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Electrochemical Investigations of Isomerism in Manganese and Group VI Dicarbonylbis[1,2-bis(diphenylphosphino)ethane] Complexes

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A series of complexes of the general formula [M(CO)$_2$(DPE)$_2$]$^{0,+,2+}$ is known (M = Mn, Cr, Mo, W; DPE = 1,2-bis(diphenylphosphino)ethane). In addition to existing in several oxidation states, some of the complexes have been isolated in cis and trans isomeric forms. Electrochemical investigations at mercury and platinum electrodes in acetone, dichloromethane, and nitromethane have given a wide variety of new synthetic, kinetic, and thermodynamic data on the complexes. The electrochemistry of the different oxidation states and isomeric forms is remarkably different and a highly specific technique for studying these complexes has been obtained. Strong evidence for the existence of the new complexes *cis*-[Cr(CO)$_2$(DPE)$_2$], *trans*-[Cr(CO)$_2$(DPE)$_2$]$^{2+}$, *trans*-Mo(CO)$_2$(DPE)$_2$, and *trans*-W(CO)$_2$(DPE)$_2$ and other complexes is presented. Evidence for the existence of *cis*-[M(CO)$_2$(DPE)$_2$]$^+$ (M = Cr, Mo, W) isomers in forms that are readily isomerized to the trans isomer has also been obtained. These complexes are stabilized considerably at low temperature. All thermodynamic data obtained are in accord with the known chemistry of the compounds. In oxidation state II, there is no evidence for stable cis isomers, while six-coordinate trans species decrease in kinetic stability in the order Cr > (Mo $\simeq$ W).

A series of complexes of the general formula [M(CO)$_2$(DPE)$_2$]$^{0,+,2+}$ has been isolated [M = Mn, Cr, Mo, W; DPE = (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$]. With manganese, the known species[1-3] are *trans*-[Mn(CO)$_2$(DPE)$_2$]$^+$ and *trans*-[Mn(CO)$_2$(DPE)$_2$]$^{2+}$. For chromium, *trans*-[Cr(CO)$_2$(DPE)$_2$] and *trans*-[Cr(CO)$_2$(DPE)$_2$]$^+$ have been reported.[4,5] With molybdenum a variety of complexes of both cis and trans forms are known. *cis*-[Mo(CO)$_2$(DPE)$_2$] and *trans*-[Mo(CO)$_2$(DPE)$_2$]$^+$ have been well characterized.[4,6] Recently, the complexes *cis*-[Mo(CO)$_2$(DPE)$_2$]$^+$ and *cis*-[Mo(CO)$_2$(DPE)$_2$]$^{2+}$ have been reported in a preliminary communication.[7] With tungsten the species *cis*-[W(CO)$_2$(DPE)$_2$] and *trans*-[W(CO)$_2$(DPE)$_2$]$^+$ are known.[4,6]

The d^6 electron configuration species [M(CO)$_2$(DPE)$_2$]$^{n+}$ (for n = 0, M = Cr, Mo; for n = 1, M = Mn) are prepared by substitution reactions. Chemical oxidation with a variety of reagents such as iodine, perchloric acid, and nitrosyl hexafluorophosphate etc. then leads to the d^5 or d^4 cationic species.[3,5-7] In some cases retention of isomerism is observed, and in others cis to trans or trans to cis rearrangements are found. The structures of the trans and cis isomers of the [M(CO)$_2$(DPE)$_2$]$^{0,+,2+}$ species are

Trans   Cis
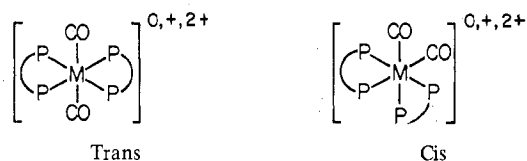
From synthetic oxidation and reduction reactions, the oxidation state of the central metal group and the particular metal group itself appears to play a significant role in the preferred stereochemistry. Electrochemical oxidation and reduction of such complexes, in general, would be expected

to be substantially more specific than chemical processes and can provide kinetic and thermodynamic information. Furthermore, the possibility of synthesizing complexes in new oxidation states or in new isomeric forms may result from electrochemical investigations. Consequently a comprehensive electrochemical investigation has been undertaken on these complexes utilizing the techniques of dc and ac polarography at a dropping mercury electrode, ac and cyclic voltammetry at Pt electrodes, and low-temperature electrochemistry. Work was carried out in a variety of solvents including acetone, dichloromethane, and nitromethane.

Experimental Section

Literature procedures were used to prepare [M(CO)$_2$(DPE)$_2$]^0 (M = Cr, Mo, W[4]) [M(CO)$_2$(DPE)$_2$]$^+$ (M = Cr,[5] Mo,[5] Mn[1]), and [Mn(CO)$_2$(DPE)$_2$]$^{2+}$.[3] *trans*-[W(CO)$_2$(DPE)$_2$]$^+$ was prepared by the method previously established for the Cr and Mo complexes.[5]

Reagents. All solvents used were of reagent grade purity. Tetraethylammonium perchlorate was used as the supporting electrolyte at a concentration of 0.1 M in acetone and nitromethane at room temperature and as a saturated solution in dichloromethane. For low-temperature work a saturated solution of the supporting electrolyte was used in all cases. All solutions were degassed with argon.

Instrumentation. (i) Polarography. All ac and dc polarograms were obtained with a Metrohm E261 Polarecord. For dc polarography a three-electrode system was used with a Metrohm E446 *iR* compensator. Three-electrode ac polarography was achieved with a Metrohm E393 ac modulator coupled to the *iR* compensator as described elsewhere.[8] An alternating potential of 10 mV rms at 50 Hz was used. The reference electrode was Ag–AgCl (0.1 M LiCl; acetone) separated from the test solution by a salt bridge containing 0.1 M tetraethylammonium perchlorate. The third or auxiliary electrode was platinum wire. Polarograms were recorded in acetone at 25° with controlled drop time of 0.20 sec obtained with a Metrohm E354 Polarographie Stand.

(ii) Ac and Cyclic Voltammetry. Ac and cyclic voltammograms were recorded at a platinum sheet working electrode in acetone, dichloromethane, and nitromethane using a PAR Model 170 electrochemistry system. The reference and auxiliary electrodes were the same as used in the polarography. Solutions were thermostated at 25° and unless otherwise stated results refer to this temperature. Low-temperature electrochemistry at −70° was carried out using an acetone–Dry Ice mixture. Scan rates of dc potential of 100 or 200 mV/sec were used in both ac and cyclic voltammetry. An alternating potential of 10 mV p-p, at frequencies between 10 and 1100 Hz, was used in the ac work. Phase-selective detection was used in the ac voltammetry. All voltammograms were recorded with a three-electrode circuit plus positive feedback circuitry to minimize ohmic losses.

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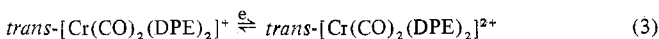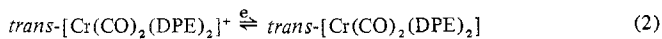(7) R. H. Reimann and E. Singleton, *J. Organometal. Chem.*, 32, C44 (1971).

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Results and Discussion

(I) Manganese. *trans*-[Mn(CO)$_2$(DPE)$_2$]$^+$ and *trans*-[Mn(CO)$_2$(DPE)$_2$]$^{2+}$. The electrochemistry at Pt is simple and extremely well defined. Figure 1 shows cyclic voltammograms of *trans*-[Mn(CO)$_2$(DPE)$_2$]ClO$_4$ in acetone and dichloromethane. A chemically reversible one-electron redox couple is obtained at rather positive potentials *vs.* Ag–AgCl. For the cyclic voltammograms, the oxidation and reduction branches gave peaks of equal height. In acetone, the peak separation at 25° was 70 mV, but in dichloromethane, 140 mV. Thus in dichloromethane some degree of irreversibility in the charge-transfer step is indicated. However, complete chemical reversibility is found in both solvents. The linear-sweep ac voltammogram of the oxidation in acetone gave a symmetrical wave with a peak potential $E_p(\sim)$ of +1.08 V *vs.* Ag–AgCl. This value will be assumed to be the reversible half-wave potential, $E^r_{1/2}$, for the d^5 ⇌ d^6 Mn(II)–Mn(I) couple. A slightly more positive value was obtained in dichloromethane.

A reversible one-electron reduction wave also with an $E^r_{1/2}$ value of +1.08 V *vs.* Ag–AgCl was found for the *trans*-[Mn(CO)$_2$(DPE)$_2$]$^{2+}$ complex in acetone. Thus the electrode process for the manganese complex is assumed to occur with retention of geometry and is described by eq 1. The half-

$$trans\text{-}[\mathrm{Mn(CO)}_2(\mathrm{DPE})_2]^+ \overset{e}{\rightleftharpoons} trans\text{-}[\mathrm{Mn(CO)}_2(\mathrm{DPE})_2]^{2+} \qquad (1)$$
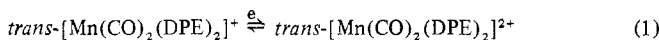
wave potential is entirely consistent with the chemical redox reactions. That is, strong oxidants are required to produce the trans dipositive cation.[3] The $E^r_{1/2}$ value for the d^5–d^6 redox couple was too positive to enable the electrode process to be studied at mercury electrodes.

(II) Chromium. (i) *trans*-[Cr(CO)$_2$(DPE)$_2$]$^+$. The electrochemistry of *trans*-[Cr(CO)$_2$(DPE)$_2$]$^+$ is also extremely well defined. One reversible reduction wave and one reversible oxidation wave were observed at Pt in acetone, dichloromethane, and nitromethane. Figure 2 shows a cyclic voltammogram of the reduction wave in acetone and Figure 3 shows both the reduction and oxidation waves in dichloromethane. At a dme, a reversible one-electron reduction wave was found corresponding to the reduction wave found at platinum. Other polarographic oxidation waves at more positive potentials were also found but were attributable to interaction with mercury. Such waves were not found at platinum. The ligand itself gave concentration-dependent adsorption-controlled and diffusion-controlled polarographic waves, attributable to the formation of mercury complexes at potentials similar to those of the additional waves observed at mercury. The ligand waves are not of interest to the current work and therefore are not reported in detail. Table I summarizes data obtained for this complex. The electrode processes are described by eq 2 and 3. Retention of geometry

$$trans\text{-}[\mathrm{Cr(CO)}_2(\mathrm{DPE})_2]^+ \overset{e}{\rightleftharpoons} trans\text{-}[\mathrm{Cr(CO)}_2(\mathrm{DPE})_2] \qquad (2)$$

$$trans\text{-}[\mathrm{Cr(CO)}_2(\mathrm{DPE})_2]^+ \overset{e}{\rightleftharpoons} trans\text{-}[\mathrm{Cr(CO)}_2(\mathrm{DPE})_2]^{2+} \qquad (3)$$

will be verified by further work. The trans dipositive cation has not been reported, and this work provides the first evidence for its existence. Endeavors to synthesize this compound are currently in progress. The $E^r_{1/2}$ value for the oxidation process suggests that oxidants of strength similar to that used to prepare the *trans*-[Mn(CO)$_2$(DPE)$_2$]$^{2+}$ species should produce the chromium(II) entity. The $E^r_{1/2}$ value for the Cr(I)–Cr(0) reduction shows that the chromium(I)
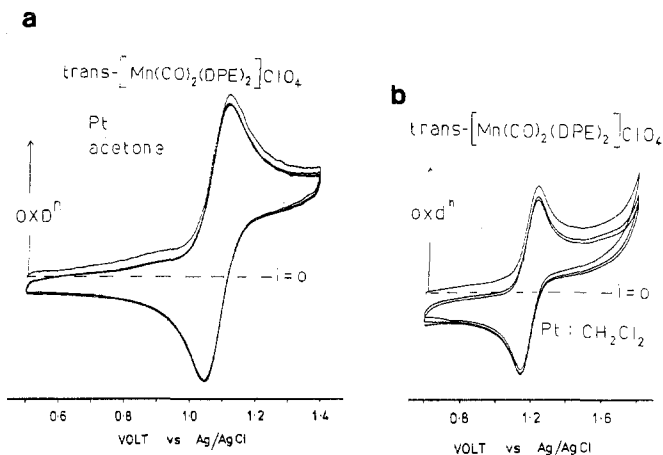

Figure 1. Cyclic voltammograms for the oxidation of *trans*-[Mn(CO)$_2$(DPE)$_2$]$^+$ in (a) acetone and (b) dichloromethane.
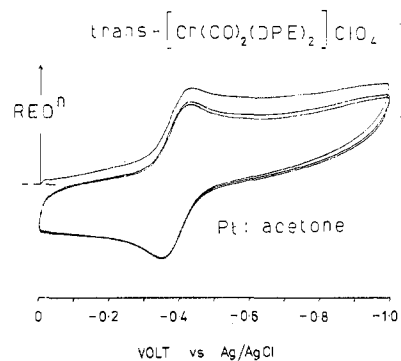

Figure 2. Cyclic voltammogram for the reduction of *trans*-[Cr(CO)$_2$(DPE)$_2$]$^+$.
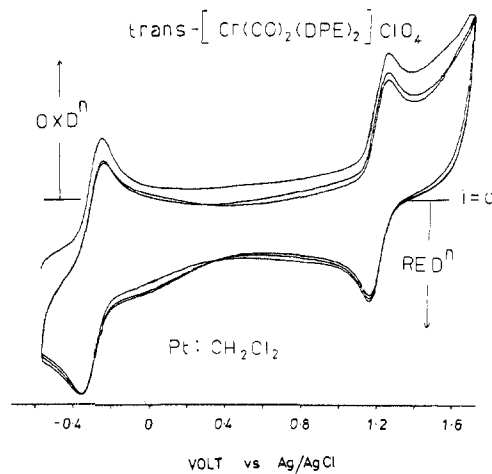

Figure 3. Cyclic voltammogram for the reduction (more negative electrode process) and oxidation (more positive electrode process) of *trans*-[Cr(CO)$_2$(DPE)$_2$]$^+$.

species should be reduced by moderately strong reductants, in agreement with the known chemistry.

(ii) [Cr(CO)$_2$(DPE)$_2$]. The electrochemistry of the nominally trans-Cr(0) complex was not as straightforward as found with previous complexes nor as would be predicted from previous discussion of the trans-Cr(I) species. The predicted behavior would be two oxidation waves

$$\text{trans-Cr(0)} \overset{e}{\rightleftharpoons} \text{trans-Cr(I)} \overset{e}{\rightleftharpoons} \text{trans-Cr(II)}$$
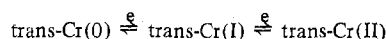
both having the same $E_{1/2}$ values as the waves given by eq 2 and 3.

Table I. Electrochemical Data^a for trans-[Cr(CO)₂(DPE)₂]ClO₄

Solvent	Polarography Dc $E_{1/2}$, V	Polarography Dc Slope,^b mV	Polarography Ac $E_p(\sim)$, V	Polarography Ac Half width,^c mV	CV redn E_p,V Cr(I)-Cr(0)	CV redn E_p,V Cr(0)-Cr(I)	CV redn $E_{1/2}$, V	CV redn Ratio of peak currents	CV oxidn E_p,V Cr(I)-Cr(II)	CV oxidn E_p,V Cr(II)-Cr(I)	CV oxidn Ratio of peak currents	CV oxidn $E_{1/2}$, V
Acetone	-0.39	64	-0.39	90	-0.42	-0.36	-0.39	1.0	1.12	1.04	1.0	1.08
Dichloromethane					-0.38	-0.28	-0.35	1.0	1.25	1.14	1.1	1.20
Nitromethane					-0.47	-0.38	-0.42	1.0	1.06	0.98	1.0	1.01

^a All potentials in volts vs. Ag–AgCl (0.1 M LiCl; acetone). ^b Slope of the plot of E vs. log [(i_d-i)/i] where i is dc current at potential E and i_d is limiting or diffusion-controlled dc current. ^c Potential separation at half-wave height which is approximately 90 mV for a reversible one-electron step. ^d Data reported at a scan rate of 200 mV/sec. ^c Potential separation at half-wave height.

Table II. Electrochemical Data^a for the Cr(CO)₂(DPE)₂ Complexes

Solvent	Poly Wave 1^b Dc $E_{1/2}$, V	Poly Wave 1^b Dc Slope,^f mV	Poly Wave 1^b Ac $E_p(\sim)$, V	Poly Wave 1^b Ac Half-width,^g mV	Poly Wave 2^c Dc $E_{1/2}$, V	Poly Wave 2^c Dc Slope,^f mV	Poly Wave 2^c Ac^e $E_p(\sim)$, V	Poly Wave 2^c Ac^e Half-width,^g mV	CV Wave 1^b E_p,V Oxidn	CV Wave 1^b E_p,V Redn	CV Wave 1^b $E_{1/2}$, V	CV Wave 2^c E_p(oxidn), V	CV Wave 2^c $E_{1/2}$, V	CV Wave 3^d E_p,V Oxidn	CV Wave 3^d E_p,V Redn	CV Wave 3^d $E_{1/2}$, V
Acetone	-0.37	64	-0.38	100	0.03	100	0.09	160	-0.34	-0.40	-0.36	0.05	0.02	1.12	1.04	1.08
Dichloromethane									-0.26	-0.36	-0.31	0.11	0.08	1.27	1.18	1.23
Nitromethane									-0.38	-0.48	-0.43	0.02	0.01	1.07	0.98	1.02

^a All potentials in volts vs. Ag–AgCl (0.1 M LiCl; acetone). ^b Oxidation: trans-Cr(CO)₂(DPE)₂ ⇌ trans-[Cr(CO)₂(DPE)₂]⁺. ^c Oxidation: cis-Cr(CO)₂(DPE)₂ ⇌ cis-[Cr(CO)₂(DPE)₂]⁺ → trans-[Cr(CO)₂(DPE)₂]⁺.[k] ^d Oxidation: trans-[Cr(CO)₂(DPE)₂]⁺ ⇌ trans-[Cr(CO)₂(DPE)₂]²⁺. ^e Ac wave exhibits shoulders. Main peak quoted. ^f Slope of the plot of E vs. log [(i_d-i)/i]. ^g Potential separation at half-wave height.

Table III.^a Electrochemical Data for trans-[Mo(CO)₂(DPE)₂]ClO₄

Solvent	Poly Dc $E_{1/2}$, V	Poly Dc Slope, mV	Poly Ac $E_p(\sim)$, V	Poly Ac Half-width, mV	CV redn E_p,V Mo(I)-Mo(0)	CV redn E_p,V Mo(0)-Mo(I)	CV redn Ratio of peak currents	CV redn $E_{1/2}$, V	Oxidn Wave 2^d E_p,V Oxidn	Wave 2^d E_p,V Redn	Wave 2^d $E_{1/2}$, V	Wave 3^e E_p,V Oxidn	Wave 3^e E_p,V Redn	Wave 3^e $E_{1/2}$, V
Acetone	-0.04	64	-0.04	96	-0.05	0.01	1.0	-0.03	1.24	1.12	1.19			
Dichloromethane					-0.02	0.08	1.0	0.03	1.34	1.27	1.30		1.22	
Nitromethane					-0.10	-0.02	1.0	-0.06	1.23	1.07	1.18			

^a Footnotes in Table I apply.

Table IV.^a Electrochemical Data^a for cis-Mo(CO)₂(DPE)₂

Solvent	Poly^b Dc $E_{1/2}$, V	Poly^b Dc Slope, mV	Poly^b Ac $E_p(\sim)$, V	Poly^b Ac Half-width, mV	CV Wave 1^c E_p,V Oxidn	Wave 1^c E_p,V Redn	Wave 1^c $E_{1/2}$, V	Wave 2^d E_p,V Oxidn	Wave 2^d E_p,V Redn	Wave 2^d $E_{1/2}$, V	Wave 3^e E_p,V Oxidn	Wave 3^e E_p,V Redn	Wave 3^e $E_{1/2}$, V
Acetone	0.28	52	0.33	90	0.03	-0.03	0.00	0.34	0.24	0.31	1.18		1.14
Dichloromethane					0.06	-0.02	0.03	0.39	0.30	0.36	1.31	1.20	1.27
Nitromethane					-0.02	-0.08	-0.04	0.33		0.30	1.24		1.19

^a Footnotes in Table I apply in addition to those below. ^b Electrode process: cis-Mo(CO)₂(DPE)₂ ⇌ cis-[Mo(CO)₂(DPE)₂]⁺ → trans-[Mo(CO)₂(DPE)₂]⁺. ^c Reduction wave seen on repetitive cycling. ^d Same electrode process as in footnote b for polarography. ^e Oxidation of trans-[Mo(CO)₂(DPE)₂]⁺.

trans-[Mo(CO)₂(DPE)₂]⁺ ⇌ trans-Mo(CO)₂(DPE)₂.

Figure 4 shows a cyclic voltammogram of the complex in dichloromethane at 25°. Clearly, three oxidative electrode processes are observed. Figures 5a and 5b show a comparison of the low-temperature cyclic voltammetry of the two most negative waves at −70° and at 25° in acetone. At low temperatures, all three electrode processes are chemically reversible with respect to cyclic voltammetry, based on the unity ratio of anodic to cathodic peak heights. This is clearly not found at 25°. At the dme two oxidation waves were observed corresponding to the two most negative waves. Data for this complex are summarized in Table II.

From the peak potentials and $E_{1/2}$ values, the most negative wave can be assigned to the oxidation

$$trans\text{-}[Cr(CO)_2(DPE)_2] \overset{e}{\rightleftharpoons} trans\text{-}[Cr(CO)_2(DPE)_2]^+ \qquad (4)$$
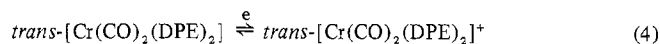
This is of course the reverse of eq 2, which describes the reduction of $trans\text{-}[Cr(CO)_2(DPE)_2]^+$. However, on the cyclics of this wave the ratio of anodic to cathodic peaks at 25° was only unity if the scan reversal potential was set at potentials less positive than that of the onset of the second oxidation wave. If the cyclic reversal potential was selected so that the other oxidation waves were included in the scan, then the cathodic branch of the most negative wave became larger than the anodic branch. Furthermore, the oxidation step

$$trans\text{-}Cr(I) \overset{e}{\rightleftharpoons} trans\text{-}Cr(II)$$
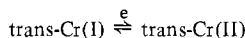
had equal anodic to cathodic peaks heights, which are larger in magnitude than the anodic branch of the most negative wave but almost equal to this wave's cathodic branch when all waves were recorded simultaneously.

Analysis of the polarographic waves, based on the assumption of equal diffusion coefficients, showed that the two most negative oxidation waves are collectively equivalent to a one-electron oxidation. Both ac and dc data show that the most negative

$$trans\text{-}Cr(0) \overset{e}{\rightleftharpoons} trans\text{-}Cr(I)$$
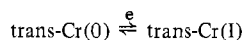
wave is reversible, but the second wave exhibits reversible charge transfer with a follow-up chemical reaction, to give an overall irreversible wave. The data at mercury electrodes are entirely consistent with the cyclic voltammetry at Pt electrodes. Apparently, two isomers of $Cr(CO)_2(DPE)_2$ were formed on its preparation. The second wave therefore corresponds to oxidation of another isomer, presumably $cis\text{-}[Cr(CO)_2(DPE)_2]$, and this electrode process is written as

$$cis\text{-}[Cr(CO)_2(DPE)_2] \overset{e}{\rightleftharpoons} cis\text{-}[Cr(CO)_2(DPE)_2]^+ \overset{k}{\rightarrow}$$
$$trans\text{-}[Cr(CO)_2(DPE)_2]^+ \qquad (5)$$
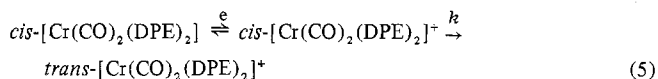
The rate constant k is fast at 25° but quite slow at −70°. All cyclic data at Pt electrodes are entirely consistent with this mechanism. At −70°, $cis\text{-}[Cr(CO)_2(DPE)_2]^+$ is therefore available for oxidation to $cis\text{-}[Cr(CO)_2(DPE)]^{2+}$, but we predict that the $E_{1/2}$ value will be close to the solvent breakdown potential.

The $E_{1/2}$ value for the trans–trans Cr(0)–Cr(I) couple indicates that the $trans\text{-}Cr(CO)_2(DPE)_2$ species will readily be oxidized, in comparison with the $trans\text{-}[Mn(CO)_2(DPE)_2]^+$ species. This is in accordance with the known chemistry.[3] Furthermore, oxidation of either isomer, according to the electrochemistry, would lead to the formation of $trans\text{-}[Cr(CO)_2(DPE)_2]^+$, although the assumed $cis\text{-}Cr(CO)_2(DPE)_2$ is predicted to be more difficult to oxidize.
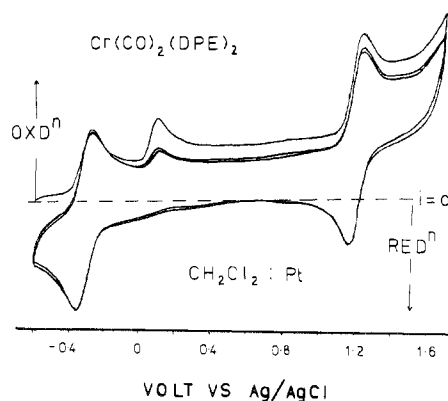

Figure 4. Cyclic voltammogram for the oxidation of a mixture of *cis*- and *trans*-$Cr(CO)_2(DPE)_2$.

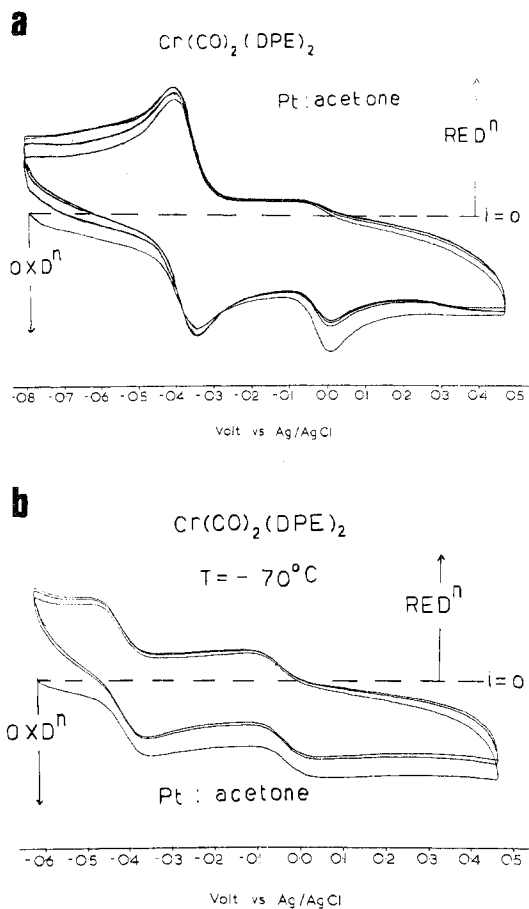**Figure 5.** Cyclic voltammograms for the two most negative waves for the oxidation of $Cr(CO)_2(DPE)_2$ at variable temperature: (a) 25°; (b) −70°.

Examination of the nominally trans $Cr(CO)_2(DPE)_2$ complex as prepared showed that it contained a mixture of red and golden yellow crystals. The product was previously washed with methyl ethyl ketone to remove the yellow tetracarbonyl. The $trans\text{-}[Cr(CO)_2(DPE)_2]^+$ species is a pale yellow so it is concluded that synthesis itself actually produced a mixture of *cis*- and *trans*-$Cr(CO)_2(DPE)_2$ in our hands. The red crystals are assigned as the trans and the golden yellow as the cis isomer.

On dissolution of the material into argon-saturated solvent an orange solution results. Polarographic data on such a solution show no cathodic current, and initially no $[Cr(CO)_2$-$(DPE)_2]^+$ species is present. On allowing oxygen to enter the system, the orange color gradually decreases in intensity

to yellow. Polarograms now contain both cathodic and anodic components. Analysis of the data reveals that the trans-Cr(0) complex has been oxidized preferentially by oxygen to the trans-Cr(I) cation leaving the cis-Cr(0) complex in solution. Monitoring of the process in an infrared cell where peaks in the CO stretching region may be assigned to each of these species confirms this mechanism.[9] The original report[4] of $Cr(CO)_2(DPE)_2$ indicated that both the cis and trans isomers could be obtained by crystallization from different solvents. The cis isomer was subsequently ascribed[5] to a mixture of trans species in zero and single-positive oxidation states since the combination of their infrared spectra (CO region) was very close to that originally reported for the cis complex. The electrochemistry shows that all three species can be formed and further work is in progress to verify the nature of the solvent-dependent equilibria implied by the original report. Data on the molybdenum complexes will provide substantial support for the above arguments as these complexes show considerable analogy with chromium.

(III) Molybdenum. (i) *trans-*$[Mo(CO)_2(DPE)_2]ClO_4$. The electrochemistry of this complex, like all of the trans isomers, is extremely well defined and straightforward. At around 0 V *vs.* Ag–AgCl a reversible one-electron reduction is observed. Figure 6a shows a cyclic voltammogram of this reduction process. Polarographically, a reversible reduction is also observed in both the ac and dc sense. Table III lists appropriate data. This electrode process is therefore assigned to the reaction given by eq 6.

$$trans\text{-}[Mo(CO)_2(DPE)_2]^+ \overset{e}{\rightleftharpoons} trans\text{-}Mo(CO)_2(DPE)_2 \qquad (6)$$
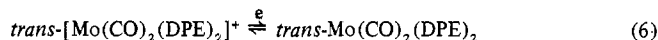
Retention of geometry during charge transfer is assumed as in previous cases. The product of the reduction, *trans-*$Mo(CO)_2(DPE)_2$, was not known prior to this work, as in zero oxidation state the cis complex has always been isolated. However, the electrochemistry suggests that reduction of the trans-Mo(I) cation should lead to a new isomer.

Reduction of *trans-*$[Mo(CO)_2(DPE)_2]^+$ with sodium amalgam in acetone and tetrahydrofuran produced a golden yellow solution. Polarographic monitoring of the reduction process is shown in Figure 7. The reduction wave is converted to an oxidation wave with the same $E_{1/2}$ value. This new species gives a pale yellow solution and, as will be shown in the next section, electrochemical behavior entirely different from that of *cis-*$Mo(CO)_2(DPE)_2$, so the new product is not the cis-Mo(0) complex. Polarographic evidence therefore conclusively demonstrates the existence of the trans isomer.

Infrared monitoring of the reduction shows the appearance of a new band at 1820 cm⁻¹ and the disappearance of the bands from the starting material. With time the band at 1820 cm⁻¹ diminishes in height and the two bands due to the cis-Mo(0) isomer appear. Thus the chemical reduction is given by eq 7.

$$trans\text{-}[Mo(CO)_2(DPE)_2]^+ \overset{Na(Hg)}{\rightleftharpoons} trans\text{-}Mo(CO)_2(DPE)_2 \xrightarrow[\text{isomerism}]{\text{slow}}$$
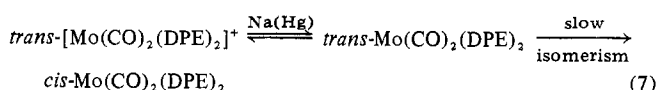$$cis\text{-}Mo(CO)_2(DPE)_2 \qquad (7)$$

Figure 6b shows the electrochemical oxidation of the complex in dichloromethane. Only a small degree of chemical reversibility was found in dichloromethane, and none was found in acetone or nitromethane. Analysis of linear-sweep

(9) F. L. Wimmer, M. R. Snow, and A. M. Bond, to be submitted for publication.
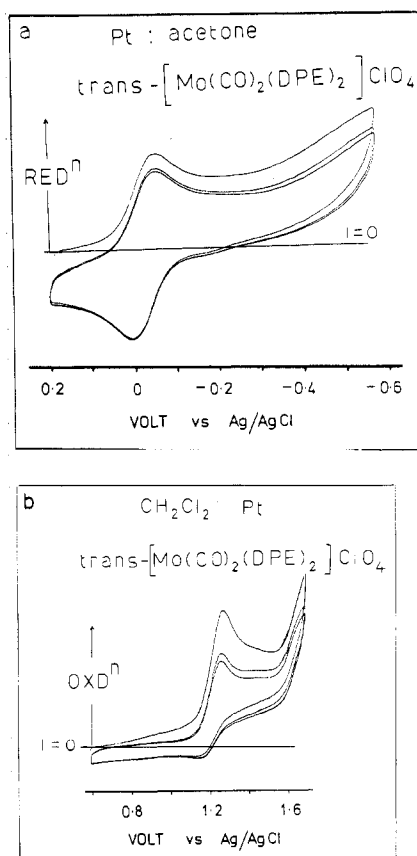
Figure 6. Cyclic voltammograms for (a) the reduction and (b) the oxidation of *trans-*$[Mo(CO)_2(DPE)_2]^+$.

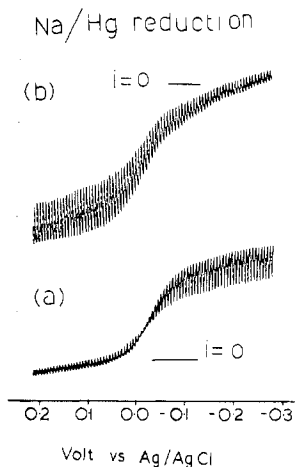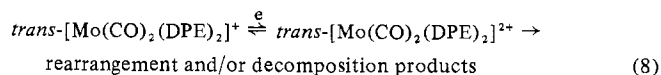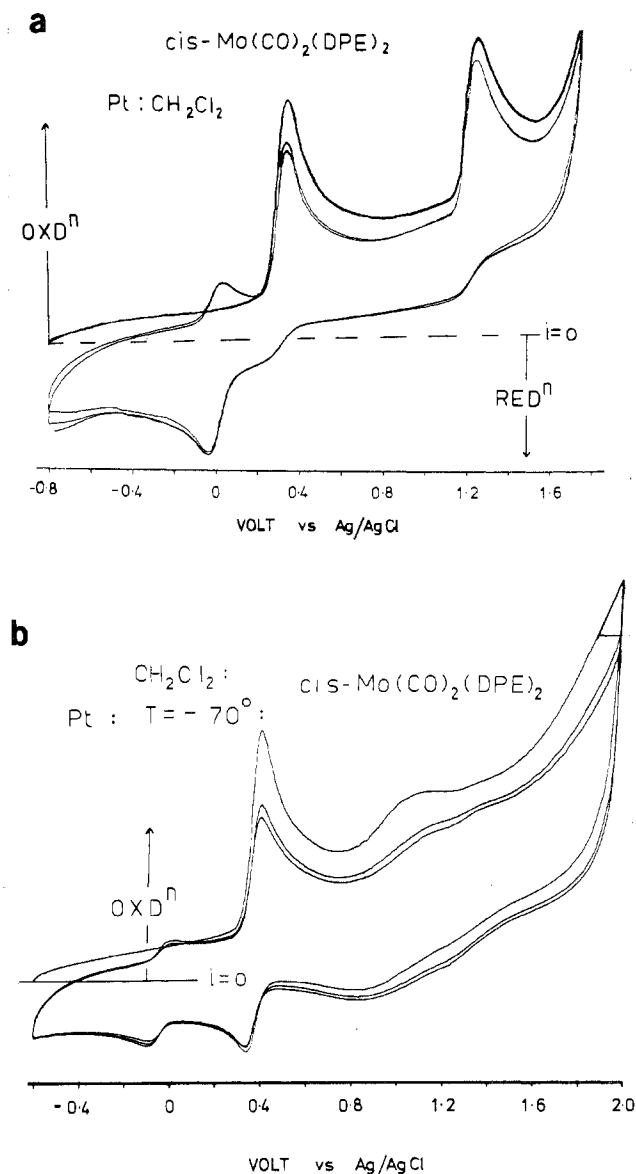**Figure 7.** Polarograms of *trans-*$Mo(CO)_2(DPE)_2$ before (a) and after (b) reduction with sodium amalgam.

ac and dc voltammograms suggests that the charge-transfer step is reversible. The oxidation process is therefore defined as

$$trans\text{-}[Mo(CO)_2(DPE)_2]^+ \overset{e}{\rightleftharpoons} trans\text{-}[Mo(CO)_2(DPE)_2]^{2+} \rightarrow$$
$$\text{rearrangement and/or decomposition products} \qquad (8)$$

(ii) *cis-*$Mo(CO)_2(DPE)_2$. Figure 8a shows a cyclic voltammogram of this *cis-*$Mo(CO)_2(DPE)_2$ complex in dichloromethane. On the first scan to positive potentials two oxidation waves are seen. On the first reverse scan three reduction waves are observed. In the second and subsequent cycles three oxidation and three reduction waves are present.
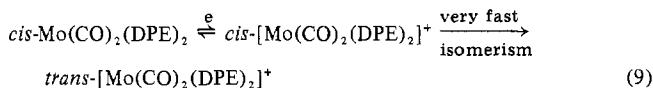
The most negative wave that grows on repetitive scans is the reversible trans-Mo(0)–trans-Mo(I) reduction couple. The

a

cis-Mo(CO)$_2$(DPE)$_2$

Pt : CH$_2$Cl$_2$

OXD^n

i = 0

RED^n

-0·8   -0·4   0   0·4   0·8   1·2   1·6

VOLT   vs   Ag/AgCl

b

CH$_2$Cl$_2$:

Pt :   T = -70° :   cis-Mo(CO)$_2$(DPE)$_2$

OXD^n

i = 0

-0·4   0   0·4   0·8   1·2   1·6   2·0

VOLT   vs   Ag/AgCl

Figure 8. Cyclic voltammogram for the oxidation of cis-Mo(CO)$_2$-(DPE)$_2$: (a) 25°; (b) -70°.

most positive oxidation step is identical with that observed with the trans-[Mo(CO)$_2$(DPE)$_2$]$^+$ complex and therefore is described by eq 8.

The additional electrode process to that found with trans-[Mo(CO)$_2$(DPE)$_2$]$^+$ is therefore identified as

$$cis\text{-Mo(CO)}_2(\text{DPE})_2 \overset{e}{\rightleftharpoons} cis\text{-[Mo(CO)}_2(\text{DPE})_2]^+ \xrightarrow[\text{isomerism}]{\text{very fast}}$$
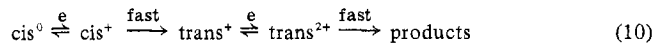
$$trans\text{-[Mo(CO)}_2(\text{DPE})_2]^+ \qquad (9)$$

The low-temperature electrochemistry is shown in Figure 8b and considerable reversibility for the cis^0-cis$^+$ couple is now observed. The rate constant for the isomerism is apparently much slower at low temperatures.

Polarographic data show one oxidation wave involving the Mo complex assignable to a reversible charge transfer with a follow-up reaction. Another more positive polarographic oxidation wave attributable to mercury-ligand interaction was also observed. This wave is not discussed. The following step is undoubtedly the cis-trans isomerism, and results at the dme are equivalent to those at platinum electrodes.

Electrochemical data for this complex are summarized in Table IV. From Figure 8 and the data in this table and com-

parison with results for the trans$^+$ complex given previously, it can be seen that the wave attributed to the oxidation of trans-[Mo(CO)$_2$(dpe)$_2$]$^+$ in eq 8 is almost identical with the most positive wave found for the cis^0 complex. This is consistent with the postulation of the rapid isomerization as given in eq 9. The entire oxidation process may therefore be represented as

$$cis^0 \overset{e}{\rightleftharpoons} cis^+ \xrightarrow{\text{fast}} trans^+ \overset{e}{\rightleftharpoons} trans^{2+} \xrightarrow{\text{fast}} \text{products} \qquad (10)$$

The product appears to be the precursor of "cis-[Mo(CO)$_2$-(DPE)$_2$]PF$_6$"[10] and may be a seven-coordinate species as frequently found in Mo and W oxidation state II in carbonyl chemistry.[11-15] No evidence for isomerism to cis-[Mo(CO)$_2$-(DPE)$_2$]$^{2+}$ was obtained from the electrochemistry.

Comparison of data in Tables II and IV shows that electrochemistry of the well-characterized and pure cis-Mo(CO)$_2$-(DPE)$_2$ complex is almost identical in every respect (except absolute $E_{1/2}$ values) with that of the assumed cis-Cr(CO)$_2$-(DPE)$_2$ species. The difference in $E_{1/2}$ values is entirely consistent with the known chemistry and these results for cis-Mo(CO)$_2$(DPE)$_2$ provide excellent substantiation for the existence of the cis-Cr(0) isomer. Voltammetry on cis-Mo(CO)$_2$(DPE)$_2$ has been briefly reported[11] along with that on other substituted metal carbonyls. Only one wave was tabulated ($E_{1/2}$ = -0.02 V vs. sce, 1 M aqueous LiCl), which we believe corresponds to the overall process of eq 9.
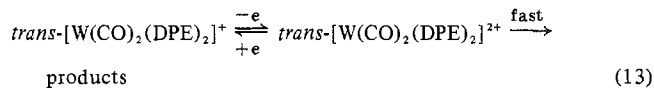
(IV) Tungsten. (i) cis-W(CO)$_2$(DPE)$_2$. The electrochemistry of this complex was very similar to that of the molybdenum analog. Table V summarizes the results from cyclic voltammetry. The first oxidation wave is

$$cis\text{-W(CO)}_2(\text{DPE})_2 \overset{-e}{\underset{+e}{\rightleftharpoons}} cis\text{-[W(CO)}_2(\text{DPE})_2]^+ \xrightarrow{\text{fast}}$$
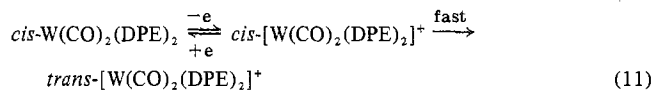
$$trans\text{-[W(CO)}_2(\text{DPE})_2]^+ \qquad (11)$$

On repetitive cycling the almost reversible trans-W(I)-trans-W(0) wave appears.

$$trans\text{-[W(CO)}_2(\text{DPE})_2]^+ \overset{+e}{\underset{-e}{\rightleftharpoons}} trans\text{-W(CO)}_2(\text{DPE})_2 \qquad (12)$$
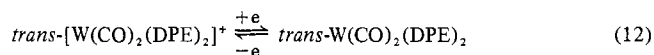
The oxidation wave at very positive potentials is also analogous to that found with molybdenum and can be written as

$$trans\text{-[W(CO)}_2(\text{DPE})_2]^+ \overset{-e}{\underset{+e}{\rightleftharpoons}} trans\text{-[W(CO)}_2(\text{DPE})_2]^{2+} \xrightarrow{\text{fast}}$$

$$\text{products} \qquad (13)$$

(ii) trans-[W(CO)$_2$(DPE)$_2$]$^+$. For this complex, one reduc-

(10) We are unable to confirm that the other species reported[7] by Reiman and Singleton is, as stated by them, cis-[Mo(CO)$_2$(DPE)$_2$]PF$_6$. We believe that it is the seven-coordinate species [Mo(CO)$_2$(DPE)$_2$F]-PF$_6$ on the basis of ^{19}F nmr spectroscopy, its electrochemistry, and reaction monitoring by infrared spectroscopy. In contrast to the transient and unstable cis-[Mo(CO)$_2$(DPE)$_2$]$^+$ species detected above the PF$_6^-$ salt produced by oxidation with NOPF$_6$ in dichloromethane[6] is stable in solution and is very difficult to oxidize or reduce further electrochemically. It is diamagnetic and gives a ^{19}F nmr signal at 11,212 Hz upfield relative to the center of the PF$_6^-$ doublet. Monitoring of this reaction by infrared spectroscopy (CO stretching region) shows that, on warming, [Mo(CO)$_2$(DPE)$_2$F]$^+$ is formed from the complex reported as cis-[Mo(CO)$_2$(DPE)$_2$]$^{2+}$. Our characterization of this last species is incomplete and details of these studies will be reported elsewhere.

(11) M. K. Lloyd, J. A. McCleverty, D. G. Orchard, J. A. Connor, M. B. Hall, I. H. Hillier, E. M. Jones, and G. K. McEwan, *J. Chem. Soc., Dalton Trans.*, 1743 (1973).

(12) R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, *J. Chem. Soc.*, 6570 (1965).

(13) J. A. Bowden and R. Colton, *Aust. J. Chem.*, **22**, 905 (1969).

(14) M. W. Anker, R. Colton, C. J. Rix, and I. B. Tomkins, *Aust. J. Chem.*, **22**, 1341 (1969).

(15) R. Colton and J. J. Howard, *Aust. J. Chem.*, **22**, 2543 (1969).

Table V. Electrochemical Data^a for cis-W(CO)$_2$(DPE)$_2$ Obtained by Cyclic Voltammetry

Solvent	Wave 1^b E_p, V Redn	Wave 1^b E_p, V Oxidn	Wave 1^b $E_{1/2}$, V	Wave 2^c E_p, V Oxidn	Wave 2^c E_p, V Redn	Wave 2^c $E_{1/2}$, V	Wave 3^d E_p, V Oxidn	Wave 3^d E_p, V Redn	Wave 3^d $E_{1/2}$, V
Acetone	−0.04	0.03	0.00	0.33	0.25	0.31	1.28		1.24
Dichloromethane	−0.01	0.06	0.04	0.36	0.26	0.34	1.31		1.26
Nitromethane	−0.10	−0.02	−0.05	0.29		0.27	1.24		1.19

^{a} Footnotes in Table I apply in addition to those below. ^{b} Reduction wave seen on repetitive cycling. trans-[W(CO)$_2$(DPE)$_2$]$^+$ $\overset{e}{\rightleftharpoons}$ trans-W(CO)$_2$(DPE)$_2$. ^{c} Electrode process: cis-W(CO)$_2$(DPE)$_2$ $\overset{e}{\rightleftharpoons}$ cis-[W(CO)$_2$(DPE)$_2$]$^+$ → trans-[W(CO)$_2$(DPE)$_2$]$^+$. ^{d} Oxidation of trans-[W(CO)$_2$(DPE)$_2$]$^+$.

tion and one oxidation wave were observed, corresponding to the equivalent electrode processes seen with the analogous trans-[Mo(CO)₂(DPE)₂]⁺. Data essentially identical with those already incorporated in Table V for cis-W(CO)₂(DPE)₂ were obtained.

Rationalization. Some qualitative rationalization of the more ready oxidation of the trans species and the preference for formation of trans species in the higher oxidation states is available from ligand field theory. The splitting scheme shown in Figure 9 for the metal-centered and full t$_{2g}$ orbitals was derived assuming the following points. (1) The relative splitting of the t$_{2g}$ levels can be best considered by representing the species as having holohedralized D_{4h} symmetry of the ligator atoms. (2) The ligand field strength of the bonding phosphine σ orbitals is greater than that of the σ orbitals of carbon monoxide. (3) The π* orbitals of carbon monoxide are better acceptors for filled metal t$_{2g}$ orbitals than are those of the phosphine.

With these assumptions the splitting of the levels shown in Figure 9 is in the same sense for the σ- and π-bonding interactions of each isomer and is always larger for the trans than for the cis isomer. This permits ready removal of up to two electrons from the trans isomer as observed electrochemically. A difference in the effective ligand fields in each isomer could arise through steric interactions between phenyl groups. We would anticipate *a priori* that this source of strain would be greater in the cis isomer and lead to an overall reduction in ligand field strength. If this is so, then this consideration would lead to a further relative separation of the orbital levels shown in the scheme.

Conclusions

This work has shown that electrochemistry is an extremely specific technique for studying isomerism exhibited by complexes of the type [M(CO)₂(DPE)₂]⁰,⁺,²⁺, where M = Mn, Cr, Mo, or W. Strong evidence has been obtained for the existence of the new complexes cis-Cr(CO)₂(DPE)₂, trans-[Cr(CO)₂(DPE)₂]²⁺, trans-Mo(CO)₂(DPE)₂,¹⁶ and trans-W(CO)₂(DPE)₂. Evidence for the existence of cis-[M(CO)₂(DPE)₂]⁺ complexes (M = Cr, Mo, W) in forms that are readily isomerized to the trans isomers has also been obtained. These complexes are

(16) Note Added in Proof. Evidence for the existence of trans-Mo(CO)₂(DPE)₂ has also been given by T. A. George and C. D. Seibold, *Inorg. Chem.*, **12**, 2548 (1973).

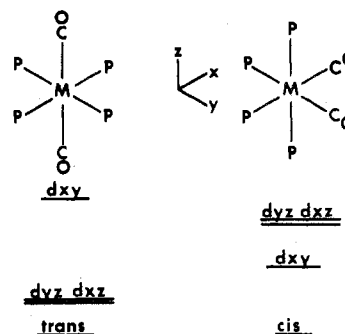**Figure 9.** Orbital level splitting scheme for trans- and cis-M(CO)₂P₄ complexes.

stabilized considerably at low temperature. In oxidation state II trans-[M(CO)₂(DPE)₂]²⁺ (M = Mo, W) species exhibit only a fleeting existence and are extremely reactive. The relative stabilities of the isomers in each oxidation state present an interesting problem. Thus the neutral cis-Mo(CO)₂(DPE)₂ is more stable than the trans isomer. The reversed stability sequence is obtained for the oxidation state I complex and generally an increase in oxidation state leads to relative stabilization of the trans isomer. We are able to rationalize the ready oxidation of trans species by consideration of bonding and steric arguments. The oxidation state II cations appear to be able to accept nucleophiles such as F⁻ to form seven-coordinate species such as [Mo(CO)₂(DPE)₂F]PF₆. This behavior is well known with other group VI–substituted carbonyl species where the seven-coordinate species are usually the only ones isolated.¹²⁻¹⁵

All electrochemical data are in accordance with the known chemistry of the complexes, with respect to $E_{1/2}$ values, and provide a quantitative thermodynamic account of previously observed chemical redox reactions. Results obtained should lead to syntheses of new complexes and further mechanistic details of this branch of carbonyl chemistry.