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Synthesis and Spectroscopic Characterization of Group 15/Group 16 Ligand Derivatives of Manganese(I) and Rhenium(I) Pentacarbonyl Halides: Influence of the Group 16 Donor Atom on Thermodynamic and Kinetic Aspects of the Oxidation of Metal Carbonyl Complexes

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The interactions of the group 7 metal carbonyl halides $\mathrm{M(CO)_5X}$ (M = Mn, X = Cl, Br; M = Re, X = Br) with mixed group 15/group 16 donor atom ligands (L-E) have been investigated. The ligands used were dpmE ($\mathrm{Ph_2PCH_2P(E)Ph_2}$, E = Se or S to give dpmSe or dpmS, respectively) and apeE ($\mathrm{Ph_2AsCH_2CH_2P(E)Ph_2}$, E = Se or S to give apeSe or apeS, respectively). The products were characterized by microanalysis and infrared and NMR (^{31}P,^{77}Se) spectroscopies. dpmE act as bidentate ligands with both metals to give $\mathrm{M(CO)_3(dpmE)X}$, but the chemistry with apeE is more variable. With 1:1 stoichiometry, $\mathrm{Mn(CO)_5X}$ gives $\mathrm{[Mn(CO)_3(apeE)X]_2}$ with monodentate apeE coordinated through arsenic, although the compounds $\mathrm{Mn(CO)_3(apeE)X}$ with chelated apeE are intermediates in the reaction. $\mathrm{Re(CO)_5Br}$ gives stable $\mathrm{Re(CO)_3(apeE)Br}$ with chelated apeE. Both metals react with 2 mol equiv of apeE to give $\mathrm{M(CO)_3(apeE)_2X}$ containing two monodentate apeE ligands. The electrochemical oxidation of the 18-electron $\mathrm{M(CO)_3(dpmE)X}$ compounds to the 17-electron $\mathrm{[M(CO)_3(dpmE)X]^+}$ cations has been compared to that of oxidation of $\mathrm{M(CO)_3(L\text{-}L)X}$ compounds (L-L = $\mathrm{Ph_2PCH_2PPh_2}$, dpm; $\mathrm{Ph_2PCH_2CH_2PPh_2}$, dpe). Replacement of phosphorus by sulfur or selenium leads to unexpectedly large thermodynamic, kinetic, and mechanistic effects. For example, the oxidation potential of $\mathrm{Mn(CO)_3(dpmSe)X}$ derivatives is shifted by 280–300 mV in the negative direction relative to $\mathrm{Mn(CO)_3(L\text{-}L)X}$. All data imply enhanced redox stability of the 17-electron cations. However, greater kinetic lability leads to ready attack by coordinating solvents such as acetonitrile and loss of carbon monoxide so that $\mathrm{[Mn(CO)_3(dpmE)X]^+}$ cannot be isolated by oxidative-controlled potential electrolysis or chemical oxidation. The difference in oxidation potentials between corresponding dpmE and L-L is remarkably constant over a wide range of carbonyl compounds including $\mathrm{M(CO)_3(dpmE)X/M(CO)_3(L\text{-}L)X}$ (M = Mn, Re) and $\mathrm{M(CO)_4(dpmE)/M(CO)_4(L\text{-}L)}$ (M = Cr, Mo, W).

Introduction

The group 7 metal pentacarbonyl halides $\mathrm{M(CO)_5X}$ (M = Mn, Re; X = Cl, Br, I) react with a variety of monodentate tertiary phosphine and arsine ligands (L) to form compounds of the types $\mathrm{M(CO)_4LX}$ and $\mathrm{M(CO)_3L_2X}$.[3-7] Reactions of $\mathrm{M(CO)_5X}$ with diphosphine ligands (L-L) give *fac*-$\mathrm{M(CO)_3(L\text{-}L)X}$ (L-L = $\mathrm{Ph_2PCH_2PPh_2}$ (dpm), $\mathrm{Ph_2P(CH_2)_2PPh_2}$ (dpe)).[8-11] The pentacarbonyl bromides are reported to react with an excess of L-L to produce $\mathrm{M(CO)(L\text{-}L)_2Br}$ in which the carbonyl and bromide groups are trans.[9,12,14] To date, there are no reports in the literature of manganese or rhenium carbonyl compounds with ligands containing both group 15 and group 16 donor atoms. In this paper, the reactions of some mixed group 15/group 16 donor ligands (L-E, E = Se, S) (L-E = $\mathrm{Ph_2PCH_2P(Se)Ph_2}$ (dpmSe), $\mathrm{Ph_2PCH_2P(S)Ph_2}$ (dpmS), $\mathrm{Ph_2As(CH_2)_2P(Se)Ph_2}$ (apeSe), $\mathrm{Ph_2As(CH_2)_2P(S)Ph_2}$ (apeS)) with $\mathrm{M(CO)_5X}$ are described, and the products are characterized by infrared and NMR (^{31}P, ^{77}Se) spectroscopic studies.

Electrochemical oxidation of the 18-electron carbonyl compounds *fac*-$\mathrm{Mn(CO)_3(L\text{-}L)X}$ (X = Cl, Br)[14,15] in dichloromethane or acetonitrile solutions at low temperatures gives *fac*-$\mathrm{[Mn(CO)_3(L\text{-}L)X]^+}$. However, at room temperature *fac*-$\mathrm{[Mn(CO)_3(L\text{-}L)X]^+}$ rapidly isomerize to *mer*-$\mathrm{[Mn(CO)_3(L\text{-}L)X]^+}$ which in turn can be reversibly reduced to *mer*-$\mathrm{Mn(CO)_3(L\text{-}L)X}$.[14,15] The electrochemical processes at ambient temperatures can be summarized in the reaction scheme

$$\begin{tikzcd}
fac\text{-}\mathrm{Mn(CO)_3(L\text{-}L)X} \arrow[r, harpoon, shift left] & fac\text{-}\mathrm{[Mn(CO)_3(L\text{-}L)X]^+} + e^- \arrow[l, harpoon, shift left] \arrow[d] \\
mer\text{-}\mathrm{Mn(CO)_3(L\text{-}L)X} \arrow[r, harpoon, shift left] & mer\text{-}\mathrm{[Mn(CO)_3(L\text{-}L)X]^+} + e^- \arrow[l, harpoon, shift left]
\end{tikzcd} \tag{1}$$

To date there are no reports of electrochemical studies of *fac*-$\mathrm{Re(CO)_3(L\text{-}L)X}$ compounds.

Also presented in this paper are the results of the voltammetric oxidation of the compounds *fac*-$\mathrm{M(CO)_3(dpmE)X}$ (M = Mn, X = Cl, Br; M = Re, X = Br; E = Se, S) and $\mathrm{M(CO)_4(dpmE)}$ (M = Cr, Mo, W). Comparisons with the analogous compounds containing the bidentate phosphorus L-L ligands studied previously[14-16] enable the thermodynamic and kinetic effects of replacing a phosphorus atom in a chelate ligand with the weaker σ donors

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Table I. Microanalytical Data

	calcd			found		
	C	H	P	C	H	P
apeS	65.8	5.1	6.5	65.7	4.9	6.6
$Mn(CO)_3(dpmS)Cl$	56.9	3.8	10.5	56.7	3.5	10.2
$Mn(CO)_3(dpmSe)Br$	49.3	3.3	9.1	49.6	3.6	9.4
$[Mn(CO)_3(apeSe)Cl]_2$	50.1	3.5	4.5	49.8	3.4	4.6
$Mn(CO)_3(apeS)_2Br$	56.6	4.1	5.3	56.4	4.2	5.2
$Re(CO)_3(dpmSe)Br$	41.3	2.7	7.6	41.1	2.9	7.8
$Re(CO)_3(apeS)Br$	42.2	2.9	3.9	42.5	3.2	3.7
$Re(CO)_3(apeSe)_2Br$	47.0	3.5	4.5	47.1	3.4	4.4

selenium or sulfur to be examined in detail. The use of a range of metals enables the general nature of any substituent effects to be considered.

Experimental Section

Materials. Chromium, molybdenum, and tungsten hexacarbonyls (Climax Molybdenum Co., Pressure Chemical Co.) and manganese and rhenium carbonyls (Strem Chemicals Inc.) were dried over P_2O_5 and used without further purification. The ligands dpm, dpe, and ape ($Ph_2As(CH_2)_2PPh_2$) (Strem Chemicals Inc.) were used as supplied. All solvents were AR grade and dried over molecular sieves.

Preparations. The ligands dpmSe, apeSe, and dpmS were prepared by the following methods. dpmSe: dpm (5 mmol) and elemental red selenium (5 mmol) were stirred in a tetrahydrofuran solution for 3 h. The solvent was removed, and the white product was recrystallized from dichloromethane/*n*-hexane. ApeSe was prepared in an analogous manner. dpmS: dpm (5 mmol) was dissolved in a minimum amount of toluene and the solution cooled to 0 °C. Sulfur (5.2 mmol) was added to the stirred solution over a period of 1 h. After the addition of sulfur was complete, the solution was stirred for a further 1 h at 0 °C. Hexane was added to the solution, and upon cooling to −15 °C crystals of dpmS precipitated from solution. The previously unreported ligand apeS was prepared by the reaction of equimolar amounts of ape and sulfur in dichloromethane solution at ambient temperatures for 2 h. $M(CO)_4(dpmE)$ (M = Cr, Mo, W)[17] and $M(CO)_4(L\text{-}L)$ (M = Cr, Mo, W)[18] were prepared by the literature methods. The compounds $M(CO)_5X$ (M = Mn, X = Cl, Br; M = Re, X = Br)[3,19] and *fac*-$Mn(CO)_3(L\text{-}L)X$ (X = Cl, Br)[20] were also prepared by the litueurature methods.

The new compounds *fac*-$M(CO)_3(dpmE)X$ (M = Mn, X = Cl, Br; M = Re, X = Br) were prepared as follows: $M(CO)_5X$ (10 mmol) and the dpmE ligand were reacted in refluxing chloroform under a nitrogen atmosphere. The reaction was monitored by infrared spectroscopy, and when all the bands in the carbonyl region due to $M(CO)_5X$ had disappeared, the reaction was stopped. The isolated products were recrystallized from chloroform/*n*-hexane. A similar method was used to prepare *fac*-$Re(CO)_3(apeE)Br$ and *fac*-$Re(CO)_3(dpm)Br$. $[Mn(CO)_3(apeE)X]_2$: $Mn(CO)_5X$ (10 mmol) and the apeE ligand (10 mmol) were reacted in refluxing chloroform under a nitrogen atmosphere for 4 h, and the yellow products were recrystallized as described above for the $M(CO)_3(dpmE)X$ compounds. $Mn(CO)_3(apeE)_2X$: $Mn(CO)_5X$ (10 mmol) and the apeE ligand (20 mmol) were reacted in refluxing chloroform for 24 h, and the products were recrystallized as described above.

$[Cr(CO)_4(dpmE)]^+$ compounds were prepared in dichloromethane solution by oxidative-controlled potential electrolysis of $Cr(CO)_4(dpmE)$ at 0.6 V vs Ag/AgCl at a platinum electrode in the dark. The compounds $[Cr(CO)_4(dpmE)](PF_6)$ were prepared by the chemical oxidation of $Cr(CO)_4(dpmE)$ in dichloromethane using $NOPF_6$ at ambient temperatures; however, these products are only stable under these conditions for approximately 10 min.

Microanalyses were performed by AMDEL Australian Microanalytical Service, and Table I contains microanalytical data for the compounds described in this paper.

Table II. Infrared Data for the Manganese(I) and Rhenium(I) Compounds

compd	ν_{CO},[a] cm^{-1}			$\nu_{P=E}$,[b] cm^{-1}
dpmSe				529
dpmS				597
apeSe				528
apeS				605
fac-$Mn(CO)_3(dpmSe)Cl$	2040	1955	1915	510
fac-$Mn(CO)_3(dpmS)Cl$	2040	1940	1915	580
fac-$Mn(CO)_3(dpmSe)Br$	2035	1955	1910	510
fac-$Mn(CO)_3(dpmS)Br$	2010	1950	1910	575
fac-$Re(CO)_3(dpmSe)Br$	2050	1950	1905	515
fac-$Re(CO)_3(dpmS)Br$	2030	1945	1895	580
[*fac*-$Mn(CO)_3(apeSe)Cl]_2$	2025	1950	1910	528
[*fac*-$Mn(CO)_3(apeS)Cl]_2$	2050	1960	1915	605
[*fac*-$Mn(CO)_3(apeSe)Br]_2$	2045	1950	1915	528
[*fac*-$Mn(CO)_3(apeS)Br]_2$	2045	1955	1920	605
fac-$Mn(CO)_3(apeSe)_2Cl$	2050	1945	1910	530
fac-$Mn(CO)_3(apeS)_2Cl$	2040	1960	1910	605
fac-$Mn(CO)_3(apeSe)_2Br$	2040	1955	1915	528
fac-$Mn(CO)_3(apeS)_2Br$	2050	1955	1920	600
fac-$Re(CO)_3(apeSe)Br$	2025	1945	1905	518
fac-$Re(CO)_3(apeS)Br$	2050	1945	1900	590
fac-$Re(CO)_3(apeSe)_2Br$	2050	1945	1900	528
fac-$Re(CO)_3(apeS)_2Br$	2040	1940	1900	605

[a] Dichloromethane solution. [b] KBr disk.

Physical Measurements. NMR spectra were recorded by using a JEOL FX 100 spectrometer with an external ^7Li lock. Phosphorus-31 NMR spectra were recorded at 40.26 MHz (reference 85% H_3PO_4) and selenium-77 at 18.99 MHz (1M H_2SeO_3 in H_2O).[21] All NMR spectra are proton-decoupled, and the high-frequency positive convention is used for chemical shifts. A JEOL NM 5471 controller was used for temperature control, and the temperatures in the probe were measured with a calibrated platinum resistance thermometer.

Infrared spectra were recorded on a Jasco A-302 spectrophotometer and calibrated against polystyrene (1601 cm^{-1}).

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

Controlled potential electrolysis experiments were performed with a PAR Model 173 potentiostat/galvanostat using a platinum gauze working electrode and a platinum auxiliary electrode separated from the bulk solution by a salt bridge containing a Vycor plug. The reference electrode was the same as that used in the voltammetric experiments. All solutions were degassed with nitrogen before measurements were taken and were kept under a nitrogen blanket during the experiments. For the experiments that were conducted in the dark, aluminium foil was wrapped around the electrochemical cell.

Results and Discussion

Synthesis and Characterization of Compounds. (a) dpmE Derivatives. Reaction of equimolar amounts of dpmSe or dpmS with $M(CO)_5X$ (M = Mn, X = Cl, Br; M = Re, X = Br) in refluxing chloroform results in the formation of yellow $M(CO)_3(dpmE)X$ compounds. Their infrared spectra exhibit three bands in the carbonyl region

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Table III. NMR Data for the Manganese(I) and Rhenium(I) Compounds in Dichloromethane Solution[a]

compd	$\delta(^{31}P)$ P(III)	$\delta(^{31}P)$ P(E)	^2J(P,P), Hz	$\delta(^{77}Se)$	^1J(Se,P), Hz	*T*, °C
dpmSe	−27.7 d	30.4 d	85	−1596 d	732	25
dpmS	−28.8 d	39.8 d	78			25
apeSe		36.4		−1656 d	732	25
apeS		44.5				25
fac-Mn(CO)$_3$(dpmSe)Cl	64.9 d	38.3 d	71	−1455 d	601	−70
fac-Mn(CO)$_3$(dpmS)Cl	57.9 d	39.8 d	66			−70
fac-Mn(CO)$_3$(dpmSe)Br	61.6 d	36.4 d	71	−1466	601	−70
fac-Mn(CO)$_3$(dpmS)Br	59.3 d	33.4 d	66			−70
fac-Re(CO)$_3$(dpmSe)Br	20.7 d	39.7 d	64	−1518 d	596	25
fac-Re(CO)$_3$(dpmS)Br	19.1 d	30.6 d	59			25
[*fac*-Mn(CO)$_3$(apeSe)Cl]$_2$		36.5		−1658 d	730	25
[*fac*-Mn(CO)$_3$(apeS)Cl]$_2$		44.2				25
[*fac*-Mn(CO)$_3$(apeSe)Br]$_2$		36.6		−1659 d	730	25
[*fac*-Mn(CO)$_3$(apeS)Br]$_2$		44.3				25
fac-Mn(CO)$_3$(apeSe)$_2$Cl		36.6		−1656 d	732	25
fac-Mn(CO)$_3$(apeS)$_2$Cl		44.0				25
fac-Mn(CO)$_3$(apeSe)$_2$Br		36.4		−1661 d	728	25
fac-Mn(CO)$_3$(apeS)$_2$Br		43.9				25
fac-Re(CO)$_3$(apeSe)Br		32.6		−1717 d	620	25
fac-Re(CO)$_3$(apeS)Br		45.4				25
fac-Re(CO)$_3$(apeSe)$_2$Br		36.8		−1659 d	728	25
fac-Re(CO)$_3$(apeS)$_2$Br		44.1				25

[a] Abbreviation: d, doublet.

consistent with *facial* stereochemistry. Each compound has one band in the P=E region (E = Se, S) at a frequency 15–25 cm^{-1} lower than for the free ligand, which is indicative of selenium or sulfur coordination.[22-24] Infrared data are given in Table II.

The phosphorus-31 NMR spectrum of *fac*-Mn(CO)$_3$(dpmSe)Br in dichloromethane solution at −70 °C (Figure 1a) is typical for *fac*-Mn(CO)$_3$(dpmE)X compounds and exhibits two doublets at δ 36.4 and 61.6. The doublet at δ 36.4 exhibits selenium-77 satellites (^1J(Se,P) = 601 Hz); hence this resonance is assigned to the phosphorus(V) atom, and its chemical shift is similar to that of the phosphorus(V) atom in the free ligand. The doublet at δ 61.6 is therefore assigned to the phosphorus(III) atom. As the temperature is raised (Figure 1b,c) the spectrum changes, indicating the labile nature of *fac*-Mn(CO)$_3$(dpmSe)Br on the NMR time scale. There are only slight changes in the appearance of the phosphorus(V) resonance, but there are marked changes in the shape of the phosphorus(III) resonance, although its position hardly alters. This suggests that this phosphorus atom remains coordinated at all times; otherwise the position of the exchange average signal would move toward the resonance position for the free ligand. Later evidence will suggest that it is the Mn–Se bond which cleaves, probably leading to a five-coordinate–six-coordinate exchange. The fast-exchange limit of the spectra of these labile molecules is not reached up to 90 °C, and they decompose above their temperature. The phosphorus-31 NMR spectra of *fac*-Re(CO)$_3$(dpmE)Br compounds exhibit two doublets at room temperature, showing them to be rigid in solution on the NMR time scale at room temperature, but the resonance due to the P(III) atom is at much lower frequency, appearing at lower chemical shift than the P(V) resonance. NMR data for the *fac*-M(CO)$_3$(dpmE)X compounds are given in Table III.

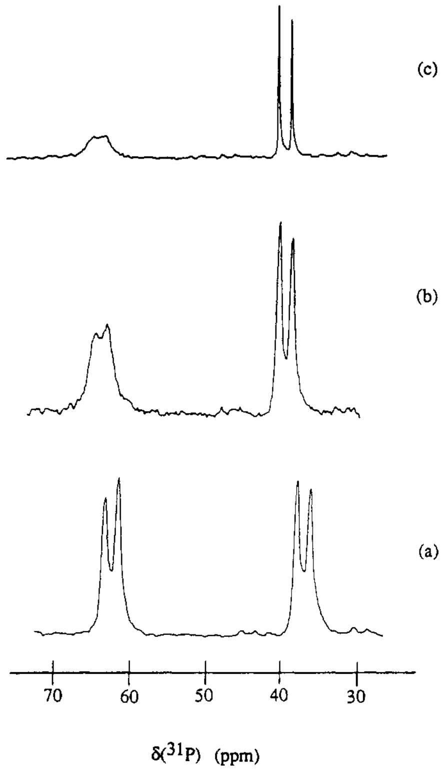

Figure 1. The phosphorus-31 NMR spectra of *fac*-Mn(CO)$_3$(dpmSe)Br in dichloromethane solution at various temperatures; (a) −70 °C, (b) 25 °C, and (c) 90 °C.

The selenium-77 NMR spectra of the *fac*-Mn(CO)$_3$(dpmSe)X compounds in dichloromethane solution at −70 °C are doublets while that of *fac*-Re(CO)$_3$(dpmSe)Br is a similar doublet at room temperature. The chemical shifts and coupling constants of the doublets are significantly different from those of the free ligand (Table III) which confirms selenium coordination. Although no such evidence is available for the compounds containing dpmS, the similar phosphorus-31 NMR spectra and the infrared spectral evidence ($\nu_{P=S}$) are sufficient to confirm coordination of sulfur in *fac*-M(CO)$_3$(dpmS)X compounds.

(b) apeE Derivatives. Reaction of equimolar quantities of apeSe or apeS with Mn(CO)$_5$X (X = Cl, Br) in refluxing chloroform forms yellow Mn(CO)$_3$(apeE)X compounds. Their infrared spectra (Table II) are consistent

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Table IV. Cyclic Voltammetric Data for the Oxidation of 5×10^{-4} M *fac*-M(CO)$_3$(dpmE)X and *fac*-Mn(CO)$_3$(L-L)X Compounds in Dichloromethane (0.1 M Bu$_4$NClO$_4$) and Acetonitrile (0.1 M Et$_4$NClO$_4$) Solutions[a-c]

	dichloromethane				acetonitrile				
					process I			process II	
	$E_p^{ox.}$,[d] V[a]	$E_p^{red.}$,[e] V[a]	$E^r_{1/2}$,[f] V[a]	T, °C	$E_p^{ox.}$,[d] V[a]	$E_p^{red.}$,[e] V[a]	$E^r_{1/2}$,[f] V[a]	$E_p^{ox.}$,[d] V[a]	T, °C
fac-Mn(CO)$_3$(dpmSe)Cl	1.04	0.96	0.99	25	0.96	0.87	0.92	1.70	−30
fac-Mn(CO)$_3$(dpmS)Cl	1.06	0.96	1.01	25	1.00	0.90	0.95	2.10	−30
fac-Mn(CO)$_3$(dpmSe)Br	1.02	0.94	0.98	25	0.96	0.90	0.93	1.80	0
fac-Mn(CO)$_3$(dpmS)Br	1.08	0.96	1.02	25	1.04	0.94	0.99	2.12	−30
fac-Re(CO)$_3$(dpmSe)Br	1.28	1.19	1.26	−50	1.15	1.07	1.11	1.50	−30
fac-Re(CO)$_3$(dpmS)Br	1.34	1.25	1.30	−50	1.21	1.13	1.17	1.82	−30
fac-Mn(CO)$_3$(dpm)Cl	1.33	1.20	1.26	25					
fac-Mn(CO)$_3$(dpe)Cl	1.31	1.21	1.26	25					
fac-Mn(CO)$_3$(dpm)Br	1.34	1.22	1.28	25					
fac-Mn(CO)$_3$(dpe)Br	1.32	1.22	1.27	25					

[a] V vs Ag/AgCl; $E_{1/2}$ for oxidation of 10^{-3} M ferrocene in CH$_2$Cl$_2$ = 0.50 V vs Ag/AgCl and CH$_3$CN = 0.41 V vs Ag/AgCl. [b] Scan rate = 200 mV s^{-1}. [c] $i_p^{ox.}/i_p^{red.} = 1.0$ as required for a chemically reversible process. [d] $E_p^{ox.}$ = oxidation potential of the forward scan in the cyclic voltammogram. [e] $E_p^{red.}$ = reduction potential of the reverse scan in the cyclic voltammogram. [f] $E^r_{1/2}$ = reversible half-wave potential calculated from the relationship $E^r_{1/2} = (E_p^{ox.} + E_p^{red.})/2$.

with facial geometry, and each compound exhibits a band in the P═E region at a frequency identical with that for the free ligand. This is indicative of noncoordination of the selenium or sulfur atoms, in marked contrast to the apparently analogous dpmE derivatives.

The NMR data for these compounds are given in Table III. Each compound exhibits phosphorus-31 and selenium-77 NMR spectra very similar to those of the free apeE ligand, confirming that the selenium and sulfur atoms are not coordinated. The spectroscopic evidence suggests that the compounds are in fact [*fac*-Mn(CO)$_3$(apeE)X]$_2$, new members of the well-known[3] series of dimeric halogen-bridged carbonyl derivatives. For a further investigation of the formation of these compounds, the reaction between equimolar quantities of Mn(CO)$_5$Br and apeSe was repeated in refluxing chloroform and monitored by phosphorus-31 NMR spectroscopy. After approximately 30-min reaction time two signals were observed at δ 36.6 and δ 30.9, each with selenium-77 satellites. The chemical shift and coupling constant of the high-frequency singlet are very similar to those of the free ligand, which is consistent with an uncoordinated selenium atom. The chemical shift of the other singlet is different from that of the free ligand, but more significantly the P═Se coupling constant is reduced to 630 Hz, which indicates a coordinated selenium atom. The reaction was allowed to proceed, and after 1 h only the signal at higher frequency remained. Hence it appears that the compound *fac*-Mn(CO)$_3$(apeSe)Br with chelated apeSe is formed but is not the favored long-term product. These reactions serve to illustrate the poor σ-donor power of selenium and sulfur in these ligands since the coordinated halogen can compete successfully to cleave the Mn–E bond to generate the halogen-bridged species. The same reactions do not occur with the corresponding dpmE complexes since the geometry of these ligands favors chelation. These differences between dpmE and apeE ligands have been observed before in other systems.[25] At room temperature the same sequence of events occurs, but the reaction times are longer than in refluxing chloroform. Attempts to separate Mn(CO)$_3$(apeSe)Br and [Mn(CO)$_3$(apeSe)Br]$_2$ failed.

Reaction of equimolar amounts of apeSe or apeS with Re(CO)$_5$Br in refluxing chloroform or at ambient temperatures leads to the formation of white Re(CO)$_3$(apeE)Br. Their infrared spectra indicate a facial arrangement of the carbonyl groups. Each compound exhibits one band in the P═E region that is shifted to lower frequency by 10–15 cm^{-1} relative to the frequency of the P═E band in the free apeE ligand, indicating that the apeE ligand is chelated, in contrast to the corresponding manganese(I) compounds. NMR data for the Re(CO)$_3$(apeE)Br compounds are given in Table III and confirm that these compounds, which are rigid in solution on the NMR time scale, contain a chelated apeE ligand.

Reaction of 2 mol of apeSe or apeS with Mn(CO)$_5$X (X = Cl, Br) in refluxing chloroform produces yellow compounds Mn(CO)$_3$(apeE)$_2$X. Their infrared spectra in both the carbonyl and P═E regions are very similar to those of [*fac*-Mn(CO)$_3$(apeE)X]$_2$ (Table II) and indicate a facial configuration with two monodentate apeE ligands coordinated through arsenic. NMR data for the *fac*-Mn(CO)$_3$(apeE)$_2$X compounds are given in Table III and confirm this proposed structure.

Reaction of 2 mol of apeSe or apeS with Re(CO)$_5$Br in refluxing chloroform leads to the formation of the white compounds Re(CO)$_3$(apeE)$_2$Br. Infrared spectra in the carbonyl and P═E regions and phosphorus-31 (for both compounds) and selenium-77 (for the apeSe derivative) NMR spectra are all indicative of the formation of compounds of the formula *fac*-Re(CO)$_3$(apeE)$_2$Br, with monodentate apeE ligands, similar to the corresponding manganese(I) compounds. Thus, although the Re–E bond in Re(CO)$_3$(apeE)Br is not attacked by the coordinated halogen to give the halo-bridged species, it is cleaved by the stronger arsenic donor of the apeE ligand.

Neither the dpmE nor apeE ligands react with M(CO)$_5$X to give analogues of Mn(CO)(L-L)$_2$X and Re(CO)(L-L)$_2$X.

Electrochemical Studies. (i) *fac*-M(CO)$_3$(dpmE)X Compounds. (a) Dichloromethane Solution. The cyclic voltammograms for the oxidation of *fac*-Mn(CO)$_3$(dpmE)X compounds at room temperature in dichloromethane (0.1 M Bu$_4$NClO$_4$) solution show one reversible oxidation process on the first and subsequent scans. Voltammetric data in dichloromethane solution are summarized in Table IV.

The diffusion-controlled limiting currents for the oxidations of *fac*-Mn(CO)$_3$(dpmE)X at a platinum rotating disk electrode are consistent with one-electron processes since the limiting currents per unit concentration are the same as that for the known one-electron oxidation of *fac*-Mn(CO)$_3$(dpm)Br.[14] The electrode processes can be described as

$$fac\text{-Mn(CO)}_3\text{(dpmE)X} \rightleftharpoons fac\text{-[Mn(CO)}_3\text{(dpEe)X]}^+ + e^- \qquad (2)$$

fac-[Mn(CO)$_3$(dpmE)X]$^+$ compounds are kinetically stable

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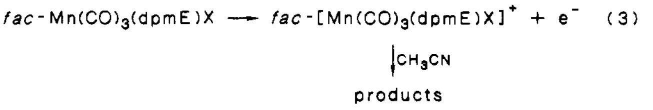
[25] Colton, R.; Panagiotidou, P. *Aust. J. Chem.* **1987**, *40*, 13.

on the voltammetric time scale at temperatures in the range +25 to −70 °C, and there is no evidence for *fac*$^+$ to *mer*$^+$ isomerization after electron transfer, in contrast to the rapid isomerization of *fac*-$[Mn(CO)_3(L\text{-}L)X]^+$.[14,15] The greater thermodynamic stability of the *fac*-$[Mn(CO)_3(dpmE)X]^+$ compounds in dichloromethane solution compared to $[Mn(CO)_3(L\text{-}L)X]^+$ compounds, is seen in the markedly lower oxidation potentials for eq 2 than for oxidation of $Mn(CO)_3(L\text{-}L)X$. Hence, the selenium and sulfur donor atoms in the chelating dpmE ligands have a large effect on the thermodynamic redox stability.

At 25 °C *fac*-$Re(CO)_3(dpmE)Br$ compounds in dichloromethane (0.1 M Bu_4NClO_4) solution give a single irreversible oxidation wave at a scan rate of 200 mV s^{-1}. When the solution is cooled to −50 °C, the process becomes chemically reversible. Data are given in Table IV. The platinum rotating disk voltammograms for the oxidation of *fac*-$Re(CO)_3(dpmE)Br$ show well-defined oxidation waves, and the limiting currents per unit concentration indicate a one-electron oxidation. Therefore the electrode processes for $Re(CO)_3(dpmE)Br$ in dichloromethane at low temperature are analogous to those of the manganese systems at room temperature.

Attempts to isolate the *fac*-$[Mn(CO)_3(dpmE)X]^+$ compounds failed. Exhaustive oxidative-controlled potential electrolysis of *fac*-$Mn(CO)_3(dpmE)X$ in dichloromethane (0.1 M Bu_4NClO_4) gives no evidence for formation of *fac*-$[Mn(CO)_3(dpmE)X]^+$ or *mer*-$[Mn(CO)_3(dpmE)X]^+$ species on the synthetic time scale since the product does not contain any carbonyl groups (infrared evidence). Similarly, chemical oxidation of *fac*-$Mn(CO)_3(dpmE)X$ with $NOPF_6$ does not lead to the formation of *fac*- or *mer*-$[Mn(CO)_3(dpmE)X]^+$ compounds. During the initial stages of the chemical oxidation a green color is observed in the solution that is the same color as *fac*-$[Mn(CO)_3(dpm)X]^+$ and thus suggests the formation of the corresponding *fac*-$[Mn(CO)_3(dpmE)X]^+$ species. However, this green color is quickly discharged, indicating decomposition of the oxidation products. No carbonyl or nitrosyl bands are observed in the infrared spectra of the final products. Hence, although the *fac*-$[Mn(CO)_3(dpmE)X]^+$ compounds are stable on the voltammetric time scale, they are unstable on the longer coulometric and synthetic time scales, and the products are not the *mer*$^+$ isomers in contrast to the behavior of the *fac*-$[Mn(CO)_3(L\text{-}L)X]^+$ compounds.

(b) Acetonitrile Solution. Cyclic voltammograms of all *fac*-$Mn(CO)_3(dpmE)X$ compounds in acetonitrile (0.1 M Et_4NClO_4) are similar and show two chemically irreversible oxidation processes on the first scan (processes I and II) at about +1.0 and +1.9 V vs Ag/AgCl, respectively, and no other processes are observed on the reverse scan or in subsequent cycles. Process II occurs at too positive a potential to be observed in dichloromethane. When the potential is switched between processes I and II, process I is observed to be almost completely chemically irreversible at room temperature. As the temperature of the solution is decreased, process I becomes partially reversible although complete reversibility is not attained at the solvent-imposed limit of −35 °C with a scan rate of 200 mV s^{-1}. The potential of the process I relative to Fc^+/Fc is similar to that of the response in dichloromethane; hence in acetonitrile, process I is due to



$$fac\text{-}Mn(CO)_3(dpmE)X \longrightarrow fac\text{-}[Mn(CO)_3(dpmE)X]^+ + e^- \quad (3)$$
$$\downarrow CH_3CN$$
$$\text{products}$$

that is, acetonitrile rapidly attacks the 17-electron cation so that the behavior of $Mn(CO)_3(dpmE)X$ is solvent-dependent, unlike the case with the analogous L-L derivatives.[14] Process II, which is due to further oxidation of manganese, remains irreversible over the temperature range +25 to −35 °C and scan rates 10–500 mV s^{-1}. The voltammetric oxidations of $Re(CO)_3(dpmE)Br$ in acetonitrile follow a similar pattern, and data are given in Table IV.

Table V. Electrochemical Data for the Oxidation of 5 × 10^{-4} M $M(CO)_4(dpmE)$ and $M(CO)_4(L\text{-}L)$ Compounds in Dichloromethane (0.1 M Bu_4NClO_4) and Acetonitrile (0.1 M Et_4NClO_4) Solutions at 25 °C[a–c]

		cyclic voltammetry			
compd	sol	$E_p^{ox.}$,[d] V	$E_p^{red.}$,[e] V	$E^r_{1/2}$,[f] V	rotating disk[g] $E^r_{1/2}$,[f] V
$Cr(CO)_4(dpmSe)$	CH_2Cl_2	0.53	0.45	0.49	0.50
$Cr(CO)_4(dpmS)$	CH_2Cl_2	0.54	0.44	0.48	0.50
$Mo(CO)_4(dpmSe)$	CH_2Cl_2	0.78	0.66	0.72	0.74
$Mo(CO)_4(dpmS)$	CH_2Cl_2	0.78	0.68	0.73	0.74
$W(CO)_4(dpmSe)$	CH_2Cl_2	0.78			
$W(CO)_4(dpmS)$	CH_2Cl_2	0.74	0.66	0.70	0.72
$Cr(CO)_4(dpmSe)$	CH_3CN	0.52	0.44	0.48	0.50
$Cr(CO)_4(dpmS)$	CH_3CN	0.53	0.48	0.51	0.52
$Mo(CO)_4(dpmSe)$	CH_3CN	0.77			
$Mo(CO)_4(dpmS)$	CH_3CN	0.80			
$W(CO)_4(dpmSe)$	CH_3CN	0.79			
$W(CO)_4(dpmS)$	CH_3CN	0.72			
$Cr(CO)_4(dpm)$[h]	CH_2Cl_2	0.86	0.70	0.78	0.80
$Cr(CO)_4(dpe)$[h]	CH_2Cl_2	0.82	0.72	0.77	0.80
$Mo(CO)_4(dpe)$[h]	CH_2Cl_2	1.10	0.88	0.99	1.01
$W(CO)_4(dpe)$[h]	CH_2Cl_2	1.06	0.96	1.01	1.02

[a–f] See footnotes to Table IV. [g] Rotation rate = 2000 rpm. [h] These data are taken from ref 16, and only the compounds giving chemically reversible processes in dichloromethane solution are considered.

(ii) $M(CO)_4(dpmE)$ Compounds. (a) Dichloromethane Solution. The $Cr(CO)_4(dpmE)$ compounds each give very similar voltammetric results, and the data are given in Table V. The cyclic voltammograms in dichloromethane (0.1 M Bu_4NClO_4) at 25 °C are consistent with chemically reversible one-electron oxidations. The shapes of the current–voltage curves and the magnitudes of the diffusion-controlled limiting currents in platinum rotating disk electrode experiments are also consistent with reversible one-electron oxidations. Thus the electrode processes are

$$Cr(CO)_4(dpmE) \rightleftharpoons [Cr(CO)_4(dpmE)]^+ + e^- \quad (4)$$

Cyclic voltammetry over the temperature range +25 to −60 °C and for scan rates 10–500 mV s^{-1} is also consistent with one-electron oxidations. These data indicate that the *cis*-$[Cr(CO)_4(dpmE)]^+$ cations are stable on the voltammetric time scale.

The $Cr(CO)_4(dpmE)$ compounds are oxidized at less positive potentials than the $Cr(CO)_4(L\text{-}L)$ compounds, similar to the parallel observations with the manganese(I) and rhenium(I) systems (Table V).

Oxidative-controlled potential electrolysis of $Cr(CO)_4(dpmSe)$ at 0.6 V vs Ag/AgCl in dichloromethane (0.1 M Bu_4NClO_4) in the presence of light produces a faint blue color close to the electrode that discharges as the material diffuses away from the electrode. In the dark, exhaustive oxidative-controlled potential electrolysis gives a deep purple solution after the passage of 1.2 ± 0.2 electrons per molecule. Monitoring the progress of the oxidation by platinum rotating disk electrode experiments shows the disappearance of the oxidative process and the generation of a reductive wave at the same potential. When the purple solution is exposed to the light, the color gradually changes to yellow (approximately 10 min). Hence the $[Cr(CO)_4(dpmSe)]^+$ cation is somewhat light sensitive but

Table VI. Infrared Data (cm^{-1}) for the $[M(CO)_3(NO)(dpmE)]^+$ Cations in Dichloromethane Solution

compound	ν_{CO}		ν_{NO}
$[Cr(CO)_3(NO)(dpmSe)]^+$	2110 m	2060 s	1735 br
$[Cr(CO)_3(NO)(dpmS)]^+$	2105 m	2040 s	1740 br
$[Mo(CO)_3(NO)(dpmSe)]^{+}$[b]	2100 m	2050 s	1715 br
$[Mo(CO)_3(NO)(dpmS)]^+$	2100 m	2050 s	1750 br
$[W(CO)_3(NO)(dpmSe)]^{+}$[b]	2105 m	2035 s	1750 br
$[W(CO)_3(NO)(dpmS)]^+$	2100 m	2050 s	1750 br

[a] Abbreviations: m, medium; s, strong; br, broad. [b] The data for these cations have been reported previously.[16]

not as sensitive as the $[Cr(CO)_4(dpm)]^+$ cation that decomposes instantly under the same conditions.[16]

Chemical oxidation of $Cr(CO)_4(dpmE)$ by $NOPF_6$ in dichloromethane at ambient temperatures gives a deep purple color due to $[Cr(CO)_4(dpmE)]^+$. In the presence of $NOPF_6$ the purple color persists at room temperature in the presence of light for approximately 10 minutes and the solution gradually turns yellow. The final yellow products are $[Cr(CO)_3(NO)(dpmE)](PF_6)$. In contrast, the chemical oxidation of $Cr(CO)_4(dpm)$ with $NOPF_6$ gives the purple $[Cr(CO)_4(dpm)]^+$ species only at low temperatures, and at room temperature the product is the yellow compound $[Cr(CO)_3(NO)(dpm)](PF_6)$.[26,27] Thus the dpmE systems allow direct observation of the substitution of $[Cr(CO)_4(dpmE)]^+$ by the nitrosyl group to give $[Cr(CO)_3(NO)(dpmE)]^+$. Infrared data are given in Table VI.

The oxidations of $M(CO)_4(dpmS)$ (M = Mo, W) in dichloromethane (0.1 M Bu_4NClO_4) over the temperature range +20 to −60 °C and for scan rates 10–500 mV s^{-1} are also consistent with chemically reversible one-electron oxidations.

The $M(CO)_4(dpmS)$ (M = Mo, W) compounds are oxidized at potentials less positive than the potentials for the oxidation of the chemically reversible $M(CO)_4(dpe)$ (M = Mo, W).

Although the $[M(CO)_4(dpmS)]^+$ (M = Mo, W) cations are stable on the short voltammetric time scale in dichloromethane (0.1 M Bu_4NClO_4), oxidative-controlled potential electrolysis in dichloromethane gives a solution that shows no voltammetric responses for the 17-electron $[M(CO)_4(dpmS)]^+$ cations, showing them to be unstable on the longer coulometric time scale. Similarly, chemical oxidation of $M(CO)_4(dpmS)$ by $NOPF_6$ produces exclusively the nitrosyl substitution products $[M(CO)_3(NO)(dpmS)](PF_6)$; infrared data are given in Table VI.

The voltammetric oxidations of $M(CO)_4(dpmSe)$ (M = Mo, W) have been reported previously.[16] $Mo(CO)_4(dpmSe)$ exhibits very unusual electrochemical behavior; it gives a chemically reversible oxidation at −10 °C that becomes irreversible at −60 °C. The oxidative cyclic voltammogram for $W(CO)_4(dpmSe)$ in dichloromethane (0.1 M Et_4NClO_4) over the temperature range +25 to −60 °C exhibits a chemically irreversible oxidation response to ~0.8 V vs Ag/AgCl and a broad reduction response at −0.8 V vs Ag/AgCl on the reverse scan.[16]

(b) Acetonitrile. In acetonitrile, cyclic voltammograms of $Cr(CO)_4(dpmE)$ exhibit a reversible couple similar to that described for a dichloromethane solution. Electrochemical data in acetonitrile are also given in Table V.

The voltammetric responses for the $M(CO)_4(dpmS)$ (M = Mo, W) compounds are modified by changing to the coordinating solvent acetonitrile. In acetonitrile (0.1 M Et_4NClO_4) the oxidations of $M(CO)_4(dpmS)$ are chemically irreversible.

Table VII. Differences between the Half-Wave Potentials ($E_{1/2}$) of Compounds Containing the dpmE Ligands and Those Containing the L-L Ligands

A (dpmE compd)	B (L-L compd)	difference $E_{1/2}(A) - E_{1/2}(B)$, V
$Cr(CO)_4(dpmSe)$	$Cr(CO)_4(dpm)$	0.49 − 0.78 = −0.29
$Cr(CO)_4(dpmSe)$	$Cr(CO)_4(dpe)$	0.49 − 0.77 = −0.28
$Cr(CO)_4(dpmS)$	$Cr(CO)_4(dpm)$	0.51 − 0.78 = −0.27
$Cr(CO)_4(dpmS)$	$Cr(CO)_4(dpe)$	0.51 − 0.79 = −0.26
$Mo(CO)_4(dpmSe)$[a]	$Mo(CO)_4(dpe)$	0.72 − 0.99 = −0.27
$Mo(CO)_4(dpmS)$	$Mo(CO)_4(dpe)$	0.73 − 0.99 = −0.26
$W(CO)_4(dpmS)$	$W(CO)_4(dpe)$	0.74 − 1.01 = −0.27
fac-$Mn(CO)_3(dpmSe)Cl$	*fac*-$Mn(CO)_3(dpm)Cl$	0.99 − 1.26 = −0.27
fac-$Mn(CO)_3(dpmS)Cl$	*fac*-$Mn(CO)_3(dpm)Cl$	1.01 − 1.26 = −0.25
fac-$Mn(CO)_3(dpmSe)Cl$	*fac*-$Mn(CO)_3(dpe)Cl$	0.99 − 1.26 = −0.27
fac-$Mn(CO)_3(dpmS)Cl$	*fac*-$Mn(CO)_3(dpe)Cl$	1.01 − 1.26 = −0.25
fac-$Mn(CO)_3(dpmSe)Br$	*fac*-$Mn(CO)_3(dpm)Br$	0.98 − 1.28 = −0.30
fac-$Mn(CO)_3(dpmSe)Br$	*fac*-$Mn(CO)_3(dpe)Br$	0.98 − 1.27 = −0.29
fac-$Mn(CO)_3(dpmS)Br$	*fac*-$Mn(CO)_3(dpm)Br$	1.02 − 1.28 = −0.26
fac-$Mn(CO)_3(dpmS)Br$	*fac*-$Mn(CO)_3(dpe)Br$	1.01 − 1.27 = −0.26

[a] This compound shows a partially reversible redox couple at 25 °C which is chemically reversible at −10 °C.[16]

Conclusions

The electrochemical results presented in this paper clearly show that the replacement of phosphorus by selenium and sulfur donor atoms in chelating ligands has a significant effect on the electrochemical behavior of the compounds. The 17-electron cations produced from the voltammetric oxidation of the 18-electron compounds containing the dpmE ligands are thermodynamically more stable in a redox sense, that is, the resultant 17-electron cation is a weaker oxidant than the analogous 17-electron cations containing the L-L ligands. This is illustrated in Table VII where the differences between the half-wave potentials ($E_{1/2}$) of corresponding dpmE and L-L compounds are given. Only compounds giving chemically reversible oxidation processes are included in the comparison. The compounds containing the dpmSe and dpmS ligands are oxidized at potentials that are respectively 280–300 and 250–270 mV less positive than the potentials required for the oxidation of the analogous L-L compounds. This shift to less positive potential is remarkable and independent of the metal. $Re(CO)_3(dpm)Br$ is irreversibly oxidized at 1.5 V vs Ag/AgCl in acetonitrile. Although a direct comparison with the reversible oxidation of $Re(CO)_3(dpmE)Br$ is not possible, approximately the same difference in potential is apparent.

Such a constant trend is not observed in the selenium-77 NMR data for the 18-electron derivatives (Table III), indicating that the observed electrochemical effect is dominated by the paramagnetic 17-electron species. The data presented in Table VII show that the chelate ring size is not important in this effect since the difference in $E_{1/2}$ between $Cr(CO)_4(dpmS)$ and $Cr(CO)_4(dpm)$ is almost the same as that between $Cr(CO)_4(dpmS)$ and $Cr(CO)_4(dpe)$. Presumably the contributing factors for this unusual stability, in the redox sense, of the 17-electron dpmE compounds are electronegativity and a balance between σ and π effects, although it is not possible to determine which effect is dominant.

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(26) Connelly, N. G. *J. Chem. Soc., Dalton Trans.* **1973**, 2183.

(27) Ashford, P. K.; Baker, P.K.; Connelly, N. G.; Kelly, R. L.; Woodley, V. A. *J. Chem. Soc. Dalton Trans.* **1982**, 477.

The greater thermodynamic stability of the 17-electron cations containing the dpmE ligands suggests that these cations should be more stable on the synthetic time scale if decomposition reactions are redox-based reactions. However, with the exception of the [Cr(CO)$_4$(dpmE)]$^+$ cations, all cations show very little, if any, stability on the synthetic time scale. The instability is clearly related to the weakening of the bond strength (M–E vs M–P) and is substitution rather than redox based. Other observations due to the weak M–E bond were noted in the preparative and spectroscopic section. The [M(CO)$_4$(dpmE)]$^+$ cations are light sensitive, and when M = Mo and W the electrochemical behavior is drastically affected by the presence of the coordinating solvent acetonitrile. The displacement of chelating ligands coordinated through sulfur donor atoms in 18-electron M(CO)$_4$(chelate) compounds by phosphine and phosphites has been well-documented.[28] Since it has already been shown that selenium and sulfur are poor donors in the zerovalent M(CO)$_4$(L-E) compounds,[25] it is plausible that in the 17-electron system the metal–selenium (sulfur) bond is cleaved in the presence of a coordinating ligand, in this case CH_3CN, and the six-coordinate cations [M(CO)$_4$(η^1-dpmE)(CH_3CN)]$^+$ are formed which in turn decompose to non-carbonyl-containing species.

It has been shown for the *fac*-[Mn(CO)$_3$(L-L)X]$^+$ cations and many other *facial* tricarbonyl cations that the *fac*$^+$ → *mer*$^+$ isomerization is fast.[6,14,15,29] In the case of the manganese(I) and rhenium(I) compounds containing the dpmE ligands, however, the presence of a selenium and sulfur donor atom stabilizes the 17-electron *fac*-[M(CO)$_3$(dpmE)X]$^+$ cations toward isomerization to the *mer*$^+$ isomers, and for the 17-electron cations containing the dpmE ligands, the *fac*$^+$ → *mer*$^+$ isomerization is not observed on the voltammetric or synthetic time scales.

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Registry No. dpmSe, 23176-19-4; dpmS, 54006-28-9; apeSe, 77386-60-8; apeS, 114582-76-2; *fac*-Mn(CO)$_3$(dpmSe)Cl, 114594-81-9; *fac*-Mn(CO)$_3$(dpmS)Cl, 114594-82-0; *fac*-Mn(CO)$_3$(dpmSe)Br, 114594-83-1; *fac*-Mn(CO)$_3$(dpmS)Br, 114594-84-2; *fac*-Re(CO)$_3$(dpmS)Br, 114594-86-4; [*fac*-Mn(CO)$_3$(apeSe)Cl]$_2$, 114594-87-5; [*fac*-Mn(CO)$_3$(apeS)Cl]$_2$, 114594-88-6; [*fac*-Mn(CO)$_3$(apeSe)Br]$_2$, 114594-89-7; [*fac*-Mn(CO)$_3$(apeS)Br]$_2$, 114594-90-0; *fac*-Mn(CO)$_3$(apeSe)$_2$Cl, 114594-91-1; *fac*-Mn(CO)$_3$(apeS)$_2$Cl, 114594-92-2; *fac*-Mn(CO)$_3$(apeSe)$_2$Br, 114594-93-3; *fac*-Mn(CO)$_3$(apeS)$_2$Br, 114594-94-4; *fac*-Re(CO)$_3$(apeSe)Br, 114614-09-4; *fac*-Re(CO)$_3$(apeS)Br, 114614-10-7; *fac*-Re(CO)$_3$(apeSe)$_2$Br, 114594-95-5; *fac*-Re(CO)$_3$(apeS)$_2$Br, 114594-96-6; *fac*-Mn(CO)$_3$(dpm)Cl, 60305-98-8; *fac*-Mn(CO)$_3$(dpe)Cl, 49695-20-7; *fac*-Mn(CO)$_3$(dpm)Br, 37523-63-0; *fac*-Mn(CO)$_3$(dpe)Br, 37523-64-1; Cr(CO)$_4$(dpmSe), 73395-81-0; Cr(CO)$_4$(dpmS), 62264-01-1; Mo(CO)$_4$(dpmSe), 73395-83-2; Mo(CO)$_4$(dpmS), 54340-52-2; W(CO)$_4$(dpmSe), 73395-82-1; W(CO)$_4$(dpmS), 62264-00-0; [Cr(CO)$_4$(dpmSe)]$^+$, 114594-98-8; [Cr(CO)$_4$(dpmS)]$^+$, 114691-52-0; [Mo(CO)$_4$(dpmSe)]$^+$, 114594-99-9; [Mo(CO)$_4$(dpmS)]$^+$, 114595-00-5; [W(CO)$_4$(dpmSe)]$^+$, 114595-01-6; [W(CO)$_4$(dpmS)]$^+$, 114595-02-7; [Cr(CO)$_3$(NO)(dpmSe)]PF$_6$, 114595-04-9; [Cr(CO)$_3$(NO)(dpmS)]PF$_6$, 114595-06-1; [Mo(CO)$_3$(NO)(dpmSe)]$^+$, 114672-92-3; [W(CO)$_3$(NO)(dpmS)]$^+$, 114595-07-2; dpm, 2071-20-7; Se, 7782-49-2; ape, 23582-06-1; S, 7704-34-9; Mn(CO)$_5$Cl, 14100-30-2; Mn(CO)$_5$Br, 14516-54-2; Re(CO)$_5$Br, 14220-21-4; [*fac*-Mn(CO)$_3$(dpmSe)Cl]$^+$, 114595-08-3; [*fac*-Mn(CO)$_3$(dpmS)Cl]$^+$, 114595-09-4; [*fac*-Mn(CO)$_3$(dpmSe)Br]$^+$, 114595-10-7; [*fac*-Mn(CO)$_3$(dpmS)Br]$^+$, 114595-11-8; [*fac*-Re(CO)$_3$(dpmSe)Br]$^+$, 114595-12-9; [*fac*-Re(CO)$_3$(dpmS)Br]$^+$, 114595-13-0; [*fac*-Mn(CO)$_3$(dpm)Cl]$^+$, 65634-85-7; [*fac*-Mn(CO)$_3$(dpm)Br]$^+$, 47752-42-1; [*fac*-Mn(CO)$_3$(dpe)Br]$^+$, 47768-35-4.

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