

Reaction Pathways in the Redox Chemistry of the $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$ and $[\{\text{Mo}(\text{CO})_2(\text{dpe})_2\}_2\text{F}]^{3+}$ ($\text{dpe} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$) Mo(II) Carbonyl Fluoride System

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Received January 21, 1998

Voltammetric oxidation of 0.45 mM $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$ ($\text{dpe} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$) in dichloromethane (0.1 M Bu_4NPF_6) at platinum and glassy carbon macro- and microdisk electrodes gives a one-electron reversible couple. Spectroelectrochemical (IR) oxidation studies on the tens of seconds time scale confirm the formation of the first Mo(III) phosphine-substituted carbonyl fluoride, $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^{2+}$. However, the compound is not stable on the longer synthetic (tens of minutes) time scale. Bulk electrolytic reduction of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$ gives *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ and F^- quantitatively, but on the voltammetric time scale an intermediate identified as *cis*- $[\text{Mo}(\text{CO})_2(\eta^1\text{-dpe})(\eta^2\text{-dpe})\text{F}]^-$ is detected which then reacts to give *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ and F^- . The existence of this and other short-lived intermediates leads to complex cyclic voltammograms which are very concentration, scan rate, and temperature dependent. The fluoride-bridged binuclear complex $[\{\text{Mo}(\text{CO})_2(\text{dpe})_2\}_2\text{F}](\text{PF}_6)_3$ is not oxidized within the potential range available, but in reductive cyclic voltammograms it is reduced predominantly to *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$, again probably via a fluoride containing intermediate. The reaction $2[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+ \rightleftharpoons [\{\text{Mo}(\text{CO})_2(\text{dpe})_2\}_2\text{F}]^{3+} + \text{F}^-$ is believed to be important in determining the concentration dependence of the redox behavior of this Mo(II) carbonyl fluoride system. The electrochemical studies reveal that carbonyl fluoride complexes may exist in a wide range of oxidation states and confirm that fluoride is relatively strongly bound in these types of systems, although in the zero valent reduced form, displacement by a phosphorus ligand does occur.

Introduction

The number of metal carbonyl fluoride derivatives known is small.¹ Initially, it was postulated that the combination of low oxidation state favoring carbonyl ligands and the high oxidation state favoring fluoride ligands meant that the probability of forming carbonyl fluoride complexes was small. For the group 6 metals, examples of unsubstituted carbonyl fluoride complexes now include $[\text{M}(\text{CO})_5\text{F}]^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$),² $\text{M}(\text{CO})_4\text{F}_2$ ($\text{M} = \text{Mo}, \text{W}$),³ $\text{Mo}(\text{CO})_3\text{F}_3$,³ $\text{Mo}(\text{CO})_3\text{F}_4$,³ and $(\text{NEt}_4)_3\text{[W}_2(\text{CO})_6\text{F}_3]$,^{2a} so that these compounds exist in oxidation states ranging from zero to four.

A number of phosphine-substituted seven-coordinate M(II) ($\text{M} = \text{Mo}$ or W) carbonyl fluorides also are known and include $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2\text{F}_3]\text{BF}_4$,⁴ $[\{\text{M}(\text{CO})_2(\text{PPh}_3)_2\}_2\text{F}_3]\text{BF}_4$,⁵ and $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$ ($\text{dpe} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$). This latter species was first gener-

ated⁶ by NOPF_6 oxidation of *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ ⁷ in dichloromethane, with the anion of the oxidant acting as the source of fluoride. It is also formed by bulk electrolytic oxidation of *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ in dichloromethane in the presence of fluoride ion.⁸ The crystal structure of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$ has been determined,⁹ and the geometry of the cation is of approximately C_{2v} symmetry with the two carbonyls and the fluoride ligand in one plane and the four phosphorus atoms in another plane approximately at right angles to the first. A brief report of the voltammetry of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$ recorded that the compound is extremely stable toward reduction but that it could be oxidized close to the solvent limit in both dichloromethane and nitromethane solutions.⁶

Wimmer and Snow also reported⁶ that when *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ and NOPF_6 were interacted in nitromethane, the resulting product was a mixture of about 20% $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$ and 80% of the fluoride-bridged binuclear complex $[\{\text{Mo}(\text{CO})_2(\text{dpe})_2\}_2\text{F}](\text{PF}_6)_3$, which could not be separated. The bridged species was shown to react with excess fluoride ion to give $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^-$

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PF₆. No previous electrochemical studies of the bridged species have been reported.

In this paper, the reductive and oxidative electrochemical properties of [Mo(CO)₂(dpe)₂F]⁺ and [Mo(CO)₂(dpe)₂]₂F³⁺ have been investigated in detail and the importance of an equilibrium reaction between the compounds has been confirmed. A moderately stable Mo(III) carbonyl fluoride has been identified upon oxidation of [Mo(CO)₂(dpe)₂F]⁺, and upon reduction, an unexpected zero valent fluoride-containing intermediate has been characterized by voltammetry and spectroelectrochemistry (IR). These electrochemical studies demonstrate that the fluoride ligand is relatively strongly bound in molybdenum and, presumably, the related tungsten carbonyl fluoride compounds.

Experimental Section

Materials. All solvents were of analytical reagent or HPLC grade. Dichloromethane was purified by drying over freshly regenerated 4A molecular sieves. Molybdenum carbonyl, dpe, and NPF₆ (Strem) were used as received.

Syntheses. *cis*-Mo(CO)₂(dpe)₂,⁷ *trans*-[Mo(CO)₂(dpe)₂]₂PF₆,⁶ [Mo(CO)₂(dpe)₂F]PF₆,⁶ and [Mo(CO)₂(dpe)₂]₂F(PF₆)₃⁶ were prepared by literature methods. The identity of [Mo(CO)₂(dpe)₂F]PF₆ was confirmed by a single-crystal X-ray diffraction study which yielded unit cell data essentially identical with those published.⁹

Electrochemical Methods. Conventional voltammetric measurements were carried out in dichloromethane (0.1 M Bu₄NPF₆) solution on a MacLab 4e computer-controlled system. The working electrode was a platinum or glassy carbon disk, radius 0.5 mm, the auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl (0.1 M Bu₄NPF₆, dichloromethane-saturated LiCl) separated from the test solution by a salt bridge. The reversible voltammetry of an approximately 1.0 mM ferrocene (Fc) solution in the same solvent was used as a reference redox couple, and all potentials are quoted relative to Fc⁺/Fc. Molecular sieves were added to electrochemical solutions to maintain dryness.

Near-steady-state voltammograms at fast scan rates were recorded in dichloromethane (0.5 M Bu₄NPF₆) on an apparatus described previously¹⁰ using a 5-μm-radius platinum microdisk working electrode and a platinum wire pseudoreference electrode.

Rotating disk voltammograms were recorded at 1.5-mm platinum or glassy carbon disk electrodes using a Metrohm 628-10 assembly at rotation speeds of 500 and 1000 revolutions (rev) min⁻¹.

Dichloromethane (0.1 M Bu₄NPF₆) solutions were purged with solvent-saturated nitrogen before voltammetric measurements and then maintained under an atmosphere of nitrogen during measurements.

Bulk electrolysis experiments were undertaken in dichloromethane with a BAS 100A electrochemical analyzer using a large platinum basket working electrode, a platinum gauze auxiliary electrode separated from the test solution by a salt bridge, and the same reference electrode as used in the voltammetric studies. The electrolytes in the bulk electrolysis experiments were Bu₄NPF₆ or Bu₄NCIO₄.

Spectroscopic Methods. ³¹P NMR spectra were recorded on a Bruker AM 300 spectrometer at 121.496 MHz. The high-frequency positive convention is used for chemical shifts with 85% H₃PO₄ as external reference. Infrared spectra were recorded on a Bruker IFS 55 FTIR spectrometer.

Infrared spectroelectrochemical experiments were carried out using a modified IR reflection-absorption spectroscopy

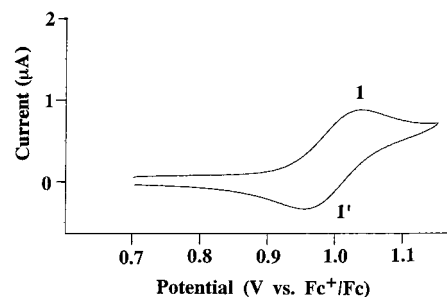
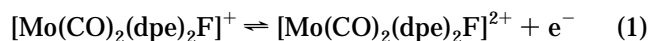


Figure 1. Oxidative cyclic voltammogram at 20 °C at a platinum electrode (radius 0.5 mm) for a 0.45 mM solution of [Mo(CO)₂(dpe)₂F]PF₆ in dichloromethane (0.1 M Bu₄NPF₆). Scan rate 100 mV s⁻¹.

(IRRAS) cell,^{11,12} mounted on a specular reflectance accessory located in the sample compartment of a Bruker IFS 55 FTIR spectrometer. The electrode arrangement consisted of a polished platinum disk working electrode (radius 2.5 mm), a platinum gauze auxiliary electrode, and a silver wire pseudoreference electrode. Electrolyses were carried out by stepping the potential of the working electrode from a rest potential to a potential sufficient to cause electrolysis, typically 200 mV past the peak potential, and single-scan IR spectra (resolution 1.0 cm⁻¹) were collected as a function of time. Electrolyses were performed with a Princeton Applied Research Corp. (PAR) (Princeton NJ) model 174A polarographic analyzer. The dichloromethane Bu₄NPF₆ electrolyte solutions were prepared as for the voltammetric experiments, and solutions were deoxygenated before syringing into the IRRAS cell. The cell itself was thoroughly flushed with nitrogen prior to addition of the sample and maintained under a nitrogen atmosphere throughout the experiments.

Results

Oxidation Studies. (i) Voltammetry. Figure 1 shows an oxidative cyclic voltammogram at a platinum electrode (radius 0.5 mm) at 20 °C and a scan rate of 100 mV s⁻¹ for a 0.45 mM solution of [Mo(CO)₂(dpe)₂F]PF₆ in dichloromethane (0.1 M Bu₄NPF₆). A single chemically reversible redox couple (couple 1, comprising oxidation process 1 and reduction process 1'; all reduction responses will be indicated by a superscript ') is observed. At this concentration, the couple has all the characteristics of a fully reversible redox process. The peak-to-peak separation and its scan rate dependence are essentially the same as that observed for the oxidation of an equimolar solution of ferrocene, and this behavior strongly suggests the existence of a Mo(III) carbonyl fluoride [Mo(CO)₂(dpe)₂F]²⁺ which is stable on the voltammetric time scale. The process at low concentrations is therefore described by eq 1. However, at a



concentration of 4.5 mM, the oxidation response becomes chemically irreversible at slow scan rates but remains reversible at high scan rates. Data obtained at different scan rates are summarized in Table 1. Clearly some non-unity-order chemical reaction accompanies the charge-transfer process at higher concentrations. The earlier report in the literature⁶ de-

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Table 1. Oxidative Cyclic Voltammetric Data at 20 °C for [Mo(CO)₂(dpe)₂F]⁺ and Fc in Dichloromethane (0.1 M Bu₄NPF₆) at a Platinum Electrode (Radius 0.5 mm)

compound	conc (mM)	scan rate (mV s ⁻¹)	E _p ^{ox} (V)	E _p ^{red} (V)	ΔE _p (V)	i _p ^{ox} /i _p ^{red}
Fc		100	0.040	-0.040	0.080	0.9
Fc		1000	0.060	-0.060	0.120	0.9
[Mo(CO) ₂ (dpe) ₂ F]PF ₆	0.45	100	1.040	0.960	0.080	0.9
	0.45	1000	1.050	0.950	0.100	0.9
	0.9	100	1.070	0.960	0.110	1.2
	0.9	1000	1.090	0.940	0.150	0.9
	4.5	100 ^a	1.110		irreversible	
	4.6	1000	1.190	0.860	0.330	2.3

^a First scan complex; data given for second cycle.

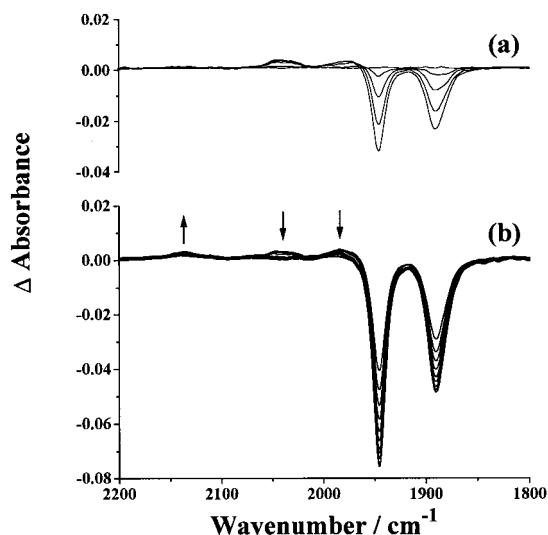


Figure 2. Changes in the IR difference spectra accompanying oxidation of [Mo(CO)₂(dpe)₂F]PF₆ in an IRRAS cell in dichloromethane (0.1 M Bu₄NPF₆): (a) first series of spectral changes, time 0–22 s; (b) second and final stage of spectral changes, time 22–94 s.

scribes the oxidation response as quasi-reversible. Cyclic voltammetric data obtained at a glassy carbon macrodisk electrode are very similar to those reported at the platinum macrodisk electrode.

(ii) Spectroelectrochemical Oxidation of [Mo(CO)₂(dpe)₂F]PF₆. The IR spectral changes that occur during the oxidation of 5.0 and 1.0 mM [Mo(CO)₂(dpe)₂F]⁺ in dichloromethane (0.1 M Bu₄NPF₆) at 1.1 V in the IRRAS cell occur in two distinct stages. Figure 2 shows difference spectra (i.e., initial spectrum before oxidation subtracted from each successive spectrum) accompanying the oxidation. The first stage (0–22 s) (Figure 2a) involves the negative growth (that is, consumption of the species) of the reactant peaks at 1945 and 1890 cm⁻¹ and the growth of two relatively weak bands of approximately equal intensities at 2040 and ~1978 cm⁻¹. These changes are consistent with the depletion of [Mo(CO)₂(dpe)₂F]⁺ within the thin layer and formation of the one-electron-oxidized product [Mo(CO)₂(dpe)₂F]²⁺. The two carbonyl bands shift by 80–100 cm⁻¹ to higher wavenumber, which is typical for the one-electron oxidation of monomeric carbonyl complexes.¹³ After consumption of ~45% of the [Mo(CO)₂(dpe)₂F]⁺, the second stage of spectral changes takes place (22–94 s). The carbonyl bands at 2040 and 1978

cm⁻¹ stop growing and begin to collapse, eventually diminishing to zero absorbance as the remainder of the [Mo(CO)₂(dpe)₂F]⁺ is oxidized, as shown by the gradual growth of the 1945- and 1890-cm⁻¹ bands to negative absorbance (Figure 2b). Concomitant with the collapse of the 2040- and 1978-cm⁻¹ bands is the growth of a weak peak at 2137 cm⁻¹, signifying the release of free CO.¹⁴ Although the lifetime of [Mo(CO)₂(dpe)₂F]²⁺ increases at low temperature (–40 °C) and low concentration, complete chemical reversibility of the oxidation cannot be achieved on the tens of seconds time scale of the spectroelectrochemical experiment.

Exhaustive bulk oxidative electrolysis at a platinum electrode of a solution of [Mo(CO)₂(dpe)₂F]PF₆ in dichloromethane (0.4 M Bu₄NPF₆) was carried out at room temperature. This experiment required 15–30 min. The IR spectrum of the resulting solution showed no absorption bands in the carbonyl region, confirming that the high-oxidation-state carbonyl fluoride is not stable on this longer time scale.

The binuclear complex [Mo(CO)₂(dpe)₂F]₂(PF₆)₃ does not show any oxidation response within the accessible potential range available at either platinum or glassy carbon macrodisk electrodes.

Reduction Studies. (i) Reductive Voltammetry of [Mo(CO)₂(dpe)₂F]PF₆. The literature⁶ suggests that [Mo(CO)₂(dpe)₂F]PF₆ cannot be electrochemically reduced in dichloromethane solution. However, we find the compound can be reduced, and there is a rich chemistry accompanying the charge-transfer process. Under conditions of conventional cyclic voltammetry, we have detected at least 10 responses, several of which can be seen upon close inspection of Figure 3. Figure 3a is the third cycle of a reductive cyclic voltammogram of [Mo(CO)₂(dpe)₂F]PF₆ and illustrates the complexity of the system. Furthermore, the nature of the cyclic voltammograms is scan rate, concentration, and temperature dependent. It is therefore necessary to present the reductive voltammetric data in a stepwise fashion so that the nature of each of the responses, and their inter-relationships, can be established.

Figure 3b shows a reductive cyclic voltammogram at 20 °C, scan rate 100 mV s⁻¹, over the restricted potential range –0.9 to –2.4 V for a 0.90 mM solution of [Mo(CO)₂(dpe)₂F]PF₆ in dichloromethane (0.1 M Bu₄NPF₆) at a platinum macrodisk electrode (radius 0.5 mm). On the first reductive scan, only one well-defined response, process 2', is observed. On the reverse scan (oxidative direction), process 3 is observed at –1.180 V. On the

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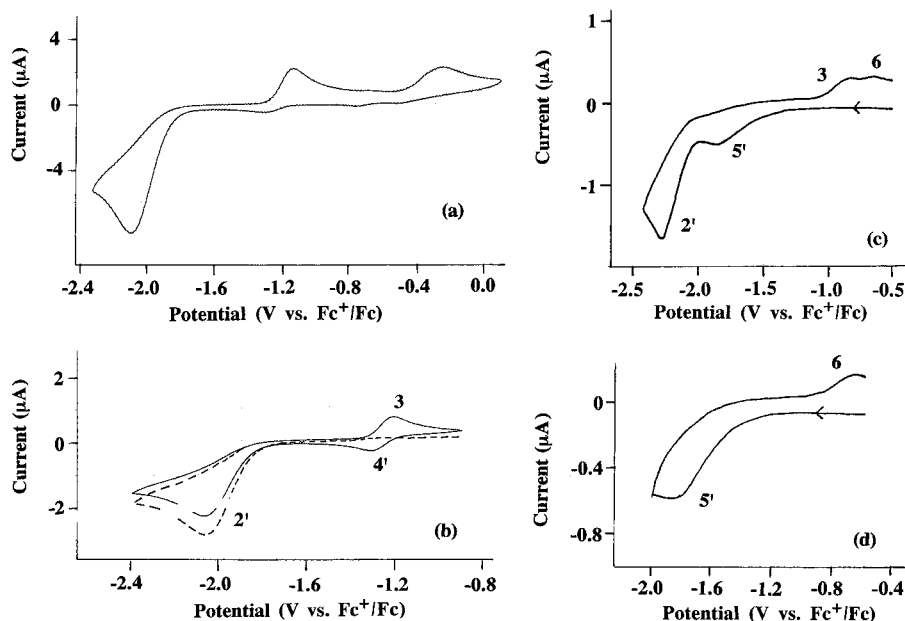


Figure 3. Reductive cyclic voltammograms at a platinum electrode (radius 0.5 mm) for solutions of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$ in dichloromethane (0.1 M Bu_4NPF_6): (a) 0.9 mM solution at 20 °C, potential range 0.1 to -2.4 V, scan rate 1000 mV s^{-1} , third cycle; (b) 0.9 mM solution at 20 °C potential range -0.9 to -2.4 V, scan rate 100 mV s^{-1} ; (- -) first cycle, (-) second cycle; (c) 0.45 mM solution at -60 °C, potential range -0.5 to -2.5 V, scan rate 1000 mV s^{-1} , first cycle; (d) 0.45 mM solution at -60 °C, potential range -0.5 to -2.0 V, scan rate 1000 mV s^{-1} , first cycle.

second cycle, a new process 4' appears in a potential region which might make it appear to be the reductive component of process 3, but later experiments show that it is not part of a simple reversible couple with process 3. Subsequent cycles of the voltammogram are similar to the second. At a rotating platinum disk electrode (500 and 1000 rev min^{-1}) the reduction current for process 2' is approximately twice that for the oxidation current for an equimolar solution of *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$, which is known^{15,16} to be a one-electron process. Thus, assuming both compounds have similar diffusion coefficients, process 2' is deduced to be a two-electron-reduction process. The identities of the species giving rise to the other processes present in cyclic voltammograms will be discussed later.

Cyclic voltammograms at a macrodisk electrode at varying scan rates (25–2000 mV s^{-1}) over the same restricted potential range show (a) process 2' never becomes reversible, and it shifts to more negative potentials as the scan rate is increased, and (b) processes 3 and 4' become more separated at fast scan rates, but the oxidation-to-reduction peak current ratio does not approach unity at fast scan rates, as would be required if processes 3 and 4' formed a simple reversible couple. Data obtained as a function of scan rate and concentration are summarized in Table 2.

Figure 3c shows a cyclic voltammogram for a 0.45 mM solution of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$ in dichloromethane (0.1 M Bu_4NPF_6) at -60 °C and a scan rate of 1000 mV s^{-1} . On the reductive scan, a new process 5' is observed at -1.870 V prior to the onset of process 2' at -2.220 V. On the reverse scan, two processes, 3 and 6, at -0.920 and -0.720 V, respectively, are observed. Processes 5' and 6 are related as shown by examination of Figure

Table 2. Data for the Second Cycles of Reductive Cyclic Voltammograms Over a Limited Potential Range at 20 °C for $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$ in Dichloromethane (0.1 M Bu_4NPF_6) at a Platinum Electrode (Radius 0.5 mm)

conc (mM)	scan rate (mV s^{-1})	peak potentials (V)			
		2'	3	4'	diff (3 - 4')
0.45	100	-2.050	-1.210	-1.300	0.090
0.9	25	-2.030	-1.210		
0.9	100	-2.040	-1.180	-1.280	0.100
0.9	1000	-2.140	-1.150	-1.320	0.170
4.5	100	-2.110	-1.200	-1.280	0.080
4.5	1000	-2.280	-1.140	-1.340	0.200

3d where the potential is switched between processes 5' and 2'. Process 3 is now absent as it is due to a product arising from process 2'. On second and subsequent cycles (not shown) over the potential range used in Figure 3c, process 4' is drawn out and well separated from the potential region of process 3, which again is consistent with these processes not being the components of a simple redox couple. Process 5' also can be detected by close examination (current range amplification) in room-temperature voltammograms over this potential range, but only on the first cycle, and its peak height is very small relative to peak heights of other processes. However, at low-temperature, process 5' remains well defined on second and subsequent cycles. Process 5' disappears on addition of fluoride as does process 6 at both room temperature and low temperatures.

Referring back to Figure 3a, it can be seen that by extending the potential range in the positive direction to 0.1 V, further responses are observed after the initial reduction. Figure 4a shows the third cycle of a reduction voltammogram of a 0.90 mM solution of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$ in dichloromethane (0.1 M Bu_4NPF_6) at a scan rate of 50 mV s^{-1} . As the current sensitivity is

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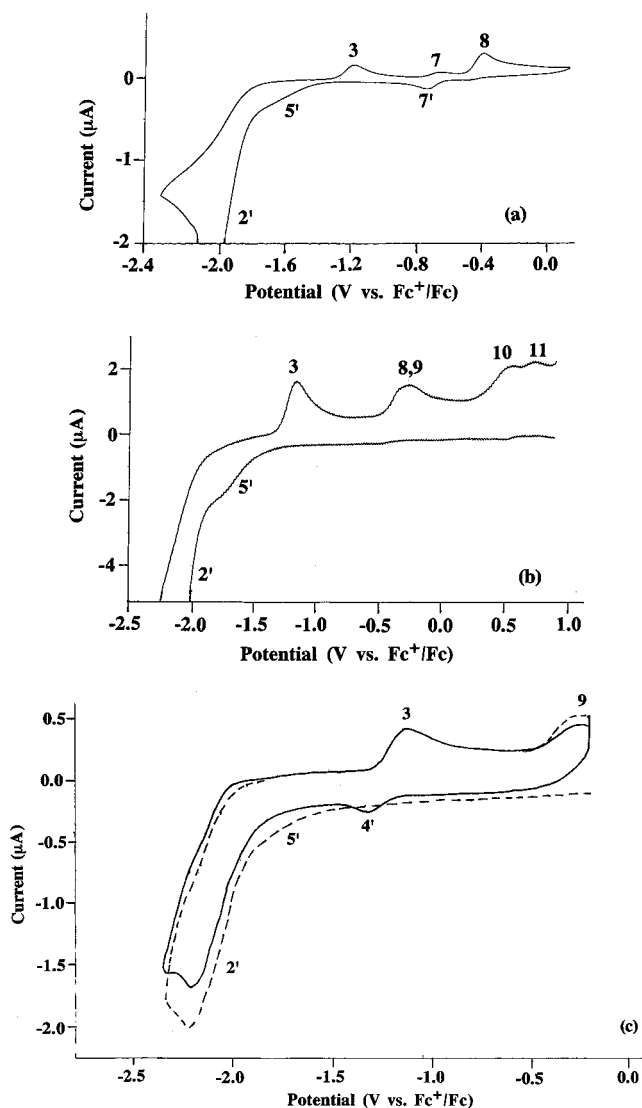
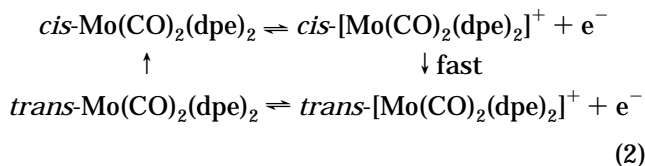


Figure 4. Reductive cyclic voltammograms at 20 °C at platinum electrodes for a 0.9 mM solution of $[\text{Mo}(\text{CO})_2(\text{dpe})_2]\text{PF}_6$ in dichloromethane (0.1 M Bu_4NPF_6): (a) third cycle, potential range 0.2 to -2.3 V, scan rate 50 mV s^{-1} , electrode radius 0.5 mm; (b) first cycle, potential range 1.0 to -2.2 V, scan rate 1000 mV s^{-1} , electrode radius 0.5 mm; (c) (---) first cycle, (—) second cycle, potential range 0.3 to -2.4 V, scan rate $10\,000$ mV s^{-1} , electrode radius 5 μm .

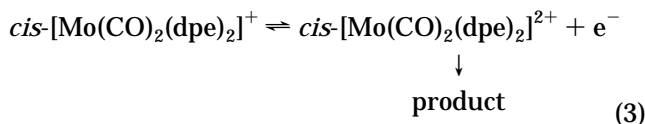
set to clearly observe the weaker responses, process 2' is off scale. With this wider potential range, a very small redox couple 7 (processes 7 and 7') and an irreversible oxidation response, process 8, are now observed. Process 7' is not present on the first reductive scan, so the species giving rise to couple 7 is a minor product, on this time scale, of the reduction of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$. Process 7' increases when oxidation process 8 is also scanned, so it is related to process 8 as well as process 2'. Under these scan conditions, the peak height of process 8 is greater than that of process 3.

Couple 7 and process 8 are unequivocally identified from their potentials and scan rate dependencies as due to the $\text{trans}-[\text{Mo}(\text{CO})_2(\text{dpe})_2]^{+/0}$ couple and oxidation of $\text{cis}-\text{Mo}(\text{CO})_2(\text{dpe})_2$, respectively.^{15,16} These species are involved in a well-known square scheme shown in eq 2 with $\text{cis}-[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+$ isomerizing completely to $\text{trans}-[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+$ on the time scale of the slow scan rate experiment. Unambiguous identification of



these processes was confirmed by separate experiments in which $\text{cis}-\text{Mo}(\text{CO})_2(\text{dpe})_2$ or $\text{trans}-[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+$ were added to solutions of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$, which caused growth of the appropriate responses.

Figure 4b shows the first scan of a reductive voltammogram commencing at 0.9 V of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$ at a scan rate of 1000 mV s^{-1} . Compared to the response in Figure 4a, process 7 is essentially absent, and the peak near -0.260 V is broadened into two barely resolved responses (8 and 9), whose overall height is now less than that of process 3. These features do not depend on the more positive starting potential. However, new oxidation processes 10 and 11 are observed as a result of commencing the scan at more positive potentials. Process 10 is identified with the known^{15,16} process



since at this scan rate, $\text{cis}-[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+$ can be oxidized at positive potentials since insufficient time is available to isomerize completely to the $\text{trans}-[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+$ isomer. Process 11 is due to further oxidation of the $\text{trans}-[\text{Mo}(\text{CO})_2(\text{dpe})_2]^+$ formed. In voltammograms at -60 °C (not shown), processes 8, 10, and 11 disappear (as does process 7) and process 9 now has the same peak height as process 3. At very fast scan rates (10 – 50 V s^{-1}) using a platinum microdisk electrode analogous behavior is observed. Figure 4c shows a cyclic voltammogram at a platinum microdisk electrode (radius 5 μm) at a scan rate of 10 V s^{-1} . On the first reductive scan, only processes 2' and 5' are observed, while on the reverse scan, processes 3 and 9 are present. On the second cycle process 4' is now apparent. At very fast scan rates (100 – $10,000$ V s^{-1}) and if the potential is switched immediately after process 5', then only process 5' and the reversible couple 8 are observed. Voltammetric data applicable to Figure 4 are summarized in Table 3.

The fast scan rate data at room temperature are equivalent to the slow scan rate data at low temperature when the potential is switched at a value that is more negative than process 2. No trans - or $\text{cis}-\text{Mo}(\text{CO})_2(\text{dpe})_2$ species are detected under these conditions, which shows that these species are produced as products of followup chemical reactions after the charge-transfer step. The fast-scan experiment outruns the kinetics of this followup reaction and the low-temperature experiment slows its rate, thus revealing that processes 3, 9, 10, and 11 are all related to the product of process 2'.

At the higher concentration of 4.5 mM $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]\text{PF}_6$, the nature of the cyclic voltammograms is significantly modified. Process 3 decreases in peak height relative to processes 2' and 8. That is, at higher concentrations a non-unity-order chemical reaction

Table 3. Reductive Cyclic Voltammetric Data at 20 °C for [Mo(CO)₂(dpe)₂F]⁺ in Dichloromethane (0.1 M Bu₄NPF₆) at a Platinum Electrode

scan rate (mV s ⁻¹)	peak potentials (V)										
	2'	3	4'	5'	7	7'	8	9	10	11	
50 (Figure 4a) ^a		-1.210		-1.660	-0.670	-0.750	-0.410				
1000 (Figure 4b) ^a		-1.16		-1.680			-0.300 ^b		0.550	0.730	
10 000 (Figure 4c) ^c	-2.220	-1.130	-1.320					-0.300			

^a Electrode radius 0.5 mm. ^b Peak very broad; processes 8 and 9 not resolved. ^c Electrode radius 5 μm.

favors the formation of Mo(CO)₂(dpe)₂ over formation of the species giving rise to process 3. In more dilute solution (0.45 mM), the reverse situation applies so that process 3 is enhanced relative to process 8.

(ii) Reductive Bulk Electrolysis at Room Temperature. [Mo(CO)₂(dpe)₂F]PF₆ (2.12 × 10⁻⁵ mol) contained in 10 mL of dichloromethane (0.1 M Bu₄NClO₄) was exhaustively reduced at a controlled potential of -2.3 V, and the progress of the electrolysis was monitored by voltammetry at a platinum rotating disk electrode (1000 rev min⁻¹). Before electrolysis, the only major reduction response was that due to process 2' with a small contribution from process 5'. As the electrolysis proceeded, the responses due to processes 2' and 5' decreased and were replaced by a response due to oxidation process 8 (oxidation of *cis*-Mo(CO)₂(dpe)₂). At the completion of the electrolysis, coulometric monitoring shows that almost two electrons (1.8 ± 0.1) are passed for each molecule of [Mo(CO)₂(dpe)₂F]⁺ in the solution. A rotating disk voltammogram shows that the height of the response due to process 8 is half that originally observed for process 2'. The sign of the current confirms that the species in solution is the expected *cis*-Mo(CO)₂(dpe)₂, and this is confirmed by IR and ³¹P NMR spectroscopies^{15,16} (ν(CO) = 1849, 1782 cm⁻¹; δ³¹P = 67.3, 47.1 ppm). In a separate experiment, [Mo(CO)₂(dpe)₂F]PF₆ was electrolytically reduced in the presence of an equimolar amount of *cis*-Mo(CO)₂(dpe)₂ and in this case the limiting current for oxidation *cis*-Mo(CO)₂(dpe)₂ in the rotating disk voltammogram was doubled after electrolysis.

(iii) Spectroelectrochemical Reduction of [Mo(CO)₂(dpe)₂F]PF₆. [Mo(CO)₂(dpe)₂F]PF₆ shows two bands in the carbonyl region at 1945 and 1890 cm⁻¹. Monitoring of the IR spectrum (difference spectra) during reduction of [Mo(CO)₂(dpe)₂F]PF₆ at -2.2 V in the IRRAS cell results in the negative growth of the bands of the reactant and formation of two intense bands at 1849 and 1782 cm⁻¹ (Figure 5) which are assigned to *cis*-Mo(CO)₂(dpe)₂.¹⁵ In addition, a broad weak band at ~1690 cm⁻¹ is observed to grow before decaying during the latter stages of the electrolysis. This behavior is consistent with the formation of a short-lived intermediate during the overall reduction of [Mo(CO)₂(dpe)₂F]⁺ to the final product *cis*-Mo(CO)₂(dpe)₂.

(iv) Reduction Voltammetry of [Mo(CO)₂(dpe)₂F](PF₆)₃. This compound cannot be prepared free of [Mo(CO)₂(dpe)₂F]PF₆ impurity.^{6a} A reductive cyclic voltammogram of a nominally 0.9 mM solution containing approximately 80% [Mo(CO)₂(dpe)₂F](PF₆)₃ and 20% [Mo(CO)₂(dpe)₂F]PF₆ at a scan rate of 100 mV s⁻¹ in dichloromethane (0.1 M Bu₄NPF₆) is shown in Figure 6. Significantly, the three processes identified in this figure have essentially identical peak potentials and characteristics of processes 5', 2', and 8

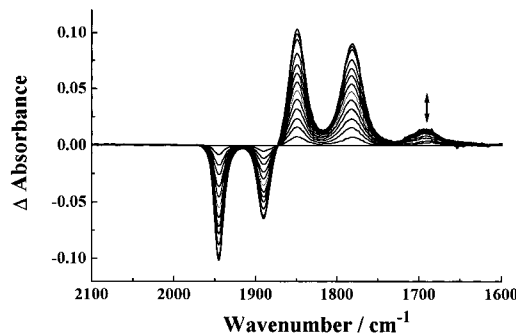


Figure 5. Changes in the IR difference spectra accompanying reduction of [Mo(CO)₂(dpe)₂F]PF₆ in an IRRAS cell in dichloromethane (0.1 M Bu₄NPF₆). The band at ~1690 cm⁻¹ grows during the initial phase of the electrolysis but then diminishes to zero absorbance as the reduction nears completion.

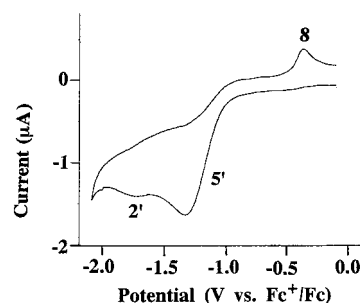


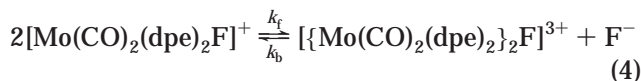
Figure 6. Reductive cyclic voltammogram at 20 °C for a 0.9 mM solution of an approximately 80:20 mixture of [Mo(CO)₂(dpe)₂F](PF₆)₃ and [Mo(CO)₂(dpe)₂F]PF₆ in dichloromethane (0.1 M Bu₄NPF₆) at a platinum electrode (radius 0.5 mm), scan rate 100 mV s⁻¹.

and subsequently are shown to have the same origin. This implies that process 5 yet to be assigned in the description of the voltammetry is now identified as being due to the reduction of [Mo(CO)₂(dpe)₂F]⁺. Under the conditions of Figure 6, processes 5' and 8 are prominent, process 2' is weak, and process 3 is not detectable. On the second cycle (not shown), redox couple 7 is also detected. This arises due to the isomerization of *cis*-[Mo(CO)₂(dpe)₂F]⁺, which is the product of process 8. Thus, process 5', previously observed as weak responses at room temperature in the voltammetry of [Mo(CO)₂(dpe)₂F]⁺, is attributed to reduction of [Mo(CO)₂(dpe)₂F]³⁺ via a kinetically complicated reaction scheme which is very scan rate, concentration, and temperature dependent. At a microdisk electrode and scan rates in the range 100–10 000 V s⁻¹, only process 5' and the reversible couple 8 are observed; because on this short electrochemical time scale, the isomerization of *cis*-[Mo(CO)₂(dpe)₂F]⁺ to *trans*-[Mo(CO)₂(dpe)₂F]⁺ is outrun. Importantly, when fluoride ion is added to the solution of [Mo(CO)₂(dpe)₂F](PF₆)₃, process 2' increases in height and process 5' disappears, until eventually the voltam-

mograms are indistinguishable from that observed for $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$ as described above. Finally, it may be noted that process 6 is only observed when voltammograms of low-concentration solutions of $[\{\text{Mo}(\text{CO})_2(\text{dpe})_2\}_2\text{F}]^+$ are recorded so that, as is the case with reduction of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$, high concentrations favor the formation of *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ rather than the presumed fluoride-containing intermediates.

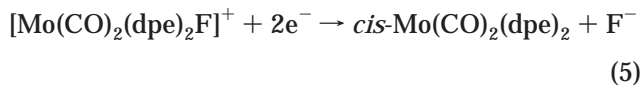
Discussion

The oxidative chemistry of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$ at low concentration (0.45 mM) gives rise to process 1 and is simple (see eq 1). This oxidation process has been adequately discussed earlier and convincingly demonstrates the existence of the first phosphine-substituted carbonyl fluoride of Mo(III), $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^{2+}$, which is stable on the voltammetric time scale but not on the longer synthetic time scale. At higher concentrations, the reaction shown in eq 4 (where k_f and k_b are the



forward and reverse rate constants for this reaction) is expected to be favored, thus leading to kinetic control of the $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$ oxidation process. It is postulated that this second-order reaction may be associated with the chemical irreversibility observed at higher concentration (also see later).

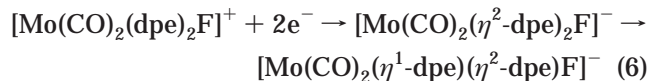
The long time scale (tens of minutes) bulk electrolytic reduction also is simple as the overall reaction amounts to quantitative reduction to the well-known *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$.



The product was identified by ^{31}P NMR and IR spectroscopies and by its electrochemical characteristics. The overall long time scale coulometric measurements show the conversion to be quantitative. However, on the shorter voltammetric time scale, the electrochemical data reveal the existence of intermediates in the overall reaction pathway. If the two-electron reduction (process 2') proceeded directly as shown in eq 5, only processes 8 and 10 and couple 7, which are due to the presence of *cis*- or *trans*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ or their cations, should be observed on subsequent cycles. All the other processes described earlier must therefore arise from the presence of short-lived intermediates. Spectroscopic evidence for a carbonyl-containing short-lived intermediate was gleaned from the reductive IRRAS experiments (Figure 5).

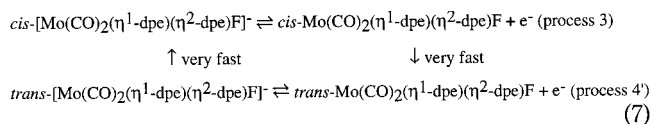
Reductions of 18e carbonyl species are almost always a two-electron process with loss of one ligand, so the product is also an 18e species with a coordination number one less than its precursor. For example, reduction of $\text{Mo}(\text{CO})_6$ leads to the formation of $[\text{Mo}(\text{CO})_5]^{2-}$, and such reductions are invariably irreversible on the voltammetric time scale.¹⁷ Since process 2' for seven-coordinate $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$ has been shown to be an irreversible two-electron reduction, it is likely that the initial product of process 2' is a six-

coordinate species and that one donor group is lost. Carbon monoxide is not the ligand lost because long time scale experiments show that *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ is generated quantitatively by reduction of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$. If fluoride were the ligand lost, then $\text{Mo}(\text{CO})_2(\text{dpe})_2$ would be the direct product of the reduction, but this is not the case. The only other possibility is that one of the dpe ligands becomes monodentate to give the 18e species $[\text{Mo}(\text{CO})_2(\eta^1\text{-dpe})(\eta^2\text{-dpe})\text{F}]^-$. Thus, process 2' is assigned to the overall reaction as shown in eq 6.



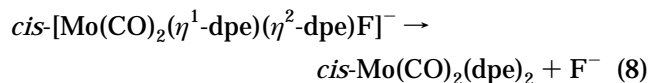
Since the product described in eq 6 is proposed to be a normal six-coordinate dicarbonyl species, it is most likely to have a *cis*-dicarbonyl geometry. The spectroelectrochemical reduction of $[\text{Mo}(\text{CO})_2(\text{dpe})_2\text{F}]^+$ revealed a short-lived intermediate (tens of seconds) with a carbonyl IR absorption at 1690 cm^{-1} . Although this is usually regarded as a very low value for a terminal carbonyl group, it is possible for such low values to occur when the species is an anion and has few carbonyl groups.¹⁸ *cis*- $[\text{Mo}(\text{CO})_2(\eta^1\text{-dpe})(\eta^2\text{-dpe})\text{F}]^-$ would have two carbonyl stretches, so it must be assumed that the second is obscured by one of the IR bands of *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$.

Process 3 is an oxidation response of *cis*- $[\text{Mo}(\text{CO})_2(\eta^1\text{-dpe})(\eta^2\text{-dpe})\text{F}]^-$, and its unusual relationship with process 4' already has been described. These processes



are not the components of a simple redox couple, but their behavior is that expected for a square reaction scheme with very fast isomerizations in both directions. It is common¹⁷ for isomerization to occur from *cis* to *trans* upon oxidation of 18e to 17e dicarbonyl complexes and for the reverse reaction to occur upon reduction. Usually isomerizations of this type are relatively slow on the voltammetric time scale, as in the *cis/trans*- $[\text{Mo}(\text{CO})_2(\text{dpe})_2]^{+/0}$ system.^{15,16} However, occasionally they occur much faster, one example being observed¹⁰ in the *cis, fac*- $[\text{Mo}(\text{CO})_3(\text{P}_2\text{P}')^{+/0}]$ system ($\text{P}_2\text{P}' = \{\text{Ph}_2\text{P}(\text{CH}_2)_2\}_2\text{-PPh}$). This is exactly the behavior shown by responses 3 and 4', so eq 7 is a reasonable summary of the processes occurring.

At conventional scan rates, small responses for $\text{Mo}(\text{CO})_2(\text{dpe})_2$ species are observed on the second cycle so the postulated product of process 2', *cis*- $[\text{Mo}(\text{CO})_2(\eta^1\text{-dpe})(\eta^2\text{-dpe})\text{F}]^-$, must rearrange slowly on the voltammetric time scale to the product that is produced quantitatively on the longer electrolysis time scale. That is,



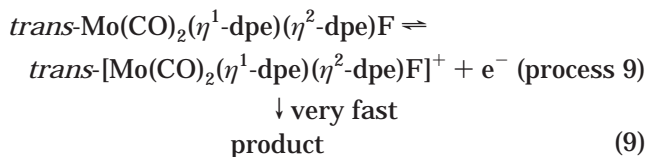
It is interesting that in the 20e species $[\text{Mo}(\text{CO})_2(\eta^2\text{-dpe})_2\text{F}]^-$ a phosphorus ligand is lost to give the stable

(17) Bond, A. M.; Colton, R. *Coord. Chem. Rev.* **1998**, *166*, 161.

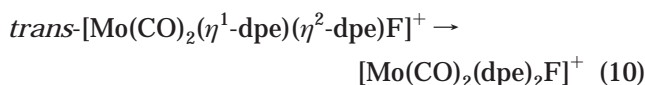
(18) Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 4447.

18e configuration, but in the 18e complex *cis*-[Mo(CO)₂(η¹-dpe)(η²-dpe)F]⁻, the phosphorus ligand then displaces the fluoride.

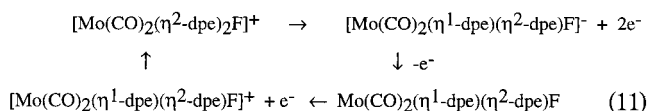
At very fast scan rates or slow scan rates at low temperature, the rearrangement in eq 8 is outpaced and further oxidation processes for *trans*-Mo(CO)₂(η¹-dpe)(η²-dpe)F generated from oxidation of *cis*-[Mo(CO)₂(η¹-dpe)(η²-dpe)F]⁻ via the square scheme (eq 7) are then clearly observed.



trans-[Mo(CO)₂(η¹-dpe)(η²-dpe)F]⁺ is a 16e species which would be expected to rapidly acquire an additional ligand to achieve the 18e configuration, and in this case the pendant phosphorus atom is the most likely candidate.



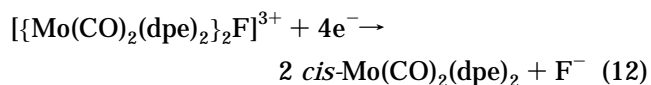
which regenerates the original carbonyl fluoride complex. Thus, if conditions are chosen for which the loss of fluoride is avoided, the system becomes chemically reversible on the voltammetric time scale



and closely resembles the behavior of the Mo(CO)₃(η¹-dpe)(η²-dpe) system which generates the seven-coordinate species [Mo(CO)₃(η²-dpe)₂]²⁺ upon oxidation, which in turn is reduced back to the starting material.¹⁹ On the longer time scale also, the system is chemically reversible, even with the loss of fluoride ion, since electrolytic reduction of [Mo(CO)₂(dpe)₂F]⁺ yields *cis*-Mo(CO)₂(dpe)₂ and fluoride ion, while bulk electrochemical oxidation of *cis*-Mo(CO)₂(dpe)₂ in the presence of fluoride gives [Mo(CO)₂(dpe)₂F]⁺.⁸

Voltammetric studies on the reduction of [Mo(CO)₂(dpe)₂F](PF₆)₃ imply that process 5' is associated with the reduction of this compound. However, while process 5' exhibits the normal peak-shaped response when [Mo(CO)₂(dpe)₂F](PF₆)₃ is the dominant species in the bulk solution, the process is drawn out when [Mo(CO)₂(dpe)₂F]PF₆ is present as the major species in the bulk solution.

This suggests that process 5' detected in the voltammograms for bulk solutions of [Mo(CO)₂(dpe)₂F]PF₆ is kinetically controlled and may be generated by the reaction given in eq 4. The back reaction of the binuclear complex with fluoride ion has been well established,⁶ but attempts to demonstrate the existence of the forward reaction by infrared spectroscopy failed. Separate IR measurements on [Mo(CO)₂(dpe)₂F]PF₆ and [Mo(CO)₂(dpe)₂F](PF₆)₃ show that the absorption coefficients of the carbonyl bands for the binuclear complex are only ~20% of those of the mononuclear complex. Given the close proximity of the bands for the two compounds, it is therefore not possible to detect small amounts of [Mo(CO)₂(dpe)₂F]³⁺ in the presence of [Mo(CO)₂(dpe)₂F]⁺ by IR spectroscopy, although small impurities of monomer in the binuclear complex are readily detected. Process 5', when generated from bulk solution containing mainly [Mo(CO)₂(dpe)₂F]⁺, is assigned to the overall reduction



although a minor reaction pathway appears to generate *trans*-Mo(CO)₂(dpe)₂ since a weak peak for process 7 is observed on the first oxidation (reverse) scan before process 8 is reached. Process 6 is most readily detected when low concentrations of [Mo(CO)₂(dpe)₂F]⁺ are present and like process 5' is not detected when significant quantity of fluoride is present in either the bulk solution or generated at the electrode surface. Process 6 is clearly associated with oxidation of a product of process 5' but not with oxidation of *cis*- or *trans*-Mo(CO)₂(dpe)₂. Little direct evidence can be presented for identification of the species giving rise to process 6, but most likely it is associated with oxidation of a fluoride-containing complex which then rapidly reacts to give *cis*- or *trans*-Mo(CO)₂(dpe)₂ and fluoride. Again, the implications are that eq 4 is important in the redox chemistry.

In summary, the electrochemical studies on the two Mo(II) carbonyl fluoride systems considered in this study reveal that the fluoride ligand is strongly bound to the metal center so that a wide range of oxidation-state carbonyl fluoride complexes (0–III) are available, although in the zero valent oxidation state, the fluoride ligand is eventually replaced by a phosphorus ligand.

Acknowledgment. We thank the Australian Research Council for general financial support and provision of an Endeavour Fellowship to D.G.H. We also thank Alison Edwards (University of Melbourne), who collected the X-ray diffraction data.

(19) (a) Bond, A. M.; Colton, R.; McGregor, K. *Inorg. Chem.* **1986**, *25*, 2378. (b) Bond, A. M.; Colton, R.; McGregor, K. *Organometallics* **1990**, *9*, 1227.