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EPR Study of Photochemical Reactions of *fac*- and *mer*-$[Cr(CO)_3(\eta^1\text{-}L_2)(\eta^2\text{-}L_2)]^+$ (L_2 = Bidentate Phosphine, Arsine, or Phosphonite Ligand)

Anne L. Rieger and Philip H. Rieger*

Department of Chemistry, Brown University, Providence, Rhode Island 02912

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Rearrangement of *fac*-$[Cr(CO)_3(\eta^2\text{-}L_2)(\eta^1\text{-}L_2)]^+$ to *mer*-$[Cr(CO)_3(\eta^2\text{-}L_2)(\eta^1\text{-}L_2)]^+$ (L_2 is a bidentate phosphine or arsine ligand) is a rapid thermally activated process. Loss of CO from *mer*-$[Cr(CO)_3(\eta^2\text{-}L_2)(\eta^1\text{-}L_2)]^+$ to form *trans*-$[Cr(CO)_2(\eta^2\text{-}L_2)_2]^+$ is shown to be a clean photochemical process, perhaps the first example of a quantitative photochemical transformation for a Cr(I) complex. The bidentate phosphonite ligand, $L_2 = (MeO)_2PCH_2CH_2P(OMe)_2$, behaves quite differently: *fac*-$[Cr(CO)_3(\eta^2\text{-}L_2)(\eta^1\text{-}L_2)]^+$ undergoes photochemical loss of CO to form a five-coordinate complex which converts slowly via thermal activation to *trans*-$[Cr(CO)_2(\eta^2\text{-}L_2)_2]^+$.

Introduction

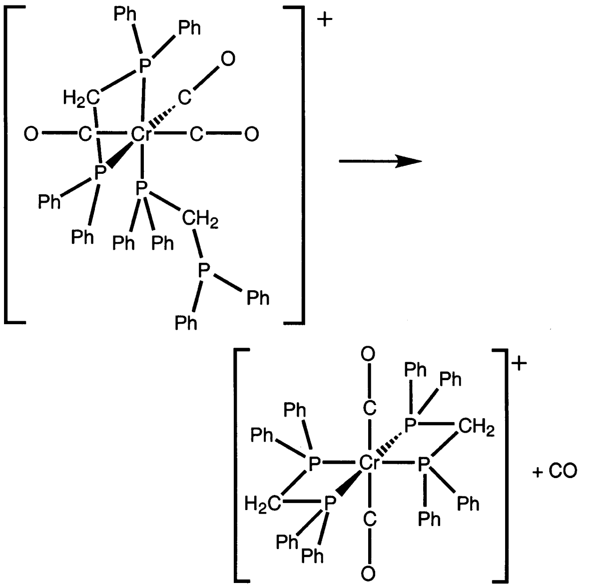
Over the course of two decades, Bond, Colton, and coworkers[1] made many electrochemical and EPR spectroscopic contributions to the chemistry of chromium(I) carbonyl phosphine, arsine, and phosphite complexes. For example, we know from the work of Bagchi, Bond, and Colton[2] that *fac*-$[Cr(CO)_3L_3]$ (L = phosphine, phosphite) is stable in the Cr(0) state but that the Cr(I) complex rapidly rearranges to the meridional conformation:

$$fac\text{-}[Cr(CO)_3L_3]^+ \rightarrow mer\text{-}[Cr(CO)_3L_3]^+ \qquad (1)$$

Rate constants for the isomerization of two complexes were measured, and analysis of the data leads to the following activation parameters: for $L = PPhMe_2$, $\Delta H^\ddagger = 9 \pm 2$ kJ mol^{-1} and $\Delta S^\ddagger = -226 \pm 8$ J mol^{-1} K^{-1}; for $L = P(OMe)_3$, $\Delta H^\ddagger = 11 \pm 1$ kJ mol^{-1} and $\Delta S^\ddagger = -220 \pm 3$ J mol^{-1} K^{-1}. These parameters show that little bond stretching is involved in the isomerization, but the large loss of entropy indicates that a very specific conformation is required: i.e., the transition state is very crowded, even for monodentate phosphines and phosphites.

Several mysteries remained from the work of Bond and Colton. We have recently provided an explanation for the failure to observe isotropic EPR spectra of *fac*-$[Cr(CO)_3L_3]^+$ or *cis*-$[Cr(CO)_2L_4]^+$,[3] but there are still a number of unsolved problems related to the mechanisms of Cr(I) reactions.

With the mechanism in mind, our attention was drawn to the reaction which converts *mer*-$[Cr(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})]^+$ to *trans*-$[Cr(CO)_2(\eta^2\text{-dppm})_2]^+$ with loss of CO:



(2)

Blagg et al.[4] reported that reaction 2 could be followed over the course of 100 min by observation of the EPR spectra of the complexes. A substantial loss of signal intensity over the course of the reaction was attributed to the disproportionation reaction

$$2\ mer\text{-}[Cr(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})]^+ \rightarrow mer\text{-}[Cr(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})] + mer\text{-}[Cr(CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})]^{2+}$$

with the dication decaying rapidly to EPR-inactive

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Table 1. Infrared Data

complex	ν/cm^{-1} obsd[a]	ν/cm^{-1} lit.[b]
mer-[Cr(CO)$_3$(η^1-dppm) (η^2-dppm)]	1948, 1850, 1830 sh	1950 w, 1850 1830 sh[d]
mer-[Cr(CO)$_3$(η^1-dppm) (η^2-dppm)]$^+$	2031 w, 1971, 1912	2036, 1972, 1912[c]
trans-[Cr(CO)$_2$(η^2-dppm)$_2$]$^+$	1871	1869[f]
fac-[Cr(CO)$_3$(η^1-dppe) (η^2-dppe)]	1927, 1836 br	1928, 1835[d]
mer-[Cr(CO)$_3$(η^1-dppe) (η^2-dppe)]		1955 w, 1850, 1830 sh[d]
mer-[Cr(CO)$_3$(η^1-dppe) (η^2-dppe)]$^+$	1965 w, 1909 br	1965 w, 1910, 1900 sh[d] (?)
trans-[Cr(CO)$_2$(η^2-dppe)$_2$]$^+$	1849	1850[g]
mer-[Cr(CO)$_3$(η^1-arphos) (η^2-arphos)]	1950 w, 1850, 1830 sh	1960 w, 1855, 1835 sh[e]
mer-[Cr(CO)$_3$(η^1-arphos) (η^2-arphos)]$^+$	2029, 1951, 1909	1970 w, 1915, 1895[e]
trans-[Cr(CO)$_2$(η^2-arphos)$_2$]$^+$	1850	
fac-[Cr(CO)$_3$(η^1-dpae) (η^2-dpae)]	1927, 1832	1930, 1830 br[e]
mer-[Cr(CO)$_3$(η^1-dpae) (η^2-dpae)]$^+$	2029w, 1925, 1911	
trans-[Cr(CO)$_2$(η^2-dpae)$_2$]$^+$	1851	
fac-[Cr(CO)$_3$(η^1-dmpm) (η^2-dmpm)]	1919, 1824	
mer-[Cr(CO)$_3$(η^1-dmpm) (η^2-dmpm)]$^+$	2029, 1961, 1896	
trans-[Cr(CO)$_2$(η^2-dmpm)$_2$]$^+$	1828	
mer-[Cr(CO)$_3$(η^1-dmpe) (η^2-dmpe)]	1919, 1826, 1817 sh	
mer-[Cr(CO)$_3$(η^1-dmpe) (η^2-dmpe)]$^+$	2023, 1952, 1900	
trans-[Cr(CO)$_2$(η^2-dmpe)$_2$]$^+$	1842	
mer-[Cr(CO)$_3$(η^1-dppbz) (η^2-dppbz)]	2008 w, 1853, 1824 sh	
mer-[Cr(CO)$_3$(η^1-dppbz) (η^2-dppbz)]$^+$	2031 w, 1907, 1882 sh	
trans-[Cr(CO)$_2$(η^2-dppbz)$_2$]$^+$	1858	
fac-[Cr(CO)$_3$(η^1-pompom) (η^2-pompom)]	1948, 1868	
fac-[Cr(CO)$_3$(η^1-pompom) (η^2-pompom)]$^+$	1967, 1871	
[Cr(CO)$_2$(η^1-pompom) (η^2-pompom)]$^+$	2011 w, 1869	
trans-[Cr(CO)$_2$ (η^2—pompom)$_2$]$^+$	1892	
mer,mer-[{Cr(CO)$_3$(η^2-dppe)}$_2$(μ-dppe)]	1950 w, 1850, 1835	1950, 1850, 1834 sh
mer,mer-[{Cr(CO)$_3$(η^2-dppe)}$_2$(μ-dppe)]$^+$	2029 w, 1957, 1909	

[a] In $CH_2Cl_2/C_2H_4Cl_2$ solution unless otherwise noted. [b] In CH_2Cl_2 solution unless otherwise noted. [c] Reference 4. [d] Reference 11. [e] Reference 5. [f] Reference 17. [g] Reference 18. [h] Reference 12. [i] Obtained by ferrocenium oxidation in a dry ice/acetone slush bath.

products. This explanation seems unlikely since, from electrochemical studies,[5] we know that $\Delta G° = 1.09$ eV (105 kJ mol^{-1}) for the disproportionation step. Subsequent experiments by Bond, Colton, and co-workers[5] showed that solutions of *mer*-[Cr(CO)$_3$(η^2-dppm)(η^1-dppm)]$^+$ were stable indefinitely when kept in the dark in a sealed tube, but the reaction was found to occur when the tube was opened or purged with argon. These authors[6] later showed that the oxidation of *fac*-[Mn(CO)$_3$(dppm)Cl] involves a photochemical *fac* → *mer* rearrangement of the Mn(I) species prior to oxidation:

$$\textit{fac}\text{-}[\mathrm{Mn(CO)_3(dppm)Cl}] \xrightarrow{h\nu} \textit{mer}\text{-}[\mathrm{Mn(CO)_3(dppm)Cl}] \rightarrow \textit{mer}\text{-}[\mathrm{Mn(CO)_3(dppm)Cl}]^+ + e^- \quad (3)$$

This result suggests that some reactions of Cr(I) complexes could be photochemical. We will show below that reaction 2, and related reactions of many Cr(I) carbonyl phosphine and arsine complexes, are indeed photochemical in nature and proceed virtually quantitatively under controlled conditions. Photochemical substitution reactions have been reported for 18-electron complexes such as Cr(CO)$_6$,[7] but this may be the first report of a quantitative photochemical reaction of a 17-electron chromium complex.

Experimental Section

Materials. Chlorinated solvents were distilled from calcium hydride under nitrogen. Hydrocarbons were dried over sodium. Diethyl ether was distilled from sodium benzophenone ketyl under nitrogen. Acetone was dried over potassium carbonate and distilled from potassium permanganate. Other solvents were used as supplied.

[Cr(CO)$_6$], [(C$_7$H$_8$)Cr(CO)$_3$], Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe), Ph$_2$PCH$_2$PPh$_3$ (dppm), Me$_2$PCH$_2$PMe$_2$ (dmpm), Me$_2$PCH$_2$CH$_2$PMe$_2$ (dmpe), 1,2-(Ph$_2$P)$_2$C$_6$H$_4$ (dppbz), and Ph$_2$AsCH$_2$CH$_2$AsPh$_2$ (dpae) were obtained from Aldrich or Strem, and Ph$_2$PCH$_2$CH$_2$AsPh$_2$ (arphos) was obtained from Pressure Chemical Co. (MeO)$_2$PCH$_2$CH$_2$P(OMe)$_2$ (pompom) was prepared by the method of King and Rhee[8,9] from Cl$_2$PCH$_2$CH$_2$PCl$_2$ (Strem). Ferrocenium tetrafluoroborate was prepared as described by Connelly and Geiger.[10] (*p*-Nitrophenyl)diazonium tetrafluoroborate (Aldrich) was recrystallized from acetone/diethyl ether.

The Cr(0) complexes were prepared by literature methods[5,6,11] or small variations thereon. All operations were performed under argon using either Schlenk techniques or a Vacuum Atmospheres drybox. The identities of the Cr(0) complexes were confirmed by mass and infrared spectra. Cr(I) complexes were prepared by ferrocenium or diazonium oxidation of Cr(0) complexes. Carbonyl stretching frequencies for the Cr(0) and Cr(I) complexes are given in Table 1. *mer,mer*-[{Cr(CO)$_3$(η^2-dppe)}$_2$(μ-dppe)] was prepared by a modification of the reported synthesis.[12] A 4:1 mixture of dppe and [(C$_7$H$_8$)Cr(CO)$_3$] was refluxed for 14 h in hexane. The supernatant was removed by needle under Ar. The solid was transferred to a Soxhlet extractor under Ar and extracted with hexane for 48 h. The extract contained mostly dppe. The extractor was then charged with degassed CH$_2$Cl$_2$ and the complex extracted into the solvent. The identity of the complex was confirmed by its infrared (Table 1) and mass spectra.

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Table 2. EPR Parameters[a]

complex	isotropic[a]	g	A
mer-[Cr(CO)$_3$(η^2-dppm)(η^1-dppm)]$^+$	2.016	2.034	24 (3 P)
	22.8 (1 P)	2.034	24
	19.6 (2 P)	1.982	21.1
trans-[Cr(CO)$_2$(η^2-dppm)$_2$]$^{+\,b}$	2.004	2.031	26.4 (4 P)^e
	25.82 (4 P)	2.014	25.0
		1.973	25.5
mer-[Cr(CO)$_3$(η^2-dppe)(η^1-dppe)]$^+$	2.025	[2.055]^c	[22.9] (3 P)^c
	22.7 (3 P)	2.037	22.0
		1.983	23.2
trans-[Cr(CO)$_2$(η^2-dppe)$_2$]$^{+\,b}$	2.015	2.027	28.5 (4 P)^e
	26.91 (4 P)	2.025	26.8
		1.980	26.5^d
mer-[Cr(CO)$_3$(η^2-arphos)(η^1-arphos)]$^+$	2.025	[2.068]^c	[24] (2 P), [21] (1 As)^c
	24 (2 P)	2.024	25, 25
	23 (1 As)	1.983	23, 23
mer-[Cr(CO)$_3$(η^1-dpae)(η^2-dpae)]$^+$	2.025	*f*	*f*
	24.3 (3 As)^d		
trans-[Cr(CO)$_2$(η^2-dpae)$_2$]$^+$	2.008	2.034	31 (4 As)
	28.5 (4 As)	2.008	31
		1.980	28
mer-[Cr(CO)$_3$(η^2-dmpe)(η^1-dmpe)]$^+$	2.016	[2.01]^c	[22] (3 P)^c
	24.3 (3 P)	2.04	26
		1.994	24.9
mer-[Cr(CO)$_3$(η^2-dmpm)(η^1-dmpm)]$^+$	2.018	*f*	*f*
	23.7 (3 P)		
trans-[Cr(CO)$_2$(η^2-dmpm)$_2$]$^+$	2.004	*f*	*f*
	26.76 (4 P)	2.011	29 (4 P)
		f	*f*
trans-[Cr(CO)$_2$(η^2-dmpe)$_2$]$^+$	2.016	2.030	28.8 (4 P)
	27.82 (4 P)	2.023	27.4
		1.993	27.4
trans-[Cr(CO)$_2$(η^2-dppbz)$_2$]$^+$	2.015	2.058^e	25.1 (4 P)^e
	26.75 (4 P)	2.019^e	27.1^e
		1.967^e	24.9^e
fac-[Cr(CO)$_3$(η^2-pompom)(η^1-pompom)]$^+$		1.990	30.7 (3 P)
		2.050	28.8
		2.050	28.8
[Cr(CO)$_2$ (η^2-pompom)(η^1-pompom)]$^+$	2.017	2.046	*f*
	13.8 (1 P)	2.021	
	24.6 (1 P)	1.987	
	31.6 (1 P)		
trans-[Cr(CO)$_2$(η^2-pompom)$_2$]$^{+\,b}$	2.023	2.049	31.1 (4 P)^e
	31.49 (4 P)	[2.029]^c	[31.5]^c
		1.991	31.9
mer,mer-[{Cr(CO)$_3$(η^2-dppe)}$_2$(μ-dppe)]$^+$	2.025	[2.049]^c	[22.4] (3 P)^c
	22.7 (3 P)	2.037	23.2
		1.989	22.5

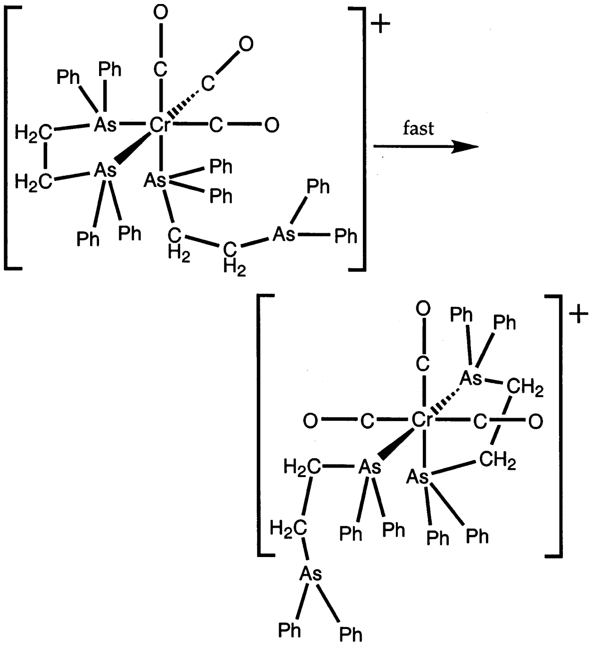
[a] Hyperfine couplings in units of 10^{-4} cm^{-1}; uncertainties are ±1 in last digit. [b] Data from ref 9. [c] Value in brackets computed from measured components and the isotropic parameters. [d] Uncertainty ±2 in last decimal place. [e] Uncertainty ±3 in last decimal place. [f] Hyperfine structure poorly resolved.

Instrumentation. EPR spectra were obtained using Bruker ER-220D or EMX X-band spectrometers equipped with a Bruker variable-temperature accessory, a Systron-Donner microwave frequency counter, and a Bruker gauss meter. Infrared spectra were recorded with a Mattson FT-IR spectrometer. Mass spectra were obtained with a Kratos MS80RFA spectrometer in positive-ion mode with fast atom bombardment using *m*-nitrobenzyl alcohol as a matrix.

Results

Bidentate Phosphines and Arsines. One-electron oxidation of *mer*-[Cr(CO)$_3$(η^1-L$_2$)(η^2-L$_2$)] (L$_2$ = dppm, dmpe, arphos, dppbz) by [Fe(η-C$_5$H$_5$)$_2$]$^+$ or [O$_2$NC$_6$H$_4$N$_2$]$^+$ in CH$_2$Cl$_2$/C$_2$H$_4$Cl$_2$ results in the corresponding Cr(I) complexes. In each case, the paramagnetic product was identified by its EPR and infrared spectra. CO stretching frequencies and EPR parameters are given in Tables 1 and 2, respectively.

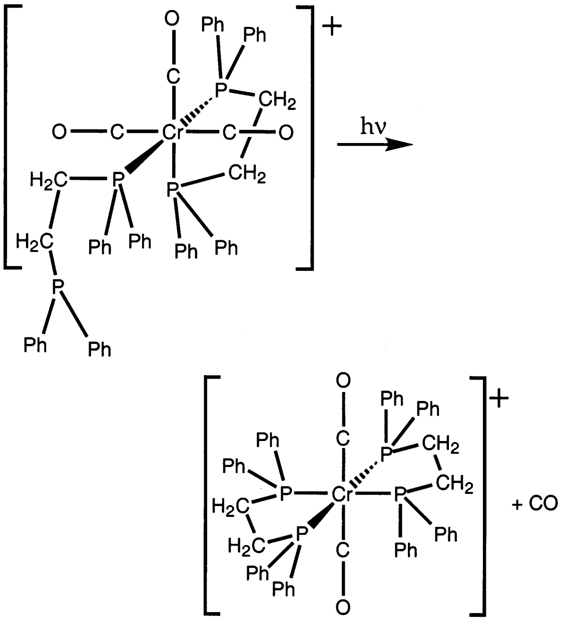
Oxidation of *fac*-[Cr(CO)$_3$(η^1-L$_2$)(η^2-L$_2$)] (L$_2$ = dpae, dppe, dmpm) results in the expected rapid rearrangement to the *mer* isomer:



(4)

In all three cases, the *mer* isomer was formed too rapidly to obtain well-resolved EPR or IR spectra of the *fac* cation.

The oxidized solutions are stable, provided they are kept air-free and in the dark. The integrated EPR signal intensity remained constant within experimental error for at least 2 h. On standing under room light for several hours, spectral features due to *trans*-[Cr(CO)$_2$(L$_2$)$_2$]$^+$ (L$_2$ = dppm, dppe, dmpm, dmpe, arphos, dpae, dppbz) can be detected. As shown in Figure 1 for the reaction the transformation is complete after several days under room light or after several minutes of illumination with 300 nm lamps in a Rayonet reactor. In all cases, the integrated intensities of the isotropic EPR spectra were



(5)

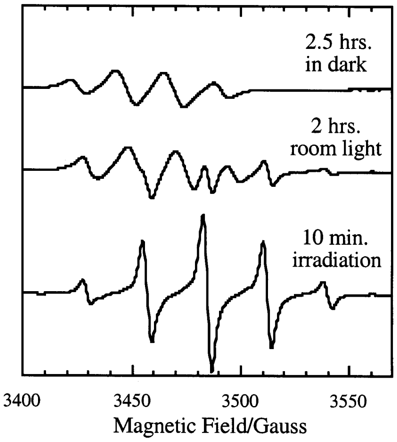


Figure 1. EPR spectra showing conversion of *mer*-$Cr[(CO)_3(\eta^2\text{-dppe})(\eta^1\text{-dppe})]^+$ to *trans*-$[Cr(CO)_2(\eta^2\text{-dppe})_2]^+$. Integrated intensities of the spectra are (top to bottom) 51, 55, and 52.

identical within experimental error before and after the transformation.

Oxidation of *mer,mer*-$[\{Cr(CO)_3(\eta^2\text{-dppe})\}_2(\mu\text{-dppe})]$ by $[Fe(\eta\text{-}C_5H_5)_2]^+$ resulted in an isotropic EPR spectrum similar to that reported by Bond et al.[12] and virtually indistinguishable from those of *mer*-$[Cr(CO)_3(\eta^2\text{-dppe})(\eta^1\text{-dppe})]^+$. However, under no circumstances did we observe the very broad line attributed to *mer,mer*-$[\{Cr(CO)_3(\eta^2\text{-dppe})\}_2(\mu\text{-dppe})]^{2+}$; indeed, the spectra remained unchanged when an excess of oxidant was employed. Furthermore, on irradiation, the spectrum of *trans*-$[\{Cr(CO)_2(\eta^2\text{-dppe})_2]^+$ was observed with a factor-of-2 decrease in integrated intensity. This suggests that the spectra of *mer*-$[Cr(CO)_3(\eta^2\text{-dppe})(\eta^1\text{-dppe})]^+$ and *mer,mer*-$[\{Cr(CO)_3(\eta^2\text{-dppe})\}_2(\mu\text{-dppe})]^{2+}$ are essentially identical: i.e., that there is negligible spin exchange through the PCH_2CH_2P bridge.

The isotropic EPR spectra of *mer*-$[Cr(CO)_3(\eta^1\text{-}L_2)(\eta^2\text{-}L_2)]^+$ (L_2 = dppm, dppe, dmpm, dmpe, dppbz) are approximate 1:3:3:1 quartets with relatively broad lines, although the spectrum of the dppm complex showed sufficient departure from 1:3:3:1 intensity ratios that a least-squares analysis of the digitized spectrum gave couplings for one unique and two equivalent ^{31}P nuclei. Lines in the other spectra were too broad to attempt such an analysis. The isotropic spectrum of the *mer* dpae cation consists of 10 lines (three approximately equivalent ^{75}As nuclei, $I = {}^3/_2$). The spectrum of the *mer* arphos cation has 6 lines (2 equivalent ^{31}P nuclei and 1 ^{75}As nucleus) with $\langle A^P\rangle = \langle A^{As}\rangle$; small variations in the line spacings suggest that the ^{31}P coupling is slightly larger than the ^{75}As coupling.

Isotropic spectra were not detected for any of the *fac* cations, consistent with previous experience: we were unable to obtain isotropic spectra for *fac*-$[Cr(CO)_3(triphos)]^+$ or *fac*-$[Cr(CO)_3(PPhMe_2)_3]^+$,[9] and Bond and co-workers saw no spectrum for solutions which almost certainly contained *fac*-$[Cr(CO)_3(PPhMe_2)_3]^+$ or *fac*-$[Cr(CO)_3\{P(OMe)_3\}_3]^+$.[2,5] The reasons for this apparent anomaly are discussed in detail elsewhere.[3]

Isotropic EPR spectra of *trans*-$[Cr(CO)_2(\eta^2\text{-}L_2)_2]^+$ all showed well-resolved ^{31}P and/or ^{75}As hyperfine coupling, and all (except the trans dppbz cation) exhibited ^{53}Cr satellites. The nine-line spectrum of the trans dpae cation has sufficiently even line spacings that $\langle A^P\rangle$ and $\langle A^{As}\rangle$ differ by no more than 0.1×10^{-4} cm^{-1}.

Frozen-solution EPR spectra range considerably in resolution. All spectra of *trans*-$[Cr(CO)_2(\eta^2\text{-}L_2)_2]^+$, except those of the arphos, dmpm, and dppbz complexes, showed well-resolved ^{31}P or ^{75}As hyperfine coupling on two of the three g components (the L_2 = dppe, dpae derivatives showed one or more resolved features for the third component). Resolution of the frozen-solution spectra of the *mer* dmpm and dppe cations and the trans dmpm cation was not sufficient to quote anisotropic parameters with certainty, although the overall shapes of the spectra suggest g components similar to those of the *mer* dppm and trans dppm cations, respectively. Frozen-solution spectra of the *mer* dppm and dppe cations and the trans dppe cation have resolved features for two of the g components and a variably resolved shoulder corresponding to the lowest-field feature of the g_{max} series. Analysis of the EPR spectra thus is straightforward. Although spectra of *mer,mer*-$[\{Cr(CO)_3(\eta^2\text{-dppe})\}_2(\mu\text{-dppe})]^+$ are slightly better resolved than those of *mer*-$[Cr(CO)_3(\eta^2\text{-dppe})(\eta^1\text{-dppe})]^+$, the EPR parameters are identical within experimental uncertainty. The frozen-solution spectrum of the *mer* dpae cation is completely unresolved, and no parameter estimates could be obtained.

Bidentate Phosphonite. Oxidation of *fac*-$[Cr(CO)_3(\eta^1\text{-pompom})(\eta^2\text{-pompom})]$ yields the corresponding *fac* cation, identified by its frozen-solution EPR spectra and the absence of an isotropic spectrum. The frozen-solution EPR spectrum is clearly axial with three hyperfine features resolved on both the $g_{\parallel}$ and $g_{\perp}$ components (the fourth features in each series overlap but are clearly present); the spectrum is better resolved than, but similar to, those of *fac*-$[Cr(CO)_3(triphos)]^+$ and *fac*-$[Cr(CO)_3(PPhMe_2)_3]^+$.[9] $g_{\parallel}$ is close to the free-electron g value as expected for a C_{3v} complex where the metal contribution to the a_1 SOMO is necessarily d_{z^2}.

Isomerization is very slow in the dark, even at room temperature. However, on irradiation for a few minutes in the Rayonet reactor, an EPR spectrum is observed which was at first thought to be that of the *mer* cation. However, further irradiation does not lead to the trans cation, and we conclude that irradiation leads to loss of CO,[7] presumably to form a square-pyramidal intermediate.[13] On standing at room temperature either in the dark or under room light, the spectrum slowly changes to that of *trans*-$[Cr(CO)_2(\eta^2\text{-pompom})_2]^+$.[9] No isotropic EPR spectrum of the *fac* cation is detected, so that no integration could be performed for the first step, but the integrated intensity remained constant over the second step. The proposed reaction steps are shown in Scheme 1.

EPR spectra of *fac*-$[Cr(CO)_3(\eta^1\text{-pompom})(\eta^2\text{-pompom})]^+$, the photolysis product, and *trans*-$[Cr(CO)_2(\eta^2\text{-pompom})_2]^+$ are shown in Figures 2 and 3, and isotropic and anisotropic parameters are given in Table 2. The isotropic spectrum obtained on photolysis of *fac*-$[Cr(CO)_3(\eta^2\text{-pompom})(\eta^1\text{-pompom}\}]^+$ consists of eight remarkably well-resolved lines, corresponding to hyperfine coupling to three nonequivalent ^{31}P nuclei, A^P = 13.8

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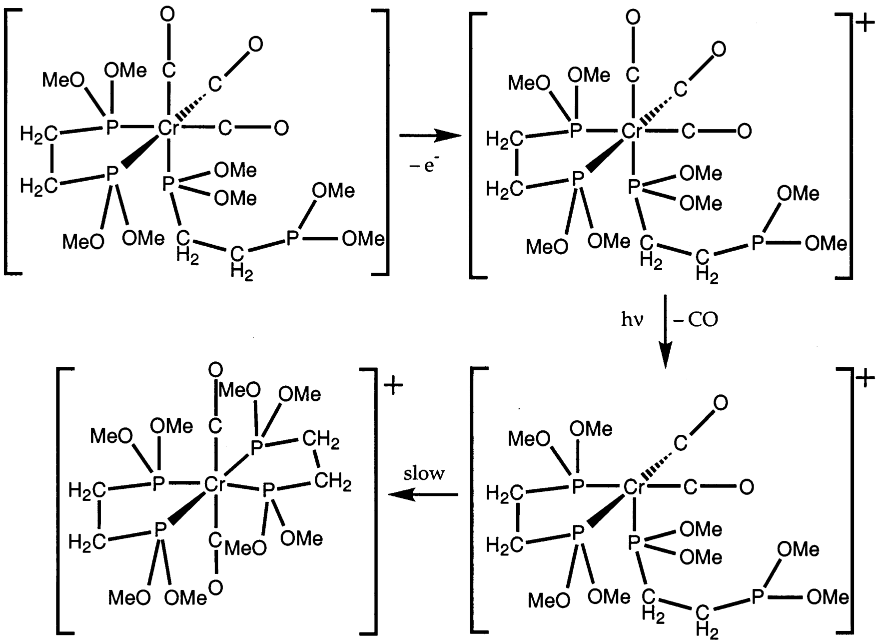
(13) There is ample precedent for isoelectronic square-pyramidal Fe(III) complexes; see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed., Wiley-Interscience: New York, 1988; p 720.

Scheme 1



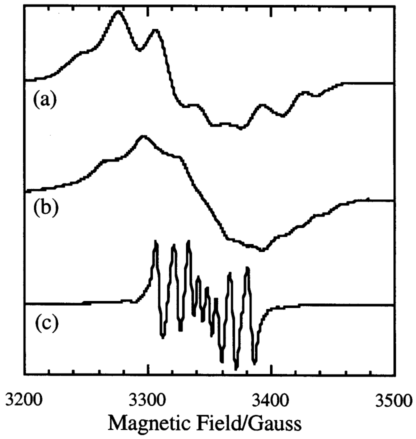


Figure 2. EPR spectra of $CH_2Cl_2/C_2H_4Cl_2$ solutions of (a) *fac*-$[Cr(CO)_3(\eta^2\text{-pompom})(\eta^1\text{-pompom})]^+$ at 120 K and the photolysis product at (b) 120 K and (c) 300 K.

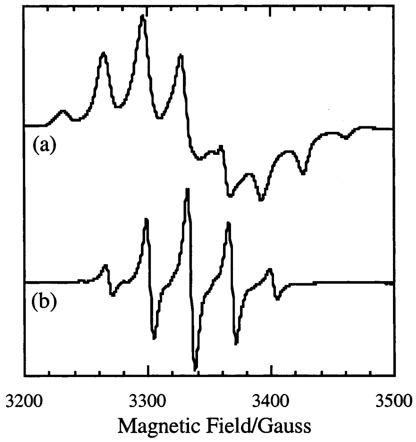


Figure 3. EPR spectra of *trans*-$[Cr(CO)_2(\eta^2\text{-pompom})_2]^+$ in $CH_2Cl_2/C_2H_4Cl_2$ at (a) 120 K and (b) 290 K.

$\times 10^{-4}$, 24.6×10^{-4}, and 31.6×10^{-4} cm^{-1}. The sharper lines may be due to the absence of the neutral precursor and the consequent absence of electron-exchange line broadening; better resolution was observed in spectra of *mer*-$[Cr(CO)_3L_3]^+$ species derived from *fac* precursors.[2]

Identification of the intermediate as *mer*-$[Cr(CO)_3(\eta^1\text{-pompom})(\eta^2\text{-pompom})]^+$ is impossible on several grounds: (i) it is surprising that it is generated photochemically; (ii) if the intermediate were the expected *mer* cation, it would be surprising to have CO loss to form the trans cation be thermally activated; (iii) other *mer* cations show three equivalent (or two small and one slightly larger) ^{31}P couplings, while the intermediate shows three quite different couplings.

This system was studied using cyclic voltammetry. A CH_2Cl_2 solution of *fac*-$[Cr(CO)_3(\eta^1\text{-pompom})(\eta^2\text{-pompom})]$ exhibits a reversible oxidation at −0.04 V vs ferrocene. On irradiation (15 min with stirring in Rayonet reactor), a new reversible couple is observed at −0.34 V, which is not the reduction of *trans*-$[Cr(CO)_2(\eta^2\text{-pompom})_2]^+$.

With the structure of the five-coordinate intermediate as shown above, an extended Hückel MO calculation[14] suggests a d_{xz}-based SOMO and d_{yz}-based HOMO. We then expect two larger, but unequal, ^{31}P couplings (P atoms on the *x* and *z* axes) and one smaller coupling (P atom on the *y* axis). This stereochemistry has the three phosphonite groups in the facial conformation, as in the starting material, and makes the slow transformation to *trans*-$[Cr(CO)_2(\eta^2\text{-pompom})_2]^+$ plausible, since the CO ligands would have to move to the *z* axis in order to allow ring closure. Alternatively, if one CO moves to the *z* axis, the product would be *cis*-$[Cr(CO)_2(\eta^2\text{-pompom})_2]^+$, which is EPR silent in liquid solution.[3] Isomerization to the trans isomer is thermodynamically favored but would probably be slow.

Discussion

Tricarbonyl Cr(I) complexes of bidentate phosphines and arsines all behave very similarly. The facial com-

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(14) Extended Hückel MO calculations were performed using the CAChe program and Alvarez parameters.

plexes isomerize to meridional ones rapidly via a thermally activated process. The meridional complexes lose CO in a photochemical process to produce *trans*-$[Cr(CO)_2(L_2)_2]^+$. Since *cis*-$[Cr(CO)_2(L_2)_2]^+$ is expected to be EPR silent in liquid solution,[3] and there is no loss in integrated EPR intensity, we can be quite certain that only the *trans*-dicarbonyl complexes are ultimately produced after photochemical loss of CO from the *mer*-tricarbonyls. However, previous work by Bond and coworkers[15] has shown that the *cis*-dicarbonyl complexes rapidly isomerize to trans, so that we cannot rule out the cis isomer as an intermediate in the photochemical process. We believe these reactions to be the first examples of photochemical reactions of 17-electron organometallics leading quantitatively to substitution products. It should be noted that the *trans*-dicarbonyls are probably not photoactive if they are analogues of *trans*-$[Cr(CO)_2(dppe)_2]^+$, which has been shown to be unaffected by light.[16]

The case of the bidentate phosphonite ligand is more complex. As discussed above, the experimental results are consistent with the formation of a five-coordinate $(CO)_2$ complex on photolysis of *fac*-$[Cr(CO)_3(\eta^2\text{-pompom})(\eta^1\text{-pompom})]^+$ followed by slow ring closure to produce the *trans*-$(CO)_2$ cation. We have no convincing evidence for this hypothesis, but the alternative—formation of the *mer*-$(CO)_3$ cation on photolysis—is not plausible.

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