be limited however by side reactions to as yet unidentified products.


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Electrochemical and Spectroscopic Study of Isomerization, Cross-Redox, and Self-Exchange Reactions in the [Cr(CO)₃P₃]⁺/⁰ Redox System

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Homogeneous and heterogeneous aspects of the redox couple [Cr(CO)$_3$P$_3$]$^{+/0}$ [P = monodentate phosphorus ligand (P(OMe)$_3$, P(OPh)$_3$, P(OMe)$_2$Ph, PMe$_2$Ph)] have been examined by polarographic, voltammetric, synthetic, magnetic, spectroscopic, and other techniques in dichloromethane solution. The tricarbonyl complexes in each oxidation state can exist in both facial (*fac*⁺ or *fac*⁰) and meridional (*mer*⁺ or *mer*⁰) forms. Under the electrochemical conditions of polarography or voltammetry, parts of the square reaction scheme

$$fac^0 \rightleftharpoons fac^+ + e^-$$
$$\Updownarrow \qquad\qquad \Updownarrow$$
$$mer^0 \rightleftharpoons mer^+ + e^-$$
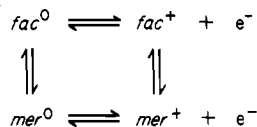
in addition to the cross-redox reaction *fac*⁺ + *mer*⁰ ⇌ *fac*⁰ + *mer*⁺, are required to explain the electrode processes at both platinum and mercury electrodes. The heterogeneous rates of electron transfer are relatively fast at either electrode. The homogeneous cross-redox reaction enables generation of *mer*-Cr(CO)$_3$P$_3$ to occur as an intermediate under conditions of oxidative controlled-potential electrolysis or chemical oxidation of *fac*⁰ isomers. Ultimately, however, the *mer*⁺ form is the sole product of these oxidation reactions irrespective of whether *fac*⁰- or *mer*⁰-Cr(CO)$_3$P$_3$ is used as the starting complex. These paramagnetic 17-electron cations can be isolated; they are light and heat sensitive and chemically reactive, readily regenerating the *mer*⁰ complexes. The electron-transfer reaction *mer*⁺* + *mer*⁰ ⇌ *mer*⁰* + *mer*⁺ has been shown by ESR and NMR measurements to be faster than the cross-redox reaction *fac*⁺ + *mer*⁰ ⇌ *fac*⁰ + *mer*⁺.

Introduction

Compounds of the type Cr(CO)$_3$P$_3$ (P = phosphorus ligand) can exist in facial or meridional isomeric forms.[3] The isomer formed with standard preparative methods usually depends on the nature of the ligand, although in some cases both isomers can be prepared. One-electron oxidation of the 18-electron Cr(CO)$_3$P$_3$ complex is expected to produce the 17-electron cation [Cr(CO)$_3$P$_3$]⁺, which could also exist in the facial or meridional forms.

To date, the majority of the redox chemistry of the chromium tricarbonyl derivatives has concerned complexes of polycyclic tridentate (P, S, or N donors) or arene ligands that fix the stereochemistry in the facial form.[4-7] In general, the arene tricarbonyl compounds showed a 1-electron reversible oxidation, and in some cases a second 1-electron reversible couple was also observed.[4-8] In the case of the tridentate ligands two reversible 1-electron oxidation processes were reported.[7] A brief report on the oxidation of Cr(CO)$_3$L$_3$ (L = nitrogen donor) complexes is also available,[8] but no discussion as to whether structural changes occur on oxidation was given. The mere observation of apparently reversible electrochemical behavior does not prove that there is no structural change accompanying electron transfer as detailed

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theoretical studies have shown.[9] However, in the particular case of the tridentate ligands noted above the observation of the reversible electrochemical behavior described enables the assignment of the processes to be made as

$$fac \rightleftharpoons fac^+ + e^- \qquad (1)$$

$$fac^+ \rightleftharpoons fac^{2+} + e^- \qquad (2)$$

with the justifiable assumption that meridional forms are unlikely because of steric restrictions. With monodentate ligands, however, similar assumptions concerning the stereochemistry assocated with the redox couples cannot be made. Thus, with this class of ligand, detailed NMR measurements on the chromium(0) tricarbonyl compounds and ESR measurements on the Cr(I) p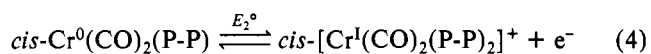roduct, or other spectroscopic or related measurements, must accompany the electrochemical investigation to enable complete assignments of the electrode processes to be made. Previous work on chromium dicarbonyl compounds $Cr(CO)_2(P-P)_2$ (where P-P is a bidentate phosphorus ligand) showed the possibility of cis/trans isomerization accompanying electron transfer,[10–12] with the oxidation process being $cis \rightleftharpoons cis^+ + e^-$ accompanied by the reaction $cis^+ \rightarrow trans^+$. This structural change following the electron transfer was inferred from the electrochemistry alone because the $E°$ values for the redox couples

$$trans\text{-}Cr^0(CO)_2(P\text{-}P)_2 \overset{E_1°}{\rightleftharpoons} trans\text{-}[Cr^I(CO)_2(P\text{-}P)_2]^+ + e^- \qquad (3)$$

and

$$cis\text{-}Cr^0(CO)_2(P\text{-}P) \overset{E_2°}{\rightleftharpoons} cis\text{-}[Cr^I(CO)_2(P\text{-}P)_2]^+ + e^- \qquad (4)$$
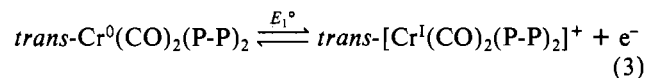
were separated by several hundred millivolts.

Theoretical and experimental studies on different geometries suggest that these kinds of electrode processes involving structural change must be common but that the nature of the geometry and the number of carbonyl groups will be critical to the reaction pathway.[13–15]

Basic information on the redox properties of tricarbonyl componds of chromium(0) is minimal in situations where isomerization may occur. In the present work, we have examined the redox behavior of $[Cr(CO)_3P_3]^{+/0}$ (P = P(OPh)$_3$, P(OMe)$_2$Ph, PMe$_2$Ph, P(OMe)$_3$) and characterized the products by elemental analysis, infrared, NMR, and ESR spectroscopy, and magnetism and conductance measurements. The chromium(0) tricarbonyl derivatives have been characterized by ^{31}P and ^{13}C NMR and infrared measurements. As will be demonstrated, all of this information is required to fully characterize the redox processes since structural changes and exchange reactions do accompany the charge-transfer process.

Experimental Section

Reagents. The ligands P(OMe)$_3$, PMe$_2$Ph, and P(OPh)$_3$ were obtained commercially and distilled before use. P(OMe)$_2$Ph was prepared by the published method.[16] Chromium tricarbonyl cycloheptatriene was prepared by the literature method from $Cr(CO)_6$ (dried over P$_2$O$_5$), freshly distilled cycloheptatriene, and freshly distilled diglyme.[17] All solvents were dried over type 4A molecular sieves. Benzene was dried by azeotroping off 50% of the volume under a N$_2$

atmosphere. Silver perchlorate was dried by dissolving in benzene followed by azeotropic distillation of the water. Tetrabutylammonium perchlorate was dried under vacuum over P$_2$O$_5$. NOPF$_6$ and NOBF$_4$ were commercial samples and used as supplied.

Preparations. Cr(CO)$_3$P$_3$ Compounds. The compounds *fac*-Cr-(CO)$_3$(P(OMe)$_3$)$_3$,[18] *mer*-Cr(CO)$_3$(P(OMe)$_3$)$_3$,[19] *mer*-Cr(CO)$_3$(P(OPh)$_3$)$_3$,[20] *mer*-Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$,[21] and *fac*-Cr(CO)$_3$-(PMe$_2$Ph)$_3$[21] were prepared as described in the literature.

mer-[Cr(CO)$_3$P$_3$]ClO$_4$ or [Cr(CO)$_3$P$_3$]PF$_6$ Compounds. The chromium(0) tricarbonyl compounds (0.003 mol) were stirred in the dark for 1 h with a slight molar excess of AgClO$_4$ in benzene. Apart from Cr(CO)$_3$P(OPh)$_3$, which requires a stronger oxidant, the reaction occurred with deposition of silver. The solution was evaporated to dryness and the oxidized chromium compound extracted with dichloromethane. Hexane was added until the solution was just turbid, the solution was then cooled to –20 °C, and pale orange flakes precipitated. Typically, a yield of approximately 30% was obtained. The compounds were moderately light and heat sensitive. All the compounds [Cr(CO)$_3$P$_3$]PF$_6$ could be prepared by using an equimolar ratio of Cr(CO)$_3$P$_3$ and NOPF$_6$ by a procedure analogous to that described above. Microanalytical data were obtained on some of the compounds. Anal. Calcd for *mer*-[Cr(CO)$_3$(PMe$_2$Ph)$_3$]ClO$_4$: C, 49.90; H, 5.12. Found: C, 48.38; H, 5.06. Calcd for *mer*-[Cr-(CO)$_3$(P(OMe)$_2$Ph)$_3$]ClO$_4$: C, 43.47; H, 4.46. Found: C, 44.05; H, 5.01. The remaining *mer*-[Cr(CO)$_3$P$_3$]$^+$ compounds could not be obtained analytically pure but were characterized by infrared spectroscopy, electrochemistry, and electron spin resonance measurements.

Instrumentation. (a) Electrochemical Measurements. All voltammograms and polarograms were recorded in dichloromethane (0.1 M Bu$_4$NClO$_4$) on a Model 174A EG&G PAR electrochemistry system. A three-electrode system was used. Controlled drop times of 0.5, 1.0, and 2.0 s were used in the polarographic measurements. In cyclic voltammetry the working electrode was a growing mercury drop or a platinum disk. The reference electrode was Ag/AgCl (CH$_2$Cl$_2$; saturated LiCl) separated from the test solution by a salt bridge containing 0.1 M tetrabutylammonium perchlorate in dichloromethane. The third or auxiliary electrode was a platinum wire. For variable-temperature cyclic voltammetry the temperature was regulated by using a dry ice/ethanol bath with varying dry ice/ethanol proportions. The temperature was monitored with a thermocouple. Controlled-potential electrolysis experiments were performed with a PAR Model 173 potentiostat/galvanostat using either a mercury-pool or platinum-gauze working electrode and a platinum auxiliary electrode separated from the bulk solution by a salt bridge containing a Vycor plug. The same Ag/AgCl reference electrode used in polarography and voltammetry was used in the electrolysis experiments.

(b) Nuclear Magnetic Resonance. All spectra were recorded on a JEOL FX-100 NMR spectrometer in CDCl$_3$. The ^{31}P spectra were recorded at 40.32 MHz with 85% H$_3$PO$_4$ as the external reference. The ^{13}C spectra were recorded at 25.47 MHz with use of tetramethylsilane as an internal reference. Chromium tris(acetylacetonate) was added to reduce the relaxation time of the ^{13}C nuclei associated with the carbonyl group. The ^{1}H spectra at 99.61 MHz were recorded by using tetramethylsilane as an internal reference.

(c) Infrared Spectra. The infrared spectra were recorded on a Jasco A-302 spectrometer and calibrated against polystyrene (1601 cm^{-1}).

(d) Electron Spin Resonance. The ESR spectra were recorded in dichloromethane and calibrated against pitch on a Varian 450/15 spectrometer with a temperature controller. The temperature was checked by using a platinum resistance thermometer.

(e) Magnetic Moments. The magnetic moments of *mer*-[Cr-(CO)$_3$(P(OMe)$_2$Ph)$_3$]$^+$ClO$_4$ and *mer*-[Cr(CO)$_3$(PMe$_2$Ph)$_3$]$^+$ClO$_4$ were determined by the Evans method[22] using the ^{1}H resonance of CH$_2$Cl$_2$ at 25 °C. They were found to be 1.84 and 1.82 μ_B, respectively, indicating that the cations have one unpaired electron (low-spin d^5 chromium(I)) and that they are not dimeric in solution.

(f) Conductivity Measurements. The molar conductances of *mer*-[Cr(CO)$_3$(PMe$_2$Ph)$_3$]ClO$_4$ and *mer*-Cr[(CO)$_3$(P(OMe)$_2$Ph)$_3$]$^+$ClO$_4$ in CH$_2$Cl$_2$ at 25 °C were found to be 1.35×10^{-3}

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Table I. Infrared Carbonyl Stretching Frequencies, ^{31}P and ^{13}C (Carbonyl) NMR Data, and ESR Data for Cr(CO)$_3$P$_3$ and [Cr(CO)$_3$P$_3$]$^+$ at 25 °C

| compd | IR^{a,b} data ν_{CO}, cm^{-1} | NMR^c data | | | ESR^f data | |
		$\delta(^{31}P)^d$	$^2J_{P-P},^e$ Hz	$\delta(^{13}C)^d$	g	hyperfine coupling, G
fac-Cr(CO)$_3$(PMe$_2$Ph)$_3$	1923 (s), 1820 (s)	14.3		229.7		
fac-Cr(CO)$_3$(P(OMe)$_3$)$_3$	1961 (s), 1869 (s)	185.0		226.2		
mer-Cr(CO)$_3$(P(OMe)$_3$)$_3$	1981 (m), 1900 (sh), 1878 (s)	196.8 (2)		226.9 (1)		
		188.3 (1)	60.3	221.3 (2)		
mer-Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$	2000 (m), 1910 (vs), 1890 (sh)	212.8 (2)	40.0	227.9 (1)		
		204.1 (1)		223.8 (2)		
mer-Cr(CO)$_3$(P(OPh)$_3$)$_3$	1973 (m), 1890 (sh), 1870 (vs)	176.2 (2)	65.6	223.7 (1)		
		166.9 (1)		218.4 (2)		
mer-[Cr(CO)$_3$(PMe$_2$Ph)$_3$]ClO$_4$	2010 (m), 1940 (sh), 1904 (s)				2.019	20 (triplet)
						36 (doublet)
mer-[Cr(CO)$_3$(P(OMe)$_3$)$_3$]ClO$_4$	2051 (m), 1988 (m), 1935 (s)				2.002	40 (average)
mer-[Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$]ClO$_4$	2042 (m), 1970 (m), 1911 (s)				1.990	33 (average)
mer-[Cr(CO)$_3$(P(OPh)$_3$)$_3$]PF$_6$	2070 (m), 1970 (s), 1918 (m)				1.980	35 (average)

^{a} In CH$_2$Cl$_2$ solution and calibrated against polystyrene, 1601 cm^{-1}. ^{b} vs = very strong; s = strong; m = medium; sh = shoulder. ^{c} In CDCl$_3$ solution. ^{d} Errors ±0.1 ppm. ^{e} Errors ±0.4 Hz. ^{f} In CH$_2$Cl$_2$ and calibrated against pitch.

Table II. Polarographic and Cyclic Voltammetric Data at Mercury Electrodes for the Oxidation of Cr(CO)$_3$P$_3$ Complexes in CH$_2$Cl$_2$ (0.1 M Bu$_4$NClO$_4$) at 20 °C^a

| compd | polarography | | | cyclic voltammetry^b | |
	drop time, s	$E_{1/2}$, V vs. Ag/AgCl	$E_{3/4} - E_{1/4}$, V	$E_p^{ox},^d$ V vs. Ag/AgCl	$E_p^{red},^d$ V vs. Ag/AgCl
mer-Cr(CO)$_3$(P(OMe)$_3$)$_3$	0.5	0.362	0.059	0.400	0.322
	1.0	0.356	0.056		
	2.0	0.357	0.057		
mer-Cr(CO)$_3$(P(OPh)$_3$)$_3$	0.5	0.739	0.056	0.784	0.674
	1.0	0.732	0.055		
	2.0	0.726	0.057		
mer-Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$	0.5	0.285	0.075	0.347	0.237
	1.0	0.287	0.070		
	2.0	0.290	0.067		
fac-Cr(CO)$_3$(P(OMe)$_3$)$_3$	0.5	0.479	0.059	0.561	0.475
	1.0	0.456	0.057		
	2.0	0.442	0.053		
fac-Cr(CO)$_3$(PMe$_2$Ph)$_3$	0.5	0.226	0.065	0.290	0.205
	1.0	0.219	0.062		
	2.0	0.214	0.060		
mer-Cr(CO)$_3$(PMe$_2$Ph)$_3$ ^{c}	2.0	−0.067	0.060	−0.005	−0.100

^{a} Concentration of compounds 10^{-3} M. ^{b} Recorded at a dropping-mercury electrode. Scan rate of 500 mV s^{-1} commenced 0.5 s after drop growth commences. ^{c} Polarographic data obtained by monitoring the controlled-potential electrolytic oxidation of *fac*-Cr(CO)$_3$-(PMe$_2$Ph)$_3$ in which this species is an observed intermediate (see text). The *mer*$^+$ + e$^-$ ⇌ *mer*^{0} redox couple was observed on second and subsequent scans enabling data to be obtained for cyclic voltammetry. ^{d} E_p^{ox} and E_p^{red} are oxidation and reduction peak potentials, respectively.

and 1.27 × 10^{-3} S cm^2 mol^{-1}, respectively, compared with 1.45 × 10^{-3} S cm^2 mol^{-1} for Bu$_4$NI under the same conditions. The complexes are thus 1:1 electrolytes.
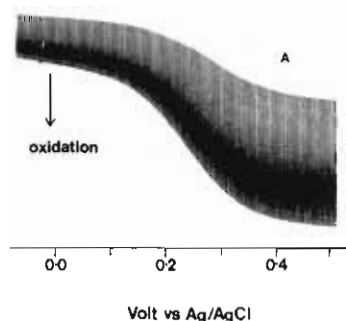
Results and Discussion

Isolation of [Cr(CO)$_3$P$_3$]$^+$ Compounds. Although the first evidence for the existence of the oxidized compounds [Cr-(CO)$_3$P$_3$]$^+$ was obtained from the electrochemical data, it is convenient to describe their isolation first. *fac*-Cr(CO)$_3$-(PMe$_2$Ph)$_3$, *mer*-Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$, and *mer/fac*-Cr-(CO)$_3$(P(OMe)$_3$)$_3$ were readily oxidized with AgClO$_4$ or NOPF$_6$ in benzene to form pale orange chromium(I) compounds. *mer*-Cr(CO)$_3$(P(OPh)$_3$)$_3$ was not oxidized with AgClO$_4$, but NOPF$_6$ was a sufficiently strong oxidant to produce the chromium(I) compound. This is in agreement with electrochemical data (see later text), showing that this is by far the hardest compound to oxidize.

The infrared spectra of the [Cr(CO)$_3$P$_3$]$^+$ compounds in dichloromethane solution all show three bands in the carbonyl region (Table I). This is consistent with the formation of the *mer* isomer (C_{2v} symmetry) as the *fac* isomer has symmetry C_{3v} and thus would be expected to show only two bands.[23] The

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infrared carbonyl stretching frequencies of the chromium(I) compounds are moved to higher frequencies relative to the analogous chromium(0) compounds. This is consistent with the chromium(I) center being less able to back-bond to the carbonyl groups.

Polarographic Oxidation of Cr(CO)$_3$P$_3$ Complexes in Dichloromethane. For each of the compounds, one very well-defined polarographic oxidation wave was observed. Table II summarizes the data. For the oxidation of *mer*-Cr-(CO)$_3$(P(OMe)$_3$)$_3$, the half-wave potential, $E_{1/2}$, was independent of drop time and $E_{3/4} - E_{1/4}$ was close to the value expected for a Nernstian electrode process. A plot of log [(i_d − i)/i] vs. E at a drop time of 2.0 s was linear with a slope of −60 mV at 20 °C (theoretical −58 mV) (i = current, i_d = diffusion-controlled limiting current, E = potential). These values confirm that on the time scale of dc polarography the oxidation process was diffusion controlled for this complex. The electrode process for *mer*-Cr(CO)$_3$(P(OPh)$_3$)$_3$ was essentially the same as for *mer*-Cr(CO)$_3$(P(OMe)$_3$)$_3$ although it is oxidized at a much more positive potential. The polarography of *mer*-Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$ approached Nernstian behavior at longer drop times, which is consistent with a quasi-reversible couple. Thus, all *mer* complexes showed reversible or quasi-reversible behavior, with no chemical steps

Figure 1. (A) Dc polarogram of the oxidation of 10^{-3} M *fac*-Cr-$(CO)_3(PMe_2Ph)_3$ in dichloromethane (0.1 M Bu$_4$NClO$_4$) at 18 °C (drop time 1 s).

Table III. Cyclic Voltammetric Data at a Platinum Electrode for Oxidation of *mer*-Cr(CO)$_3$P$_3$ in CH$_2$Cl$_2$ (0.1 M Bu$_4$NClO$_4$) at 20 °C^a

compd	scan rate, mV/s	E_p^{ox}, V vs. Ag/AgCl	E_p^{red}, V vs. Ag/AgCl	$(i_p)^{ox}/(i_p)^{red}$
mer-Cr(CO)$_3$-(P(OMe)$_3$)$_3$^{b}	500	0.406	0.285	1.0
	200	0.400	0.288	1.0
	100	0.397	0.290	1.0
	50	0.394	0.294	0.9
mer-Cr(CO)$_3$-(P(OPh)$_3$)$_3$^{c}	500	0.870	0.625	1.0
	200	0.827	0.645	1.0
	100	0.810	0.665	0.9
	50	0.784	0.678	0.8
mer-Cr(CO)$_3$-(P(OMe)$_2$Ph)$_3$^{d}	500	0.410	0.225	1.0
	200	0.375	0.245	1.0
	100	0.370	0.255	1.0
	50	0.365	0.265	1.0

^{a} $(i_p)^{ox}/(i_p)^{red}$ is the ratio of peak oxidation and peak reduction current, respectively. Other symbols are as defined in Table II. ^{b} A second irreversible oxidation wave was observed at 1.46 V. ^{c} No further oxidation observed prior to solvent limit. ^{d} A second irreversible oxidation process was observed at 1.28 V.

accompanying the charge transfer.

The polarograms of the complexes *fac*-Cr(CO)$_3$(P(OMe)$_3$)$_3$ and *fac*-Cr(CO)$_3$(PMe$_2$Ph)$_3$ (Figure 1A) had shapes close to those expected for reversible couples, but for *fac*-Cr(CO)$_3$-(PMe$_2$Ph)$_3$ $E_{1/2}$ became slightly less positive at longer drop times, in contrast to the *mer* complexes described above for which $E_{1/2}$ was almost independent of drop time. The compound *fac*-Cr(CO)$_3$(P(OMe)$_3$)$_3$ showed an even stronger drop time dependence than *fac*-Cr(CO)$_3$(PMe$_2$Ph)$_3$ consistent with a quasi-reversible charge-transfer step followed by a chemical reaction. The quotient i_d/c (c = concentration) was approximately the same for all compounds and corresponded to a 1-electron oxidation.

Cyclic Voltammetry at the Mercury Electrode. Table II summarizes the data. The cyclic voltammograms at a growing-mercury-drop electrode for all the *mer* compounds were consistent with quasi-reversible 1-electron oxidation processes; the typical cyclic voltammogram of *mer*-Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$ is shown in Figure 1B (supplementary material). The mere observation of a single oxidation process with apparently rapid electron transfer does not permit an assignment of the electrode process as a *mer*$^{+/0}$ redox couple.[9,13] The compound Cr(CO)$_3$(P(OMe)$_3$)$_3$ is unusual since it exists as both facial and meridional isomers that can be studied independently. The *mer* isomer showed similar voltammetric behavior to that of the other *mer* compounds (Table III). However, the cyclic voltammogram of *fac*-Cr(CO)$_3$(P-(OMe)$_3$)$_3$ showed behavior distinctly different from that observed for the *mer* isomer. On the first oxidative scan a chemically irreversible oxidation process was observed at about 0.56 V (vs. Ag/AgCl), which was a more positive potential than that observed for the oxidation of *mer*-Cr(CO)$_3$(P-

Table IV. Cyclic Voltammetric Data for Oxidation of *fac*-Cr(CO)$_3$(PMe$_2$Ph)$_3$ at a Platinum Electrode at Variable Temperatures and Scan Rates in CH$_2$Cl$_2$ (0.1 M Bu$_4$ClO$_4$)^{a,e}

temp, °C	scan rate, mV/s	$E_p^{ox,b}$ V vs. Ag/AgCl	$E_p^{red,b}$ V vs. Ag/AgCl	$E_p^{ox,c}$ V vs. Ag/AgCl	$E_p^{red,c}$ V vs. Ag/AgCl
18	500	0.34	ca. 0.18	0.00	-0.13
	200	0.31	d	-0.01	-0.12
	100	0.28	d	-0.02	-0.11
	50	0.26	d	-0.03	-0.10
-15	500	0.36	0.15	0.01	-0.15
	200	0.33	0.17	-0.02	-0.13
	100	0.31	0.17	-0.03	-0.11
	50	0.30	0.17	-0.03	-0.09
-43	500	0.40	0.13	0.03	-0.17
	200	0.37	0.13	-0.02	-0.18
	100	0.31	0.16	-0.03	-0.13
	50	0.30	0.17	d	d
-57	500	0.46	0.09	d	d
	200	0.36	0.12	d	d
	100	0.34	0.17	d	d
	50	0.31	0.15	d	d

^{a} Symbols are as defined in Table III. ^{b} For process

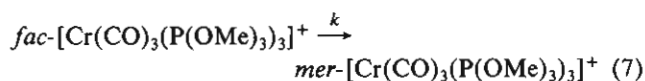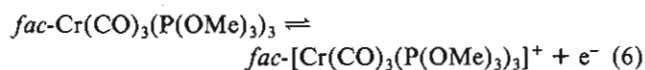$$fac \rightleftharpoons fac^+ + e^-$$
$$\downarrow$$
$$mer^+$$
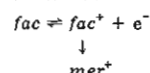
^{c} For process *mer* $\rightleftharpoons$ *mer*$^+$ + e$^-$ observed as a consequence of process b. ^{d} No peak observed under stated experimental conditions. ^{e} A second irreversible oxidation process was also observed at 1.06 V.

(OMe)$_3$)$_3$. (Compare parts a and b of Figure 2 (supplementary material).) On the first reverse scan and in subsequent cycles the redox couple
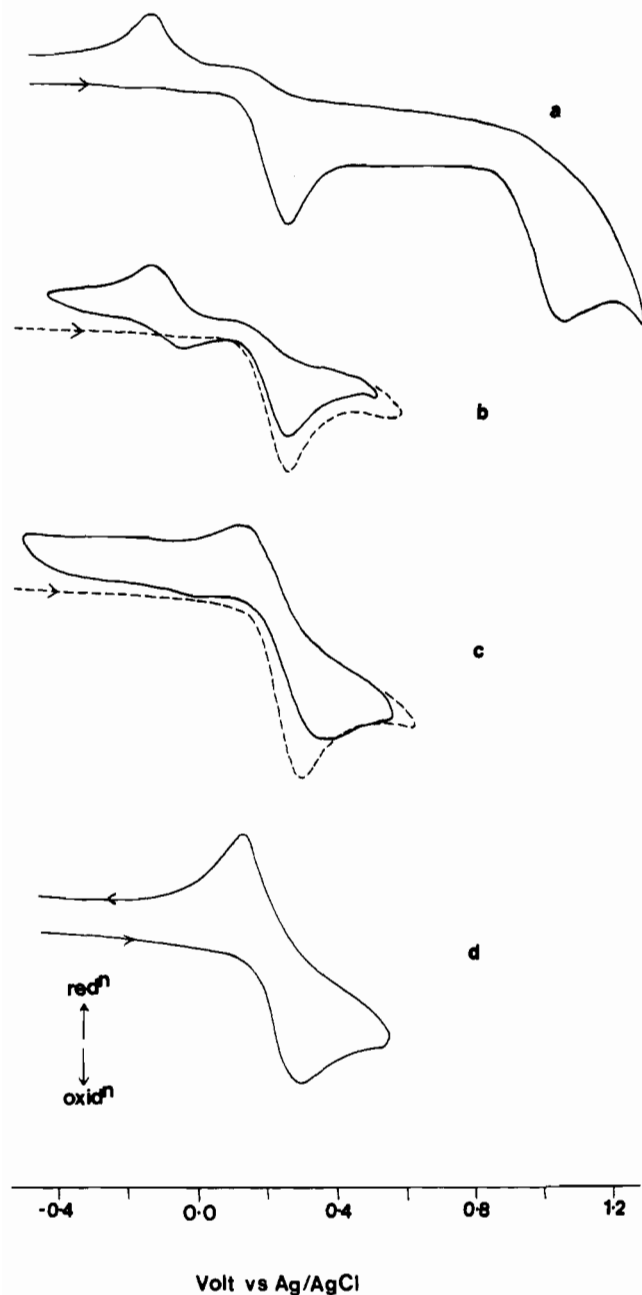
$$mer\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ + e^- \rightleftharpoons$$
$$mer\text{-}Cr(CO)_3(P(OMe)_3)_3 \quad (5)$$
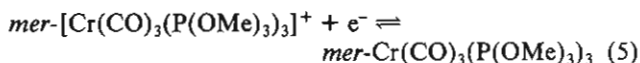
was observed (identical with that for *mer*-Cr(CO)$_3$(P-(OMe)$_3$)$_3$) as well as the wave at 0.56 V. This demonstrated that an isomerization process occurred after the electron transfer, and the process may be written in its simplest form as
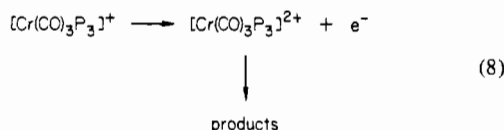
$$fac\text{-}Cr(CO)_3(P(OMe)_3)_3 \rightleftharpoons$$
$$fac\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ + e^- \quad (6)$$

$$fac\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ \xrightarrow{k}$$
$$mer\text{-}[Cr(CO)_3(P(OMe)_3)_3]^+ \quad (7)$$

In the cyclic voltammetry of *fac*-Cr(CO)$_3$(PMe$_2$Ph)$_3$, similar processes to those described above for *fac*-Cr(CO)$_3$(P(OMe)$_3$)$_3$ were observed even though *mer*-Cr(CO)$_3$(PMe$_2$Ph)$_3$ has not been isolated. However, the assignment for the new couple was confirmed by reductive cyclic voltammetry on isolated *mer*-[Cr(CO)$_3$(PMe$_2$Ph)$_3$]ClO$_4$. These results demonstrate that *mer*-Cr(CO)$_3$(PMe$_2$Ph)$_3$ can exist in solution at least on the time scale of the electrochemical experiments.

Cyclic Voltammetry at a Platinum Electrode. Table III summarizes the data for the oxidative cyclic voltammetry at a platinum electrode for the complexes *mer*-Cr(CO)$_3$P$_3$. Figure 3 (supplementary material) shows the cyclic voltammogram of *mer*-Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$. The constant surface area of the platinum electrode made the degree of chemical reversibility easier to measure than for the growing-mercury-drop electrode. The ratio of oxidation and reduction currents was close to unity at all scan rates, implying that the oxidation products were stable on the time scale of cyclic voltammetry. A second irreversible 1-electron oxidation step was observed for *mer*-Cr(CO)$_3$(P(OMe)$_3$)$_3$ and *mer*-Cr-(CO)$_3$(P(OMe)$_2$Ph)$_3$ (Table III). No chemical reversibility could be observed for this step at temperatures down to -78 °C even in the presence of excess ligand or under an atmo-

Figure 4. Cyclic voltammograms for the oxidation of a 10^{-3} M solution of fac-Cr(CO)₃(PMe₂Ph)₃ in dichloromethane (0.1 M Bu₄NClO₄; scan rate 100 mV/s): (a) 18 °C; (b) 18 °C without second oxidation process; (c) −43 °C; (d) −57 °C.

Table V. Cyclic Voltammetric Data for Oxidation of fac-Cr(CO₃)₃(P(OMe)₃)₃ at a Platinum Electrode at Variable Temperatures and Scan Rates in CH₂Cl₂ (0.1 M Bu₄NClO₄)[a]

temp, °C	scan rate, mV/s	$E_p^{ox,b}$ V vs. Ag/AgCl	$E_p^{red,b}$ V vs. Ag/AgCl	$E_p^{ox,c}$ V vs. Ag/AgCl	$E_p^{red,c}$ V vs. Ag/AgCl
22	500	0.600	≈0.48	0.403	0.258
	200	0.545	≈0.47	0.385	0.275
	100	0.525	d	0.360	0.300
	50	0.510	d	0.350	0.317
3	500	0.62	≈0.45	0.425	0.275
	200	0.565	≈0.47	0.415	0.295
	100	0.555	d	0.395	0.310
	50	0.543	d	0.365	0.323
−28	500	0.640	0.430	0.390	0.290
	200	0.610	0.455	0.415	0.315
	100	0.587	0.470	0.420	0.325
	50	0.582	0.472	0.400	0.327
−50	500	0.662	0.433	d	d
	200	0.635	0.458	d	d
	100	0.617	0.472	d	d
	50	0.603	0.484	d	d

[a] A second irreversible oxidation process was also observed at 1.46 V. Symbols as in Table IV.

mer^+ was observed. This indicated that, once formed, mer^0 can exist in a mixture with the fac^0 isomer. This ready generation of the mer^0 isomer is an important aspect of the ESR spectroscopic measurements (see below). All data reported, therefore, refer to freshly prepared solutions. Figure 4c shows that at −43 °C very little isomerization occurs and at −57 °C (Figure 4d) no isomerization was detected, confirming that the fac^+ isomer can exist at low temperatures. Thus, at low temperature the electrode process can be represented by eq 9. Table IV summarizes the data for fac-Cr(CO)₃(PMe₂Ph)₃

$$fac^0 \rightleftharpoons fac^+ + e^- \qquad (9)$$

at a range of temperatures. At low temperatures the rate of electron transfer, k_s, was slowed down leading to larger peak to peak separations in cyclic voltammograms.

Data for fac-Cr(CO)₃(P(OMe)₃)₃ are summarized in Table V. The separation of the $E_{1/2}$ values for the $fac^{+/0}$ and $mer^{+/0}$ couples was much smaller than for the Cr(CO)₃P(Me₂Ph)₃ system.

The electrochemical data provide strong evidence that the mer^+ isomer was formed after oxidation of both fac-Cr-(CO)₃(PMe₂Ph)₃ and fac-Cr(CO)₃(P(OMe)₃)₃, although spectroscopic evidence was required to confirm all details. The electrochemical behavior was similar in both acetone and acetonitrile, implying that the solvent did not play a dominant role in either thermodynamic or kinetic aspects of the redox process. This is a characteristic of intramolecular isomerization reactions as noted for dicarbonyl complexes.[12]

Electrochemistry of the Product of Electrolysis. Oxidative controlled-potential electrolysis or chemical oxidation of Cr-(CO)₃P₃ with AgClO₄, NOBF₄, or NOPF₆ in an electrochemical cell produced a product with electrochemical behavior consistent with the electrode processes discussed above. Figure 5 (supplementary material) shows current-sampled polarographic monitoring of the NOBF₄ oxidation of mer-Cr-(CO)₃(P(OMe)₂Ph)₃ with increasing concentration of NOBF₄. As expected for a reversible process, the 1-electron oxidation converted to a 1-electron reduction with the same $E_{1/2}$ value.

An authentic sample of mer-[Cr(CO)₃(P(OMe)₂Ph)₃]⁺ exhibited electrochemical behavior identical with that produced by in situ generation. Under polarographic conditions a reversible 1-electron reduction was observed at the same $E_{1/2}$ as the oxidation of mer-Cr(CO)₃(P(OMe)₂Ph)₃. A reductive cyclic voltammetric experiment on mer-[Cr(CO)₃(P-(OMe)₂Ph)₃]⁺ClO₄ at a platinum electrode was conducted in the following manner. The initial potential was set at 1.0 V

sphere of CO gas and with scan rates of up to 5 V s⁻¹. The formally chromium(II) cation formed was very reactive as it was generated at very positive potentials. This oxidation process has not been characterized but can be written as

$$[Cr(CO)_3P_3]^+ \longrightarrow [Cr(CO)_3P_3]^{2+} + e^-$$

$$\downarrow \qquad (8)$$

$$products$$

At room temperature, fac-Cr(CO)₃(PMe₂Ph)₃ showed cyclic voltammetric behavior at platinum similar to that described above for mercury, except for a second 1-electron irreversible oxidation step at a more positive potential (Figure 4a). For a fresh solution there was no evidence of any mer compound on the first oxidative scan (Figure 4b), but after several cyclic voltammograms had been performed on the same solution a small oxidation peak corresponding to oxidation of mer^0 to

(relative to Ag/AgCl) where no current flowed. Scanning toward 0.0 V produced a reduction current (peak potential, E_p^{red}), and on the reverse positive direction scan the corresponding 1-electron oxidation wave (E_p^{ox}) was observed. The positions of E_p^{ox} and E_p^{red} were coincident with those observed commencing with the mer^0 compound (Figure 2, supplementary material). Thus, the reduction process is

$$mer^+ + e^- \rightleftharpoons mer^0 \qquad (10)$$
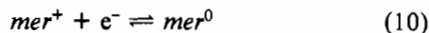
This assignment was unequivocally confirmed by scanning in the positive potential direction from 1.0 V and observing the chromium(I) → chromium(II) oxidation (eq 8). Similar results were obtained for the other mer^+ compounds.

For the complexes mer-[Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$]ClO$_4$ and mer-[Cr(CO)$_3$(PMe$_2$Ph)$_3$]ClO$_4$ the cyclic voltammograms showed no evidence for the $fac^{+/0}$ couple even after many cycles.

Current-sampled polarographic monitoring of the NOBF$_4$ oxidation of fac-Cr(CO)$_3$(P(OMe)$_3$)$_3$ is shown in Figure 6. Figure 6a shows the polarographic oxidation wave ($E_{1/2}$ = 0.43 V (vs. Ag/AgCl) of fac-Cr(CO)$_3$(P(OMe)$_3$)$_3$ before the addition of any oxidant. Figure 6b shows the polarographic oxidation 5 min after the addition of NOBF$_4$. A new wave appeared with an $E_{1/2}$ value of 0.35 V, which is the $E_{1/2}$ for the $mer^{+/0}$ couple. This new wave had both reductive and oxidative components, showing that the mer^+ isomer had been generated as a product and that mer^0 was also present in the solution. In Figure 6c the major species was the mer^0 isomer, and in Figure 6d, 20 min after the addition of NOBF$_4$, only the $mer^{+/0}$ couple was observed and no fac-Cr(CO)$_3$(P-(OMe)$_3$)$_3$ remained. Ultimately only the mer^+ isomer was present in solution since the polarographic wave became completely reductive in nature. The cation [Cr(CO)$_3$(P-(OMe)$_3$)$_3$]$^+$ generated by oxidative controlled-potential electrolysis with polarographic monitoring showed the same behavior. The polarographic monitoring of the oxidation of fac-Cr(CO)$_3$(PMe$_2$Ph)$_3$ gave similar results except that a much smaller proportion of the mer^0 isomer was observed as an intermediate.

The direct conversion $fac^0 \rightarrow mer^0$ does not occur on the time scale of these oxidation experiments for either fac-Cr-(CO)$_3$(P(OMe)$_3$)$_3$ or fac-Cr(CO)$_3$(PMe$_2$Ph)$_3$, as shown by electrochemical, infrared, and NMR measurements in dichloromethane at room tempearture. Therefore, the mer^+ species is an essential component of the pathway, generating the mer^0 isomer as an intermediate in the oxidation step.

Since the E° ($\approx E_{1/2}$) for the $fac^{+/0}$ redox couple occurs at a more positive potential than the E° for the $mer^{+/0}$ couple, it follows that the reaction

$$fac^0 + mer^+ \xrightleftharpoons{K_1} fac^+ + mer^0 \qquad (11)$$
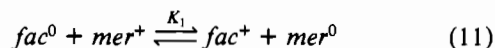
where K_1 is an equilibrium constant lies substantially to the left for the Cr(CO)$_3$(P(OMe)$_3$)$_3$ and Cr(CO)$_3$(PMe$_2$Ph)$_3$ systems in a thermodynamic sense.

Thermodynamically the equilibrium constant for the reaction

$$fac^+ \xrightleftharpoons{K_2} mer^+ \qquad (12)$$

lies substantially to the right, but the equilibrium

$$fac^0 \xrightleftharpoons{K_3} mer^0 \qquad (13)$$

can lie to the left or the right depending on the identity of the ligand. Consequently, after oxidation to the fac^+ isomer, isomerization occurs rapidly to generate the mer^+ species. Under these conditions mer^0 may be produced via the cross-redox reaction between fac^0 and mer^+ (eq 11) even though the reaction in eq 13 is not thermodynamically favored. A possible reaction mechanism for generation of the mer^0 species is shown
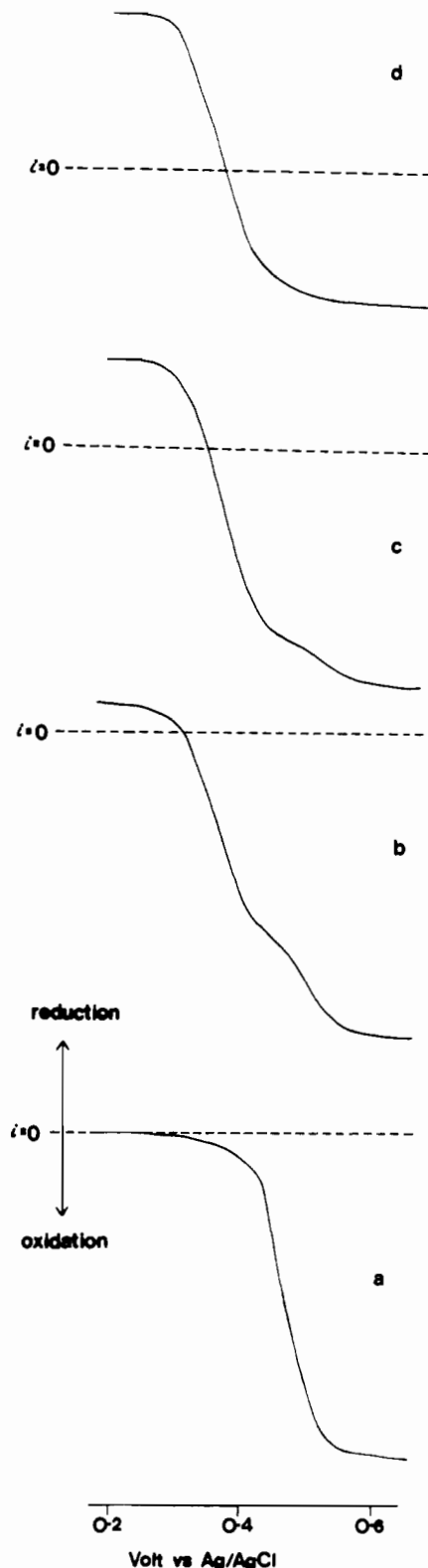

Figure 6. Current-sampled dc polarograms in dichloromethane (0.1 M Bu$_4$NClO$_4$) at 18 °C for an initially 10^{-3} M solution of fac-Cr-(CO)$_3$(P(OMe)$_3$)$_3$ with increasing concentration of NOBF$_4$ (drop time 0.5 s).

in Scheme I. More of the mer^0 isomer was seen as an intermediate in the oxidation of fac-Cr(CO)$_3$(P(OMe)$_3$)$_3$ than in the case of fac-Cr(CO)$_3$(PMe$_2$Ph)$_3$ because the equilibrium constant, K_1, is smaller for Cr(CO)$_3$(P(OMe)$_3$)$_3$, K_1 being a measure of the difference between the E°'s of the $fac^{+/0}$ and $mer^{+/0}$ couples. Furthermore, the equilibrium process

$$fac^0 \xrightleftharpoons{K_3} mer^0$$

Scheme I

$$fac^0 + mer^+ \xrightleftharpoons{\text{fast}} mer^0 + fac^+$$
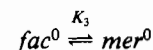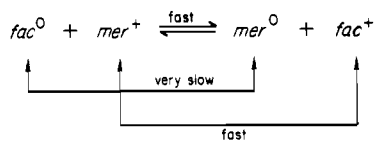
is more favored for this complex. The observation of the mer^0 complex as an intermediate via a cross-redox reaction must be the result of a kinetic barrier in the reaction mechanism since the concentration of mer^0 at equilibrium would be extremely small. It is of course possible that some form of catalysis induced by light or a trace impurity such as water may also be operative. Ultimately, of course, the mer^+ complex will be the product of oxidation since any oxidant (or controlled potential) sufficiently strong to oxidize fac^0 will also be able to oxidize mer^0, both oxidation steps leading to mer^+. If electrochemical oxidation is used instead of a chemical oxidant the additional kinetic parameters describing the heterogeneous electron transfer must be incorporated into Scheme II, where (k_s) represents the heterogeneous charge-transfer rate constant 1 or 2, α_n is the charge-transfer coefficient of the electrode process, k_n and k_{-n} are homogeneous rate constants for isomerization steps, and the crossed arrows represent the cross-redox reaction

$$fac^+ + mer^0 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} fac^0 + mer^+$$
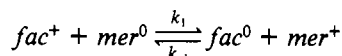
with k_1 and k_{-1} being second-order homogeneous rate constants.

NMR Spectra of the Chromium(0) Compounds. The ³¹P and ¹³C NMR data are given in Table I. For fac-Cr(CO)₃-(P(OMe)₃)₃ and fac-Cr(CO)₃(PMe₂Ph)₃ the ³¹P{¹H} NMR spectra showed a singlet and the ¹³C{¹H} NMR spectra of the carbonyl groups showed a complex multiplet due to coupling the magnetically inequivalent phosphorus nuclei. The ³¹P NMR spectra of the mer compounds showed varying degrees of second-order effects. The spectra were quite readily solved as A₂B types. In the carbonyl region, the ¹³C spectra consisted of two multiplets, one at lower frequency of intensity 2 and one at higher frequency of intensity 1. For Cr(CO)₃(P-(OMe)₃)₃ the ³¹P NMR spectrum of a mixture of fac and mer isomers showed separate signals. All these data show that both the fac^0 and mer^0 isomers are rigid on the NMR time scale.

ESR Spectra of [Cr(CO)₃P₃]⁺ and Exchange Reactions for the [Cr(CO)₃P₃]⁺/⁰ System. The ESR data are given in Table I. The ESR spectrum of mer-[Cr(CO)₃(PMe₂Ph)₃]⁺ at 273 and 233 K in dichloromethane are shown in Figure 7A. The spectra were essentially similar at the two temperatures although better resolution was obtained at 233 K. The spectrum can be interpreted as a doublet of triplets due to ³¹P hyperfine coupling and is consistent with a mer chromium(I) cation. No hyperfine coupling to chromium (⁵³Cr, $I = {}^3/_2$, 9.55%) was observed. Figure 7B shows the ESR spectra at various temperatures for the mer-[Cr(CO)₃(P(OMe)₂Ph)₃]⁺ cation. At room temperature the signal was a broad singlet, and at lower temperatures a relatively well-resolved spectrum was observed. It has been shown that electron transfer between [Cr(η⁶-arene)₂]⁺ and Cr(η⁶-arene)₂[24,25] or [Cr(bpy)₃]⁺ and Cr(bpy)₃[26] causes spectral changes of just this type. Thus, it is suggested that the spectrum at room temperaature is the fast exchange limit and at low temperatures the slow exchange limit for the electron transfer between mer-[Cr(CO)₃(P(OMe)₂Ph)₃]⁺ and traces of mer-Cr(CO)₃(P(OMe)₂Ph)₃, which are always

(24) Elschenbroich, C.; Zenneck, U. *J. Organomet. Chem.* **1978**, *160*, 125.
(25) (a) Li, T. T-T.; Brubaker, C. H., Jr. *J. Organomet. Chem.* **1981**, *216*, 223. (b) Li, T. T-T.; Weaver, M. J.; Brubaker, C. H., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 2381.
(26) Saji, T.; Aoyagui, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2101.
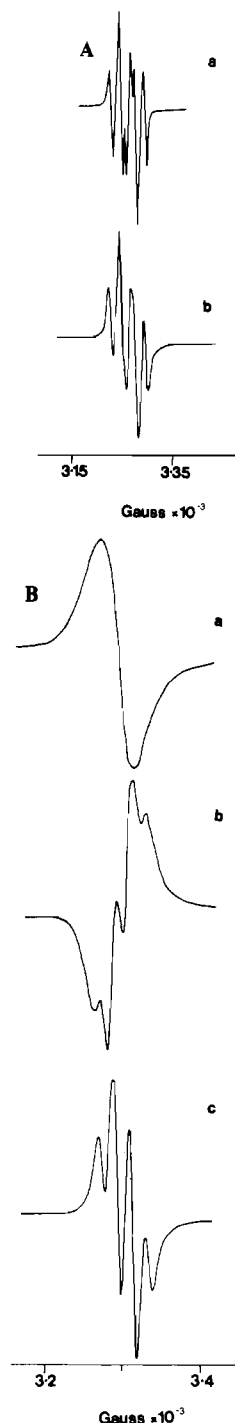
**Figure 7.** ESR spectra of (A) mer-[Cr(CO)₃(PMe₂Ph)₃]⁺ at (a) 273 K and (b) 213 K and (B) mer-[Cr(CO)₃(P(OMe)₂Ph)₃]⁺ at (a) 298 K, (b) 273 K, and (c) 213 K in dichloromethane.

present in the solution, since reaction with light and/or moisture generates the chromium(0) complex. Electron transfer between oxidized and reduced components would only be fast on the ESR time scale if the oxidized and reduced species are isostructural.[27] In the case of the Cr(CO)₃(P-(OMe)₂Ph)₃ system, the mer isomer is favored in both the 18- and 17-electron complexes and therefore fast electron transfer leading to line broadening in the ESR spectrum according to

$$mer^+ + mer^{0*} \xrightleftharpoons{\text{very fast}} mer^0 + mer^{+*} \qquad (14)$$
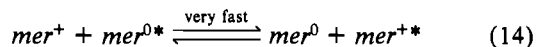
is very likely to occur. In contrast, the fac isomer of Cr-(CO)₃(PMe₂Ph)₃ is the thermodynamically favored form for
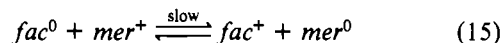
(27) Libby, W. F. *J. Phys. Chem.* **1952**, *56*, 863.

Scheme II
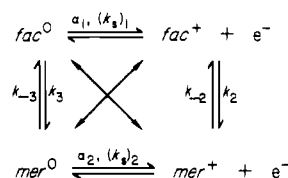
the 18-electron complex, whereas the *mer* isomer is favored in the 17-electron complex and hence the electron transfer (cross-redox reaction)

$$fac^0 + mer^+ \xrightarrow{\text{slow}} fac^+ + mer^0 \qquad (15)$$

that may occur under these conditions will have different thermodynamic constraints and is likely to be slow on the ESR time scale. This explains why the ESR spectrum of *mer*-[Cr(CO)$_3$(PMe$_2$Ph)$_3$]$^+$ is sharp.

In order to confirm the above hypothesis, *fac*-Cr(CO)$_3$-(PMe$_2$Ph)$_3$ was added to a solution of *mer*-[Cr(CO)$_3$-(PMe$_2$Ph)$_3$]$^+$. No change was observed in the spectrum even at large molar concentrations of the *fac*^{0} isomer relative to the *mer*$^+$ isomer. Similarly, addition of *fac*-Cr(CO)$_3$(P(OMe)$_3$)$_3$ to *mer*-[Cr(CO)$_3$(P(OMe)$_3$)$_3$]$^+$ produced only a very small amount of line broadening in the ESR spectrum,[28] but addition of *mer*-Cr(CO)$_3$(P(OMe)$_3$)$_3$ caused the spectrum to broaden to a much greater extent, as expected with a second-order homogeneous electron-transfer reaction. Figure 8 shows the effect of adding increasing amounts of *mer*-Cr(CO)$_3$(P-(OMe)$_3$)$_3$ to *mer*-[Cr(CO)$_3$(P(OMe)$_3$)$_3$]$^+$ at 233 K. The other complexes that were isolated in the *mer* isomeric form in both oxidation states showed the same evidence for electron-transfer phenomena in their ESR spectra.
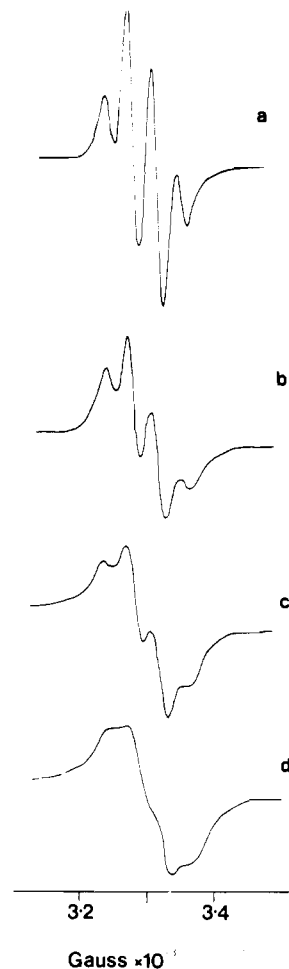
Study of the Exchange for the [Cr(CO)$_3$P$_3$]$^{+/0}$ System by ^{1}H NMR. To further illustrate the exchange reactions discussed in the previous section, proton NMR experiments on the [Cr(CO)$_3$P$_3$]$^{+/0}$ system were performed for P = P-(OMe)$_2$Ph and PMe$_2$Ph in CDCl$_3$.

The ^{1}H{^{31}P} NMR of *mer*-Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$ consisted of two signals (δ 3.45, intensity 2; δ 3.30, intensity 1) with full width at half-height ($w_{1/2}$) of about 1 Hz. Addition of small amounts of the compound *mer*-[Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$]$^+$ caused line broadening of these two resonances and a shift to higher frequency. Further additions of the chromium(I) compound enhanced the line broadening and shift to higher frequency. A solution of *mer*-[Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$]$^+$ alone gave a resonance at approximately δ 5.6 ($w_{1/2}$ = 340 Hz; the two resonances could not be resolved). In accordance with the work of Elschenbroich and Zennick[24] the observed spectra represent the fast exchange limit on the NMR time scale between *mer*-[Cr(CO)$_3$(P(OMe)$_2$Ph)$_3$]$^+$ and *mer*-Cr(CO)$_3$-(P(OMe)$_2$Ph)$_3$, and these results are consistent with the ESR data after allowance is made for the different time domains.

In contrast, addition of *mer*-[Cr(CO)$_3$(PMe$_2$Ph)$_3$]$^+$ to *fac*-Cr(CO)$_3$(PMe$_2$)Ph)$_3$ (δ 1.41) did not lead to the observation of exchange even with a large excess of the chromium(I) compound.[29] Thus, the cross-redox exchange reaction (eq 15) is slow on NMR time scale, and the data are consistent with the observations made with ESR and electrochemical techniques.

Conclusions

Examination of the [Cr(CO)$_3$P$_3$]$^{+/0}$ redox couple by electrochemical and spectroscopic techniques reveals: (1) All of

(28) The ^{31}P spectrum of *fac*-Cr(CO)$_3$(P(OMe)$_3$)$_3$ in CH$_2$Cl$_2$ always shows the presence of a trace of the *mer*^{0} complex.

(29) Although no chemical exchange was observed, the expected paramagnetic broadening occurred at large concentrations of *mer*-[Cr(CO)$_3$-(PMe$_2$Ph)$_3$]$^+$. The internal reference and the ^{1}H{^{31}P} resonance of the compound broadened at the same rate verifying that the process involved was not chemical exchange.

3·2   3·4

Gauss ×10

Figure 8. ESR spectrum in dichloromethane of *mer*-[Cr(CO)$_3$(P-(OMe)$_3$)$_3$]$^+$ at 233 K is shown before the addition of *mer*-Cr-(CO)$_3$(P(OMe)$_3$)$_3$ (a) and after the addition of approximately a 1 molar quantity (b), 3 molar quantity (c), and large excess (d) of *mer*-Cr(CO)$_3$(P(OMe)$_3$)$_3$.

the moieties *mer*^{0}, *mer*$^+$, *fac*^{0}, and *fac*$^+$ are important in the redox chemistry. (2) Heterogeneous electron transfer is rapid and occurs between isostructural *mer*$^{+/0}$ or *fac*$^{+/0}$ redox couples. (3) The 17-electron system is kinetically labile with respect to the 18-electron situation in that *fac*$^+$ → *mer*$^+$ isomerization occurs rapidly whereas the *fac*^{0} → *mer*^{0} isomerization processes are very slow. Both the *fac*^{0} and *mer*^{0} isomers are rigid on the NMR time scale. (4) The homogeneous reaction *fac*^{0} + *mer*$^+$ ⇌ *fac*$^+$ + *mer*^{0} contributes to the electrochemical oxidation of the *fac*^{0} complexes. (5) The electron-exchange homogeneous reaction *mer*$^+$ + *mer*^{0}* ⇌ *mer*^{0} + *mer*$^+$* is extremely fast. (6) Structural change accompanying the oxidation, *mer*-Cr(CO)$_3$P$_3$ to *mer*-[Cr-(CO)$_3$P$_3$]$^+$, are probably very small whereas those accompanying oxidation of *fac*-Cr(CO)$_3$P$_3$ are obviously large, with an intramolecular isomerization following charge transfer.