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 - (18) That significant metal–ligand stabilization is occurring is evident in the relative energies of the π-bonded (η³, η³), half-sandwich (η¹, η³), and σ-bonded (η¹, η¹) structures (Table I). Bridging of one ligand (IIIa → IIIb) costs 117 kcal/mol while bridging the second ring (IIIb → IIIc) costs only an additional 22 kcal/mol.
 - (19) This is shown by the short Be–ring distance in IIIc (1.52 Å), comparable to those in η³-cyclopentadienylberyllium derivatives (1.48–1.53 Å).⁵ VIIIb, with four fewer valence electrons than IIIc has a longer Be–ring distance (1.71 Å).
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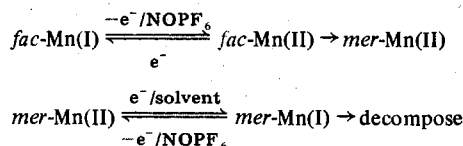
Investigation of Isomerization and Oxidation–Reduction Reactions of Halotricarbonylbis(diphenylphosphino)methanemanganese(I) Complexes Using Chemical and Electrochemical Techniques

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Electrochemical and chemical investigations of Mn(CO)₃dpmX [dpm = Ph₂PCH₂PPh₂, X = Cl, Br] have allowed the elucidation of the structural, kinetic, and thermodynamic properties of the [Mn(CO)₃dpmX]^{0,+} system. The equilibrium *fac*-Mn(I) + *mer*-Mn(II) ⇌ *mer*-Mn(I) + *fac*-Mn(II) is shown to lie substantially to the left. The various isomers for this system have all been individually identified and characterized by a variety of physical measurements. Electrochemistry is demonstrated to be particularly valuable in distinguishing the different species as well as providing information about redox properties. The reactions occurring in solution are summarized by the equations



The most interesting feature of this system is that both *mer*- and *fac*-[Mn(CO)₃dpmX]⁺ are low spin, as shown by ESR and direct magnetic susceptibility measurements (*mer* only). Reduction of Mn(I) (2e) and oxidation of Mn(II) were also observed.

Introduction

A study¹ of a series of complexes of the type Mn(CO)₃(PR₃)₂X has shown that they can exist in two distinct isomeric forms and that the rate of isomerism from *cis* to *trans* (referring to the phosphine groups) increases with increasing size of R. The complexes Mn(CO)₃dpmX cannot of course isomerize in this manner because of the bidentate nature of dpm, but isomerism from facial to meridional (referring to

carbonyls), which always accompanies the *cis*–*trans* type noted above, is still possible. However, only facial isomers of Mn(CO)₃dpmX have been previously reported.²

In two separate publications Reimann and Singleton have reported two compounds to result from the oxidation of Mn(CO)₃dpmBr with NOPF₆: one green³ and one violet.⁴ Both were described as *fac*-[Mn(CO)₃dpmBr]⁺, but there is only one possible isomer with this formula. Violet *fac*-

$[\text{Mn}(\text{CO})_3\text{dpmBr}]^+$ was said to be an oxidant which retained its facial arrangement upon reduction to $\text{Mn}(\text{CO})_3\text{dpmBr}$, even though the complexes $[\text{Mn}(\text{CO})_3(\text{PR}_3)_2\text{Br}]^+$ reduced exclusively to *mer*- $\text{Mn}(\text{CO})_3(\text{PR}_3)_2\text{Br}$.⁴ No mention of the green complex was made in this later study. Thus, according to the literature, redox reactions of the $[\text{Mn}(\text{CO})_3\text{dpmX}]^+ - \text{Mn}(\text{CO})_3\text{dpmX}$ system would not appear to involve isomerism.

The only other reported reaction of a manganese(I) carbonyl complex being oxidized to a Mn(II) complex is $[\text{Mn}(\text{CO})_2(\text{dpe})_2]^+ \rightarrow [\text{Mn}(\text{CO})_2(\text{dpe})_2]^{2+}$. In this case both complexes are trans and the Mn(II) complex is low spin.⁵

The complexes $[\text{M}(\text{CO})_2(\text{L-L})_2]^{0,+2+}$ [$\text{L-L} = \text{dpm}, \text{dpe}$ ($\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$); $\text{M} = \text{Cr}, \text{Mo}, \text{W}$] have been studied by both chemical and electrochemical techniques^{6,7} and were shown to isomerize rapidly after oxidation. Electrochemical techniques proved very valuable in elucidating the structures of all of the isomers observed in this dicarbonyl system and in establishing the mechanism of the redox reaction. It appeared worthwhile, therefore, to investigate the $\text{Mn}(\text{CO})_3\text{dpmX}$ system in an effort to study the possible isomerism and also to investigate whether electrochemistry of tricarbonyl systems would be as valuable as it had proved to be in the earlier study of the group 6 metal dicarbonyl system.

Experimental Section

$\text{Mn}(\text{CO})_3\text{dpmX}$ complexes were prepared by interaction of dpm and $\text{Mn}(\text{CO})_5\text{X}$ as described in the literature.⁸ All reagents used were of reagent grade purity. Tetraethylammonium perchlorate was used as the supporting electrolyte at a concentration of 0.1 M. For electrochemical measurements all solutions were degassed with argon. Unless otherwise stated, data were recorded at $22 \pm 2^\circ\text{C}$.

All polarograms and voltammograms were recorded using a PAR electrochemistry system, Model 170. A three-electrode system was used. The working electrode in polarography was a dropping mercury electrode with a controlled drop time of 0.5 s. In voltammetry the working electrode was platinum wire. The reference electrode was Ag-AgCl (0.1 M LiCl, acetone) separated from the test solution by a salt bridge containing acetone (0.1 M tetraethylammonium perchlorate). The third or auxiliary electrode was a platinum wire.

All infrared spectra were recorded on a Unicam SP 1200 instrument and calibrated against polystyrene (1601 cm^{-1}). A Varian 450/15 spectrometer was used to record the ESR spectra.

Results and Discussion

(i) **Electrochemical Oxidation.** The oxidation of $\text{Mn}(\text{CO})_3\text{dpmX}$ occurs at fairly positive potentials and cannot be studied at mercury electrodes. Discussion of the oxidation steps is therefore restricted to voltammetry at platinum electrodes in acetonitrile, although some data are tabulated for acetone solutions.

Figure 1a shows a cyclic voltammogram for oxidation of $\text{Mn}(\text{CO})_3\text{dpmCl}$ at room temperature (22°C). In the first positive-going potential scan two chemically irreversible oxidation processes are seen (electrode processes I and II). From the first negative-going scan and in all subsequent cycles, a chemically reversible process (electrode process III) occurs at less positive potentials than the initial oxidation process. If the potential of the cyclic voltammogram is switched at a potential between processes I and II (Figure 1b) then the reversible couple seen on subsequent scans remains, demonstrating that electrode process III is derived from the product of the first oxidation step. The electrochemistry of $\text{Mn}(\text{CO})_3\text{dpmBr}$ is essentially the same as that for $\text{Mn}(\text{CO})_3\text{dpmCl}$ and the general nomenclature $\text{Mn}(\text{CO})_3\text{dpmX}$ will therefore be used in subsequent discussion.

The freezing point of acetonitrile is -42°C , but of course it is a little lower in the presence of tetraethylammonium perchlorate. Using an acetone/dry ice mixture, the acetonitrile solution containing 0.1 M Et_4NClO_4 and 10^{-3} M $\text{Mn}(\text{CO})_3\text{dpmX}$ was frozen. The solid was allowed to melt slowly

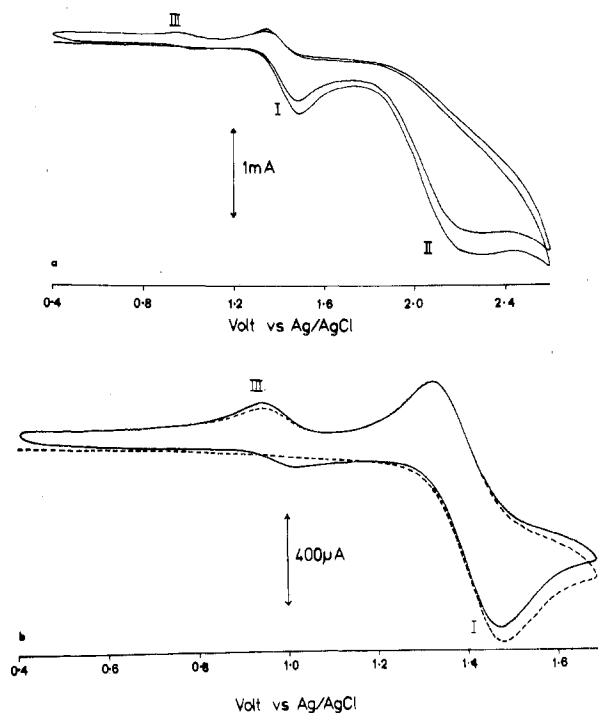


Figure 1. (a) Cyclic voltammogram for oxidation of $\text{Mn}(\text{CO})_3\text{-dpmCl}$ in acetonitrile (0.1 M Et_4NClO_4) at a platinum electrode; $T = 22^\circ\text{C}$; scan rate 500 mV/s. (b) Cyclic voltammogram for (a) but scan reversed after electrode process I.

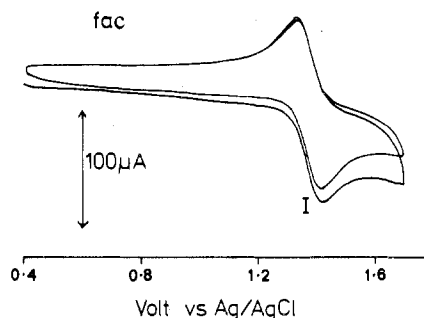


Figure 2. Low-temperature cyclic voltammogram for oxidation of $\text{Mn}(\text{CO})_3\text{dpmCl}$ at platinum in acetonitrile solution (0.1 M $\text{Et}_4\text{-NClO}_4$); $T = -35^\circ\text{C}$; scan rate 500 mV/s.

and when the solution reached a temperature of -35°C , cyclic voltammograms were recorded. Figure 2 shows that electrode process I now occurs as a chemically reversible couple at this temperature and that electrode process III is now absent. At -35°C electrode process II remains irreversible. Electrochemical parameters for the compounds described in this paper are summarized in Table I.

The starting material $\text{Mn}(\text{CO})_3\text{dpmX}$ is known to exist in the facial form. At low temperatures the reversibility of electrode process I means that probably the isostructural oxidation state II complex *fac*- $[\text{Mn}(\text{CO})_3\text{dpmX}]^+$ is formed and is quite stable on the electrochemical time scale at these temperatures, although this stability is lost at room temperature. Thus at -35°C the electrode processes can be summarized as

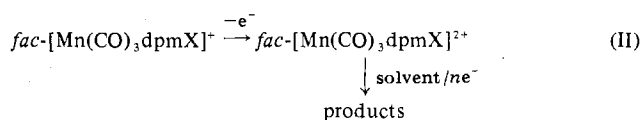
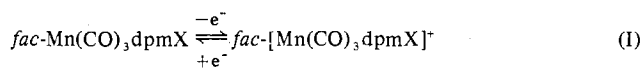


Table I. Electrochemical Data for the Mn(CO)₃dpmX System^a

(a) Oxidation (Pt) Cyclic Voltammetry							
	Electrode process	Mn(CO) ₃ dpmCl			Mn(CO) ₃ dpmBr		
		E _p ^{ox}	E _p ^{red}	E _{1/2}	E _p ^{ox}	E _p ^{red}	E _{1/2}
Acetonitrile	I	1.48	1.35	1.44	1.49	1.38	1.46
	II	2.29		2.14	2.20		2.10
	III	1.02	0.95	0.98	1.05	0.98	1.01
Acetone	I	1.41	1.29	1.38	1.47	1.34	1.45
	III	0.98	0.92	0.93	1.07	0.95	0.99

(b) Reduction (Pt) Cyclic Voltammetry							
	Electrode process	Mn(CO) ₃ dpmCl			Mn(CO) ₃ dpmBr		
		E _p ^{red}	(E _p ^{ox}) ₁	(E _p ^{ox}) ₂	E _p ^{red}	(E _p ^{ox}) ₁	(E _p ^{ox}) ₂
Acetonitrile		-1.20	-0.76	-0.34	-1.20	-0.77	-0.35
Acetone		-1.27			-1.27		

(c) Reduction (Hg) Polarography			
		Mn(CO) ₃ dpmCl	Mn(CO) ₃ dpmBr
Acetonitrile	E _{1/2}	-1.24	-1.18
	E _{1/2} - E _{3/4}	61 mV	60 mV
Acetone	E _{1/2}	-1.32	-1.23
	E _{1/2} - E _{3/4}	80 mV	80 mV

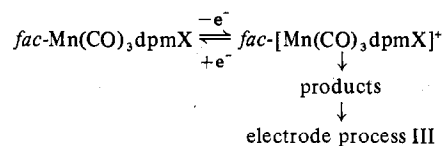
^a T = 22 °C; supporting electrolyte 0.1 M Et₄NClO₄. All potentials are given in volts vs. Ag-AgCl. Scan rate used for cyclic voltammetry was 500 mV/s.

Table II. Infrared Spectra (Carbonyl Region) (cm⁻¹)^a

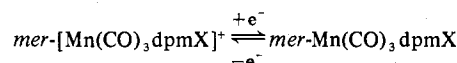
	[Mn(CO) ₃ dpmCl] ^{0,+}			[Mn(CO) ₃ dpmBr] ^{0,+}		
	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹	cm ⁻¹
<i>fac</i> -Mn(CO) ₃ dpmX	2028 s	1952 s	1916 s	2026 s	1950 s	1917 s
<i>mer</i> -[Mn(CO) ₃ dpmX] ⁺	2120 m	2081 w	2031 s	2124 m	2085 w	2032 s
<i>mer</i> -Mn(CO) ₃ dpmX	2031 s	1958 s	1918 sh	2030 s	1956 s	1920 sh

^a All spectra recorded in dichloromethane solution.

However at 22 °C electrode process I is modified to give



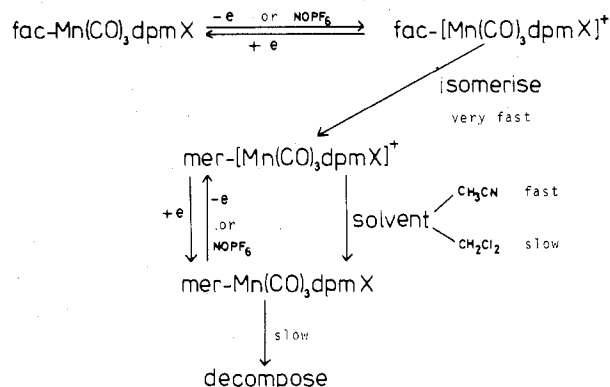
On the basis of previous work^{6,7} it was suspected that at room temperature *fac*-[Mn(CO)₃dpmX]⁺ isomerized and that the *mer*-[Mn(CO)₃dpmX]⁺ produced gave rise to electrode process III which would then be written as



If correct, this would also require that the only isolable product from the oxidation of *fac*-Mn(CO)₃dpmX at room temperature would be *mer*-[Mn(CO)₃dpmX]⁺ and not the facial isomer as reported^{2,3} and that, likewise, the product obtained from the reduction of [Mn(CO)₃dpmX]⁺ would also be the *mer* isomer of Mn(CO)₃dpmX rather than the facial.

It was thought that a controlled-potential oxidation of Mn(CO)₃dpmX would allow isolation of [Mn(CO)₃dpmX]ClO₄ and that the structural form of this product could then be elucidated by physical measurements. Accordingly, a 2.7 × 10⁻³ M solution of Mn(CO)₃dpmCl was electrolyzed at +1.7 V in acetonitrile. Assuming the oxidation involves a one-electron oxidation, 11.7 C should be required for exhaustive electrolysis to zero current. However, after 50 C had been passed through the cell, the current had dropped only slightly below its initial value. The originally yellow solution turned orange during the electrolysis. The stirring was stopped and a red color was observed at the electrode; the red color returned to yellow as it reached the bulk of the solution. When the potential across the cell was removed, the

Scheme I



solution quickly became yellow. Thus it was not possible to isolate or completely characterize the oxidation products using electrochemistry alone.

(ii) **Chemical Oxidation.** Mn(CO)₃dpmBr has been oxidized previously³ in benzene to give a green complex formulated as *fac*-[Mn(CO)₃dpmBr]PF₆; a violet compound formulated in the same way was later isolated by carrying out the oxidation in dichloromethane solution.⁴ The infrared spectra of both compounds (carbonyl region) showed bands at 2124 (s), 2085 (m), and 2032 (vs) cm⁻¹.

We have repeated both of these preparations with *fac*-Mn(CO)₃dpmCl and have been able to isolate the same red complex from both solvents. Its infrared spectrum is the same as that reported by Reimann and Singleton for [Mn(CO)₃dpmBr]PF₆. The spectra for this compound and for *fac*-Mn(CO)₃dpmCl are shown in Figure 3 and summarized in Table II. The only possible isomers of [Mn(CO)₃dpmX]^{0,+} are facial and meridional; both are of C₃ symmetry and three

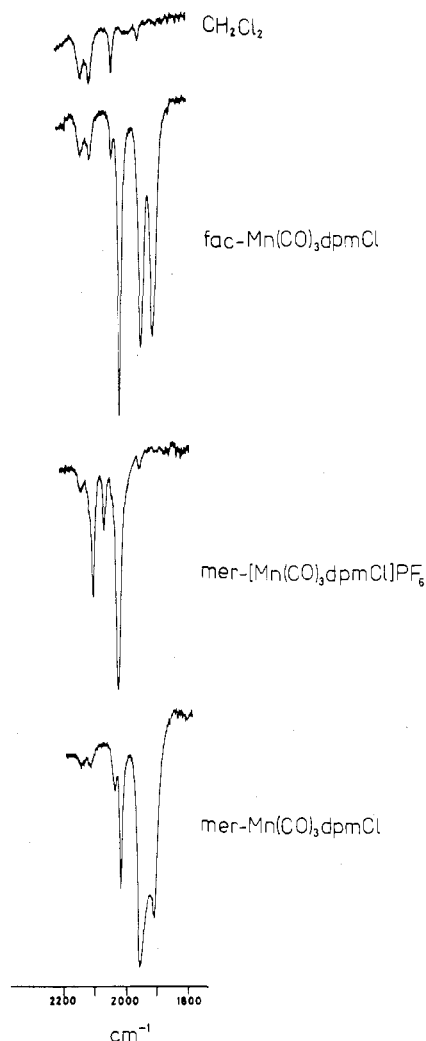
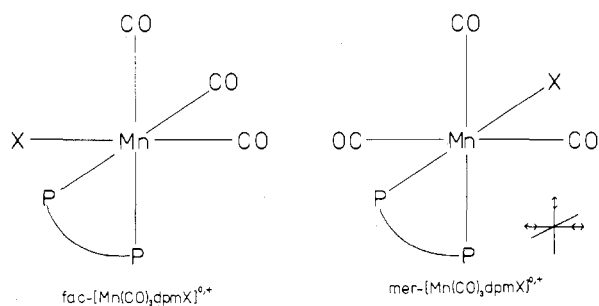


Figure 3. Infrared spectra (carbonyl region) of isomers of $[\text{Mn}(\text{CO})_3\text{dpmX}]^{0+}$.

carbonyl stretches would be expected ($2A' + A''$). However, the symmetric vibrations of the *mer* isomer do not involve a change in dipole moment and would be expected to be weak.¹ Examination of Figure 3 and the previous electrochemical evidence makes it certain that the isomer obtained at room temperature is *mer*- $[\text{Mn}(\text{CO})_3\text{dpmCl}]\text{PF}_6$ and not the facial isomer as claimed.^{3,4} The structures of the two isomers are shown below.



As is expected from the potential required to produce it, *mer*- $[\text{Mn}(\text{CO})_3\text{dpmCl}]^+$ is an oxidant and it is reduced very rapidly in acetonitrile, or more slowly in dichloromethane, to give a yellow solution. This has been noted before, but again we believe the product has been wrongly formulated.⁴ The infrared spectrum (Figure 3) strongly suggests that it is *mer*- $\text{Mn}(\text{CO})_3\text{dpmCl}$ rather than *fac*- $\text{Mn}(\text{CO})_3\text{dpmCl}$, whose spectrum is also shown for comparison. A cyclic voltam-

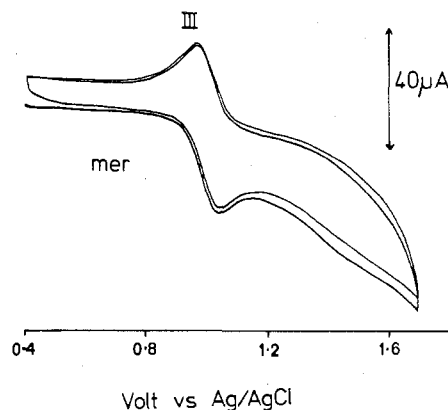


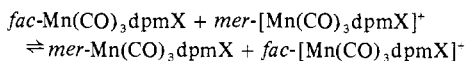
Figure 4. Cyclic voltammogram for oxidation at platinum of *mer*- $\text{Mn}(\text{CO})_3\text{dpmCl}$ in acetonitrile (0.1 M Et_4NClO_4); $T = 22^\circ\text{C}$; scan rate 500 mV/s.

mogram of *mer*- $[\text{Mn}(\text{CO})_3\text{dpmCl}]\text{PF}_6$ was recorded in acetonitrile and this is shown in Figure 4. The solution had become yellow before the voltammogram could be taken, so the species in solution was the reduction product. Electrode process I is completely absent thus showing unequivocally that the reduction product is *mer*- $\text{Mn}(\text{CO})_3\text{dpmCl}$; since electrode process I is known to be due to the facial isomer.

The previously described coulometric experiment is clearly consistent with this result. When *fac*- $\text{Mn}(\text{CO})_3\text{dpmCl}$ is oxidized at the electrode at room temperature, it quickly produces *mer*- $[\text{Mn}(\text{CO})_3\text{dpmCl}]^+$ which is then reduced by the solvent to *mer*- $\text{Mn}(\text{CO})_3\text{dpmCl}$ which can then be re-oxidized in a cyclic fashion. Thus, the oxidizable species is never exhausted and the current decays only very slowly due to slow decomposition of *mer*- $\text{Mn}(\text{CO})_3\text{dpmCl}$.

The reduction of *mer*- $[\text{Mn}(\text{CO})_3\text{dpmCl}]\text{PF}_6$ by acetonitrile can be prevented by the addition of NO^+PF_6^- . However, decomposition occurs via an unknown carbonyl intermediate to give a colorless solution which, according to infrared evidence, contained no metal carbonyl derivatives.

We believe that a complete description of the isomerization and redox reactions of the $\text{Mn}(\text{CO})_3\text{dpmX}/[\text{Mn}(\text{CO})_3\text{dpmX}]^+$ couple can now be given. The results are summarized by the series of equations given in Scheme I. Examination of E° ($\approx E_{1/2}$) values (see Table I) for both the *fac*/*fac*⁺ and *mer*/*mer*⁺ couples show that the equilibrium for the reaction



lies almost exclusively to the left. The observed isolation of *fac*- $\text{Mn}(\text{CO})_3\text{dpmX}$ and *mer*- $[\text{Mn}(\text{CO})_3\text{dpmX}]^+$ from this system is therefore not unexpected. Isolation of *mer*- $\text{Mn}(\text{CO})_3\text{dpmX}$ appears to be possible only because its isomerization is kinetically very slow. In contrast, the isomerization of *fac*- $[\text{Mn}(\text{CO})_3\text{dpmX}]^+$ is very fast and it cannot be isolated at room temperature. However, the pathway of isomerization (*fac*⁺ \rightarrow *mer*⁺) could be quenched either by using cyclic voltammetry with scan rates of 500 V/s at room temperature or by cooling the solution to -35°C , where isomerization is not observed at scan rates of 100 mV/s.

It can be seen from the E° values that the manganese(II) complexes would act as oxidizing agents powerful enough to oxidize many solvents. Oxidation of chloroform and ethanol has already been observed⁴ and the presence of water may well affect the reaction as water is relatively easy to oxidize. For example, *mer*- $[\text{Mn}(\text{CO})_3\text{dpmCl}]^+$ was reduced only very slowly in dichloromethane solution unless very dilute (10^{-4} M) solutions were studied. The reaction was then very fast suggesting that traces of water may be important.

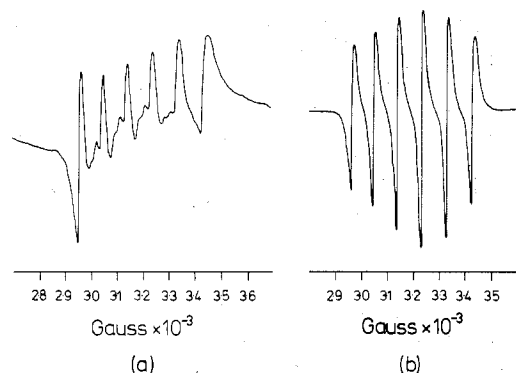


Figure 5. ESR spectra: (a) *mer*-[Mn(CO)₃dpmCl]PF₆ in a frozen glass of acetonitrile at 77 K; (b) *mer*-[Mn(CO)₃dpmCl]PF₆ in acetonitrile at 22 °C.

Electrode process II has not been studied in detail although it was noted that it could not be made chemically reversible under any conditions of scan rate (up to 500 V/s) or temperature (down to -40 °C). This is not unexpected for a 16-electron system produced at such positive potentials.

(iii) **Properties of the Manganese(II) Complexes.** Almost all manganese(II) compounds are high spin and they are very weakly colored due to the fact that there are no spin-allowed transitions. The strong red color of *mer*-[Mn(CO)₃dpmX]⁺ and the green (see below) color of *fac*-[Mn(CO)₃dpmX]⁺ immediately suggested that they may be low spin, a possibility also suggested by a consideration of the nature of the ligands coordinated to the metal.

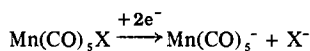
Voltammetry at -35 °C had shown that *fac*-[Mn(CO)₃dpmCl]⁺ is stable at this temperature. Accordingly, a solution of NOPF₆ in acetonitrile was added to a frozen solution of *fac*-Mn(CO)₃dpmCl in a silica tube suitable for ESR measurements. A very dark green color formed at the interface. Repeated thawing and freezing, without allowing the temperature to exceed -35 °C, enabled all of the original yellow color to be replaced by green. The ESR spectrum of *fac*-[Mn(CO)₃dpmCl]PF₆ was then recorded in a frozen glass of acetonitrile at liquid nitrogen temperature. The solution was then allowed to warm to room temperature and the resulting red solution of *mer*-[Mn(CO)₃dpmCl]⁺ was then refrozen. No reversion to the green facial isomer was observed. The ESR spectrum of *mer*-[Mn(CO)₃dpmCl]PF₆ in a frozen glass of acetonitrile at 77 K was recorded and it was found to be almost identical with that of the facial isomer. This spectrum is shown in Figure 5a. A room-temperature ESR spectrum of *mer*-[Mn(CO)₃dpmCl]PF₆ in acetonitrile is shown in Figure 5b. The room-temperature spectrum has six sharp lines [⁵⁵Mn, 100%, *I* = 5/2] with *g* = 2.003 and a nuclear hyperfine coupling constant of 91.5 G. Because of the symmetry of [Mn(CO)₃dpmX]⁺ this spectrum is consistent with low-spin manganese(II), since even small deviations from octahedral symmetry lead to marked broadening of the spectrum in high-spin manganese(II) due to zero-field splitting effects.⁹ The low-spin state for Mn(II) was confirmed by a direct measurement of the magnetic susceptibility of solid *mer*-[Mn(CO)₃dpmCl]PF₆ by the Gouy method which gave an effective magnetic moment of 1.82 μ_B at room temperature. The added complexity in the ESR spectra recorded in frozen glasses is attributed to a nonrandom distribution of crystals in the glass.

It is interesting to note that no hyperfine structure due to the phosphorus atoms [³¹P, 100%, *I* = 1/2] was observed, indicating that little electron density is delocalized onto the phosphorus atoms from manganese, in marked contrast to

trans-[Mo(CO)₂(dpm)₂]⁺ which displays phosphorus coupling.⁷

Low-spin Mn(II) is rare. The ESR spectrum of [Mn(CO)₂(dpe)₂]²⁺ was observed but the only detail reported was a *g* value of 2.08.⁵ Fantucci et al.¹⁰ have made low-spin Mn(CNR)₆²⁺ but in this case the ESR cannot enable us to make a distinction between high-spin and low-spin because the complexes have *O_h* symmetry.

(iv) **Reduction of Mn(CO)₃dpmX.** Polarographic data for the reduction of Mn(CO)₃dpmX are summarized in Table I. The shape of the waves and the variation of potential indicate considerable solvent dependence for the reduction step. The reduction of Mn(CO)₅X has been shown to give a two-electron reduction step in acetonitrile^{11,12}



We have confirmed that this occurs also in acetone by controlled-potential electrolysis at a mercury pool electrode and by identifying Mn(CO)₅⁻ by its published¹³ infrared spectrum. In the case of Mn(CO)₅Br the release of bromide ion was confirmed polarographically.

The limiting current of dc polarograms per unit concentration in acetone was the same for Mn(CO)₅X and *fac*-Mn(CO)₃dpmX. Coulometry at a mercury pool electrode in acetone also confirmed that the reduction of Mn(CO)₃dpmX is a two-electron step with liberation of 1 mol of halide (detected polarographically for the bromide). The electrolyzed solution was brown and contained carbonyl compounds (infrared evidence), but it rapidly turned yellow, especially after the potential was removed from the cell. Cyclic voltammograms for the reduction of Mn(CO)₅Br and *fac*-Mn(CO)₃dpmBr in acetone were recorded at platinum and mercury electrodes. For Mn(CO)₅Br the reverse scan clearly shows the presence of Mn(CO)₅⁻ but for Mn(CO)₃dpmBr two waves were seen on the reverse scan at mercury and none at platinum. The expected Mn(CO)₃dpm⁻ species, derived from a simple two-electron reduction and loss of halide, therefore does not appear to be obtained even at the electrode, although it is probably an intermediate in the reduction. Under these circumstances the reduction products of Mn(CO)₃dpmBr could not be identified.

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Registry No. *fac*-Mn(CO)₃dpmCl, 60305-98-8; *fac*-Mn(CO)₃dpmBr, 37523-63-0; *mer*-[Mn(CO)₃dpmCl]PF₆, 60306-00-5; *mer*-[Mn(CO)₃dpmBr]PF₆, 60325-43-1; *mer*-Mn(CO)₃dpmCl, 60325-41-9; *mer*-Mn(CO)₃dpmBr, 60325-44-2.

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