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Electrochemistry of 1-Phenyldibenzophosphole Complexes of Group 6 Metal Carbonyls

Emil B. Milosavljević,[1a] Ljiljana Solujić,[1a] Salina Affandi,[1b] and John H. Nelson*,[1b]

Institute of Chemistry, Faculty of Sciences, University of Belgrade, P.O. Box 550, 11001 Belgrade, Yugoslavia, and Department of Chemistry, University of Nevada, Reno, Nevada 89557

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The electrochemistry of a series of complexes of the type $(DBP)_nM(CO)_{6-n}$ (DBP = 1-phenyldibenzophosphole; M = Cr, Mo, W; n = 1–3) has been investigated by cyclic voltammetry, differential pulse polarography, and controlled potential electrolysis in propylene carbonate and/or dichloromethane solutions. Both the oxidations and reductions of these complexes are one-electron processes. The stabilities of the oxidized 17-electron species increase in the sequences $(DBP)M(CO)_5$ < *cis*-$(DBP)_2M(CO)_4$ < *mer*-$(DBP)_3M(CO)_3$ and $Mo(1+) \simeq W(1+) < Cr(1+)$, and they are slightly less stable in propylene carbonate than in dichloromethane. Electrochemical investigations of the *fac*-$(DBP)_3M(CO)_3$ complexes indicate an ECE mechanism wherein the oxidized species rapidly isomerize to the corresponding *mer*-$(DBP)_3M(CO)_3^+$ complexes with rates that increase in the order Cr < Mo < W. Low-temperature measurements enabled determination of the cross-redox equilibrium constants and rate constants for these isomerizations. The redox potentials were evaluated with respect to their correlation or lack thereof with the following spectroscopic data: IR (ν_{CO}); NMR ($\delta(^{13}C)$ and $\delta(^{17}O)$ for carbonyl ligands, $\delta(^{31}P)$ (phosphole ligands), $\delta(^{95}Mo)$); and UV (MLCT transitions). The correlations found are discussed with regards to the various effects influencing spectroscopic and electrochemical measurements.

Introduction

There is considerable current interest in the electrochemistry of 18-electron complexes of the type $L_nM(CO)_{6-n}$ (L = monodentate phosphorus donor; M = Cr, Mo, W).[2] Several recent publications have also addressed the kinetics of the chemical step that generally follows heterogeneous electron transfer for complexes of this type,[2c,3-5] but there is at present little systematic information regarding the relative kinetic stabilities of the oxidized 17-electron species for a series of $L_nM(CO)_{6-n}$ complexes. For this reason, we have paid special attention to the kinetics of the decomposition and/or isomerization of the oxidized species, investigating in detail the effects of the central metal, the number of coordinated phosphole ligands, and the solvent on the aforementioned kinetics. In this work, electrochemical and various spectroscopic measurements are compared with regards to their sensitivity to structural and electronic changes. Comparisons of electrochemical data with other physical parameters have been extensively reported,[2d,6] and except for one recent report,[2d] systematization of the various relationships has been difficult because, among other reasons, electrochemical measurements have been performed under a variety of conditions. In addition, few investigations have studied the effects of the central metal on these relationships.

Experimental Section

The preparation of the compounds and most of the spectroscopic measurements have been previously described.[7] The UV spectra were obtained on CH_2Cl_2 solutions in 1-cm quartz cells with a Cary-14 spectrophotometer on solutions ranging from 1×10^{-5} to 1×10^{-3} M.

Electrochemical Measurements. Cyclic voltammograms were recorded in dichloromethane containing 0.1 M tetrabutylammonium perchlorate (TBAP) and/or in propylene carbonate containing 0.1 M tetraethylammonium perchlorate (TEAP) using an EG&G PAR electrochemical system consisting of a Model RE0037 recorder, a Model 173 potentiostat, and a Model 175 universal programmer. A three-electrode system with instrumental IR compensation was used throughout. The working electrode was either a platinum disk or a hanging drop mercury electrode (HMDE). (The reductions of the 18-electron metal species were followed with the HMDE only.) The reference electrodes for dichloromethane/TBAP and propylene carbonate/TEAP systems were Ag/AgCl (saturated LiCl in dichloromethane) and aqueous calomel, respectively. The test solution was separated from the reference electrode by a salt bridge containing a Vycor plug and was filled with the corresponding solvent/supporting electrolyte system. Temperature regulation for the 25 °C and −10 °C experiments was achieved with a Brinkman Lauda K-2/R temperature controller with the electrochemical cell immersed in the constant temperature bath. The low-temperature experiments were performed at −78 °C (dry ice/acetone) and were recorded only on the dichloromethane/TBAP system. Oxygen-free nitrogen saturated with solvent vapors was used to thoroughly purge and blanket the solution being analyzed, before and during recording of the voltammograms, respectively. The concentrations of the complexes for electrochemical studies were in the 10^{-3}–10^{-4} M range.

The differential pulse polarography experiments were performed on an EG&G PAR 174A polarographic analyzer with a Model SMDE 303 dropping mercury electrode. Controlled-potential electrolysis experiments were performed with the Model 173 potentiostat/galvanostat connected to a Model 179 digital coulometer. The three-electrode configuration consisted of a platinum-gauze working electrode, a platinum auxiliary electrode separated from the bulk solution by a salt bridge containing a Vycor plug, and the same reference electrodes as used in the voltammetric experiments.

As recommended by IUPAC[8] for electrochemistry in nonaqueous solvents, the ferricinium ion (Fc^+)/ferrocene (Fc) couple was employed as the reference, and all potentials reported herein are given vs this couple. As suggested by Gagnê et al.,[9] whenever

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(1) (a) University of Belgrade. (b) University of Nevada, Reno.

(2) See for example: a) Connely, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 2. (b) Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275. (c) Bond, A. M.; Colton, R.; Keverkodes, J. E. *Inorg. Chem.* **1986**, *25*, 749 and references cited therein. (d) Morris, R. H.; Earl, K. A.; Luck, R. L.; Lazarowych, N. J.; Sella, A. *Inorg. Chem.* **1987**, *26*, 2674 and references cited therein.

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Table I. Electrochemical and Spectroscopic Data of Complexes Investigated

compd	$E_{1/2}^{\text{ox.}a}$ (+/0) (V vs Fc^+/Fc)	$E_{PC}^{\text{red.}b}$ (0/−) (V vs Fc^+/Fc)	$\nu_{CO}(A_1^1)$ (cm^{-1})	$\delta(^{13}C)^{c,f}$	$\delta(^{31}P)^{c,f}$	MLCT (nm)
$Cr(CO)_6$	1.04	−2.71	2100	211.2		280.1
$Cr(DBP)(CO)_5$	0.76	−2.26	2066	216.9	49.05	304.9
cis-$Cr(DBP)_2(CO)_4$	0.37	−2.42	2007	222.8	48.32	314.9
mer-$Cr(DBP)_3(CO)_3$	−0.19	−2.58	1953	227.9	57.58	335.6
fac-$Cr(DBP)_3(CO)_3$	0.12^e	−2.46	1935	220.2	48.32	332.8
$Mo(CO)_6$	1.14	−2.54	2120	200.7		289.0
$Mo(DBP)(CO)_5$	0.915^d	−2.37	2073	205.8	29.25	303.9
cis-$Mo(DBP)_2(CO)_4$	0.555	−2.56	2019	211.6	30.43	322.1
mer-$Mo(DBP)_3(CO)_3$	0.055	−2.67	1972	215.8	36.35	322.0
fac-$Mo(DBP)_3(CO)_3$	0.31^e	−2.60	1947	217.5	26.58	326.8
$W(CO)_6$	1.20	−2.42	2120	191.4		288.6
$W(DBP)(CO)_5$	0.95^d	−2.36	2072	196.5	9.26	305.8
cis-$W(DBP)_2(CO)_4$	0.57	−2.54	2016	202.3	9.51	320.0
mer-$W(DBP)_3(CO)_3$	0.06	−2.71	1964	207.6	12.11	330.0
fac-$W(DBP)_3(CO)_3$	0.29^e	−2.59	1943	208.8	8.48	340.1

[a] In propylene carbonate containing 0.1 M TEAP, at 25 °C; ν = 200 mV·s^{-1}; Pt-disk working electrode. [b] In propylene carbonate containing 0.1 M TEAP, at 25 °C; ν = 500 mV~s^{-1}; hanging mercury drop working electrode. [c] Weighted average. [d] E_{p_a} only, fast follow-up chemical step. [e] E_{p_a} only, fast isomerization to the meridional isomer. [f] Reference 7.

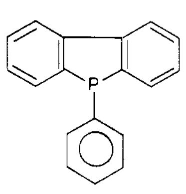
possible, ferrocene was used as an internal standard to compensate for the junction potential variability among experiments.

TEAP (Fluka, purum) and TBAP (Fluka, purum) were recrystallized from ethanol/water and dried under vacuum at 100 °C overnight. Propylene carbonate (Aldrich) was vacuum distilled and dried over Linde 4Å molecular sieves. Dichloromethane ("Baker Analyzed" reagent) was distilled from P_4O_{10} under nitrogen and stored over Linde 4-Å molecular sieves.

Results and Discussion

Effects of the Degree of Substitution in $(DBP)_nM(CO)_{6-n}$. The systems studied provide information concerning the effect of the value of n on the thermodynamic aspects of the redox processes. Under favorable conditions, electrochemical measurements can provide information about the relative energies of the highest occupied molecular orbitals (HOMO) and/or the lowest unoccuppied molecular orbitals (LUMO). For a series of complexes $[Mn(CO)_{6-n}(CNPh)_n]^+$ (n = 1–6) it was found that the HOMO energies correlate linearly with experimentally determined $E_{1/2}^{\text{ox.}}$ values.[10] With the assumption that this holds true for the compounds investigated in this work, the potentials for the process $M(0) \rightleftharpoons M(1+) + e^-$ relate to the HOMO energies and the potentials for the $M(0) + e^- \rightleftharpoons M(1-)$ process relate to the LUMO energies.

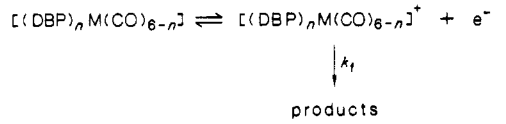
From Table I, in which all the pertinent data are presented, it may be seen that the introduction of the first DBP ligand lowers both the oxidation and reduction potentials for all three series of complexes. The oxidation potentials for all three metals change by about the same amount. This means that the introduction of the first phosphole has the same effect on the energies of the HOMO irrespective of the central metal ion. A much greater change occurs for the reduction potentials with a decrease in $\Delta E^{\text{red.}}$ as the metal increases in size; $\Delta E^{\text{red.}}$ = 0.45 V (Cr) > 0.17 V (Mo) > 0.06 V (W).



DBP

Further substitution of carbon monoxide by DBP in the series raises the energy of both the HOMO and the LUMO, so that the *cis*-$(DBP)_2M(CO)_4$ complexes are easier to oxidize and more difficult to reduce than the $(DBP)M(CO)_5$ species. This trend continues from the *cis*-$(DBP)_2M(CO)_4$ to the *mer*-$(DBP)_3M(CO)_3$ complexes. It is noteworthy that the differences between the oxidation and reduction potentials with an increasing number of DBP ligands are approximately the same for the three series of compounds. Also, one notes that the oxidation potential decrease in the sequence $(DBP)M(CO)_5$ > *cis*-$(DBP)_2M(CO)_4$ > *fac*-$(DBP)_3M(CO)_3$ > *mer*-$(DBP)_3M(CO)_3$ is greater than the corresponding changes in the reduction potentials and that these changes vary little with the identity of the metal. The metal does affect the redox potentials, and it is always easier to oxidize and reduce the chromium complex than either the molybdenum or tungsten analogue.

Kinetic Stabilities of the 17-Electron Species. The usual diagnostic criteria utilized in cyclic voltammetry point out that the mechanism of the oxidation of the 18-electron compounds is as illustrated in reaction 1.[11] The



$$[(DBP)_nM(CO)_{6-n}] \rightleftharpoons \underset{\displaystyle \text{products}}{\underset{\displaystyle \downarrow k_f}{[(DBP)_nM(CO)_{6-n}]^+}} + e^- \qquad (1)$$

reversible electron transfer is followed by an apparently irreversible chemical step; apparently irreversible, since it is possible that on the time domain of the electrochemical experiment the back-reaction is not significant.

The rate constant (k_f) may be calculated from a cyclic voltammetry experiment by the method of Nicholson and Shain.[11] They have demonstrated that the ratio of the cathodic and anodic peak currents (i_{p_c}/i_{p_a}) is a function of the product $k_f\tau$ (where τ is the time from $E_{1/2}$ to the switching potential). The ratio of peak currents was determined from a single cyclic voltammogram by Nicholson's semiempirical procedure.[12] The rate constant may be independently calculated and/or checked from experiments performed at various scan rates and switching potentials. The data obtained at 25 °C are presented in Table II from which several conclusions may be inferred. The stability of the 17-electron species increases with an

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(10) Fenske, R. F.; Sarapu, A. C. *Inorg. Chem.* **1975**, *14*, 247.

(11) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

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Table II. Rate Constants of the Chemical Processes Following the Heterogeneous Oxidations at 25 °C[a]

	K_f (s^{-1})			
	Cr		Mo	
complex	PC[b]	CH_2Cl_2	PC[b]	CH_2Cl_2
$M(DBP)(CO)_5$	0.46 ± 0.07	0.14 ± 0.01	*d*	
cis-$M(DBP)_2(CO)_4$	(7.1 ± 0.6) × 10^{-2}	(5.1 ± 0.6) × 10^{-2}	1.63 ± 0.01	0.52 ± 0.09
mer-$M(DBP)_3(CO)_3$	*c*		(2.3 ± 0.02) × 10^{-2}	(6 ± 1) × 10^{-3}
fac-$M(DBP)_3(CO)_3$	*d*		*d*	

[a] See text for details. [b] PC = propylene carbonate. [c] Stable species. [d] Too fast to measure.

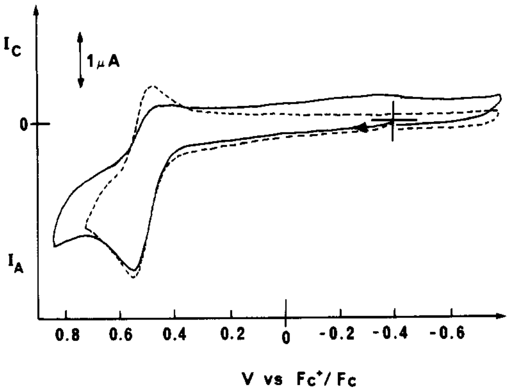

Figure 1. Cyclic voltammograms (ν = 500 $mV \cdot s^{-1}$) for the oxidation of *cis*-$(DBP)_2Mo(CO)_4$ in propylene carbonate (0.1 M TEAP) at 25 °C: (–) $C_{complex} = 8 \times 10^{-4}$ M; (- - -) $C_{complex} = 8 \times 10^{-4}$ M, $C_{DBP} = 8 \times 10^{-4}$ M.

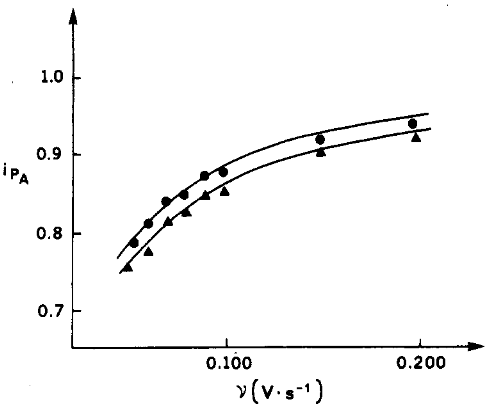

Figure 2. Effect of scan rate on the i_{p_c}/i_{p_a} ratio for the oxidation of *cis*-$(DBP)_2Cr(CO)_4$ in CH_2Cl_2 (0.1 M TBAP) at 25 °C (▲): $C_{complex} = 6 \times 10^{-4}$ M. The solid line is the theoretical curve[11] for an EC mechanism with k_f = 0.051 s^{-1}. Effect of scan rate on the i_{p_c}/i_{p_a} ratio for the oxidation of *cis*-$(DBP)_2Cr(CO)_4$ in CH_2Cl_2 (0.1 M TBAP) at 25 °C in the presence of free DBP (●): $C_{complex} = 6 \times 10^{-4}$ M; $C_{DBP} = 3 \times 10^{-3}$ M. The solid line is the theoretical curve[11] for an EC mechanism with k_f = 0.042 s^{-1}.

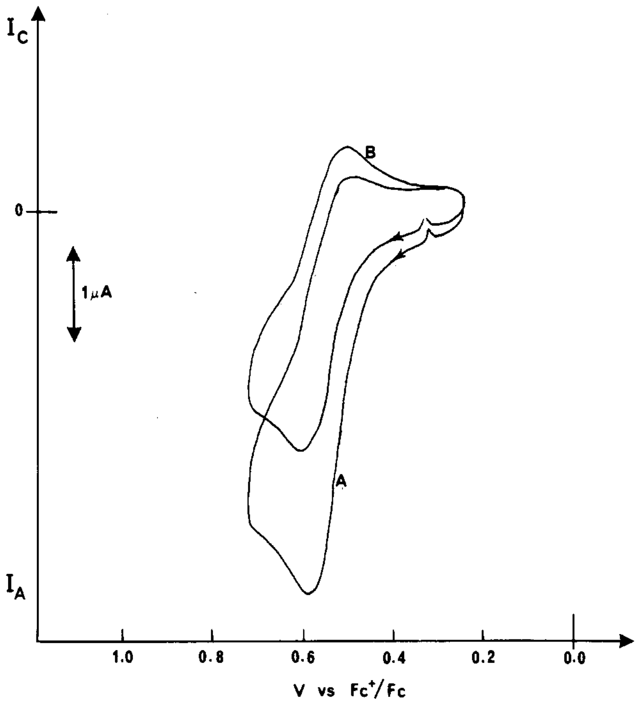

Figure 3. Cyclic voltammograms (ν = 500 $mV \cdot S^{-1}$) for the oxidation of 5×10^{-4} M *cis*-$(DBP)_2Mo(CO)_4$ in propylene carbonate (0.1 M TEAP) at 25 °C (A) and at –10 °C (B).

increase in the number of coordinated DBP ligands. The Cr(1+) complexes are more stable than the Mo(1+) or W(1+) complexes (some of the W complexes were slightly adsorbed on the Pt-working electrode so that only qualitative kinetic information could be obtained from this series). The oxidized species are more stable in dichloromethane than in the more polar propylene carbonate.

It is noteworthy that the 17-electron species show different stability trends than do the 18-electron complexes. Atwood et al.[13] have found that for some similar chromium complexes, thermal dissociation of the phosphorus ligand is faster for the $(R_3P)_2Cr(CO)_4$ than for the $(R_3P)Cr(CO)_5$ complexes.

In order to establish the mechanism of the chemical step that follows the heterogeneous electron transfer, we performed the cyclic voltammetry experiments in the presence of excess DBP and under a CO atmosphere. It was found that the observed forward rate constant ($k_{f,obsd}$) decreased with an increase in the concentration of excess DBP whereas excess CO had no effect. Also, $E_{1/2}$ decreases with an increase in the ratio of free DBP to complex. For example, for Cis-$(DBP)_2Cr(CO)_4$, $E_{1/2}$ is 0.37 V, for a 1:1 ratio of DBP to $(DBP)_2Cr(CO)_4$, $E_{1/2}$ = 0.366 V, for a 2:1 ratio, $E_{1/2}$ = 0.362 V, and for a 5:1 ratio, $E_{1/2}$ = 0.362 V. Similar results were obtained for the other complexes. These experiments together with the data previously presented suggest the electrochemical mechanism shown in reaction 2.

$$\begin{tikzcd}[(DBP)_nM(CO)_{6-n}] \arrow[r, leftrightharpoons] & {[(DBP)_nM(CO)_{6-n}]^+ + e^-} \arrow[d, leftrightharpoons, "k_{f,obs}"] & (2) \\ & {[(DBP)_{n-1}M(CO)_{6-n}]^+ + DBP} & \end{tikzcd}$$

The effects of excess DBP and temperature on the cyclic voltammetry of *cis*-$[(DBP)_2M(CO)_4]$ are shown in Figures 1–3. Other complexes behaved similarly. From Figures 1 and 2 it may be seen that the addition of DBP increases the i_{p_c}/i_{p_a} ratio. There is also a small increase in the anodic peak current that could indicate a slight dissociation of DBP from the neutral starting complex. Figure 3 shows

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[13] Atwood, J. D.; Woukulich, M. J.; Sonnenberger, D. C. *Acc. Chem. Res.* **1983**, *16*, 350.

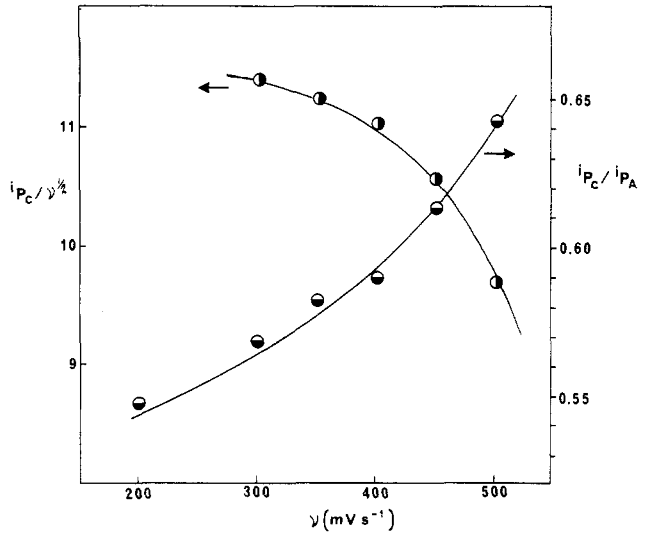

Figure 4. Effect of scan rate on the i_{p_c}/i_{p_a} ratio for the oxidation of 5×10^{-4} M *cis*-$(DBP)_2Mo(CO)_4$ in propylene carbonate (0.1 M TEAP) at 25 °C. The solid lines are the theoretical curves[11] for an EC mechanism with $k_f = 1.63$ s^{-1}.

that with a decrease in temperature i_{p_c}/i_{p_a} increases, as expected. Also, as shown in Figures 2 and 4, the i_{p_c}/i_{p_a} ratio increases with an increase in scan rate as expected.[11] Moreover, chemical oxidants such as I_2[14] or S_8[15] have been used synthetically to remove phosphorus donors from Cr, Mo, and W carbonyl complexes.

Isomerization Induced by Oxidation. As has been noted for similar complexes[2c,16-18] the *fac*-$(DBP)_3M(CO)_3$ complexes isomerize to the meridional isomers on oxidation. This has been theoretically predicted by Mingos.[19] His calculations led to the prediction that both electronic and steric factors favor the formation of meridional isomers in the 17-electron system. Since the potentials of the fac$^+$/fac^0 and mer$^+$/mer^0 couples, as theoretically predicted,[20] are different and since this isomerization is rapid, the systems are very well-suited for study by cyclic voltammetry.

Figure 5 shows the two-cycle cyclic voltammograms of *fac*-$(DBP)_3Mo(CO)_3$ as a function of temperature. The first anodic scan shows no wave due to oxidation of the meridional isomer which indicates that if isomerization of *fac*-$(DBP)_3Mo(CO)_3$ occurs, it is a very slow process. Upon oxidation of the facial isomer, very rapid isomerization occurs, and at 25 °C there is no return reduction peak. At −78 °C the rate of isomerization is significantly reduced and the return reduction peak is clearly evident. Continued cathodic scan shows the reduction peak for *mer*-$(DBP)_3Mo(CO)_3{}^+$, and subsequent anodic scan shows the wave due to the oxidation of *mer*-$(DBP)_3Mo(CO)_3$ and a decreased peak current for the oxidation of the facial isomer. The corresponding chromium and tungsten complexes behave similarly.

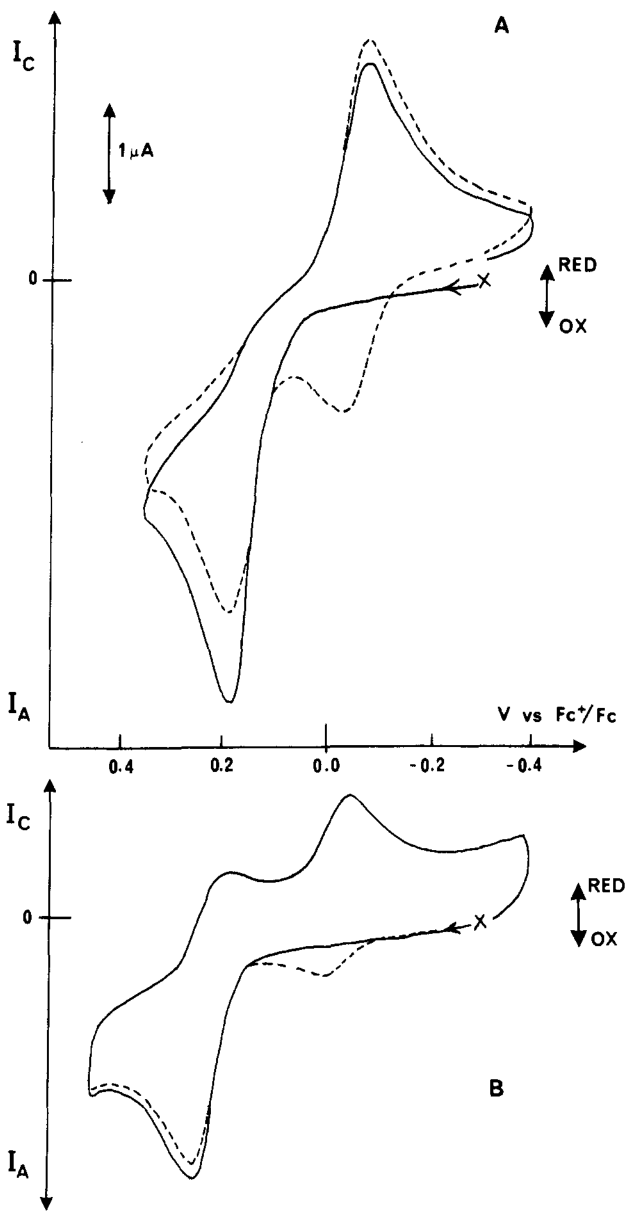

Figure 5. Cyclic voltammograms (ν = 200 mV·s^{-1}) for the oxidation of *fac*-$(DBP)_3Mo(CO)_3$ in dichloromethane (0.1 M TBAP) at 25 °C (A) and at −78 °C (B): (—) first cycle, (- - -) second cycle.

Table III. Thermodynamic and Kinetic Data for Tris(phosphole) Complexes[a]

		$E_{1/2}$ (V vs Fc$^+$/Fc)	K_f (s^{-1})	k_{eq}[c]
Cr	meridional	−0.27		2.1×10^8
	facial	0.05	0.26 ± 0.03	
Mo	meridional	−0.01		3.7×10^6
	facial	0.24	0.86 ± 0.03	
W	meridional	−0.01		
	facial	0.25	*d*	6×10^6[e]

[a] Obtained from the low-temperature (−78 °C) cyclic voltammetry experiments in CH_2Cl_2 containing 0.1 M TBAP. [b] ν = 200 mV·s^{-1}; Pt-disk working electrode. [c] See text for details. [d] Too high to be determined even at this temperature. [e] Approximate value.

It is possible to determine the $E_{1/2}$ values for both fac$^+$/fac and mer$^+$/mer couples at lower temperatures. As a result it is possible to calculate the values for the cross-redox equilibrium constants for reaction 3, from relation 4.[21]

$$\mathrm{mer}^0 + \mathrm{fac}^+ \overset{k_{eq}}{\rightleftharpoons} \mathrm{mer}^+ + \mathrm{fac}^0 \qquad (3)$$

$$k_{eq} = \exp\{F/RT[E_{1/2}(\mathrm{fac}) - E_{1/2}(\mathrm{mer})]\} \qquad (4)$$

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Table IV. MLCT Energies and $\Delta E_{ox./red.}$ for the $(DBP)_nM(CO)_{6-n}$ Complexes

complex type	Cr[a]		Mo[b]		W[c]	
	$\Delta E_{ox./red.}$ (V)	MLCT (eV)[d]	$\Delta E_{ox./red.}$ (V)	MLCT (eV)	$\Delta E_{ox./red.}$	MLCT (eV)
$M(CO)_6$	3.75	4.43	3.68	4.29	3.62	4.30
$(DBP)M(CO)_5$	3.02	4.07	3.29	4.08	3.31	4.05
cis-$(DBP)_2M(CO)_4$	2.79	3.94	3.12	3.85	3.11	3.87
mer-$(DBP)_3M(CO)_3$	2.39	3.70	2.73	3.73	2.77	3.76
fac-$(DBP)_3M(CO)_3$	2.58	3.73	2.91	3.79	2.88	3.64

[a] MLCT = 0.5585ΔE + 2.351 (r^2 = 0.982). [b] MLCT = 0.6205ΔE + 1.996 (r^2 = 0.953). [c] MLCT = 0.7275ΔE + 1.641 (r^2 = 0.918). [d] 1 eV = 8066 cm^{-1}.

These constants, along with other thermodynamic and kinetic data for all three pairs of tris isomers, obtained from cyclic voltammetry experiments (average of at least three) performed at −78 °C, are summarized in Table III. These data show that the cross redox equilibrium constant for the chromium compound is about 2 orders of magnitude greater than for the corresponding molybdenum and tungsten compounds. Bond et al.[16] observed the same trend for $(PhPMe_2)_3M(CO)_3$ (M = Cr and Mo) complexes. At low temperatures the rates of the fac$^+$ to mer$^+$ isomerizations are sufficiently reduced to be determined from cyclic voltammetry experiments in a previously described way. In these experiments the final potential is chosen to be before the onset of the reduction potential of the meridional 17-electron species. In the calculations it is assumed that the rate of the back-reaction is negligible. Bond et al.[2c] have found for the system

$$fac\text{-}[\{P(OMe)_3\}_3Cr(CO)_3]^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} mer\text{-}[\{P(OMe)_3\}_3Cr(CO)_3]^+$$

that k_2 is 3 orders of magnitude greater than k_{-2}. The calculated isomerization constants (Table III) show that this constant is more than 3 times greater for the Mo species than for the corresponding Cr one. Thus, here also, the chromium species are more stable than either the molybdenum or tungsten analogues. *fac*-$(DBP)_3W(CO)_3^+$ isomerizes to *mer*-$(DBP)_3W(CO)_3^+$ very rapidly even at −78 °C. The cathodic wave for the fac$^+$ species is very small even at high scan rates, so that the isomerization rate constant cannot be accurately determined in this case, but it is obviously greater than for the molybdenum species. The same trend was previously reported[5] for the rates of cis$^+$ and trans$^+$ isomerization of $(dppe)_2M(CO)_2$ (M = Cr, Mo, W).

It has been noted[2c,22] that cis–trans isomerizations of $L_2M(CO)_4$ also occur upon oxidation. This process may not be seen by cyclic voltammetry since it has been predicted[20] that the $E_{1/2}$ values for the cis$^+$/cis^0 and trans$^+$/trans^0 couples should be very similar. In order to determine whether this isomerization occurs for the DBP complexes, we performed controlled potential electrolysis experiments on *cis*-$(DBP)_2Cr(CO)_4$. A dichloromethane solution of this complex was completely oxidized and subsequently reduced. Infrared analysis of the solution showed no ν_{CO} bands for the trans isomer. Additionally, we have been repeatedly unsuccessful in attempts at the synthesis of *trans*-$(DBP)_2M(CO)_4$ by a variety of methods.[7] This may be attributed to strong stabilizing interactions between two mutually cis DBP ligands as shown by X-ray crystallography.[7]

Electrochemistry of the Reduction Processes. Seurat[23] has shown that $Cr(CO)_6$ undergoes one-electron reduction to $Cr(CO)_6^-$. The peak currents, as well as the half peak widths ($W_{1/2}$)[24] obtained for this species and for $(DBP)Cr(CO)_5$ by differential pulse polarography on a dropping mercury electrode, were comparable. This indicates that the reduction of $(DBP)Cr(CO)_5$ is also a one-electron process. The reduced species of all the complexes investigated decompose very rapidly. That one of the decomposition products is DBP may be inferred from the cyclic voltamettry experiments. The anodic scan after the reduction of, for example, $(DBP)W(CO)_5$ gives a small wave at around 0 V vs Fc$^+$/Fc (ΔE = 105 mV, ν = 500 mV·s^{-1}). This wave probably corresponds to the oxidation of mercury facilitated by the presence of DBP. When the cathodic scan is stopped just before the onset of the reduction process and then continued in a positive direction, the peak corresponding to mercury oxidation is just barely visible and it is shifted anodically compared to the previous experiment. This indicates that the reduced species $(DBP)W(CO)_5^-$ dissociates DBP to a much greater extent than does $(DBP)W(CO)_5$.

It should be noted that exactly the same $E_{1/2}$ values for the oxidation $M(0) \rightleftharpoons M(1+) + e^-$ were obtained on both platinum and hanging mercury drop electrodes for those processes that were accessible with the latter. This indicates that the nature of the electrode does not influence the heterogeneous charge transfer.

Correlation of Electrochemical and Spectroscopic Data: Metal–Ligand Charge-Transfer Transitions (MLCT). To a first aproximation, the redox potentials allow an assessment of the relative energies of the HOMO's and LUMO's in a series of complexes. If both the reduction and oxidation are one electron processes, the difference in the potentials should correlate with the energies of the HOMO–LUMO electronic transition.[25–27] For d^6 complexes in an octahedral ligand field, the lowest energy electronic transition is from filled metal d orbitals to the unoccupied lowest π^* orbital of the ligand(s) (MLCT).[28] Hence, we would expect to find a correlation of the type E_{op} (eV) = $\Delta E_{ox./red.}$ (V) + χ between the energy of the MLCT transition (E_{op}) and the difference in energy between the oxidation and reduction potentials ($\Delta E_{ox./red.} = E_{1/2}^{ox.} - E_{pc}^{red.}$). Very good correlations were found for all three series of complexes (Table IV). In these correlations, a lowering in the energy of the MLCT and a decrease in $\Delta E_{ox./red.}$ corresponds to an increase in n in the series $(DBP)_nM(CO)_{6-n}$. When these MLCT energies are

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(21) Relation (4) assumes equal diffusion coefficients for the oxidized and reduced species. See: Rieger, P. H. *Electrochemistry*; Prentice-Hall; Englewood Cliffs, NJ, 1987; p 242.

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compared with $\Delta E_{\text{ox./red.}}$, it may been seen that the differences increase from $M(CO)_6$ to *mer*-$(DBP)_3M(CO)_3$. These values are always greater than 0.6 V and comprise contributions to the Frank–Condon energy from intra- and intermolecular vibrations in the medium.[27] Though these correlations are quite good ($r^2 \geq 0.918$), they are improved if the sterically encumbered *fac*-$(DBP)_3M(CO)_3$ complexes are not included ($r^2 \geq 0.945$). Steric effects are well-known to give rise to difficulties in ligand additivity relationships.[6,20,29]

Carbonyl Stretching Frequencies (ν_{CO}). It is well-known that the global electron density on a transition-metal center influences the strength of M–L retrodative π-bonding to good π-acceptor ligands such as CO. This retrodative π-bonding is reflected in a weakening of the CO bond and a shift to lower energy of ν_{CO}. The oxidation potential of a complex is a measure of the global electron density at the metal center, and as a result we could expect to find a correlation between $E_{1/2}^{\text{ox.}}$ and ν_{CO} as discussed in detail recently.[2d,30] Very good correlations (facial isomers omitted) of these two parameters of the form ν_{CO} (cm^{-1}) = $AE_{1/2}^{\text{ox.}} + B$ were found where for Cr, Mo, and W; A, B, and the correlation coefficients r^2 are 121.24, 1971.48, and 0.990; 133.88, 1956.8, and 0.985; and 135.09, 1949.1, and 0.991, respectively. Thus, it is possible to predict the oxidation potential from the value of ν_{CO} for the A_1^1 or highest energy C–O vibration.

NMR Chemical Shifts. $\delta(^{13}C)$ and $\delta(^{31}P)$. NMR chemical shifts may be influenced by inductive and resonance effects which is also frequently the case with oxidation potentials. In such cases direct correlation between NMR chemical shifts and electrochemical data could be expected. Since the NMR chemical shift is affected by the electron density in the immediate vicinity of the observed nucleus and the electrochemical oxidation of the complexes involves removal of an electron from the HOMO which is largely metal in character, we might expect to observe a correlation between the chemical shifts of the nuclei bound to the metal (^{13}C of the carbonyls and ^{31}P of DBP) and $E_{1/2}^{\text{ox.}}$. Very good correlations (facial isomers omitted) are observed between the weighted average $\delta(^{13}C)$ or $\delta(^{31}P)$ and oxidation potentials. The ^{13}C correlations are of the form $\delta(^{13}C) = AE_{1/2}^{\text{ox.}} + B$ where for Cr, Mo, and W; A, B, and the correlation efficients r^2 are −13.290, 226.30, and 0.969; −13.575, 217.56, and 0.957; and −14.006, 209.18, and 0.979, respectively. It should be noted, however, that the ^{31}P chemical shifts change very little throughout a series. Similar correlations have been previously observed and discussed.[6] In all these correlations the chemical shift of the observed nucleus moves upfield as the oxidation potential increases for the $\delta(^{13}C)$ correlations and the opposite is true for the $\delta(^{31}P)$ correlations. This suggests that the M–CO bonding is largely retrodative and the M–P bonding dative in nature.

$\delta(^{95}Mo)$. The molybdenum-95 chemical shift is largely determined by the paramagnetic term[31] which is inversely related to ΔE (the energy of the lowest electronic transition). Hence, one could expect to find a linear relation between $\Delta E_{\text{ox./red.}}$ and $\delta(^{95}Mo)$[7] as was found for the MLCT energies. A good correlation is observed of the from $\delta(^{95}Mo) = A\Delta E_{\text{ox./red.}} + B$ where A, B, and r^2 are −434.90, −302.67, and 0.803, respectively. This correlation is markedly improved if the facial isomer is omitted whence $A = -236.15$, $B = -995.20$, and $r^2 = 0.91$.

Electrochemistry and the Donor Ability of DBP. Chatt et al.[32] have proposed a scale of ligand donor abilities based upon the ligand constant $P_L = E_{1/2}^{\text{ox.}}[LCr(CO)_5] - E_{1/2}^{\text{ox.}}[(Cr(CO)_6]$. Using the value of $E_{1/2}^{\text{ox.}} = 0.992$ for $PPh_3Cr(CO)_5$[33] we compute $P_L = -0.048$ for PPh_3 and $P_L = -0.28$ for DBP. This suggests that DBP is a better donor than PPh_3 toward Cr(0) which is consistent with bond distances determined by X-ray crystallography.[7]

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Registry No. $Cr(CO)_6$, 13007-92-6; $[Cr(CO)_6]^+$, 54404-20-5; $[Cr(CO)_6]^-$, 84695-79-4; $Cr(DBP)(CO)_5$, 114860-43-4; $[Cr(DBP)(CO)_5]^+$, 114944-45-5; $[Cr(DBP)(CO)_5]^-$, 114944-55-7; *cis*-$Cr(DBP)_2(CO)_4$, 114860-44-5; [*cis*-$Cr(DBP)_2(CO)_4]^+$, 114944-46-6; [*cis*-$Cr(DBP)_2(CO)_4]^-$, 114944-56-8; *mer*-$Cr(DBP)_3(CO)_3$, 114860-45-6; [*mer*-$Cr(DBP)_3(CO)_3]^+$, 114944-47-7; [*mer*–$Cr(DBP)_3(CO)_3]^-$, 774944-57-9; *fac*-$Cr(DBP)_3(CO)_3$, 114925-26-7; [*fac*-$Cr(DBP)_3(CO)_3]^+$, 115014-51-2; [*fac*-$Cr(DBP)_3(CO)_3]^-$, 115014-54-5; $Mo(CO)_6$, 13939-06-5; $[Mo(CO)_6]^+$, 114944-48-8; $[Mo(CO)_6]^-$, 87189-64-8; $Mo(DBP)(CO)_5$, 111267-08-4; $[Mo(DBP)(CO)_5]^+$, 114944-49-9; $[Mo(DBP)(CO)_5]^-$, 114944-58-0; *cis*–$Mo(DBP)_2(CO)_4$, 114860-47-8; [*cis*–$Mo(DBP)_2(CO)_4]^+$, 114944-50-2; [*cis*–$Mo(DBP)_2(CO)_4]^-$, 114944-59-1; *mer*-$Mo(DBP)_3(CO)_3$, 114860-48-9; [*mer*-$Mo(DBP)_3(CO)_3]^+$, 114944-51-3; [*mer*-$Mo(DBP)_3(CO)_3]^-$, 114944-60-4; *fac*-$Mo(DBP)_3(CO)_3$, 114925-27-8; [*fac*-$Mo(DBP)_3(CO)_3]^+$, 115014-52-3; [*fac*-$Mo(DBP)_3(CO)_3]^-$, 115014-55-6; $W(CO)_6$, 14040-11-0; $[W(CO)_6]^+$, 112908-02-8; $[W(CO)_6]^-$, 114944-61-5; $W(DBP)(CO)_5$, 71248-95-8; $[W(DBP)(CO)_5]^+$, 114944-52-4; $[W(DBP)(CO)_5]^-$, 114944-62-6; *cis*-$W(DBP)_2(CO)_4$, 114860-49-0; [*cis*-$W(DBP)_2(CO)_4]^+$, 114944-53-5; [*cis*-$W(DBP)_2(CO)_4]^-$, 114944-63-7; *mer*-$W(DBP)_3(CO)_3$, 114860-50-3; [*mer*-$W(DBP)_3(CO)_3]^+$, 114944-54-6; [*mer*-$W(DBP)_3(CO)_3]^-$, 114944-64-8; *fac*-$W(DBP)_3(CO)_3$, 114925-28-9; [*fac*-$W(DBP)_3(CO)_3]^+$, 115014-53-4; [*fac*-$W(DBP)_3(CO)_3]^-$, 115014-56-7; Hg, 7439-97-6; Pt, 7440-06-4.

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