on $Ni(C_2H_4)^{19}$) rather than a $Ni(3d_\pi) \rightarrow$ olefin(π^*) MLCT assignment.

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Registry No. Ni(ethylene), 61160-51-8; Ni(ethylene)$_2$, 52392-74-2; Ni(ethylene)$_3$, 50696-82-7; Ni(propene), 67316-83-0; Ni(propene)$_2$, 67316-84-1; Ni(propene)$_3$, 67316-85-2; Ni(but-1-ene), 67316-86-3; Ni(but-1-ene)$_2$, 67316-87-4; Ni(but-1-ene)$_3$, 67316-88-5; Ni(isobutene), 67316-89-6; Ni(isobutene)$_2$, 67316-90-9; Ni(isobutene)$_3$, 67316-91-0; Ni(*cis*-but-2-ene), 67316-92-1; Ni(*cis*-but-2-ene)$_2$, 67316-93-2; Ni(*cis*-but-2-ene)$_3$, 67316-94-3; Ni(*trans*-but-2-ene), 67337-41-1; Ni(*trans*-but-2-ene)$_2$, 67337-42-2; Ni(*trans*-but-2-ene)$_3$, 67337-43-3; Ni(hex-1-ene), 67316-95-4; Ni(hex-1-ene)$_2$, 67316-96-5; Ni(hex-1-ene)$_3$, 67316-97-6; Ni(vinyl chloride), 67316-98-7; Ni(vinyl chloride)$_2$, 67316-99-8; Ni(vinyl chloride)$_3$, 67317-00-4; Ni(vinyl fluoride), 67317-01-5; Ni(vinyl fluoride)$_2$, 67317-02-6; Ni(vinyl fluoride)$_3$, 67317-03-7; Ni(chlorotrifluoroethylene), 67317-04-8; Ni(chlorotrifluoroethylene)$_2$, 67317-05-9; Ni(chlorotrifluoroethylene)$_3$, 67328-93-2; Ni(allyl chloride), 67317-06-0; Ni(allyl chloride)$_2$, 67317-07-1; Ni(allyl chloride)$_3$, 67317-08-2; Ni(perfluoroethylene), 63833-65-8; Ni(perfluoroethylene)$_2$, 63833-64-7; Ni(perfluoroethylene)$_3$, 63833-63-6.

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Chemical and Electrochemical Studies of Tricarbonyl Derivatives of Manganese and Rhenium

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The interaction of manganese and rhenium pentacarbonyl halides with monodentate arylphosphines and related ligands has been reinvestigated. Tetracarbonyl and tricarbonyl derivatives were obtained, and in those cases where the tricarbonyl species obtained by direct interaction was facial, thermal, electrochemical, or chemical oxidation–reduction techniques were used to obtain the corresponding meridional isomers. Electrochemical and chemical oxidations of the tricarbonyl complexes clearly demonstrate the existence of metal(II) complexes. Relative to metal(I) they are kinetically very labile, powerful oxidants, light sensitive and unstable with respect to loss of carbon monoxide. Additionally, *fac* M(II) isomerizes to *mer* M(II) at a far greater rate than the corresponding isomerization in oxidation state I.

Introduction

In a recent study[1] it was shown that chemical and electrochemical oxidation of *fac*-$Mn(CO)_3$dpmX (dpm = $Ph_2PCH_2PPh_2$; X = Cl, Br) at room temperature gave *mer*-$[Mn(CO)_3dpmX]^+$ which could be readily reduced to otherwise inaccessible *mer*-$Mn(CO)_3$dpmX. With a related series of complexes containing other bidentate ligands[2] it was demonstrated that in the 17-electron configuration (manganese-(II)) the complexes were kinetically very labile, as well as light sensitive, and that many reactions of interest occurred. However, to date, similar studies on isoelectronic 17-electron rhenium complexes or complexes containing monodentate ligands have not been described, so that the generality of the above observations in group 7 transition-metal carbonyl halides is unknown. This paper reports the extension of electrochemical and chemical studies on the isomerization and redox behavior of complexes of the type $[M(CO)_3L_2X]^{0,+}$ (M = Mn, Re) containing monodentate ligands L, where L is an arylphosphine, -arsine, or -stibine or an aryl phosphite.

Some details of the properties of the 18-electron $M(CO)_3L_2X$ complexes (L as above) are known. Wilkinson and co-workers[3,4] claimed that interaction of $Re(CO)_5X$ and $Mn(CO)_5X$ with ligands such as triphenylphosphine gave in each case *fac*-$M(CO)_3L_2X$. However, later investigators[5,6] have shown that in fact the product is usually *mer*-$Mn(CO)_3L_2X$ in the case of manganese, but rhenium does produce the facial isomers. Thus, the existence of different isomers is already documented. Furthermore, in a relevant series of kinetic studies, Basolo and co-workers[7–9] showed that ligand exchange with *fac*-$Mn(CO)_3[P(OPh)_3]_2X$ or substitution of

Table I. Carbonyl Stretching Frequencies (CH_2Cl_2 Solution)

compd	ν_{CO}, cm^{-1}
mer-$Mn(CO)_3(PPh_3)_2Br$	1948, 1916 m[a]
mer-$Mn(CO)_3(ppt)_2Br$	1943, 1912 m
mer-$Mn(CO)_3(pmt)_2Br$	1943, 1910 m
mer-$Mn(CO)_3[P(OPh)_3]_2Br$	1990, 1947 m
mer-$Mn(CO)_3(AsPh_3)_2Br$	1950, 1910 m
mer-$Mn(CO)_3(SbPh_3)_2Br$	1946, 1908 m
fac-$Mn(CO)_3[P(OPh)_3]_2Br$	2046, 1995, 1946
fac-$Mn(CO)_3(SbPh_3)_2Br$	2016, 1948, 1912
fac-$Re(CO)_3(PPh_3)_2Cl$	2028, 1944, 1894
fac-$Re(CO)_3(PPh_3)_2Br$	2029, 1949, 1906
fac-$Re(CO)_3(pmt)_2Cl$	2029, 1943, 1899
fac-$Re(CO)_3(pmt)_2Br$	2030, 1950, 1901
fac-$Re(CO)_3[P(OPh)_3]_2Cl$	2057, 1994, 1935
fac-$Re(CO)_3[P(OPh)_3]_2Br$	2052, 1991, 1930
mer-$Re(CO)_3(PPh_3)_2Cl$	1944, 1894 m
mer-$Re(CO)_3(PPh_3)_2Br$	1949, 1901 m
mer-$Re(CO)_3(pmt)_2Cl$	1943, 1900 m
mer-$Re(CO)_3(pmt)_2Br$	1940, 1897 m
mer-$Re(CO)_3[P(OPh)_3]_2Cl$	1994, 1936 m

[a] m = medium; all other peaks strong.

$Mn(CO)_4LX$ produced *mer*-$Mn(CO)_3L_2X$ via a dissociative mechanism involving a five-coordinate intermediate. Finally, Reimann and Singleton have examined the reactions of $Mn(CO)_5Br$ with a series of alkylphosphines and alkyl phosphites,[10,11] and they considered some oxidation reactions of the resulting tricarbonyls. Reference to their results in comparison to ours will be made at appropriate points in the text. In summary, while some of the kinetic and thermodynamic details are known about the 18-electron complexes, very little is known about the 17-electron oxidation state II complexes or the redox behavior of the $[M(CO)_3L_2X]^{0,+}$ system.

Experimental Section

Carbon, hydrogen, halogen, phosphorus, and arsenic analyses were by the Australian Microanalytical Service, Melbourne, Australia. $Mn(CO)_5Br$ was prepared by direct interaction of $Mn_2(CO)_{10}$ and bromine at 42 °C as described previously.[12] $Re(CO)_5X$ and all ligands were commercial samples and were used without further purification. All solvents were of AR grade. Infrared spectra were recorded on a Unicam SP 1200 spectrophotometer, proton NMR spectra on a Perkin-Elmer R12 spectrometer, carbon and phosphorus NMR spectra on a Jeol FX 100 multinuclear pulsed Fourier transform spectrometer, and ESR spectra on a Varian 450/15 instrument.

For electrochemical measurements dichloromethane was used as solvent and all solutions were degassed using argon. Tetraethylammonium perchlorate was used as the supporting electrolyte at a concentration of 0.07 M. All data were obtained at 22 ± 2 °C. Voltammograms were recorded using either a PAR electrochemistry system, Model 170, or a PAR polarographic analyzer, Model 174. A three-electrode system was used and the working electrode was a platinum wire. The reference electrode was Ag/AgCl (saturated LiCl in CH_2Cl_2) separated from the test solution by a salt bridge containing tetraethylammonium perchlorate (0.07 M in CH_2Cl_2). The third, or auxiliary electrode, was a platinum wire.

Tetracarbonyl Complexes. Equimolar quantities of $Mn(CO)_5Br$ and the appropriate ligand L [L = PPh_3, $P(p\text{-tolyl})_3$ = ppt, $P(m\text{-tolyl})_3$ = pmt, $AsPh_3$, $SbPh_3$, $P(OPh)_3$] were refluxed in chloroform or dichloromethane for 1–2 h. These known compounds[7] were isolated by evaporation of the solvent and recrystallization from a dichloromethane–hexane mixture. The rhenium complexes required about 12 h of refluxing in chloroform for their formation, but they were not isolated. Their infrared spectra are similar to those of the manganese compounds.[13]

mer **Manganese Tricarbonyl Complexes.** These were prepared by a modification of a previously reported[8] method. $Mn(CO)_5Br$ and 2 molar equiv of any ligand (except $SbPh_3$ and $P(OPh)_3$), or, alternatively, $Mn(CO)_4LBr$ and a further mole of ligand, were refluxed in chloroform for 16–24 h. The compounds were isolated by evaporation of the solvent and recrystallization from a dichloromethane–hexane mixture. Infrared spectra and analyses are given in Tables I and II.

fac **Manganese Tricarbonyl Complexes.** When the reaction described above is carried out with $SbPh_3$ or $P(OPh)_3$[8] as the ligand, the product is *fac*-$Mn(CO)_3L_2Br$ (Table I) and it is formed after about 4 h of reflux. The stibine complex has previously been reported by the same reaction in the absence of solvent.[6] The products were isolated and purified as above. Refluxing a solution of these complexes in chloroform for 12 h [$P(OPh)_3$][8] or 2 days ($SbPh_3$) gave *mer*-$Mn(CO)_3L_2Br$.

fac **Rhenium Tricarbonyl Complexes.** Interaction of $Re(CO)_5X$ with 2 molar equiv of any of the ligands gave *fac*-$Re(CO)_3L_2X$ in approximately 12 h in chloroform. The compounds were isolated as above. Some of these complexes had been prepared previously[3] by interaction of the components without any solvent.

mer **Rhenium Tricarbonyl Complexes.** Refluxing a suspension of *fac*-$Re(CO)_3(pmt)_2X$ in *n*-heptane for 2 days gave *mer*-$Re(CO)_3(pmt)_2X$, but this method was not successful for the other complexes. Chemical oxidation of *fac*-$Re(CO)_3L_2X$ with $NOPF_6$ in dichloromethane solution gave a reddish purple color which rapidly disappeared in bright sunlight. In some cases (see text), after removal of excess $NOPF_6$, *mer*-$Re(CO)_3L_2X$ was isolated from the solution using the methods described above.

ESR Spectrum of Manganese(II) Complexes. Although manganese(II) complexes were observed electrochemically, they could not be isolated (see text). However, the ESR spectrum of the oxidation product of *mer*-$Mn(CO)_3(ppt)_2Br$ was obtained in the following way. A solution of the complex in dichloromethane was cooled to −78 °C in an ESR tube and a cooled solution of $NOPF_6$ in acetonitrile was added. By successively warming the solution to about −38 °C and recooling to −78 °C, oxidation proceeded to give a purple coloration at the interface of the solutions. The ESR spectrum of this preparation showed a regular six-line spectrum which is consistent only[1] with a low-spin configuration for a complex of such low symmetry as $[Mn(CO)_3(ppt)_2Br]^+$.

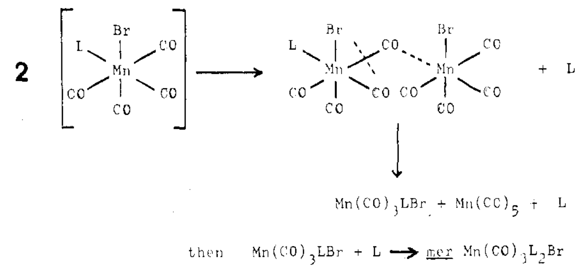
Results and Discussion

Reactions of $Mn(CO)_5Br$. Bromopentacarbonylmanganese(I) in dichloromethane reacted with 1 mol of a variety of ligands to give $Mn(CO)_4LBr$ [L = PPh_3, $P(p\text{-tolyl})_3$, $P(m\text{-tolyl})_3$, $AsPh_3$, $SbPh_3$, $P(OPh)_3$]. Their infrared spectra show unequivocally that they are all cis isomers as reported previously.[5,6] Reaction of the tetracarbonyls with an additional mole of ligand in refluxing chloroform for approximately 12

Table II. Analytical Data

compd	% calcd C	% calcd H	% calcd Hal	% calcd P	% found C	% found H	% found Hal	% found P
mer-$Mn(CO)_3(PPh_3)_2Br$	63.0	4.0	10.7	8.3	60.8	4.0	10.8	8.2
mer-$Mn(CO)_3(ppt)_2Br$	65.3	5.1	9.7	7.5	64.0	5.2	9.8	7.2
mer-$Mn(CO)_3[P(OPh)_3]_2Br$	55.8	3.6	9.5	7.4	55.8	3.8	9.2	7.7
fac-$Mn(CO)_3[P(OPh)_3]_2Br$	55.8	3.6	9.5	7.4	54.2	3.7	10.4	7.5
fac-$Re(CO)_3(PPh_3)_2Cl$	56.4	3.6	4.3	7.5	56.2	3.8	4.5	7.5
fac-$Re(CO)_3(PPh_3)_2Br$	53.6	3.4	9.2	7.1	53.2	3.3	9.1	7.0
fac-$Re(CO)_3(pmt)_2Cl$	59.1	4.6	3.8	6.8	58.9	4.9	4.1	6.9
fac-$Re(CO)_3(pmt)_2Br$	56.4	4.4	8.4	6.5	56.6	4.6	8.3	6.7
fac-$Re(CO)_3[P(OPh)_3]_2Cl$	50.6	3.2	3.8	6.7	50.3	3.5	3.4	6.6
fac-$Re(CO)_3[P(OPh)_3]_2Br$	48.2	3.1	8.3	6.4	47.8	3.2	8.3	6.1
mer-$Re(CO)_3[P(OPh)_3]_2Cl$	50.6	3.2		6.7	49.6	3.3		6.5

Scheme I



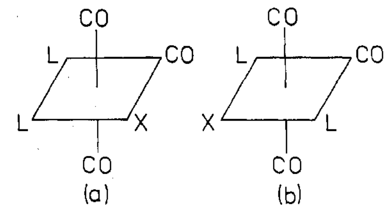


Figure 1. *mer*-cis and *mer*-trans isomers of $M(CO)_3L_2X$.

h gave $Mn(CO)_3L_2Br$ as the only carbonyl-containing species. Except when L = $SbPh_3$ and $P(OPh)_3$ (see below), the infrared spectra of the complexes show that they are *mer* isomers (Table I).

Arguments based on electronic considerations[14] would suggest that the electronically favored *fac*-$Mn(CO)_3L_2X$ should first be formed by substitution of $Mn(CO)_4LBr$ with further L, and it was thought that steric pressures may have been the cause of the isomerization to *mer*. However, all attempts at detecting the supposed intermediate facial isomer by infrared spectroscopy and electrochemistry (see below) failed. It was then found that heating a solution of $Mn(CO)_4PPh_3Br$ alone in chloroform gave *mer*-$Mn(CO)_3(PPh_3)_2Br$ and $Mn(CO)_5Br$ (which was identified by both infrared spectroscopy and electrochemistry). In addition, some $MnCl_2$ was usually observed, but we have shown that $Mn(CO)_5Br$ is readily oxidized in boiling chlorocarbon solvents.[15] The mechanism of this ligand-transfer reaction, which can be written in a formal way as

$$2Mn(CO)_4LBr \rightarrow mer\text{-}Mn(CO)_3L_2Br + Mn(CO)_5Br$$

is unknown, but it could involve the formation of a carbonyl-bridged dimer and dissociation of a phosphine group as shown in Scheme I.

The postulated five-coordinate intermediate $Mn(CO)_3LBr$ is the same as that assumed by Basolo and co-workers[7-9] to exist in solution during ligand-exchange reactions of the type

$$fac\text{-}Mn(CO)_3[P(OPh_3)]_2X + 2PPh_3 \rightarrow mer\text{-}Mn(CO)_3(PPh_3)_2X$$

It is therefore not necessary to postulate the facial isomer as an intermediate in the formation of the meridional isomer. It would appear that steric forces determine the course of the reaction. In cases where the facial isomer is possible (see below) the facial $Mn(CO)_3L_2Br$ is formed quite rapidly by direct substitution of the tetracarbonyl. However, in cases where steric interaction prevents formation of the facial isomer, the reaction proceeds much more slowly to give the *mer* isomer with $Mn(CO)_5Br$ as the other product.

With triphenyl phosphite[7] and triphenylstibine[6] it has been reported that the product obtained with $Mn(CO)_5Br$ and 2 mol of ligand is *fac*-$Mn(CO)_3L_2Br$. These results have been confirmed; their infrared spectra show three strong bands of similar intensity. In both cases the *mer* isomer may be obtained by refluxing the *fac* complex in chloroform.

Reactions of $Re(CO)_5X$. Complexes of the type $Re(CO)_4LX$ were readily prepared by refluxing equimolar quantities of the ligand and $Re(CO)_5X$ in chloroform for about 2 h. In contrast to the behavior of manganese, however, reaction with a further mole of ligand in refluxing chloroform produced in all cases *fac*-$Re(CO)_3L_2X$.

In the case of the bulkiest ligand, pmt, the facial isomer can be converted to the corresponding isomer, *mer*-$Re(CO)_3(pmt)_2X$, by refluxing in heptane for 1–2 days, but the other complexes did not isomerize under these conditions.

We suggest that the principal reason for the different stereochemistries observed for the tricarbonyl complexes of manganese and rhenium is steric in nature. An important point to be made is that the steric crowding is not concerned directly with the six donor atoms but rather with the interaction of the bulky ligands themselves. Thus, all the phosphines give *mer*-$Mn(CO)_3L_2Br$, but triphenyl phosphite and triphenylstibine give facial isomers. The relief of steric strain with the phosphite is obvious, but with $SbPh_3$ the principal effect is the increased separation of the phenyl groups due to the larger group 5 donor. Similar examples of the relief of steric interaction by *increasing* the size of the donor atom have been reported in group 6 carbonyl chemistry.[16] With the larger rhenium atom all the ligands gave facial tricarbonyl derivatives, although with the bulkiest ligand the meridional derivative could be produced by thermal methods, presumably for steric reasons. These arguments are also consistent with other observations in the literature; for example, $Mn(CO)_5X$ gave *fac*-$Mn(CO)_3L_2X$ with the less sterically active alkylphosphines.[10] Freni and co-workers[17] found that *fac*-$Re(CO)_3(PPh)_2I$ could be converted to the *mer* isomer at 150 °C and that for various phosphorus ligands, more phosphorus donor atoms could be coordinated to rhenium as the steric influence of the substituents decreased.

NMR Studies. Infrared spectroscopy distinguishes between facial and meridional isomers of $M(CO)_3L_2X$, but it does not readily distinguish between the two *mer* isomers (Figure 1). However, on the basis of dipole moment studies, Basolo, Angelici, and Poë[8] concluded that the $Mn(CO)_3L_2X$ compounds were *mer*-trans. We have confirmed this result by multinuclear NMR studies.

The compounds *mer*-$Mn(CO)_3(PPh_3)_2Br$, *mer*-$Mn(CO)_3[P(OPh_3)]_2Br$, and *mer* $Re(CO)_3[P(OPh)_3]_2Cl$ all show a single resonance in their ^{31}P NMR spectra. This singlet in each spectrum is consistent with either the *mer*-trans configuration or, much less likely, a fluxional molecule, in which case ^{31}P NMR would not distinguish between *mer*-trans and *mer*-cis. However, the ^{13}C NMR spectrum of *mer*-$Re(CO)_3[P(OPh)_3]_2Cl$ shows that the molecule is stereochemically rigid and, therefore, the ^{31}P NMR spectra are only consistent with the *mer*-trans configuration. The ^{13}C spectrum of the rhenium compound shows a carbonyl signal consisting of two triplets of relative intensity 2:1 which independently proves the *mer*-trans configuration. Proton NMR studies on the pmt complexes are of some interest. It has previously been shown[18] in group 6 carbonyl chemistry that when two pmt groups are mutually cis to each other, there is a chemical shift of the methyl resonance of approximately δ 0.2 upfield from the free-ligand resonance. However, when only one pmt group is present, or two are mutually trans, the methyl resonance occurs slightly downfield relative to the free ligand. $Mn(CO)_4pmtBr$, *mer*-$Mn(CO)_3(pmt)_2Br$, and *mer*-$Re(CO)_3(pmt)_2X$ all showed a methyl resonance almost coincident with that of the free ligand, but for *fac*-$Re(CO)_3(pmt)_2X$ the resonance occurs well upfield of the free ligand, thus demonstrating that this method of determining isomer configuration is generally valid. All NMR data are recorded in Table III.

Electrochemical Studies. All electrochemical studies on the tricarbonyl complexes were performed in dichloromethane (0.07 M NEt_4Cl_4) at platinum electrodes. A cyclic volt-

Table III. Multinuclear NMR Data

^{31}P NMR[a]		
mer-$Re(CO)_3[P(OPh)_3]_2Cl$	103.1 ppm	
mer-$Mn(CO)_3(PPh_3)_2Br$	54.1 ppm	
mer-$Mn(CO)_3[P(OPh)_3]_2Br$	129.8 ppm	
^{13}C NMR[b]		
mer-$Re(CO)_3[P(OPh)_3]_2Cl$ carbonyl resonances	186.7 ppm (intens 2) 183.9 ppm (intens 1)	
^{1}H NMR[c]		
	δ(methyl)	Δ[d]
free pmt	2.28	
$Mn(CO)_4pmtBr$	2.29	−0.01
$Re(CO)_4pmtCl$	2.30	−0.02
$Re(CO)_4pmtBr$	2.29	−0.01
mer-$Mn(CO)_3(pmt)_2Br$	2.29	−0.01
mer-$Re(CO)_3(pmt)_2Cl$	2.30	−0.02
mer-$Re(CO)_3(pmt)_2Br$	2.29	−0.01
fac-$Re(CO)_3(pmt)_2Cl$	2.14	+0.14
fac-$Re(CO)_3(pmt)_2Br$	2.13	+0.15

[a] All resonances at low frequency relative to external H_3PO_4 reference. [b] Resonances at low frequency relative to internal Me_4Si reference. [c] All resonances downfield from Me_4Si internal standard. [d] $\Delta = \delta$[methyl(free ligand)] − δ[methyl(complex)].

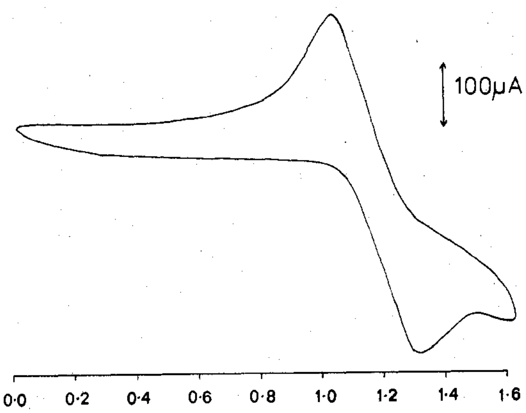


Figure 2. Cyclic voltammogram for oxidation of *mer*-$Mn(CO)_3(pmt)_2Br$ in dichloromethane (0.07 M Et_4NClO_4); T = 22 °C; scan rate 500 mV s^{-1}.

ammogram of a solution of *mer*-$Mn(CO)_3(pmt)_2Br$ is shown in Figure 2. The couple is only quasi-reversible since the peak-to-peak separation is 270 mV (instead of the theoretical value of 56 mV). All the other *mer* Mn(I) complexes gave similar results as shown in Table IV, except that the triphenyl phosphite complex oxidized at a significantly more positive potential.

Deviations from Nernstian behavior are due to the slow electron transfer from the compound to the electrode. A computer program has been written[19] which enables digital simulation[20] of the observed cyclic voltammogram using predetermined rate constants for the electron-transfer step. The results are essentially identical with the original work of Shain and Nicholson.[21] This program has been applied to this system and the values of the rate constants, k_s, which reproduce the peak-to-peak separations are also given in Table IV. In Figure 3 the comparison and theoretical curves for *mer*-$Mn(CO)_3(pmt)_2Br$ are shown. The excellent agreement verifies that the slow-electron-transfer mechanism fully accounts for the waves obtained without invoking any chemical complications. The computer program also allows evaluation of the thermodynamically significant $E°$ value of the couple and these are also tabulated.

The results show that Mn(II) is stable on the electrochemical time scale. In addition, because the couples are

Table IV. Electrochemical Data for Oxidation (Pt) Cyclic Voltammetry of *mer*-$M(CO)_3L_2X$ in CH_2Cl_2

complex	E_p^{Ox}, V	E_p^{Red}, V	$E°$, V	10^3k_s, cm s^{-1}
mer-$Mn(CO)_3(PPh_3)_2Br$	1.37	1.10	1.23	1.5
mer-$Mn(CO)_3(ppt)_2Br$	1.24	1.06	1.15	4.0
mer-$Mn(CO)_3(pmt)_2Br$	1.31	1.04	1.17	1.5
mer-$Mn(CO)_3(AsPh_3)_2Br$	1.33	1.02	1.17	1.0
mer-$Mn(CO)_3(SbPh_3)_2Br$	1.40	1.14	1.26	1.5
mer-$Mn(CO)_3P(OPh_3)_2Br$	1.78	1.44	1.43	1.2
mer-$Re(CO)_3(PPh_3)_2Cl$	1.66	1.32	1.49	0.7
mer-$Re(CO)_3(pmt)_2Cl$	1.65	1.33	1.49	0.9
mer-$Re(CO)_3(pmt)_2Br$	1.56	1.31	1.43	1.7

[a] All potentials are given in volts vs. Ag/AgCl; $T = 22 \pm 2$ °C; scan rate 500 mV s^{-1}; supporting electrolyte 0.07 M Et_4NClO_4. k_s is the heterogeneous charge transfer rate constant for electron transfer.

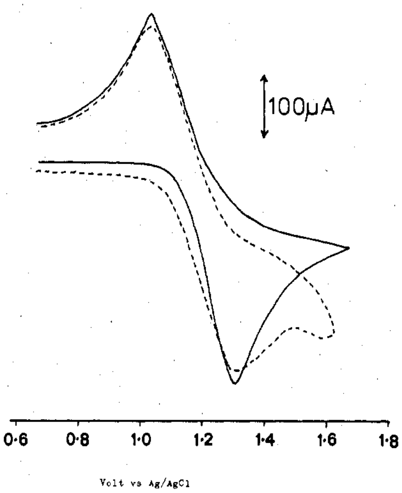


Figure 3. Cyclic voltammogram for oxidation of *mer*-$Mn(CO)_3(pmt)_2Br$: —, digital simulation using $k_s = 1.5 \times 10^{-3}$ cm s^{-1}; - - -, observed cyclic voltammogram, not corrected for background current.

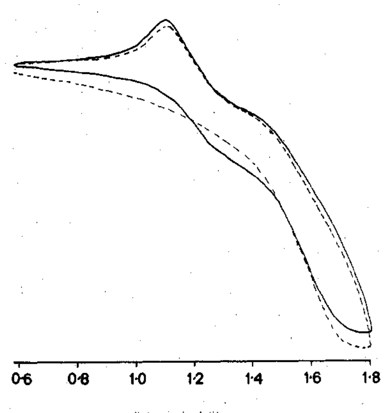


Figure 4. Cyclic voltammogram for oxidation of *fac*-$Mn(CO)_3(SbPh_3)_2Br$: - - -, first scan; —, second and subsequent scans; in dichloromethane (0.07 M Et_4NClO_4); T = 22 °C; scan rate 500 mV s^{-1}.

chemically reversible, the Mn(II) product is certainly *mer*-$[Mn(CO)_3L_2Br]^+$ and the couple can be simply written as

$$mer\text{-}Mn(CO)_3L_2Br \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} mer\text{-}[Mn(CO)_3L_2Br]^+$$

This is consistent with earlier results in the $Mn(CO)_3$(L-L)Br systems (L-L is a chelating diphosphine or diarsine).[1,2]

The electrochemical oxidation of *fac*-$Mn(CO)_3(SbPh_3)_2Br$ also shows interesting analogies with the $Mn(CO)_3$(L-L)Br system. Figure 4 shows the cyclic voltammogram for this complex in dichloromethane. On the first positive-going scan an oxidation wave was observed at about 1.68 V relative to Ag/AgCl, but no corresponding reduction peak was observed on the reverse scan. Instead, a reduction was observed at about 1.08 V and on the second forward-going scan the other half of this quasi-reversible couple appeared at about 1.35 V. These results show that *fac*-$[Mn(CO)_3(SbPh_3)_2Br]^+$ is totally unstable on the electrochemical time scale and that it decomposes to a new species showing a quasi-reversible couple at less positive potentials. Previous results in the $Mn(CO)_3dpmX$ system[1] suggested that isomerization to *mer*-$[Mn(CO)_3(SbPh_3)_2Br]^+$ had occurred and that the new peaks are due to the *mer* Mn(I)–*mer* Mn(II) couple. This assignment was confirmed by running a cyclic voltammogram of an authentic sample of *mer*-$Mn(CO)_3(SbPh_3)_2Br$. The reactions occurring with *fac*-$Mn(CO)_3(SbPh_3)_2Br$ can be summarized by the equations

$$\textit{fac}\ \mathrm{Mn(I)} \xrightarrow{-e^-} \textit{fac}\ \mathrm{Mn(II)} \xrightarrow{\text{fast}} \textit{mer}\ \mathrm{Mn(II)}$$

$$\textit{mer}\ \mathrm{Mn(II)} \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} \textit{mer}\ \mathrm{Mn(I)}$$

This result is in contrast with the conclusions of Reimann and Singleton,[11] who claimed that with dpm and alkylphosphines the manganese(II) product is facial. We have already demonstrated[1] that with dpm the product isolated in manganese(II) is the meridional isomer.

As noted earlier, it was at one stage thought that the conversion of $Mn(CO)_4LBr$ to *mer*-$Mn(CO)_3L_2Br$ might proceed via a *fac*-$Mn(CO)_3L_2Br$ intermediate and efforts were made to detect this species electrochemically, without success. On examining the cyclic voltammogram of a refluxed solution of $Mn(CO)_4PPh_3Br$, peaks were observed corresponding to the *mer* Mn(I)–*mer* Mn(II) couple, together with an extra wave which was shown to be due to $Mn(CO)_5Br$ by comparison with the cyclic voltammogram of an authentic sample. Inspection of the infrared spectrum of the solution confirmed this assignment.

The potentials required to oxidize *fac*-$Re(CO)_3L_2X$ are on the limit of the working range of dichloromethane. However, it was just possible to detect the oxidation of *fac*-$Re(CO)_3L_2X$, and the appearance of a quasi-reversible couple at less positive potentials on the reverse scan suggested the formation of *mer*-$Re(CO)_3L_2X$ similar to the manganese case. Subsequently, *mer*-$Re(CO)_3L_2X$ complexes were isolated by chemical oxidation of *fac*-$Re(CO)_3L_2X$ followed by reduction of the product (see below) and their cyclic voltammograms were recorded and confirmed the assignment of the peaks observed in the electrochemical oxidation of *fac*-$Re(CO)_3L_2X$. It will be noted (Table IV) that the $E°$ for the *mer* (I)–*mer* (II) couple is significantly more positive for rhenium than for the corresponding manganese compounds. This difference is entirely consistent with our observations in group 6 carbonyl chemistry where molybdenum and tungsten complexes were more difficult to oxidize than their chromium analogues.[22,23]

Chemical Oxidations. In the $Mn(CO)_3dpmX$ system, oxidation of *fac*-$Mn(CO)_3dpmX$ with $NOPF_6$ led to the isolation of *mer*-$[Mn(CO)_3dpmX]^+$, and its subsequent reduction gave otherwise inaccessible *mer*-$Mn(CO)_3dpmX$.[1] In the manganese complexes studied here the *mer* isomers are already available and the only aim of the chemical oxidation was isolation of solid manganese(II) derivatives. Although purple solutions of *mer*-$[Mn(CO)_3L_2Br]^+$ could be prepared by oxidation with $NOPF_6$, the products could not be isolated since they were unstable on the synthetic time scale, even though they were readily observable on the electrochemical time scale. In contrast, Reimann and Singleton[11] were able to isolate solid Mn(II) products using alkylphosphines. Chemical oxidation of *fac*-$Mn(CO)_3(SbPh_3)_2Br$ by $NOPF_6$ in dichloromethane followed by reduction of the product gave *mer*-$Mn(CO)_3(SbPh_3)_2Br$, but isolation of the intermediate Mn(II) species was again not possible. The cyclic voltammogram of the reaction mixture (Figure 5) clearly shows the presence of considerable quantities of *mer*-$Mn(CO)_3(SbPh_3)_2Br$ together with some remaining facial isomer.

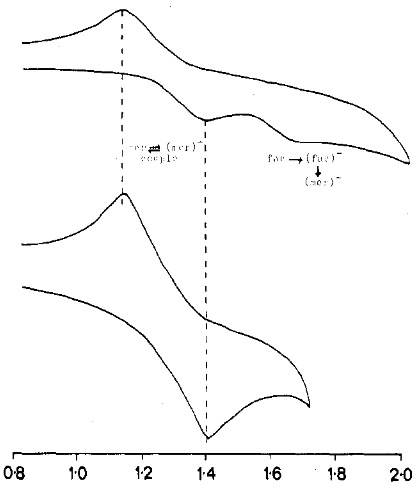


Figure 5. Cyclic voltammograms after addition of $NOPF_6$ for the oxidation of *fac*-$Mn(CO)_3(SbPh_3)_2Br$ (top) and *mer*-$Mn(CO)_3(SbPh_3)_2Br$ (bottom). Both were taken in dichloromethane (0.07 M Et_4NClO_4); $T = 22$ °C; scan rate 500 mV s^{-1}.

Chemical oxidation of *fac*-$Re(CO)_3L_2X$ with $NOPF_6$ gave a variety of results depending on the complex studied. With $Re(CO)_3(PPh_3)_2Cl$, $NOPF_6$ gave a purple solution (presumably Re(II)) which was rapidly decolorized in bright sunlight to give a solution containing *mer*-$Re(CO)_3(PPh_3)_2Cl$. With *fac*-$Re(CO)_3(PPh_3)_2Br$, reaction with $NOPF_6$ in dichloromethane in sunlight gave *mer*-$Re(CO)_3(PPh_3)_2Br$, but if the reaction was carried out in the dark, a mixture of *mer*-$Re(CO)_3(PPh_3)_2Br$ and $Re(CO)_4PPh_3Br$ resulted. With the pmt ligand, *fac*-$Re(CO)_3(pmt)_2Cl$ gave on oxidation, even in the sunlight, a mixture of meridional tricarbonyl and the tetracarbonyl species, and with the corresponding bromo derivatives no evidence for the formation of *mer*-$Re(CO)_3(pmt)_2Br$ was obtained; the product appeared to contain no carbonyl groups and was not investigated further. Our rationale for these complicated reactions is that there are two competing reactions involving Re(II), just as has been shown previously to occur in the $Mn(CO)_3(L\text{-}L)X$ systems.[2] The rhenium(II) carbonyl complexes are light sensitive and are rapidly photochemically reduced in dichloromethane to Re(I). In the absence of light the rhenium(II) carbonyl complexes slowly decompose with loss of carbon monoxide which reacts with remaining *fac*-$Re(CO)_3L_2X$ to give the observed tetracarbonyl species. It has been confirmed that carbon monoxide does indeed react with the tricarbonyl complexes. As noted earlier, the most convenient method of preparing *mer*-$Re(CO)_3(pmt)_2X$ is by refluxing the facial isomer in heptane.

Mechanism of Isomerization. An interesting feature of this system is that isomerization can occur in both oxidation state I and oxidation state II of the metal, but the rates are very different. In the thermal method, in which the metal always stays in oxidation state I, refluxing for several hours, or, in extreme cases, 1–2 days, is required. It has been shown that this process occurs via the dissociative mechanism discussed earlier. In the isomerization involving oxidation, either chemical or electrochemical, fast isomerization occurs in oxidation state II. For the series $Mn(CO)_3(L\text{–}L)X^{0,+}$ complexes,[2] oxidation state II isomerization is believed to occur

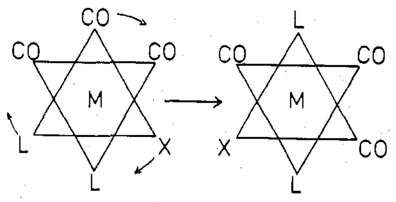


Figure 6. Internal twist mechanism of *fac*-$M(CO)_3L_2X$ to *mer*-trans-$M(Co)_3L_2X$.

via a twist mechanism on the basis of measurements of the entropy of activation, due to the nonsolvent dependence of the rate constants, and for other reasons. By analogy we believe the fast isomerization in oxidation state II in $[M(CO)_3L_2X]^+$ also occurs via a twist mechanism of the type shown in Figure 6.

Conclusions

From the above studies it seems apparent that the 17-electron manganese(II) and rhenium(II) complexes are in general extremely kinetically labile, powerful oxidants and are very light sensitive. In all cases, therefore, they can be classified as much more reactive complexes than the corresponding 18-electron metal(I) compounds. This clearly has significant synthetic consequences as has been demonstrated in this work and enables a range of otherwise inaccessible complexes to be made.

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Registry No. *mer*-$Mn(CO)_3(PPh_3)_2Br$, 15662-31-4; *mer*-$Mn(CO)_3(ppt)_2Br$, 67124-88-3; *mer*-$Mn(CO)_3(pmt)_2Br$, 67113-79-5; *mer*-$Mn(CO)_3[P(OPh)_3]_2Br$, 15614-85-4; *mer*-$Mn(CO)_3(AsPh_3)_2Br$, 63527-66-2; *mer*-$Mn(CO)_3(SbPh_3)_2Br$, 67145-45-3; *fac*-$Mn(CO)_3[P(OPh)_3]_2Br$, 19195-71-2; *fac*-$Mn(CO)_3(SbPh_3)_2Br$, 63511-08-0; *fac*-$Re(CO)_3(PPh_3)_2Cl$, 25246-23-5; *fac*-$Re(CO)_3(PPh_3)_2Br$, 54082-96-1; *fac*-$Re(CO)_3(pmt)_2Cl$, 67145-44-2; *fac*-$Re(CO)_3(pmt)_2Br$, 67145-43-1; *fac*-$Re(CO)_3[P(OPh)_3]_2Cl$, 25045-02-7; *fac*-$Re(CO)_3[P(OPh)_3]_2Br$, 49742-38-3; *mer*-$Re(CO)_3(PPh_3)_2Cl$, 19394-85-5; *mer*-$Re(CO)_3(PPh_3)_2Br$, 51446-58-3; *mer*-$Re(CO)_3(pmt)_2Cl$, 67113-78-4; *mer*-$Re(CO)_3(pmt)_2Br$, 67113-77-3; *mer*-$Re(CO)_3[P(OPh)_3]_2Cl$, 67145-42-0; $Mn(CO)_4(pmt)Br$, 67113-76-2; $Re(CO)_4(pmt)Cl$, 67113-75-1; $Re(CO)_4(pmt)Br$, 67113-74-0; pmt, 6224-63-1; ^{13}C, 14762-74-4.

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Polarographic Studies of the Geometric Isomers of the Bis(diethylenetriamine)cobalt(III) and -cobalt(II) Cations in Acetone

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Extensive studies have been made previously on the kinetically inert geometric isomers of $[Co^{III}(dien)_2]^{3+}$ (dien = the tridentate ligand diethylenetriamine); however, virtually no information has been available on the corresponding isomers of $[Co^{II}(dien)_2]^{2+}$. Electrochemical reduction of the cobalt(III) complexes has been studied by dc polarography, differential pulse polarography, cyclic voltammetry, and controlled-potential electrolysis. Results have enabled equilibrium constants for the redox and isomer distribution to be calculated. Two reduction waves are found for each of the meridional (*mer*), symmetrical facial (*s-fac*), and unsymmetrical facial (*u-fac*) isomers. The step (*mer*, *u-fac*, *s-fac*) $[Co^{III}(dien)_2]^{3+} + e^- \rightleftharpoons$ (*mer*, *u-fac*, *s-fac*) $[Co^{II}(dien)_2]^{2+}$ occurs with retention of geometry on the electrochemical time scale. With respect to redox behavior, the *s-fac*-$[Co^{III}(dien)_2]^{3+}$ species is the hardest to reduce and the *mer*-$[Co^{II}(dien)_2]^{2+}$ cation is the hardest to oxidize. In oxidation state II the complexes are kinetically labile and under conditions of controlled-potential electrolysis, the thermodynamically favored *mer*-$[Co^{II}(dien)_2]^{2+}$ species is the only species found. Calculations suggest that compared with oxidation state III, the stability of the meridional form is considerably enhanced with respect to the facial isomers. On further reduction no cobalt(I) complexes are found and a two-electron step leading to formation of cobalt metal occurs: (*mer*, *u-fac*, *s-fac*) $[Co^{II}(dien)_2]^{2+} + 2e^- \rightarrow Co + 2dien$. With the N-methylated complex $[Co^{III}(medien)_2]^{3+}$ (medien = $NH_2CH_2CH_2N(CH_3)CH_2CH_2NH_2$) stabilization of the *s-fac* isomer is enhanced remarkably and it is the only isomer detected in either oxidation state III or II.

Introduction

Isomerism in complexes of the type $[Co^{III}(dien)_2]^{3+}$ (dien = the tridentate ligand diethylenetriamine) has been studied extensively since Mann[4] first isolated the complex cation as the iodide salt.

The geometric isomers shown in Figure 1 may be designated in terms of the facial or meridional arrangement of the ligands. An additional specification *u-fac* (unsymmetrical) and *s-fac*

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