voltammograms (scan rate of 200 mV s^{-1} , 5 mm diameter glassy carbon disk electrode, temperature $0 \text{ }^\circ\text{C}$) of (a) $1 \text{ mM } [\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}](\text{SO}_3\text{CF}_3)$ and (b) $1 \text{ mM } [\text{Mo}(\text{CO})_2(\text{dpe})_2](\text{SO}_3\text{CF}_3)$ in butyronitrile ($0.2 \text{ M Bu}_4\text{PF}_6$).

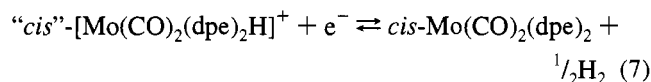
complexes **4–6** at low temperature, whereas the response for $[\text{W}(\text{CO})_2(\text{dpe})_2\text{H}]^{2+}$ is close to reversible even at $0 \text{ }^\circ\text{C}$ (scan rate of 200 mV s^{-1}). It is interesting to discuss the reason for this metastable behavior. A hydrogen atom bound as a hydride ligand with partial negative charge will not be able to dissipate the positive charge upon bond elongation, and a high kinetic barrier may result. A pathway leading to a positive polarization on the hydrogen atom may involve isomerization of the complex or may require more basic solvent media. An electrochemical study of cationic hydride complexes with related mechanistic features was recently reported by Pombeiro et al.¹⁹

The reduction responses for complexes **1–6** remain irreversible under all experimental conditions examined. At elevated temperatures, the molybdenum complexes **3** and **4** exhibit a sigmoidal step at about $-1.5 \text{ V vs Fc}^+/\text{Fc}$ (Figure 3) corresponding to a non-diffusion-controlled reduction process. Since this response is characteristic for platinum electrodes and is not observed at glassy carbon electrodes, this process may be interpreted as a catalytic prewave. One of the products of the irreversible reduction of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}]^+$ can be readily identified by cyclic voltammetry (Figure 4). Two product oxidation processes at -0.45 (small) and -0.30 V (large) vs Fc^+/Fc are observed on the reverse or positive potential scan direction regime of cyclic voltammograms. The small signal is attributable to a surface-based process (absorption). However, the major signal corresponds to oxidation of $\text{cis-Mo}(\text{CO})_2(\text{dpe})_2$, which can therefore be assumed to be generated directly from

reduction of the hydride complex. The formation of $\text{cis-Mo}(\text{CO})_2(\text{dpe})_2$ via isomerization of the $\text{trans-Mo}(\text{CO})_2(\text{dpe})_2$ complex is unlikely on the voltammetric time scale. If the trans isomer had been formed, then a reversible $\text{trans-}[\text{Mo}(\text{CO})_2(\text{dpe})_2]^{0/+}$ process (Figure 4b) should have been observed. In contrast, the trans isomer was formed by chemical deprotonation,^{7,21} and presumably, the difference must be explained by the mechanism for the reduction process. In one possible reduction pathway, metal–hydrogen bond cleavage may be facilitated via a fast preequilibrium reaction (eq 6). NMR data



show that some of the seven-coordinate metal hydride complexes are fluxional, so that this is a plausibly fast preequilibrium reaction. An alternative mechanism involving metal–hydrogen bond cleavage seems unlikely, particularly since $\text{trans-}[\text{Mo}(\text{CO})_2(\text{dpe})_2]$ is not the product and no H/D exchange occurs, as will be shown later. It is therefore proposed that the preequilibrium reaction is followed by reduction to produce hydrogen and $\text{cis-Mo}(\text{CO})_2(\text{dpe})_2$ (eq 7). The “ trans ” isomer



in eq 6 corresponds to the trans -related structure (capped octahedron) of the seven-coordinate metal hydride complex. However, the “ cis ” isomer in eqs 6 and 7 is only one of several possible isomers having seven-coordinate geometry that are energetically similar. A difference in reduction potential for “ trans ” and “ cis ” isomers, corresponding to the difference in trans- and $\text{cis-M}(\text{CO})_2(\text{P-P})_2$ redox potentials, would allow preferential reduction of the “ cis ” isomer. The mechanism proposed in this work is consistent with the strong temperature and scan rate dependence of the reduction process, with the shift in potential being governed by the rate of the isomerization. However, mechanistic details concerning the formation of hydrogen are unknown.

An important method of confirming mechanistic aspects of reactions involves the use of isotopes. Isotope (H/D) effects may be especially significant for hydride complexes. Isotope effects are expected to be minimal with respect to thermodynamic redox potentials of hydride complexes but may alter the rate of proton exchange reactions associated with electron transfer if such reactions are rate determining, as has been postulated in the case of oxidation of complexes **1–6**. Consequently, the complex $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{D}]\text{SO}_3\text{CF}_3$ (**4b**) was prepared and its spectroscopy and voltammetry compared with those of complex **4**. $^1\text{H-NMR}$ spectra show that H/D exchange of **4b** in the presence of trifluoroacetic acid in dichloromethane/methanol is negligible even at $60 \text{ }^\circ\text{C}$. The expected and characteristic broad $^2\text{D-NMR}$ resonance was observed. (See Synopsis figure.) The degree of deuteration is conveniently and accurately determined by electropray mass spectrometry. A content of 16% hydrogen and 84% deuterium is found from the isotope pattern of the intact ion (Figure 5). Importantly, the voltammetry of compound **4b** differs from that of compound **4** with respect to the degree of chemical reversibility, so that a normal isotope effect is detected. In Figure 6 cyclic voltammograms of compounds **4** and **4b** are shown to have measurably different oxidation and reduction peak current ratios at $0 \text{ }^\circ\text{C}$ using a scan rate of 2000 mV s^{-1} . The conclusion is therefore

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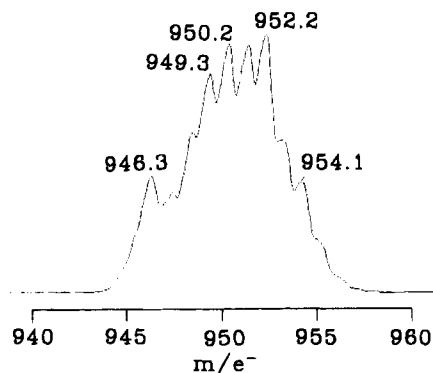


Figure 5. Electrospray mass spectrum for $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{D}](\text{SO}_3\text{CF}_3)$ (**4b**) dissolved in a 1:10 dichloromethane:methanol mixture.

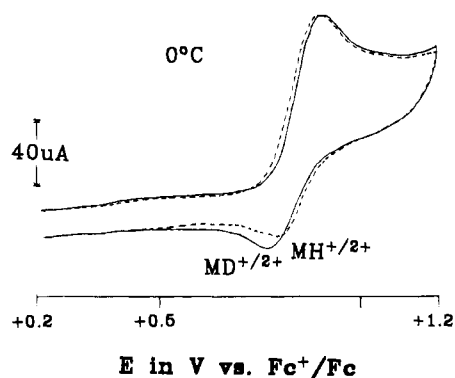


Figure 6. Comparison of cyclic voltammograms obtained for oxidation of 1 mM $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}](\text{SO}_3\text{CF}_3)$ (**4**) (dashed) and 1 mM $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{D}](\text{SO}_3\text{CF}_3)$ (**4b**) in butyronitrile (0.2 M NBu_4PF_6) at 0 °C using a scan rate of 2000 mV s^{-1} and a 5 mm diameter glassy carbon disk electrode.

reached that reactions involving the metal–hydrogen bond are thermodynamically or kinetically important components of the oxidation reaction.

The difference between the reversible redox potentials (E°

Table 3. Differences in Thermodynamic Acidity of MH^+ and MH^{2+} Calculated from the Reversible Potentials ($E_{1/2}$ Values) for the $\text{trans}^{0/+}$ and the $\text{MH}^{+/2+}$ Processes

	$E_{1/2}(\text{trans}^{0/+})$, V^a	$E_{1/2}(\text{MH}^{+/2+})$, V^a	$\text{p}K_a(\text{MH}^+) -$ $\text{p}K_a(\text{MH}^{2+})$
$[\text{Cr}(\text{CO})_2(\text{dpm})_2\text{H}]^+$ (1)	-1.25	0.52	30.0
$[\text{Cr}(\text{CO})_2(\text{dpe})_2\text{H}]^+$ (2)	-1.04	0.70	29.5
$[\text{Mo}(\text{CO})_2(\text{dpm})_2\text{H}]^+$ (3)	-0.92	0.73	27.9
$[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{H}]^+$ (4)	-0.68	0.87	26.2
$[\text{W}(\text{CO})_2(\text{dpm})_2\text{H}]^+$ (5)	-0.95	0.75	28.8
$[\text{W}(\text{CO})_2(\text{dpe})_2\text{H}]^+$ (6)	-0.68	0.82	25.4

^a V vs Fc^+/Fc calculated from the expression $E_{1/2} = E_p^{\text{ox}} - 0.028$ (V vs Fc^+/Fc).

values) for the processes $\text{trans-M}^{0/+}$ and $\text{MH}^{+/2+}$ provides a direct thermodynamic measure of the change in acidity that occurs upon oxidation (eq 8²²). Since the oxidation of

$$\text{p}K_a(\text{MH}^+) - \text{p}K_a(\text{MH}^{2+}) = \frac{F}{2.3RT} [E^\circ(\text{MH}^{+/2+}) - E^\circ(\text{trans-M}^{0/+})] \quad (8)$$

complexes **4–6** can be observed as reversible reactions, their redox potentials can be evaluated directly from the relationship $E_{1/2} \approx E^\circ$. For complexes **1–3**, E° values may be approximated from the peak potentials and by assuming that a similar mechanism applies for all compounds. Calculation based on eq 8 (Table 3) illustrates that the dicationic hydride complexes must be regarded as extremely strong acids.

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