

**Chemical and Electrochemical Oxidation of
mer/fac-Cr(CO)₃(η¹-L-L)(η²-L-L) Containing a Pendant Donor
 Atom: ESR Studies of the Cations
mer-[Cr(CO)₃(η¹-L-L)(η²-L-L)]⁺ and *trans*-[Cr(CO)₂(η²-L-L)₂]⁺
 (L-L = Bidentate Group 15 Ligand)**

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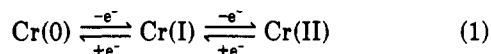
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Reactions between Cr(CO)₃(C₇H₈) and Ph₂PCH₂CH₂AsPh₂ (ape) and Ph₂AsCH₂CH₂AsPh₂ (dae) give *mer*-Cr(CO)₃(η¹-ape)(η²-ape) and *fac*-Cr(CO)₃(η¹-dae)(η²-dae), respectively. Phosphorus-31 NMR studies show that the monodentate ape ligand is coordinated through phosphorus. Upon electrochemical oxidation in dichloromethane (0.1 M Bu₄NClO₄) at platinum electrodes, *mer*-Cr(CO)₃(η¹-ape)(η²-ape) is reversibly oxidized to *mer*-[Cr(CO)₃(η¹-ape)(η²-ape)]⁺ whilst *fac*-Cr(CO)₃(η¹-dae)(η²-dae) gives *fac*-[Cr(CO)₃(η¹-dae)(η²-dae)]⁺, which rapidly isomerizes to *mer*-[Cr(CO)₃(η¹-dae)(η²-dae)]⁺. In addition, for each complex a further irreversible 1-electron process is observed at very positive potentials. ESR studies on several *mer*-[Cr(CO)₃(η¹-L-L)(η²-L-L)]⁺ cations (L-L = bidentate group 15 ligand), electrochemically generated in a sealed tube within the ESR microwave cavity, show that they decompose very slowly to *trans*-[Cr(CO)₂(η²-L-L)₂]⁺. The rate of decomposition to *trans*-[Cr(CO)₂(η²-L-L)₂]⁺ is faster in a nonsealed tube with nitrogen purging. The ESR spectra of the tricarbonyl and dicarbonyl 17-electron cations show both phosphorus and arsenic hyperfine structure with very similar values for the coupling constants. Chemical oxidation of *mer/fac*-Cr(CO)₃(η¹-L-L)(η²-L-L) with an equimolar (or greater) quantity of AgClO₄ also gives *mer*-[Cr(CO)₃(η¹-L-L)(η²-L-L)]⁺. In one case, (L-L = Ph₂PCH₂PPh₂(dpm)), when 0.5 molar equiv of AgClO₄ is used, a diamagnetic intermediate silver complex is identified by phosphorus-31 NMR spectroscopy. In the presence of excess of AgClO₄, the rate of decomposition of *mer*-[Cr(CO)₃(η¹-L-L)(η²-L-L)]⁺ to *trans*-[Cr(CO)₂(η²-L-L)₂]⁺ is greatly enhanced, further confirming that the silver ion is a noninnocent oxidant when a pendant donor atom is present.

Introduction

Chemical and electrochemical studies on the oxidation of octahedral 18-electron chromium carbonyl complexes have been widely reported.⁴⁻⁸ Commonly, two 1-electron oxidation processes are observed on the voltammetric time scale, as in eq 1. Typically, the chromium(I) compound



is an octahedral 17-electron species that can sometimes be isolated and characterized as a moderately stable compound.^{5,7,9} In certain cases, a chromium(II) 16-electron octahedral species can be identified as a transient species on the voltammetric time scale,^{4,5} but in others, such as the oxidation of Cr(CO)₃(arene), even the 17-electron species is rapidly attacked by the electrolyte (e.g. perchlorate) to give an overall irreversible 2-electron process¹⁰



If the less strongly coordinating [PF₆]⁻ is used as the supporting electrolyte anion, the 17-electron compound [Cr(CO)₃(arene)]⁺ can then be readily identified as an intermediate on the voltammetric time scale in the overall 2-electron process (synthetic time scale). In the area of zerovalent chromium carbonyl oxidation chemistry, a picture is emerging of the key role of the 17-electron intermediates in the overall 2-electron oxidation process.^{8,11}

To date, almost all the chemical and electrochemical oxidation studies on zerovalent chromium carbonyl complexes have been concerned with compounds of monodentate or fully coordinated bidentate and tridentate ligands so that after oxidation the 17- or 16-electron (coordinatively unsaturated) species are prone to nucleophilic attack by solvent or electrolyte, etc. Recently, synthetic investigations have increased the range of complexes of the kind *mer/fac*-M(CO)₃(η¹-L-L)(η²-L-L) (where M = Cr, Mo, W and L-L = Ph₂PCH₂PPh₂ (dpm), Ph₂PCH₂CH₂PPh₂ (dpe), etc.) which contain a pendant phosphorus donor atom.⁸ Upon electrochemical oxidation that phosphorus

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Table I. Electrochemical Data Obtained at a Platinum Electrode in Dichloromethane (0.1 M Bu₄NClO₄) at 20 °C under Conditions of Cyclic Voltammetry (Scan Rate 200 mV s⁻¹)^a

starting material	process 1 (<i>mer</i> ^{+/0})			process 2 <i>E</i> _p ^{ox}	process 3 (<i>fac</i> ^{+/0})		
	<i>E</i> _p ^{ox}	<i>E</i> _p ^{red}	<i>E</i> ^o		<i>E</i> _p ^{ox}	<i>E</i> _p ^{red}	<i>E</i> ^o
<i>mer</i> -Cr(CO) ₃ (η ¹ -ape)(η ² -ape)	-0.290	-0.390	-0.340	0.750			
<i>fac</i> -Cr(CO) ₃ (η ¹ -dae)(η ² -dae)	-0.285	-0.420	-0.350	0.915	0.035	-0.225	-0.095

^a All potentials vs Fc⁺/Fc; *E*_{1/2} = 0.50 V vs Ag/AgCl.

atom can act as a very well defined "internal nucleophile", giving a great deal more control over the pathway of chemical attack than is usually the case when solvent or supporting electrolyte acts as the nucleophile. The isolated products of these electrochemical oxidation reactions are relatively stable seven-coordinate 18-electron M(II) species [M(CO)₃(η²-L-L)₂]²⁺ for molybdenum and tungsten,¹² but not for chromium where the 17-electron species *mer*-[Cr(CO)₃(η¹-L-L)(η²-L-L)]⁺ is the only stable carbonyl-containing species seen on the electrochemical time scale.⁸

In the present work, we have prepared and characterized *mer*-Cr(CO)₃(η¹-ape)(η²-ape) (ape = Ph₂AsCH₂CH₂PPh₂) and *fac*-Cr(CO)₃(η¹-dae)(η²-dae) (dae = Ph₂AsCH₂CH₂AsPh₂). The role of the pendant arsenic atom after 1-electron oxidation of the complexes has been examined in detail by electrochemical techniques. Electron spin resonance spectroscopy has been used to fully characterize the 17-electron cations derived from these and closely related Cr(CO)₃(η¹-L-L)(η²-L-L) compounds. Reaction of Cr(CO)₃(η¹-L-L)(η²-L-L) with AgClO₄ provides the same final products as electrochemical oxidation. However, rates of reaction and detection of a diamagnetic intermediate in one case show that in the presence of a pendant donor atom Ag⁺ is not an innocent oxidant.

Experimental Section

Preparations. *mer*-Cr(CO)₃(η¹-ape)(η²-ape) was prepared from Cr(CO)₃(C₇H₉)¹³ (1.0 mmol) and ape (2.5 mmol) by refluxing in ethanol under a nitrogen atmosphere. The yellow solid that precipitated after 8 h was collected by filtration and recrystallized from dichloromethane/*n*-hexane. *fac*-Cr(CO)₃(η¹-dae)(η²-dae) was prepared in a similar manner, and other similar compounds were prepared by literature methods.⁸

The cations *mer*-[Cr(CO)₃(η¹-L-L)(η²-L-L)]⁺ and *trans*-[Cr(CO)₂(η²-L-L)₂]⁺ were prepared chemically or electrochemically as described in the text.

Instrumentation. Conventional cyclic voltammograms were recorded in dichloromethane (0.1 M Bu₄NClO₄) or acetone (0.1 M Et₄NClO₄) by using an EG and G PAR Model 174A polarographic analyzer. A three-electrode system was used with a platinum-disk working electrode (radius 0.9 mm) and a platinum-wire auxiliary electrode. The reference electrode was Ag/AgCl (CH₂Cl₂; saturated LiCl) and was separated from the test solution by a salt bridge containing the appropriate solvent and electrolyte. For variable-temperature cyclic voltammetry, the temperature was regulated over the range +25 to -65 °C by using a dry ice/acetone bath and the temperature was monitored with an alcohol thermometer. For rotating platinum-disk experiments, a Beckman Model 1885 platinum rotating-disk electrode (RDE) (radius 3 mm) was used at a rotation rate of 2000 rpm with the same auxiliary and reference electrodes as above. The reversible redox couple Fc⁺/Fc (Fc = (C₅H₅)₂Fe) was frequently measured to check the stability of the reference electrode, and all results are quoted against this reference.

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 that used in the voltammetric experiments.

Phosphorus-31 NMR spectra were recorded in dichloromethane solution by using a JEOL FX 100 spectrometer at 40.32 MHz, and chemical shifts were referenced against 85% H₃PO₄ by using the high-frequency positive-sign convention. Infrared spectra were recorded in dichloromethane solution on a Jasco A-302 spectrophotometer and calibrated against polystyrene (1601 cm⁻¹).

In situ simultaneous ESR-electrochemical studies were carried out at various temperatures in a sealed microcell described previously.¹⁴ The cell was placed within a Varian E231 cavity of an X-band ESR spectrometer. Alternatively, solutions that had been electrolyzed in a conventional electrochemical cell with oxygen removed by nitrogen purging were transferred at ambient temperature to the spectrometer. AgClO₄ was used as the chemical oxidant in some experiments, with the reaction pathways being monitored by ESR and phosphorus-31 NMR techniques.

Results and Discussion

Characterization of the Compounds. The infrared spectrum of Cr(CO)₃(η¹-ape)(η²-ape) shows absorptions at 1960 (w), 1855 (s), and 1835 (sh) cm⁻¹, consistent with the meridional isomer. Its phosphorus-31 NMR spectrum in dichloromethane consists of two doublets of equal intensity at δ 95.9 and 68.1 ppm (*J*_{P,P} = 15 Hz). The combined infrared and NMR evidence show that only one meridional isomer, a η¹-ape P-bonded species, is formed, but it is difficult to determine whether the phosphorus atoms are *cis* or *trans* to each another. Monitoring the preparation reaction by phosphorus-31 NMR spectroscopy showed that *fac*-Cr(CO)₃(η¹-ape)(η²-ape) (η¹-ape P-bonded isomer) is formed as an intermediate.

The infrared spectrum of Cr(CO)₃(η¹-dae)(η²-dae) shows two strong bands at 1930 and 1830 (br) cm⁻¹, which show it to be the facial isomer. These assignments were confirmed by the electrochemical studies described below.

Electrochemical Studies. Electrochemical data are summarized in Table I.

(a) *mer*-Cr(CO)₃(η¹-ape)(η²-ape). The electrochemical behavior of *mer*-Cr(CO)₃(η¹-ape)(η²-ape) is very similar to that of *mer*-Cr(CO)₃(η¹-dpm)(η²-dpm),⁸ giving two 1-electron processes at room temperature, which is typical of meridional tricarbonyl complexes.^{7,8,15,16} That is, the cyclic voltammogram for a 1 × 10⁻³ M dichloromethane solution (0.1 M Bu₄NClO₄) of *mer*-Cr(CO)₃(η¹-ape)(η²-ape) at 20 °C exhibits a chemically reversible redox couple with a half-wave potential (approximately *E*^o potential) of -0.34 V vs Fc⁺/Fc (process 1) and a second irreversible response (process 2) is observed with a peak potential of 0.75 V vs Fc⁺/Fc (scan rate 200 mV s⁻¹). Process 2 remains irreversible at all scan rates between 50 and 500 mV s⁻¹, over the temperature range +25 to -65 °C. Oxidative voltammograms at a platinum RDE at 20 °C exhibit two sigmoidal responses corresponding to processes 1 and 2. The limiting current per unit concentration observed for pro-

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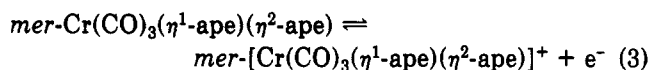
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Table II. ESR Data in Dichloromethane

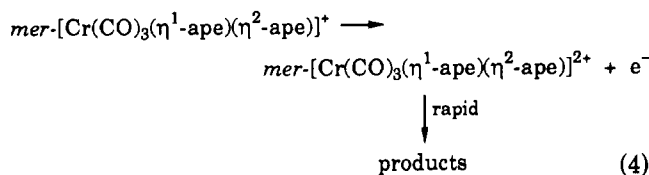
species	prepn	no. of lines	intensity ratios ^a	E_{av}	hyperfine constant	line width, mT
<i>mer</i> -[Cr(CO) ₃ (η ¹ -dpm)(η ² -dpm)] ⁺	electrochem, -40 °C	4	1:2:1, 1:1	2.02	$a_1(P) = 2.35$ $a_2(P) = 2.10$	1.50
<i>trans</i> -[Cr(CO) ₂ (η ² -dpm) ₂] ⁺	chemical, room temp	5	1:4:6:4:1	2.00	$a(P) = 2.74$	0.39
<i>mer</i> -[Cr(CO) ₃ (η ¹ -dpe)(η ² -dpe)] ⁺	electrochem, -40 °C	4	1:2:1, 1:1	2.03	$a_1(P) = 2.73$ $a_2(P) = 2.10$	1.00
<i>trans</i> -[Cr(CO) ₂ (η ² -dpe) ₂] ⁺	chemical, room temp	5	1:4:6:4:1	2.01	$a(P) = 2.82$	0.45
<i>mer</i> -[Cr(CO) ₃ (η ¹ -ape)(η ² -ape)] ⁺	electrochem, -40 °C	6	1:3:4:4:3:1	2.03	$a(P) = a(As) = 2.45$	1.80
<i>trans</i> -[Cr(CO) ₂ (η ² -ape) ₂] ⁺	chemical, room temp	9	1:4:8:12:14:12:8:4:1	2.01	$a(P) = a(As) = 2.90$	0.50
<i>mer</i> -[Cr(CO) ₃ (η ¹ -dae)(η ² -dae)] ⁺	electrochem, -40 °C	10	1:3:6:10:12:12:10:6:3:1	2.02	$a(As) = 2.50$	2.00
<i>trans</i> -[Cr(CO) ₂ (η ² -dae) ₂] ⁺	chemical, room temp	13	1:4:10:20:31:40:44:40:31:20:10:4:1	2.02	$a(As) = 3.0$	0.50

^aTheoretical ratios are given. Experimental values are very similar to the theoretical values in all cases.

cess 1 is very similar to that observed for the known 1-electron oxidation of *mer*-Cr(CO)₃(η¹-dpm)(η²-dpm).⁸ Thus, process 1 may be assigned as



and process 2 as



No additional processes are observed on the reverse scans of cyclic voltammograms corresponding to reduction of a transient [Cr(CO)₃(η²-ape)₂]²⁺ species at -78 °C, as was the case after the two 1-electron oxidations of Cr(CO)₃(η¹-dpe)(η²-dpe).⁸ Similar responses are observed in acetone (0.1 M Et₄NClO₄).

Oxidative controlled-potential electrolysis at a platinum electrode of a 1 × 10⁻³ M dichloromethane solution (0.1 M Bu₄NClO₄) of *mer*-Cr(CO)₃(η¹-ape)(η²-ape) at 0.00 V vs Fc⁺/Fc at 20 °C, in the absence of light and under a carbon monoxide atmosphere, confirms that 1 ± 0.1 electron/molecule is transferred during the oxidation step. The reductive cyclic voltammogram of this oxidized solution shows a chemically reversible redox couple, with the positions of E_p^{red} and E_p^{ox} being coincident with process 1, showing that *mer*-[Cr(CO)₃(η¹-ape)(η²-ape)]⁺ is stable on the bulk electrolysis time scale. The second oxidation process (process 2) remains after the 1-electron oxidation. The infrared spectrum of a dichloromethane solution of *mer*-[Cr(CO)₃(η¹-ape)(η²-ape)]⁺ shows three bands in the carbonyl region that are similar in appearance to those of *mer*-Cr(CO)₃(η¹-ape)(η²-ape) but shifted to higher frequencies (1970 (w), 1915 (s), 1895 (sh) cm⁻¹).

(b) *fac*-Cr(CO)₃(η¹-dae)(η²-dae). The oxidative electrochemistry of *fac*-Cr(CO)₃(η¹-dae)(η²-dae) is typical for a facial tricarbonyl complex and serves to confirm the stereochemistry of the complex. Figure 1 shows a cyclic voltammogram for a 1 × 10⁻³ M solution of the complex in dichloromethane (0.1 M Bu₄NClO₄) at a platinum electrode at a scan rate of 200 mV s⁻¹. On the first oxidative scan, a response (process 3) is observed followed by an adsorption peak (symmetrical peak shape). On the reduction scan, two responses (processes 3' and 1') are observed, and on the second oxidative scan, a new response (process 1) is observed. All four responses appear in all successive scans. There is in addition a further oxidative response (process 2) at very positive potential that is irreversible under all conditions studied. This response is assigned to further oxidation followed by fast decompo-

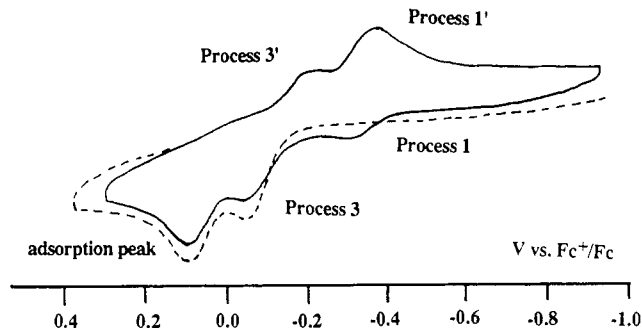


Figure 1. Oxidative cyclic voltammogram at a platinum electrode for a 1 × 10⁻³ M solution of *fac*-Cr(CO)₃(η¹-dae)(η²-dae) in dichloromethane (0.1 M Bu₄NClO₄) at 20 °C: (---) first scan; (—) second scan. Scan rate: 200 mV s⁻¹.

sition of the products (similar to eq 4), and it was not studied further.

The electrochemical behavior is explained as follows. On the first oxidative scan *fac*-Cr(CO)₃(η¹-dae)(η²-dae) is oxidized (process 3) to *fac*-[Cr(CO)₃(η¹-dae)(η²-dae)]⁺ which, like many facial 17-electron species, is unstable^{7,15,17,18} and rather rapidly isomerizes to *mer*-[Cr(CO)₃(η¹-dae)(η²-dae)]⁺. On the reverse scan, responses 3' and 1' are due to the reduction of the remaining *fac*⁺ and the newly formed *mer*⁺ species, respectively, to give the *fac*⁰ and *mer*⁰ compounds at the electrode surface. On the second oxidative scan, responses due to the oxidation of both these species are observed. This interpretation is supported by studies at various scan rates (the faster the scan rate, the less isomerization can occur and so process 1,1' is reduced in size) and also by holding the potential at 0.2 V vs Fc⁺/Fc for about 20 s after the oxidation scan, which greatly increases the size of process 1' on the subsequent reduction scan.

ESR Spectroscopy. All ESR data are given in Table II. In order to fully understand the ESR spectra of the *ape* derivatives, it is helpful to first consider the spectra of the corresponding diphosphine derivatives.

The derivative ESR spectrum of dichloromethane or acetone solutions of *mer*-[Cr(CO)₃(η¹-dpm)(η²-dpm)]⁺, produced by electrochemical oxidation at -50 °C of *mer*-Cr(CO)₃(η¹-dpm)(η²-dpm)⁸ within the microwave cavity of the spectrometer, consists of a broad quartet with intensity ratios close to 1:3:3:1. The unpaired electron is coupled to the three nonequivalent coordinated phosphorus atoms (³¹P, $I = 1/2$, 100%) with similar hyperfine constants. Computer simulation was able to distinguish one unique

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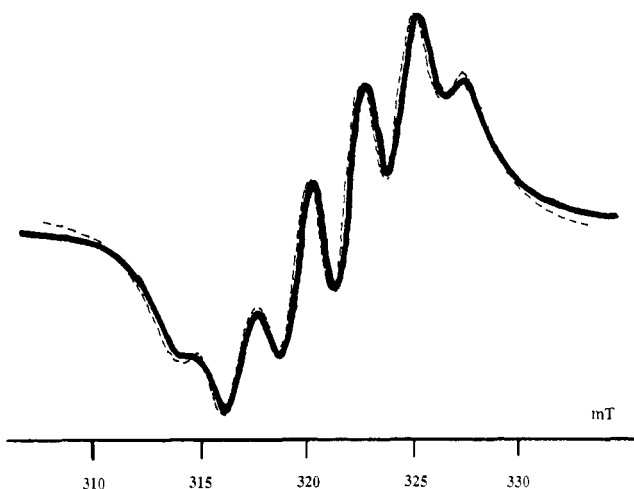
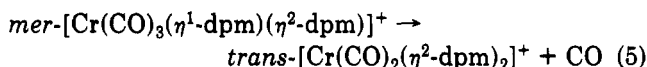


Figure 2. ESR spectrum of $mer\text{-}[\text{Cr}(\text{CO})_3(\eta^1\text{-ape})(\eta^2\text{-ape})]^+$: (—) experimental; (---) simulation.

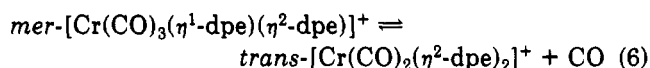
and two effectively identical hyperfine constants, as shown in Table II.

The solution of $mer\text{-}[\text{Cr}(\text{CO})_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})]^+$, if kept in a sealed tube in the dark, was found to be stable at 25 °C over several days. This is in marked contrast with an earlier report,¹⁹ which indicated the cation to be unstable on a short time scale. However, if the tube was not sealed, the spectrum did very slowly decay to a 1:4:6:4:1 quintet, which is identical with that previously reported⁹ for $trans\text{-}[\text{Cr}(\text{CO})_2(\eta^2\text{-dpm})_2]^+$. Purging the solution with argon causes more rapid (a few hours) formation of $trans\text{-}[\text{Cr}(\text{CO})_2(\eta^2\text{-dpm})_2]^+$ by the reaction



Bubbling carbon monoxide through the solution for a few minutes does not reverse the reaction. The formation of $trans\text{-}[\text{Cr}(\text{CO})_2(\eta^2\text{-dpm})_2]^+$ was confirmed by observation of a carbonyl stretching mode at 1875 cm^{-1} and a chemically reversible electrochemical reduction response at -1.18 V vs Fc^+/Fc , both of which agree with literature values.^{6,9}

The ESR spectrum of $mer\text{-}[\text{Cr}(\text{CO})_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+$, generated by electrolysis of $fac\text{-Cr}(\text{CO})_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$ in a sealed tube within the cavity of the spectrometer at -50 °C, is approximately a quartet, very similar to that of the corresponding dpm derivative. However, as the temperature is raised to 10 °C, a quintet appears together with the quartet and these changes are reversible with temperature. If the solution is purged with argon for a few minutes, only the sharp quintet is observed at any temperature. This signal is due to $trans\text{-}[\text{Cr}(\text{CO})_2(\eta^2\text{-dpe})_2]^+$, the sharp quintet originating from the unpaired electron coupling with four equivalent phosphorus-31 nuclei. Its identity was confirmed by its infrared spectrum and electrochemical behavior.^{6,9} Thus, in this case the reaction



is temperature dependent and reversible on a relatively short time scale in a sealed tube, which prevents the loss of carbon monoxide. The difference in the labilities of the dpe and dpm systems is not yet understood.

Oxidation of $fac\text{-Cr}(\text{CO})_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$ with 1 mol of AgClO_4 also produces $mer\text{-}[\text{Cr}(\text{CO})_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+$, as

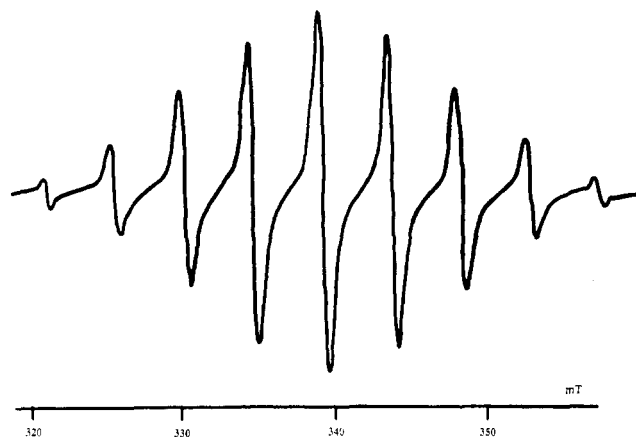


Figure 3. ESR spectrum of $trans\text{-}[\text{Cr}(\text{CO})_2(\eta^2\text{-ape})_2]^+$.

identified by the characteristic ESR spectrum. However, the reaction with AgClO_4 is quite complex relative to the electrochemical oxidation (see later discussion).

The ESR spectrum of $mer\text{-}[\text{Cr}(\text{CO})_3(\eta^1\text{-ape})(\eta^2\text{-ape})]^+$, produced by the electrochemical 1-electron oxidation of $mer\text{-Cr}(\text{CO})_3(\eta^1\text{-ape})(\eta^2\text{-ape})$ in dichloromethane solution (0.1 M Bu_4NClO_4) within the microwave cavity of the ESR spectrometer at -40 °C, is shown in Figure 2. It is a six-line spectrum (intensity ratios 1:3:4:4:3:1), and a good fit was obtained by computer simulation by assuming that the unpaired electron is distributed over one arsenic (^{75}As , $I = 3/2$, 100%) and two phosphorus atoms, with both nuclei contributing almost the same hyperfine coupling constant.

On the other hand, oxidation of $mer\text{-Cr}(\text{CO})_3(\eta^1\text{-ape})(\eta^2\text{-ape})$ with AgClO_4 at room temperature results in the rapid formation of $trans\text{-}[\text{Cr}(\text{CO})_2(\eta^2\text{-ape})_2]^+$, as evidenced by a sharp nine-line ESR spectrum (Figure 3) with the intensity ratios close to the theoretical values 1:4:8:12:14:12:8:4:1, which is to be expected if the unpaired electron is distributed over two arsenic and two phosphorus atoms, again with almost the same hyperfine coupling constant.

The proposed similarity of the hyperfine coupling constants to phosphorus and arsenic in the ape derivatives is confirmed by comparing the values in Table II with those for the diphosphine (dpm, dpe) and diarsine (dae) derivatives, which may be assigned unambiguously.

Chemical or electrochemical oxidation of $fac\text{-Cr}(\text{CO})_3(\eta^1\text{-dae})(\eta^2\text{-dae})$ with AgClO_4 at -40 °C results in the formation of $mer\text{-}[\text{Cr}(\text{CO})_3(\eta^1\text{-dae})(\eta^2\text{-dae})]^+$. The ESR spectrum consists of 10 lines and with the help of computer simulation was found to have the relative intensity ratio 1:3:6:10:12:12:10:6:3:1, which is the expected pattern if the unpaired electron is delocalized equally over three arsenic atoms. If the mer^+ species is allowed to stand for about 2 h at room temperature, an additional number of sharp lines appear and the spectrum then appears to show a mixture of $mer\text{-}[\text{Cr}(\text{CO})_3(\eta^1\text{-dae})(\eta^2\text{-dae})]^+$ and $trans\text{-}[\text{Cr}(\text{CO})_2(\eta^2\text{-dae})_2]^+$. The $trans^+$ species has a sharper spectrum with 13 lines due to the unpaired electron being coupled to four equivalent arsenic nuclei. In general, the mer^+ species show line widths between 3 and 4 times those of the $trans^+$ species.

Reactions of Chromium Complexes with AgClO_4 .

The 1-electron electrochemical oxidation of $\text{Cr}(\text{CO})_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})$ complexes at platinum electrodes is relatively straightforward, producing $mer\text{-}[\text{Cr}(\text{CO})_3(\eta^1\text{-L-L})(\eta^2\text{-L-L})]^+$, which then very slowly decompose to $trans\text{-}[\text{Cr}(\text{CO})_2(\eta^2\text{-L-L})_2]^+$. However, the reaction with AgClO_4 , which often acts as a 1-electron oxidant, is not simple when a pendant donor atom is available.

(19) Blagg, A.; Carr, S. W.; Cooper, G. R.; Dobson, I. D.; Gill, J. B.; Goodall, D. C.; Shaw, B. L.; Taylor, N.; Boddington, T. *J. Chem. Soc., Dalton Trans.* 1985, 1213.

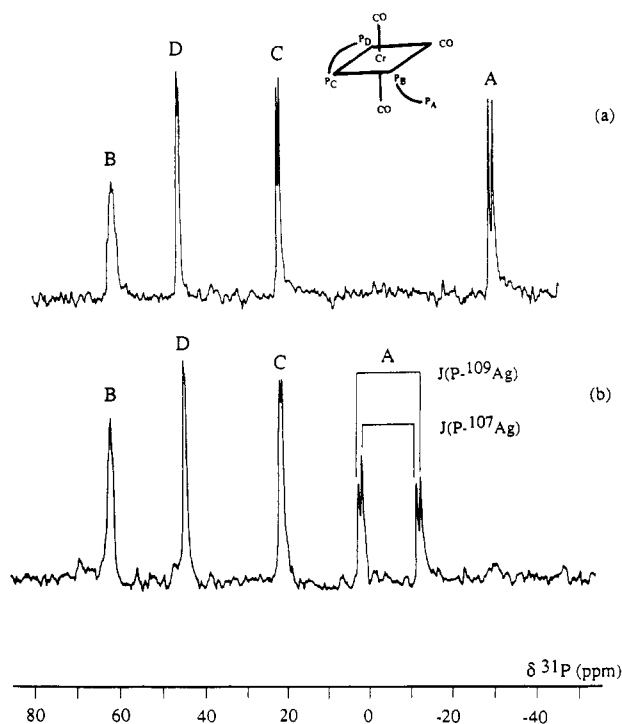
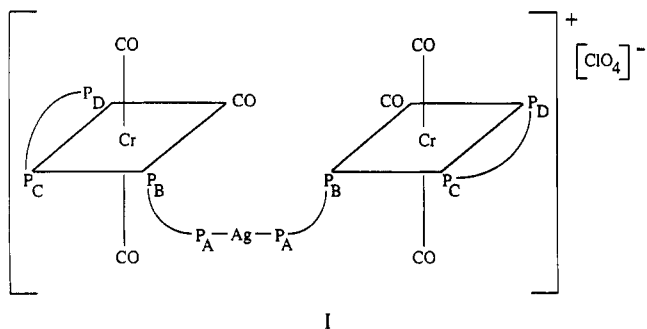


Figure 4. Phosphorus-31 NMR spectra in dichloromethane solution: (a) *mer*-Cr(CO)₃(η¹-dpm)(η²-dpm) at 20 °C; (b) the same solution after reaction with 0.5 mol of AgClO₄ at (-50 °C).

(a) *mer*-Cr(CO)₃(η¹-dpm)(η²-dpm). Solutions of *mer*-Cr(CO)₃(η¹-dpm)(η²-dpm) react with equimolar amounts of AgClO₄, producing *mer*-[Cr(CO)₃(η¹-dpm)(η²-dpm)][ClO₄]⁺, but reaction with only 0.5 mol of AgClO₄ gives a completely different reaction and produces a diamagnetic rather than paramagnetic product.

Figure 4a shows the phosphorus-31 NMR spectrum at -50 °C for a dichloromethane solution of *mer*-Cr(CO)₃(η¹-dpm)(η²-dpm), while Figure 4b shows the spectrum at -50 °C of the same solution after reaction with 0.5 mol of AgClO₄. The positions of the three resonances B, C, and D remain almost unchanged, but resonance A, due to the uncoordinated phosphorus atom P_A in *mer*-Cr(CO)₃(η¹-dpm)(η²-dpm), has disappeared and a new multiplet showing ^{107,109}Ag coupling appears at higher frequency. Structure I is proposed for this complex. The silver-



phosphorus coupling constants are comparable with those previously reported.²⁰ The reaction is probably related

to that reported by Shaw and co-workers²¹ between *fac*-M(CO)₃(η¹-dpm)(η²-dpm) (M = Mo, W) or *mer*-M(CO)₃(η¹-dpm)(η²-dpm) (M = Cr, W) and 0.25 mol equiv of [Ag₄Cl₄(PPh₃)₄] to give the species *fac*- or *mer*-[Cr(CO)₃(η²-dpm)M(μ-dpm)AgCl] (M = Cr, Mo, W), respectively.

(b) *mer*-[Cr(CO)₃(η¹-dpm)(η²-dpm)]⁺. The addition of 0.5 mol of AgClO₄ to a dichloromethane or acetone solution of *mer*-[Cr(CO)₃(η¹-dpm)(η²-dpm)]⁺ causes an increase in the rate of decomposition of *mer*-[Cr(CO)₃(η¹-dpm)(η²-dpm)]⁺ to *trans*-[Cr(CO)₂(η²-dpm)₂]⁺, resulting in a mixture of *mer*-[Cr(CO)₃(η¹-dpm)(η²-dpm)]⁺ and *trans*-[Cr(CO)₂(η²-dpm)₂]⁺ cations in solution, as shown by electrochemical and ESR studies. If an excess of AgClO₄ is used, a greater proportion of the *trans*⁺ species is observed in solution. Hence, the AgClO₄ concentration has a substantial effect on the conversion rate of *mer*-[Cr(CO)₃(η¹-dpm)(η²-dpm)]⁺ to *trans*-[Cr(CO)₂(η²-dpm)₂]⁺.

(c) *mer*-Cr(CO)₃(η¹-ape)(η²-ape). Reaction of *mer*-Cr(CO)₃(η¹-ape)(η²-ape) with equimolar amounts of AgClO₄ in dichloromethane or acetone solution produces *mer*-[Cr(CO)₃(η¹-ape)(η²-ape)]⁺, and reaction with 0.5 mol of AgClO₄ results merely in a mixture of this compound and the starting material. Addition of a large excess of AgClO₄ leads to catalytic formation of *trans*-[Cr(CO)₂(η²-ape)₂]⁺, implying that a complex of the kind given in structure I may also be formed as a precursor to the catalysis.

(d) *fac*-Cr(CO)₃(η¹-dae)(η²-dae). The reaction sequence is similar to that described for *mer*-Cr(CO)₃(η¹-ape)(η²-ape).

Conclusions

The presence of a pendant donor atom enables the electrochemically produced *mer*-[Cr(CO)₃(η¹-L-L)(η²-L-L)]⁺ species to undergo a carbonyl displacement reaction to give *trans*-[Cr(CO)₂(η²-L-L)₂]⁺, in which the 17-electron configuration is retained. Additionally, the pendant donor atom can coordinate with the silver ion so that AgClO₄ does not necessarily act solely as an innocent 1-electron chemical oxidant. Rather, coordination to the pendant donor group may occur in competition with or in parallel with oxidation to give a silver complex with chromium still in the zero-valent state. This complex may then be oxidized in the presence of excess silver to give an additional pathway to the formation of *trans*-[Cr(CO)₂(η²-L-L)₂]⁺. Complexes of the types [Ag(PR₂R')₂][ClO₄]⁺ and [Ag(AsR₂R')₂][ClO₄]⁺ (R and R' = alkyl and aryl groups) have recently been isolated and characterized by X-ray diffraction techniques.²²

Registry No. *mer*-[Cr(CO)₃(η¹-ape)(η²-ape)], 134736-57-5; *fac*-[Cr(CO)₃(η¹-dae)(η²-dae)], 134780-99-7; Cr(CO)₃(C₇H₉), 12083-24-8; *mer*-[Cr(CO)₃(η¹-ape)(η²-ape)]⁺, 134736-58-6; *trans*-[Cr(CO)₂(η²-dpm)₂]⁺, 53152-35-5; *trans*-[Cr(CO)₂(η²-dpe)₂]⁺, 66700-95-6; *mer*-[Cr(CO)₃(η¹-dpe)(η²-dpe)]⁺, 102132-80-9; *trans*-[Cr(CO)₂(η²-dpe)₂]⁺, 37757-28-1; *fac*-[Cr(CO)₃(η¹-dpe)(η²-dpe)]⁺, 102132-78-5; *trans*-[Cr(CO)₂(η²-ape)₂]⁺, 134736-59-7; *mer*-[Cr(CO)₃(η¹-dae)(η²-dae)]⁺, 134736-60-0; *mer*-[Cr(CO)₃(η¹-dpm)(η²-dpm)], 93401-94-6; [(CO)₃(η²-dpe)Cr(μ-dpm)Ag(μ-dpm)Cr(η²-dpm)(CO)₃ClO₄], 134736-62-2; *trans*-[Cr(CO)₂(η²-dae)₂]⁺, 134736-63-3; *mer*-[Cr(CO)₃(η¹-dpm)(η²-dpm)]⁺, 98152-90-0.

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