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Reaction Pathways of Geometrically Constrained 17-Electron *cis*-$[M(CO)_4(L\text{-}L)]^+$ Cations (M = Cr, Mo, W; L-L = Bidentate Ligand)[†]

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Oxidation of *cis*-$M(CO)_4(L\text{-}L)$ (where M = Cr, Mo, W and L-L is a bidentate ligand with P, As, or Se donor atoms) leads to generation of geometrically constrained 17-electron cations *cis*-$[M(CO)_4(L\text{-}L)]^+$, which cannot lower their energy by isomerization to the *trans*$^+$ configuration, as is the case with $[M(CO)_4L_2]^+$ and related complexes (L = monodentate P or As ligand). In this work, a marked contrast in reaction pathways between geometrically constrained compounds and other classes of compounds is shown to exist. The relative stability of *cis*-$[Cr(CO)_4(dpm)]^+$ in dichloromethane allows complete characterization of its chemical and electrochemical behavior; it undergoes photocatalytic reduction, substitution, redox, and disproportionation reactions, all of which regenerate $Cr(CO)_4(dpm)$. Other *cis*-$[Cr(CO)_4(L\text{-}L)]^+$ species are much less stable. The voltammetric oxidations (scan rates 50–500 mV s^{-1}) of $Mo(CO)_4(L\text{-}L)$ (L-L = dpe, dpmSe) are very unusual. While these species approach chemical reversibility at ambient temperatures in dichloromethane, anomalous temperature dependence leads to the observation of complete chemical irreversibility at −78 °C and the concomitant appearance of a new reduction response, well removed from the potential of the reversible process. In the presence of Cl^-, PPh_3, or L-L the one-electron voltammetric response is converted into an irreversible two-electron process (L-L = dpe) or an irreversible one-electron process (L-L = dpmSe). Other molybdenum and tungsten complexes give chemically irreversible one-electron oxidative voltammetric responses in both dichloromethane and acetonitrile. In acetonitrile, a second one-electron-oxidation process may be observed at very positive potentials. Reaction of *cis*-$M(CO)_4(L\text{-}L)$ with $NOPF_6$ produces $[M(CO)_3NO(L\text{-}L)]^+$ rather than *cis*-$[M(CO)_4(L\text{-}L)]^+$. Mechanisms for the chemical and electrochemical oxidation processes are presented in terms of pathways that allow a lowering of energy associated with the formation of 17-electron geometrically constrained *cis*-$[M(CO)_4(L\text{-}L)]^+$ cations.

Introduction

The chemistry of octahedral group 6 metal tetracarbonyl complexes, $M(CO)_4L_2$ (M = Cr, Mo, W; L = monodentate ligand) in their zerovalent 18-electron configuration has been widely studied. In particular, the influence of the ligands coordinated to the metal has been a major area of investigation with respect to isomeric form, rates of exchange of ligands, and structural properties.[3-7]

Oxidation of group 6 carbonyl derivatives and the relationship to isomeric form has been considered theoretically. Mingos[8] has argued that in the 17-electron (+1) oxidation state, the *trans*$^+$ isomer for dicarbonyl complexes and the *mer*$^+$ isomer for tricarbonyl complexes are heavily favored over their *cis*$^+$ and *fac*$^+$ counterparts. With monodentate ligands, the complexes $M(CO)_4L_2$ can be formed in both *cis*^{0} and *trans*^{0} 18-electron configurations. Experimentally, upon oxidation of *cis*-$M(CO)_4L_2$, isomerization to *trans*-$[M(CO)_4L_2]^+$ is observed,[9,10] indicating that *trans*-$[M(CO)_4L_2]^+$ is favored. The substantial stability of the *trans*$^+$ form is also exhibited in the *trans*-$[Cr(CO)_4(PPh_3)_2]^{+/0}$ system.[11] Geometrical preferences upon oxidation for tetracarbonyl complexes have yet to be considered in detail from a theoretical viewpoint.

For a bidentate ligand (L-L), the stereochemistry is fixed as *cis* in both the 18- and 17-electron situations. On the basis of the data for *cis*-$[M(CO)_4L_2]^+$ complexes where rapid isomerization occurs, it can be predicted that the cation is geometrically constrained so that the preferred geometry cannot be attained. This is anticipated to result in greater reactivity toward substitution, disproportionation, and other reactions that may relieve any electronic or steric strain.

Some evidence for unusual properties of $[M(CO)_4(L\text{-}L)]^+$ is indicated in the work of Connelly.[12,13] Whereas oxidation of *cis*- or *trans*-$M(CO)_4L_2$ with $NOPF_6$ always produced[10,11] the *trans*-$[M(CO)_4L_2]^+$ cations, the same oxidation reaction of $M(CO)_4(dpe)$ (M = Mo, W) gave $[M(CO)_3(NO)(dpe)](PF_6)$. However, the oxidation of $Cr(CO)_4(dpe)$ gave the isolable, but unstable, cation $[Cr(CO)_4(dpe)]^+$.[12] Reaction of $M(CO)_4(dpe)$ with $AgClO_4$ gave $[Ag\{M(CO)_4(dpe)\}_2]^+$ (M = Mo, W), but with chromium the cation $[Cr(CO)_4(dpe)]^+$ was identified as the product.[13] Analogous products were obtained from the chemical oxidation of $M(CO)_4(dpm)$ (M = Cr, Mo, W).[13] Thus, NO generally replaces CO in $M(CO)_4(L\text{-}L)$ (M = Mo, W) while silver ion reacts to form the stable silver complexes noted above rather than giving a one-electron-oxidation product.

In a brief report[13] on the electrochemical oxidation of $M(CO)_4(L\text{-}L)$ (L-L = dpe, dpm) it was suggested that oxidation of $Cr(CO)_4(L\text{-}L)$ was reversible, oxidation of $Mo(CO)_4(dpm)$ was chemically irreversible and oxidations of $M(CO)_4(dpe)$ (M = Mo, W) were reversible in dichloromethane. As part of an examination of the influence of electronic effects of bidentate ligands, Cook and Morse[14] also claimed that $M(CO)_4(dpe)$ (M = Cr, Mo) underwent reversible electrochemical oxidations in dichloromethane, but in CH_3CN they found the oxidation of $Mo(CO)_4(dpe)$ to be irreversible. These data again indicate considerable differences from the results of $M(CO)_4L_2$ voltammetric oxidation studies where reversible one-electron processes are generally observed.

To provide a framework to test the validity of the concept of modified reaction pathways induced by geometrical constraints, we have examined the oxidative chemistry and electrochemistry of a series of $M(CO)_4(L\text{-}L)$ (M = Cr, Mo, W) complexes with

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[†] Abbreviations for names of L-L ligands: dpm, $Ph_2PCH_2PPh_2$; dpe, $Ph_2CH_2CH_2PPh_2$; dam, $Ph_2AsCH_2AsPh_2$; dae, $Ph_2AsCH_2CH_2AsPh_2$; ape, $Ph_2PCH_2CH_2AsPh_2$; dpmSe, $Ph_2PCH_2P(Se)Ph_2$; dmpe, $Me_2PCH_2CH_2PMe_2$.

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Table I. Electrochemical Data[a] for the Oxidation of 1×10^{-3} M $Cr(CO)_4(L\text{-}L)$ Complexes at 20 °C

		cyclic voltammetry[b,c]			rot. disk[d,e]	
complex	solvent	E_p^{ox},[f] V	E_p^{red}, V	$E_{1/2}$, V	$(E_{3/4} - E_{1/4})$, mV	$E_{1/2}$, V
$Cr(CO)_4(dpm)$	CH_2Cl_2	0.88	0.72	0.80	100	0.82
	CH_3CN	0.89 (1.65)	0.79	0.84	90	0.86
$Cr(CO)_4(dpe)$	CH_2Cl_2	0.84	0.74	0.79	85	0.82
	CH_3CN	0.91 (1.65)	0.79	0.85	80	0.87
$Cr(CO)_4(dae)$	CH_2Cl_2	0.94	0.76	0.85	100	0.87
	CH_3CN	0.92 (1.69)	0.84	0.88	80	0.89
$Cr(CO)_4(ape)$	CH_2Cl_2	0.91	0.76	0.84	85	0.83
	CH_3CN	0.92 (1.61)	0.83	0.88	80	0.89

[a] $E_{1/2}$ for oxidation of 10^{-3} M ferrocene in CH_2Cl_2 = 0.52 V; $E_{1/2}$ for this oxidation in CH_3CN = 0.39 V vs. Ag/AgCl. The potentials for oxidation of the complexes in CH_3CN have been adjusted for this difference in junction potentials to allow direct comparison of the data in both solvents. [b] Scan rate 200 mV s^{-1}. [c] E_p^{ox} = oxidation potential of forward scan in cyclic voltammogram; E_p^{red} = reduction potential of reverse scan of cyclic voltammogram; $E_{1/2}$ = calculated reversible half-wave potential. [d] $E_{3/4}$ and $E_{1/4}$ = potential at three-fourth and one-fourth of the limiting current value, respectively. [e] 2000 rpm. [f] Values in parentheses are for the second oxidation process (see text).

a variety of bidentate ligands containing phosphorus, arsenic, and selenium donor atoms.

Experimental Section

Materials. Chromium, molybdenum, and tungsten hexacarbonyls (Climax Molybdenum Co., Pressure Chemical Co.) were dried over P_2O_5 and used without further purification. The ligands dpm, dpe, dam, dae, and ape (Strem Chemical Co.) were used as supplied while dpmSe was prepared as described previously.[15] All solvents were AR grade and dried over molecular sieves.

Preparations. $M(CO)_4(L\text{-}L)$ were prepared by standard literature methods for L-L = dpm,[16] dpe,[16] dam,[17] dae,[18] and dpmSe.[19] $M(CO)_4(ape)$ complexes were prepared analogously. $[Cr(CO)_4(dpm)]^+$ was prepared in dichloromethane solution by oxidative controlled-potential electrolysis of $Cr(CO)_4(dpm)$ at 1.0 V vs. Ag/AgCl at a platinum electrode in the dark. The compound $[Cr(CO)_4(dpm)](PF_6)$ was prepared by the oxidation of $Cr(CO)_4(dpm)$ in dichloromethane using $NOPF_6$ as described in the literature.[13]

Physical Measurements. Infrared spectra were recorded on a Jasco A-302 spectrophotometer and calibrated against polystyrene (1601 cm^{-1}). Phosphorus-31 proton-decoupled NMR spectra were recorded at 40.26 MHz on a JEOL FX 100 spectrometer and referenced against external 85% H_3PO_4. The high frequency positive convention was used. ESR spectra were recorded on a Varian 450/15 spectrometer.

Cyclic voltammograms were recorded at 20 ± 1 °C, unless otherwise stated in dichloromethane (0.1 M Bu_4NClO_4) or acetonitrile (0.1 M Et_4NClO_4) using a EG&G PAR Model 174 polarographic analyzer. A three-electrode system was used with the working and auxiliary electrodes being platinum wire or disks. The reference electrode was Ag/AgCl (CH_2Cl_2; saturated LiCl) and was separated from the test solution by a salt bridge containing 0.1 M Bu_4NClO_4 in CH_2Cl_2. Frequent calibration of this reference electrode was carried out against a standard ferrocene solution. For variable-temperature cyclic voltammetry, the temperature was regulated by using a dry ice/acetone bath and monitored with a thermocouple. For rotating platinum-disk experiments, a Metrohm platinum rotating electrode with variable rotation rates was used with the same auxiliary and reference electrodes as above.

Controlled-potential electrolysis experiments were performed with a PAR Model 173 Potentiostat/Galvanostat using a platinum-gauze working electrode and a platinum auxiliary electrode separated from the bulk solution by a salt bridge containing a Vycor plug. The reference electrode was the same as used in the voltammetric experiments. All solutions were degassed with nitrogen before measurements were taken and were kept under a nitrogen blanket during the experiments. Unless otherwise stated, all oxidative experiments were conducted in the dark since the cationic products are very light sensitive.

Results

Electrochemical Oxidation of $Cr(CO)_4(dpm)$ in Dichloromethane and Acetonitrile. All the chromium complexes studied give similar voltammetric results, and the data are summarized in Table I. The $Cr(CO)_4(dpm)$ complex will be discussed in most detail as its cation exhibits the greatest stability. Chemical reaction pathways can be followed with isolated samples in contrast to other complexes where only voltammetric monitoring is possible.

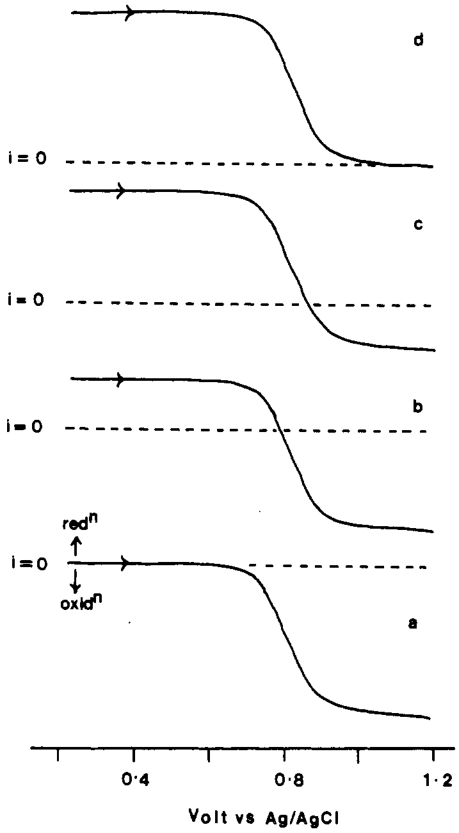

Figure 1. Voltammograms at a platinum rotating disk electrode (2000 rev min^{-1}) monitoring the course of controlled-potential oxidation (1.2 V vs. Ag/AgCl) of a 5×10^{-4} M solution of $Cr(CO)_4(dpm)$ in CH_2Cl_2 (0.1 M Bu_4NClO_4) in the dark: (a) prior to electrolysis; (b, c) during electrolysis; (d) at the end of the electrolysis.

Cyclic voltammograms for the oxidation of $Cr(CO)_4(dpm)$ in dichloromethane at a platinum electrode showed shapes that are consistent with a chemically reversible one-electron oxidation.[20] The shape of the current–voltage curve and the diffusion-controlled limiting current in platinum rotating disk electrode experiments are also consistent with a reversible one-electron oxidation.

Cyclic voltammetry over the temperature range −60 to +25 °C and for scan rates of 20–500 mV s^{-1} is also consistent with a simple one-electron oxidation. This result suggests that a *cis*$^+$ cation exists on the electrochemical time scale for the chromium dpm derivative, which is consistent with the results of chemical oxidation reported by Connelly et al.,[13] who isolated the reactive $[Cr(CO)_4(pdm)]^+$ cation.

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[20] The chemically reversible oxidation is *cis*-$Cr(CO)_4(dpm) \rightarrow$ *cis*-$[Cr(CO)_4(dpm)]^+ + e^-$. We have included cis to emphasize the unusual nature of this cation.

In the presence of light, oxidative controlled-potential electrolysis of $Cr(CO)_4(dpm)$ at 1.0 V vs. Ag/AgCl at a platinum-gauze working electrode in dichloromethane produces a faint blue color close to the electrode, consistent with the formation[13] of the cation *cis*-$[Cr(CO)_4(dpm)]^+$, but as this blue material diffuses away from the electrode, the color vanishes. Oxidative controlled-potential electrolysis with aluminum foil wrapped around the cell and monitored by rotating platinum-disk experiments shows the disappearance of the oxidative process and generation of a reduction wave at the same potential (Figure 1), and the solution becomes deep purple. Exposure of the oxidized solution to sunlight results in immediate loss of color and, within experimental error, (infrared and platinum rotating disk electrode experiments), leads to quantitative conversion back to the 18-electron $Cr(CO)_4(dpm)$ complex. Thus the cation is light sensitive, similar to other 17-electron cations.[11,21,22] This experiment confirms the previous observations of Connelly et al.,[13] although these workers did not refer specifically to photoreduction.

Coulometric monitoring of the controlled-potential electrolysis experiments in CH_2Cl_2 in the dark gives n values for electron transfer of 1.3 ± 0.2 electron/molecule. The value of $n > 1$ is consistent with a small component of a regenerative mechanism occurring on the time scale of electrolysis.

On standing in the dark, a solution of $[Cr(CO)_4(dpm)]^+$, prepared by controlled-potential electrolysis, undergoes slow decomposition and generates 50 ± 5% of the equivalent amount of $Cr(CO)_4(dpm)$, which is consistent with the occurrence of a disproportionation reaction of the type shown in eq 1. Similar

$$2\,cis\text{-}[Cr(CO)_4(dpm)]^+ \rightarrow cis\text{-}Cr(CO)_4(dpm) + Cr(II) + 4CO + dpm \quad (1)$$

disproportionation reactions have been observed in other systems.[23-25] The overall stoichiometry is fully confirmed since the infrared spectrum of the solution after slow decomposition in the dark shows in the carbonyl region only bands due to $Cr(CO)_4(dpm)$, while ^{31}P NMR spectroscopy confirms the presence of $Cr(CO)_4(dpm)$ and free dpm in equimolar quantities. Thus, two modes of reactivity exist for $[Cr(CO)_4(dpm)]^+$: rapid light-induced reduction and also slow disproportionation in the dark. The purple cation is light sensitive even in the solid state so that attempts to record the infrared spectrum in solution, or as the solid, always give carbonyl absorbances for both the 17- and 18-electron species. UV-visible spectra for the 17-electron cation cannot be recorded since the light source induces complete reduction. Thus, only techniques that do not use a light source appear to be available to study the *cis*-$[Cr(CO)_4(dpm)]^+$ cation. The magnetic susceptibility, measured in solution by the Evans method,[26] shows the compound to be paramagnetic, but a quantitative estimate of the magnetic moment was not possible because of partial decomposition. ESR is an ideal technique to confirm the presence of this paramagnetic species, and the observed spectrum is a symmetrical 1:2:1 triplet ($g = 2.009$, $A = 6.9$ G) due to hyperfine coupling to the equivalent phosphorus atoms.

Some chemical reactions of $[Cr(CO)_4(dpm)]^+$ serve to characterize the behavior of this class of compound. The reaction of $[Cr(CO)_4(dpm)]^+$ with Bu_4NI leads to quantitative conversion to $Cr(CO)_4(dpm)$ (voltammetric, ESR and NMR evidence) consistent with a simple redox reaction giving $Cr(CO)_4(dpm)$ and iodine (identified by color).

Electrochemical parameters for the 18-electron chromium system at a rotating platinum-disk electrode are unaltered with respect to limiting current and $E_{1/2}{}^r$ (reversible half-wave potential) on addition of PPh_3 or dpm or on bubbling carbon monoxide through the solution, even when these reagents are present in considerable excess. Furthermore, cyclic voltammograms remain chemically reversible. However, in contrast, additions of Et_4NCl or $(Ph_3BzP)^+Cl^-$ do alter the electrochemical behavior. As shown in Figure 2a, the limiting current at the rotating platinum-disk electrode doubles in height in the presence of a small stoichiometric excess of chloride ion. Further additions of chloride produce no further change in the voltammograms. Cyclic voltammograms (Figure 2b) also increase in height, and the reverse peak disappears. That is, in the presence of chloride, the oxidation process is a chemically irreversible two-electron step.

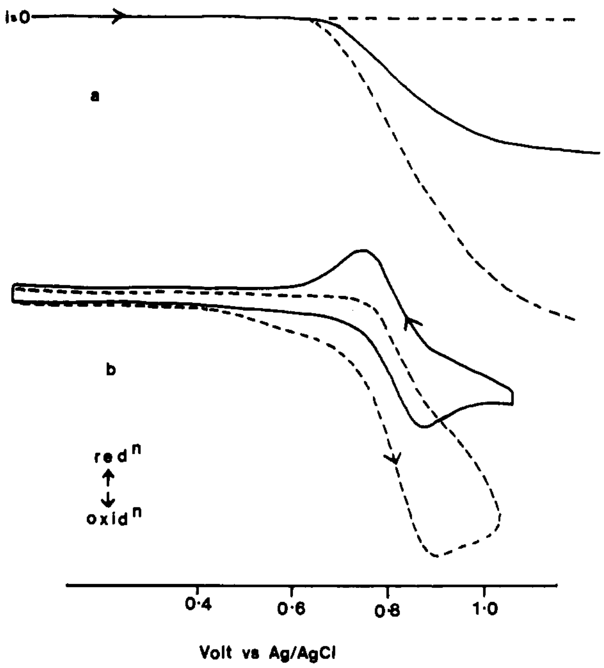

Figure 2. Voltammograms at platinum electrodes under conditions of (a) rotating disk electrode voltammetry (2000 rev min^{-1}) and (b) cyclic voltammetry (scan rate 200 mV s^{-1}) for 5×10^{-4} M $Cr(CO)_4(dpm)$ in CH_2Cl_2 (0.1 M Bu_4NClO_4) before (—) and after (- - -) addition of about 10^{-3} M Cl^- at 20 °C.

Addition of Cl^- to an isolated sample of $[Cr(CO)_4(dpm)](PF_6)$ discharges the purple color almost immediately, producing ≃50% of $Cr(CO)_4(dpm)$ (voltammetric and NMR evidence) and some unidentified non-carbonyl-containing products. A gas, assumed to be carbon monoxide, is also evolved.

Despite the fact that on the voltammetric time scale no evidence can be found for reaction of PPh_3 and dpm with $[Cr(CO)_4(dpm)]^+$, on the synthetic time scale these reagents also react with the cation to give 50 ± 5% of $Cr(CO)_4(dpm)$ together with carbon monoxide and an unidentified non-carbonyl-containing residue. Oxidative controlled-potential electrolysis of $Cr(CO)_4(dpm)$ in CH_2Cl_2 in the presence of 1 molar equiv of dpm, gives an n value of 1.9 ± 0.2 electron/molecule.

We confirmed that chemical oxidation of $Cr(CO)_4dpm$ by $NOPF_6$ in CH_2Cl_2 at temperatures below 0 °C with a vigorous stream of nitrogen passing through the solution gives the deep purple complex $[Cr(CO)_4(dpm)](PF_6)$.[13] However, at room temperature and without the nitrogen purge, nitrosyl substitution occurs to form $[Cr(CO)_3(NO)(dpm)](PF_6)$.[13] This reaction with NO is in marked contrast to systems such as *cis*/*trans*-$M(CO)_4L_2$,[9-11] *cis*-$M(CO)_2(L\text{-}L)_2$,[27,28] and *fac*/*mer*-$M(CO)_3L_3$,[22,29] where reaction with $NOPF_6$ produces the corresponding *trans* or *mer* cations, respectively, without nitrosyl substitution.

In acetonitrile, cyclic voltammograms of $Cr(CO)_4(dpm)$ exhibit a reversible couple at 0.84 V vs. Ag/AgCl similar to that described for a dichloromethane solution. This result, as with many others, is in contrast to the behavior of the corresponding molybdenum

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Table II. Infrared Data[a,b] for $[M(CO)_3(NO)(L\text{-}L)]^+$ Cations in Dichloromethane Solution

complex	ν_{CO}, cm^{-1}		ν_{NO}, cm^{-1}
$[Cr(CO)_3(NO)(dpm)]^+$	2100 m	2045 s	1755 br
$[Cr(CO)_3(NO)(dpe)]^+$	2110 m	2050 s	1757 br
$[Cr(CO)_3(NO)(dae)]^+$	2107 m	2035 s	1757 br
$[Cr(CO)_3(NO)(ape)]^+$	2095 m	2040 s	1756 br
$[Mo(CO)_3(NO)(dpm)]^+$	2110 m	2040 s	1730 br
$[Mo(CO)_3(NO)(dpe)]^+$	2105 m	2035 s	1730 br
$[Mo(CO)_3(NO)(dpmSe)]^+$	2100 m	2040 s	1715 br
$[W(CO)_3(NO)(dpm)]^+$	2102 m	2060 s	1717 br
$[W(CO)_3(NO)(dpe)]^+$	2104 m	2060 s	1722 br
$[W(CO)_3(NO)(dpmSe)]^+$	2105 m	2035 s	1750 br

[a] Calibrated against polystyrene at 1601 cm^{-1}. [b] Key: m = medium; s = strong; br = broad.

and tungsten complexes, which will be discussed later. In addition, a second irreversible one-electron oxidation with a peak potential (scan rate = 200 mV s^{-1}) at 1.65 V vs. Ag/AgCl is observed that is too positive to be observable in dichloromethane. This process represents oxidation of the Cr(I) cation and was not investigated further. The blue 17-electron cation $[Cr(CO)_4(dpm)]^+$ is somewhat less stable in acetonitrile than in dichloromethane, even when the solution is kept in darkness.

Oxidative controlled potential electrolysis of $Cr(CO)_4(dpm)$ in CH_3CN at either 0.95 V vs. Ag/AgCl or at potentials more positive than the second oxidation process, are both consistent with a two-electron oxidation step. After both electrolyses there is no blue color, and no electrochemical evidence for $[Cr(CO)_4(dpm)]^+$ in solution. The overall oxidation process is therefore

$$Cr(CO)_4(dpm) \xrightarrow{CH_3CN} Cr(II) + 4CO + dpm + 2e^- \quad (2)$$

All the above reactions must be conducted in the dark to reproduce the quoted data.

Electrochemical Oxidation of Other $Cr(CO)_4(L\text{-}L)$ Complexes in CH_2Cl_2. On the short time scale of cyclic voltammetry, data in dichloromethane for all the chromium complexes are similar to that for $Cr(CO)_4dpm$ (Table I). However, for longer time scale experiments, such as controlled-potential electrolysis, considerable differences exist.

After controlled-potential electrolysis of $Cr(CO)_4(dpe)$ or oxidation with $NOPF_6$, both at −60 °C in dichloromethane in the presence of Bu_4NClO_4 as an electrolyte, a small reductive component corresponding to the generation of a minor amount of $[Cr(CO)_4(dpe)]^+$ is observed for the voltammogram at a platinum rotating disk electrode. At room temperature or at 0 °C, however, the cation decomposes completely on the coulometric time scale and no reductive response is observed after exhaustive oxidative electrolysis. For the systems $[Cr(CO)_4(L\text{-}L)]^{+/0}$ (L-L = ape, dae), the cations are observed on the voltammetric time scale, but they are unstable on the electrochemical synthetic time scale at all temperatures. $NOPF_6$ oxidation in the presence of 0.1 M Bu_4NClO_4 also fails to produce these cations. No voltammetric response at the expected potentials is observed for the oxidized solutions.

Oxidative controlled potential electrolysis in the dark of the appropriate $Cr(CO)_4(L\text{-}L)$ complex yields an *n* value of 1.2 ± 0.2 electron/molecule. A two-electron oxidation resulting from disproportionation was expected due to the lack of evidence for longer time scale stability for the cations $[Cr(CO)_4(L\text{-}L)]^+$. Oxidation with $NOPF_6$ in CH_2Cl_2 at room temperature affords well-defined nitrosyl complexes $[Cr(CO)_3(NO)(L\text{-}L)]^+$, as shown by IR data in Table II. By contrast, Connelly[12] reported formation of only $[Cr(CO)_4(dpe)]^+$ by $NOPF_6$ oxidation of $Cr(CO)_4(dpe)$. Thus, in our hands, either the cation $[Cr(CO)_4(dpm)]^+$ or the nitrosyl substitution product $Cr(CO)_3(NO)(dpe)$ is produced, depending upon whether or not the solution is purged with nitrogen. This is what Connelly et al.[13] reported for the corresponding dpm system. We also find that the presence of electrolyte decreases considerably the stability of $[Cr(CO)_4(dpm)]^+$ and $[Cr(CO)_4(dpe)]^+$ toward decomposition. This explains the apparent inconsistencies in $NOPF_6$ oxidative data monitored electrochemically in the presence of 0.1 M Bu_4NClO_4 and monitored by visual inspection (color) without electrolyte.

Table III. Electrochemical Data[a–c] for the Oxidative Cyclic Voltammetry of 1 × 10^{-3} M $M(CO)_4(L\text{-}L)$ Complexes at 20 °C

	CH_2Cl_2		CH_3CN[f]
complex	E_p^{ox}, V	E_p^{red}, V	E_p^{ox}, V
$Mo(CO)_4(dpm)$	0.99		0.98 (1.94)
$Mo(CO)_4(dpe)$	1.12	0.90	1.05
$Mo(CO)_4(dae)$	1.14		1.06 (1.86)
$Mo(CO)_4(dpmSe)$	0.78	0.66	0.82
$W(CO)_4(dpm)$	0.99		0.94
$W(CO)_4(dpe)$	1.08	0.98	1.09
$W(CO)_4(dae)$	1.13		1.08
$W(CO)_4(ape)$	1.12		1.10
$W(CO)_4(dpmSe)$	0.71		0.75 (1.85)

[a] See footnotes to Table I.

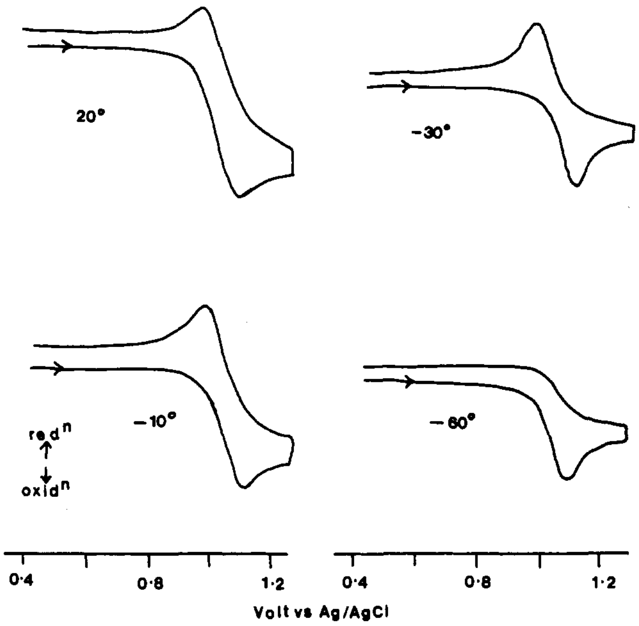

Figure 3. Cyclic voltammograms at a platinum electrode for a solution of 5 × 10^{-4} M $Mo(CO)_4(dpe)$ in CH_2Cl_2 (0.1 M Bu_4NClO_4) showing the temperature dependence of the response.

Electrochemical Oxidation of $M(CO)_4(L\text{-}L)$ (M = Mo, W). The cyclic voltammetric data for $M(CO)_4(L\text{-}L)$ complexes are summarized in Table III.

While other authors[13,14] have referred to the oxidation of $Mo(CO)_4(dpe)$ as a chemically reversible one-electron process, the temperature dependence of the cyclic voltammograms is not consistent with that simple reaction. The temperature dependence of the oxidative cyclic voltammograms for the complex $Mo(CO)_4(dpe)$ is shown in Figure 3. The temperature dependence of the oxidation process is typical for those of $M(CO)_4(dpe)$ (M = Mo, W) and $Mo(CO)_4(dpmSe)$. The processes become irreversible at very low temperatures and are only reversible (in the sense of equal oxidation and reduction peak currents) at one particular temperature at a given scan rate for each complex. These temperatures are 0 °C for $Mo(CO)_4(dpe)$, 18 °C for $W(CO)_4(dpe)$, and −10 °C for $Mo(CO)_4(dpmSe)$ at a scan rate of 200 mV s^{-1}. This type of behavior is very unusual. Systems that are chemically irreversible at room temperature commonly show enhanced chemical reversibility at lower temperatures. In this case, however, the temperature dependence is much more complex: we observe a new process at less positive potentials on the reverse (reductive) scan at low temperatures for $Mo(CO)_4(dpmSe)$ (Figure 4a) and $W(CO)_4(dpe)$. This confirms that a product other than *cis*-$[M(CO)_4(L\text{-}L)]^+$ is produced. Dilution of the electrolyte to 0.01 M leads to a small increase in chemical reversibility at low temperatures.

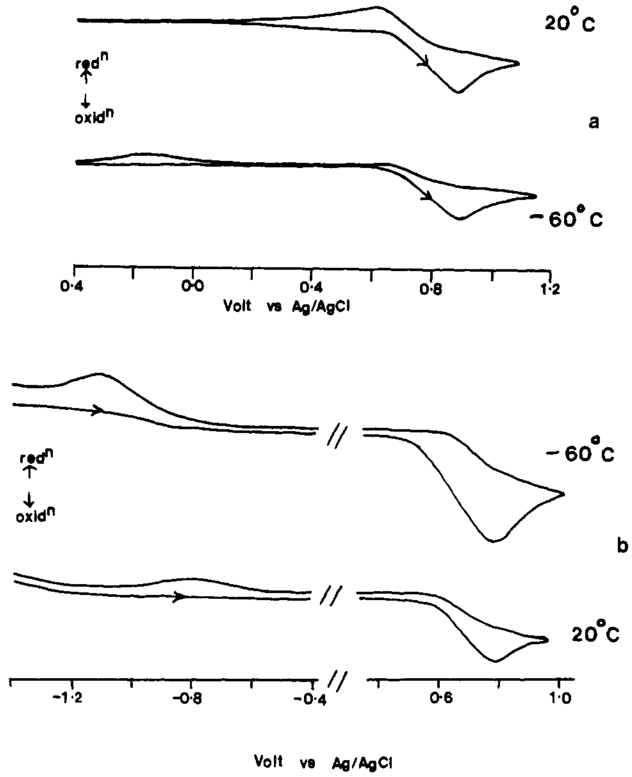

Figure 4. Cyclic voltammograms at platinum electrodes (scan rate 200 mV s^{-1}) in dichloromethane (0.1 M Bu_4NClO_4) over a wide potential range for compounds showing anomalous behavior: (a) 5 × 10^{-4} M $Mo(CO)_4$(dpmSe); (b) 5 × 10^{-4} M $W(CO)_4$(dpmSe).

At a platinum rotating disk electrode the diffusion-controlled limiting current is consistent with a one-electron-oxidation process. Bubbling carbon monoxide through the solution has no effect on the electrochemical response. The limiting current at the rotating platinum-disk electrode is doubled for oxidation of $Mo(CO)_4$(dpe) in the presence of dpe and increases to a lesser extent when PPh_3 or the appropriate ligand is added to the other systems. Under cyclic voltammetry, such an addition leads to a marked increase in the oxidative current and complete loss of the reductive component of the cyclic voltammogram. These data contrast with those for the corresponding chromium complexes for which addition of PPh_3 or free ligand causes no change in the electrochemical response on the voltammetric time scale. For $Mo(CO)_4$(dpmSe), voltammograms are independent of PPh_3 concentration. However on addition of dpmSe the limiting current of the rotating platinum-disk electrode response and the cyclic voltammetric peak height decrease slightly with increasing concentration as the reverse scan reduction peak decreases. With a 2 mol excess the height decreases to 0.75 times its original value (rotation rate 2000 rpm) and 0.9 (cyclic voltammetry scan rate = 200 mV s^{-1}). That is, the rate of reaction of $Mo(CO)_4$(dpmSe) with ligand is much slower than that for $Mo(CO)_4$(dpe) on addition of ligand and the mechanism is different.

The compounds $M(CO)_4$(L-L) (M = Mo, L-L = dpm, dae; M = W, L-L = dpm, dae, ape, dpmSe) all give chemically irreversible oxidations on the voltammetric time scale under all conditions of temperature (+20 to -60 °C) and scan rates (10-500 mV s^{-1}) examined. Despite the observed chemical irreversibility, the limiting current observed at a rotating platinum-disk electrode is consistent with a one-electron oxidation in the absence of PPh_3 or free ligand but, with the exception of $W(CO)_4$(dpmSe), becomes a two-electron oxidation in the presence of these ligands. In the case of $W(CO)_4$(dpmSe), no alteration to the response is observed on addition of a large excess of PPh_3 and only a relatively small decrease is observed on addition of dpmSe. On the reverse reductive scan a peak is observed well removed from the oxidation process (Figure 4b for $W(CO)_4$(dpmSe)). The position of the reductive response is highly temperature dependent.

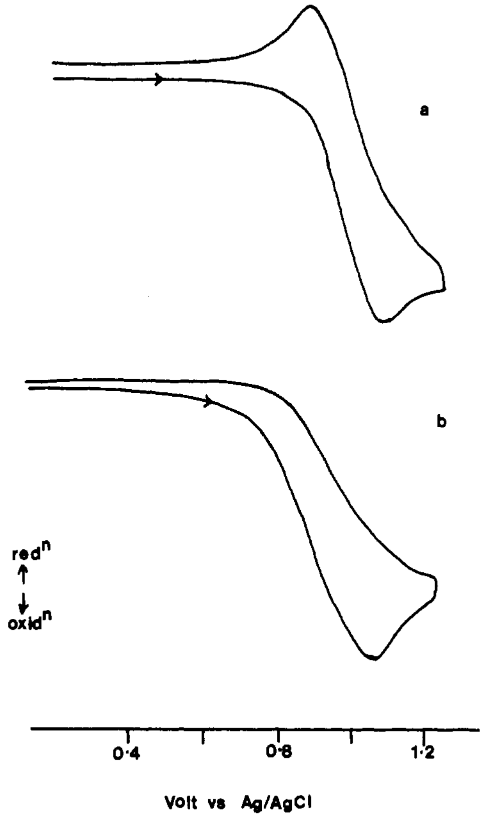

Figure 5. Cyclic voltammograms at a platinum electrode (scan rate 200 mV s^{-1}) for 5 × 10^{-4} M $Mo(CO)_4$(dpe) in (a) CH_2Cl_2 (0.1 M Bu_4NClO_4) and (b) CH_3CN (0.1 M Et_4NClO_4) at 20 °C.

Oxidative controlled-potential electrolysis at 1.2 V vs. Ag/AgCl for all the $Mo(CO)_4$(L-L) complexes and $W(CO)_4$(dpe) give *n* values of 1.6 ± 0.3. After the electrolyses the solutions give no voltammetric responses at positive potentials, and this behavior parallels that described earlier for $Cr(CO)_4$(L-L) complexes (L-L = ape, dae). In the presence of ligand, *n* values of 2.2 ± 0.1 are obtained.

In the case of $W(CO)_4$(L-L) (L-L = dpm, dae), which are examples of totally irreversible electrode processes at all temperatures, apparent *n* values considerably less than 1 are obtained when the oxidative current flow ceases. However, this is not an exhaustive electrolysis; instead, the products of oxidation foul the electrode and prevent further electrolysis. Vigorous cleaning of the electrode allows the oxidation to continue to a small degree before fouling reoccurs. Surface reactions therefore prohibit exhaustive oxidative controlled-potential electrolysis experiments of many of the tungsten compounds. However, for $W(CO)_4$(dpmSe) an *n* value of 1.98 ± 0.05 is obtained.

In the presence of Cl^- and Br^- the limiting current per unit concentration at a platinum rotating disk increases in magnitude. Presumably, the process is converted to a two-electron step, although this is difficult to ascertain due the close proximity of the complex and the halide oxidation waves.

With $NOPF_6$ oxidation of $M(CO)_4$(L-L) (M = Mo, W, L-L = dpm, dpe, dpmSe), the product is exclusively the nitrosyl substitution product $M(CO)_3(NO)$(L-L) (IR data, Table II) while the remaining complexes produce unidentified products that exhibit no carbonyl or nitrosyl bands in their infrared spectra. There is no evidence for a 17-electron cation $[M(CO)_4(L\text{-}L)]^+$ even on the voltammetric time scale at low temperature, which may be compared with other systems that can isomerize following oxidation.[10,22,27-29]

Voltammetric data (Table III) for the complexes $M(CO)_4$(dpe) and $Mo(CO)_4$(dpmSe), which show the anomalous variable-temperature chemical reversibility in dichloromethane, are modified by changing to the coordinating solvent acetonitrile as shown in Figure 5. Controlled potential electrolysis in CH_3CN gives *n* values of 2.05 ± 0.05. On the long time scale two electrons are transfered compared with one at short time scales. The complexes $Mo(CO)_4(dpm)$, $Mo(CO)_4(dae)$, and $W(CO)_4(dpmSe)$ exhibit a second one-electron oxidation at very positive potentials in acetonitrile.

Discussion

Data reported in this paper support the hypothesis formulated in the introduction that geometrically constrained 17-electron *cis*-$[M(CO)_4(L\text{-}L)]^+$ complexes are highly reactive compared to other group 6 carbonyl complexes such as *cis*-$M(CO)_4L_2$,[9,10] *cis*-$M(CO)_2(L\text{-}L)_2$,[27,28] *fac*-$M(CO)_3L_3$,[29] and *fac*-$M(CO)_3(\eta^1\text{-}L\text{-}L)(\eta^2\text{-}L\text{-}L)$,[30] which can and do relieve strain by isomerization to *trans*$^+$ and *mer*$^+$ configurations, respectively. A similar situation applies to group 6 arene chemistry where complexes of the type $[M(CO)_3(\text{arene})]^+$ are forced to retain a facial geometry instead of the thermodynamically favored lower energy *mer*$^+$ configuration.[31-33]

In the absence of an isomerization pathway leading to lower energy, a series of alternative reaction pathways can occur to produce formally 18-electron compounds or other structurally rearranged species that include photoreduction and disproportionation.

In the presence of coordinating ligands that are not readily oxidized, voltammetric data are substantially modified. Coulometric data are consistent with a two-electron process. With the exception of L-L = dpmSe, an overall reaction scheme accounting for the data in the presence of a coordinating ligand is

$$2\,cis\text{-}M(CO)_4(L\text{-}L) \rightleftharpoons 2\,cis\text{-}[M(CO)_4(L\text{-}L)]^+ + 2e^- \xrightarrow[\frac{1}{2}(L\text{-}L)\,=\,P]{Cl^-,\ PPh_3,\ \text{or}} [M(CO)_4(L\text{-}L)P]^{2+} + cis\text{-}M(CO)_4(L\text{-}L) \quad (3)$$

where $[M(CO)_4(L\text{-}L)P]^{2+}$ is a seven-coordinate oxidation state II compound. Seven-coordinate 18-electron complexes in oxidation state II are common for molybdenum and tungsten[34,35] and complexes closely related to $[M(CO)_4(L\text{-}L)P]^{2+}$ are known. For example, $[Mo(CO)_2(dmpe)_2Cl](PF_6)_2$ has been isolated and characterized by X-ray diffraction,[36] and $[M(CO)_3(dpm)_2]^{2+}$ has been postulated to be the product of oxidation of $M(CO)_3(\eta^1\text{-}dpm)(\eta^2\text{-}dpm)$.[30] However, in the case of chromium, seven-coordinate complexes are rare,[35] and this pathway is not favored.

Oxidation with $NOPF_6$ produces the 18-electron complex $[M(CO)_3(NO)(L\text{-}L)]^+$ rather than the 17-electron compound $[M(CO)_4(L\text{-}L)]^+$, and this reaction represents a special case of the reaction of the 17-electron cation with a coordinating ligand. The reactor sequence can be envisaged as in eq 4.

$$\underset{18\ \text{electron}}{M(CO)_4(L\text{-}L)} \rightarrow \underset{17\ \text{electron}}{[M(CO)_4(L\text{-}L)]^+} + NO \rightarrow$$
$$\underset{20\ \text{electron}}{[M(CO)_4(NO)(L\text{-}L)]^+} \rightarrow \underset{18\ \text{electron}}{[M(CO)_3(NO)(L\text{-}L)]^+} + CO \quad (4)$$

In the absence of coordinating ligands it is clear that as yet uncharacterized reactive intermediates can be formed. The remarkable temperature dependence of voltammetric data, electrolyte effects, etc. all indicate considerable complexity. Ring opening and closing of $M(CO)_4(\eta^1\text{-}L\text{-}L)$ complexes has been well documented in flash photolysis experiments[37-41] and in 18-electron substitution reactions of sulfur chelates by phosphines and phosphites.[42] The formation of $[M(CO)_4(\eta^1\text{-}L\text{-}L)]^+$ intermediates that are in reversible equilibrium with $[M(CO)_4(\eta^2\text{-}L\text{-}L)]^+$ at ambient temperatures but not at low temperatures where alternative decomposition pathways occur seems very plausible and would be consistent with the very unusual voltammetric data.

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