Paramagnetic Transition-metal Carbonyls and Cyanides. Part 5.[1] Electron Spin Resonance Spectra of Cations and Anions derived from Decacarbonyl-dimanganese and -dirhenium

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Exposure of $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$ to ^{60}Co γ rays at 77 K gives paramagnetic species whose e.s.r. spectra show the presence of two strongly coupled metal nuclei. Analysis of the spectra shows that the unpaired electron is located in the metal–metal bond, but this could be σ or σ^*. The same centres were formed when solutions in 2-methyltetrahydrofuran containing *NNN'N'*-tetramethyl-*p*-phenylenediamine were exposed to u.v. light, and hence the σ^* formulation is favoured. A second centre having two sets of features in the $g = 6$ region has been detected in irradiated $[Mn_2(CO)_{10}]$. This shows strong hyperfine coupling to one ^{55}Mn nucleus and weak coupling to another. This centre is thought to be from a cationic species in which one manganese atom has acquired an $S = \frac{5}{2}$ configuration. The structure is similar to that postulated for cationic centres formed from pentacarbonylhalogenomanganese compounds.

IN previous parts of this series we have demonstrated that exposure of diamagnetic transition-metal carbonyl compounds to ionizing radiation is a powerful method for preparing paramagnetic derivatives whose structure can frequently be probed by e.s.r. spectroscopy.[1-3] Our studies supplement those of Turner and his co-workers[4] who have used i.r. spectroscopy to study photolysis products of transition-metal carbonyls, and also those of Hudson *et al.*[5] who have adapted the spin-trapping technique to study homolyses induced by u.v. radiation.

We have briefly reported the formation of a paramagnetic centre in $[Mn_2(CO)_{10}]$ by exposure to ^{60}Co γ-rays,[6] but we know of no other such study for this carbonyl or for decacarbonyldirhenium. However, the photolysis of $[Mn_2(CO)_{10}]$ has been rather widely studied. The first stage in the photolysis is the formation of two $[Mn(CO)_5]$ fragments which have been detected by the spin-trapping technique,[5] but interest has centred around a species characterized by a six-line spectrum with $A(^{55}Mn) = 93$ G. This was originally assigned to $[Mn(CO)_5]$,[7] and this conclusion has recently been supported by Kwan and Kochi.[8] However, our own attempts to obtain an e.s.r. spectrum for $[Mn(CO)_5]$ in a sublimed sample of $[Mn_2(CO)_{10}]$ failed, despite the fact that in the presence of dioxygen the paramagnetic peroxide $[Mn(CO)_5(O_2)]$ was readily detected.[9] We concluded that $[Mn(CO)_5]$ must be undergoing efficient spin relaxation that broadens its e.s.r. spectrum beyond the limits of detection. Hudson *et al.*[9] also concluded that the 93-G species could not be $[Mn(CO)_5]$, and proposed that a manganese(II) ^6S centre was responsible [equation (1)]. This conclusion has been firmly supported by a combined study that has conclusively demonstrated that the species is in a ^6S state.[10] The presence of $[Mn(CO)_5]^-$ as the gegenion was also demonstrated.

$$3[Mn_2(CO)_{10}] + 12\ \text{solvent} \xrightarrow{h\nu} 2[Mn(\text{solvent})_6]^{2+} + 4[Mn(CO)_5]^- + 10CO \quad (1)$$

EXPERIMENTAL

Decacarbonyl-dimanganese and -dirhenium were obtained from Strem Chemicals Inc., Danvers, Mass., and were used without further purification. These were studied as finely ground powders and as solutions frozen in liquid nitrogen in the form of small beads. Samples were exposed to ^{60}Co γ-rays at 77 K in a Vickrad source at a dose rate of 2.5 Mrad h^{-1} for periods of up to 10 h.† Photolysis experiments were carried out with the sample in a quartz Dewar in the e.s.r. cavity using a high-pressure mercury lamp. E.s.r. spectra were recorded on a Varian E3 spectrometer at 77 K using a quartz liquid-nitrogen Dewar inserted into the e.s.r. cavity. Samples were annealed at >77 K in the Dewar flask with continuous monitoring of the e.s.r. spectra and were recooled to 77 K for detailed study whenever necessary.

RESULTS AND DISCUSSION

Irradiation of finely powdered $[Mn_2(CO)_{10}]$ at 77 K gave an axially symmetric paramagnetic centre containing two magnetically equivalent manganese nuclei [Table 1 and Figure 1(*a*)], which was tentatively identi-

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† Throughout this paper: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

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[3] M. C. R. Symons and D. N. Zimmerman, *J.C.S. Dalton*, 1975, 2545.

[4] See, for example, M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. (A)*, 1971, 2939: M. Poliakoff and J. J. Turner, *J.C.S. Dalton*, 1974, 2276; R. N. Perutz and J. J. Turner, *J. Amer. Chem. Soc.*, 1975, **97**, 4971, 4800; *Inorg. Chem.*, 1975, **14**, 262; J. K. Burdett, M. A. Graham, R. N. Perutz, M. Poliakoff, A. J. Rest, J. J. Turner, and R. F. Turner, *J. Amer. Chem. Soc.*, 1975, **97**, 4805.

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[10] A. Hudson, M. F. Lappert, J. J. MacQuitty, B. K. Nicholson, H. Zainal, G. R. Luckhurst, C. Zannoni, S. W. Bratt, and M. C. R. Symons, *J. Organometallic Chem.*, 1976, **110**, C5.

fied as the radical anion $[Mn_2(CO)_{10}]^-$.[6] In addition to this centre we detected a signal in the $g = 6$ region,

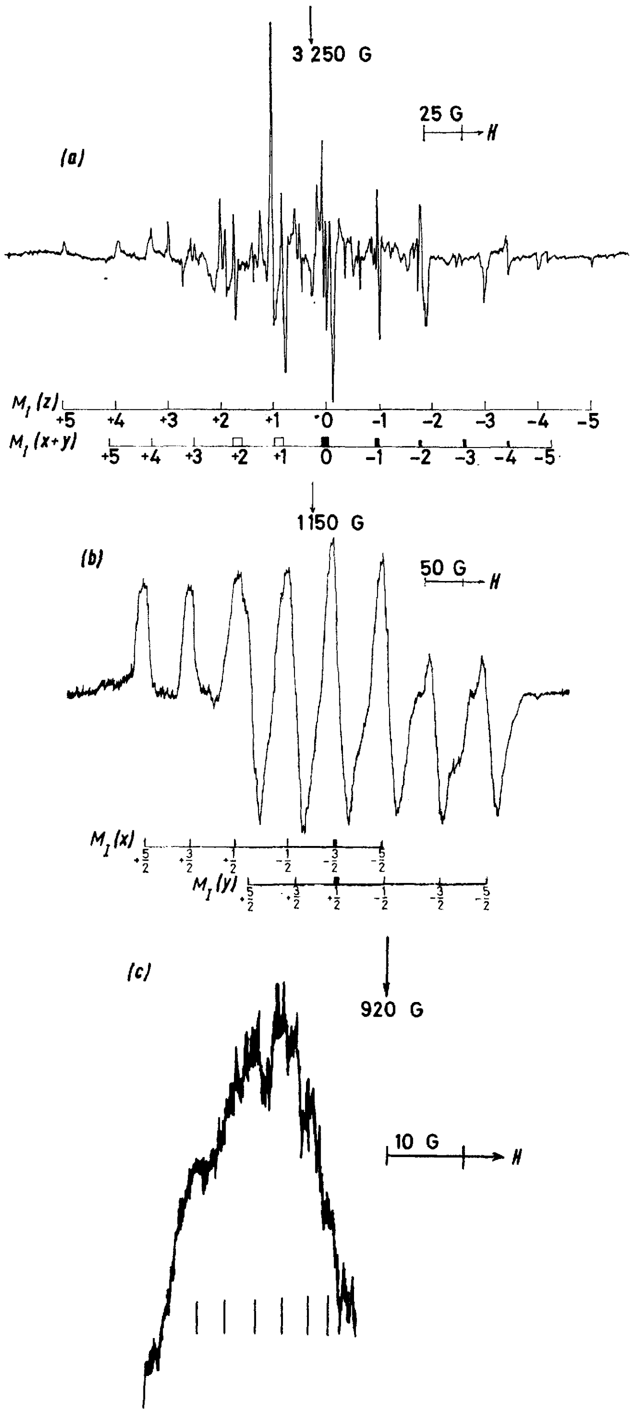

FIGURE 1 First-derivative X-band e.s.r. spectra for $[Mn_2(CO)_{10}]$ after exposure to ^{60}Co γ-rays at 77 K, showing (*a*) features assigned to $[Mn_2(CO)_{10}]^-$, (*b*) features assigned to an electron-loss centre, possibly $[Mn_2(CO)_{10}]^+$, and (*c*) the first low-field feature for this centre

similar to those found in the pentacarbonylhalogenomanganese compounds[2] [Figure 1(*b*)]. This consists of six x and y features, obviously the result of hyperfine coupling to ^{55}Mn (100% abundance, $I = \frac{5}{2}$). There is evidence of a further coupling of *ca.* 5 G to the second manganese nucleus. Data for these species are given, together with data for the pentacarbonylhalogenomanganese centres, in Table 2. Unfortunately, the z features were not detected, probably because of overlap with the central lines.

TABLE 1

E.s.r. parameters assigned to the anions of $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$

Centre	$g_\parallel$	$g_\perp$	$A_\parallel/G$	$A_\perp/G$	$A_{iso.}/G$	$2B/G$
$[Mn_2(CO)_{10}]^-$	1.999	1.998	(+) 34.9	(−) 29.2	(−) 7.8	(+) 42.7
$[Re_2(CO)_{10}]^-$	1.983	1.959	(+) 183	0, ±4	(+) 61	(+) 122

Exposure of $[Re_2(CO)_{10}]$ in 2-methyltetrahydrofuran (mthf) to γ-rays at 77 K produced maroon beads having an e.s.r. spectrum consisting of 11 parallel features and a broad central feature (after annealing to remove solvent radicals) (Figure 2). This is indicative of a radical containing two equivalent rhenium nuclei. [The magnetic isotopes of rhenium, ^{185}Re (37.1%) and ^{187}Re (62.9%), both with $I = \frac{5}{2}$, have such similar magnetic moments that transitions from each are normally coincident.] The lack of any discernible perpendicular hyperfine structure puts $A_\perp$ between the limits of ±4 G.

TABLE 2

E.s.r. parameters assigned to the cations (^6S) formed from $[Mn_2(CO)_{10}]$ and $[Mn(CO)_5X]$ (X = halide).[3] The z features were always hidden under other more intense lines in the $g = 2$ region

Host	g_x	g_y	$A_x(^{55}Mn)/$ G	$A_y(^{55}Mn)/$ G	$A_{ligand}/$ G
$[Mn_2(CO)_{10}]$	5.35	6.02	60	65	*ca.* 5(^{55}Mn)
$[Mn(CO)_5Cl]$	5.61	6.01	85	86	*ca.* 2(^{35}Cl)
$[Mn(CO)_5Br]$	5.65	6.82	83	83	*ca.* 12(^{81}Br)
$[Mn(CO)_5I]$	5.89	6.78	85	85	*ca.* 10(^{127}I)

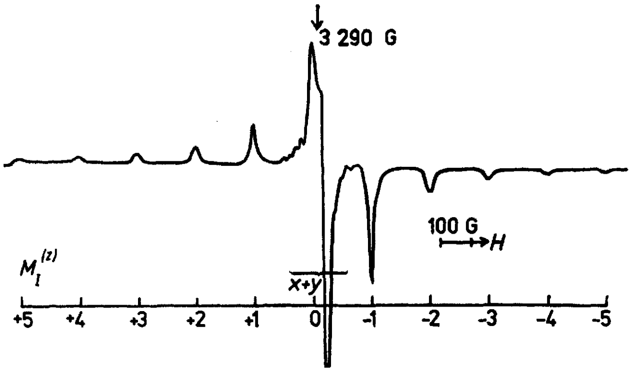

FIGURE 2 First-derivative X-band e.s.r. spectra for $[Re_2(CO)_{10}]$ in mthf glass after exposure to ^{60}Co γ-rays at 77 K, after annealing to remove signals from solvent radicals, showing features assigned to $[Re_2(CO)_{10}]^-$ anions

For both decacarbonyls in mthf, the normal blue-black colour characteristic of trapped electrons was absent after irradiation. This suggests that the electrons ejected from the solvent are effectively captured by the solutes, and hence that the signals in the $g = 2$ region are due to the anions. In order to test the validity of this electron-gain hypothesis, photolysis experiments were conducted on frozen solutions with and without small amounts of *NNN'N'*-tetramethyl-*p*-phenylenediamine (tmpd), a photosensitive source of electrons. No paramagnetic centres were observed on photolysis in the absence of tmpd, but with tmpd e.s.r. signals characteristic of the tmpd cation and the dirhenium or dimanganese centre described above were observed.

The $g = 2$ *Centres.*—We are satisfied that, for $[Mn_2(CO)_{10}]$, this is the primary anion $[Mn_2(CO)_{10}]^-$. The results strongly suggest that the unpaired electron is in a metal–metal σ^* orbital. We cannot be sure that CO ligands have not been lost, but if they have then both manganese atoms must have been equally affected, which seems to us to be improbable. Unfortunately the spectra were never sufficiently intense to reveal any ^{13}C satellite features.

As with the pentacarbonyl halides,[3] the only reasonable sign combination for the hyperfine components is $A_{\parallel}$ positive and $A_{\perp}$ negative. The resulting isotropic coupling for ^{55}Mn is an unusually small negative value which suggests considerable admixture of the (Mn) 4*s* atomic orbitals. This in turn suggests that the $3d_z$ orbitals are involved, since unless there has been a major loss of symmetry this is the only *d* orbital which can combine with 4*s*. This is confirmed by the positive sign of the dipolar coupling ($2B$) (Table 1). (Since orbital magnetic contributions are small, $2B$ and $A_{iso.}$ were calculated using $3A_{iso.} = A_{\parallel} + 2A_{\perp}$ and $A_{\parallel} = A_{iso.} + 2B$.) The $2B$ values divided by $2B^0$, the calculated coupling for unit occupancy of $3d_{z^2}$ (109 G),* gives an approximate orbital population of *ca.* 0.39 for each $3d_{z^2}$ orbital. If the 'normal' spin-polarization value for $A_{iso.}$ is taken as -80 G, then using A^0 (4*s*) = 1 128 G we find $a_{4s}^2 \approx 0.06$.

Similarly for $[Re_2(CO)_{10}]^-$, we find, using $A_{\perp} \approx 0$, $A_{iso.} = \pm 61$ G and $2B \approx \pm 122$ G. Accepting the positive signs by analogy with the manganese compound, and using $2B^0 = 198$ G,* we find $a_{5d_{z^2}}^2 \approx 0.61$. Similarly, using the calculated A^0 value of 3 200 G and making allowance for spin polarization, we arrive at a value of *ca.* 0.08 for a_{6s}^2. The high value for the d_{z^2} population may arise because of our inability to estimate $A_{\perp}$ accurately, but it is not uncommon to find an overestimate of spin density from $2B$ values for heavy atoms,[11] and we feel that these results are quite acceptable in terms of the proposed structure. They may indicate a decreased delocalization on to the axial CO groups for the rhenium compound.

The negative shifts for $g_{\perp}$ are also indicative of a σ^* rather than a σ structure. They may stem from a small occupancy of the outer *p* manifold, but in addition we invoke coupling to empty π^* orbitals formed from the $d_{xz,yz}$ pair and the π^* CO orbitals. The smaller negative shifts in $g_{\parallel}$ are less readily interpreted, since, in first order, free-spin *g* values are predicted.

The $g = 6$ *Species.*—This centre, formed from $[Mn_2(CO)_{10}]$, is not formed in mthf glasses, which suggests that it is an electron-loss centre. The same conclusion was drawn for the very similar centres formed from the pentacarbonyl halides.[3] As stressed previously,[3] two features (*x* and *y*) in the $g = 6$ region are most unexpected for electron-loss centres formed from these carbonyls. For the halides, electron loss from the halide ligands was expected and would have been in accord with photoelectron spectra for the parent compounds.[12] Also, the results are incompatible with a hole in the $3d_{xz,yz}$ level. After eliminating $S = \frac{1}{2}$ and $\frac{3}{2}$ centres, we were forced to conclude that the centres had an $S = \frac{5}{2}$ structure, which is in accord with two apparent *g* values in the $g = 6$ region and one in the $g = 2$ region.

Electron loss from $[Mn_2(CO)_{10}]$ might be expected to give either a σ structure, with one electron in the Mn–Mn bond, or some structure with the hole largely confined to the ligands. In fact, one of the $[Mn(CO)_5]$ groups seems to have taken the place of the halide ion in the pentacarbonylhalogenomanganese compounds, and the other has again acquired a ^6S state by losing an electron with concomitant unpairing of the remaining 3*d* electrons. Clearly, the zero-field parameter, *D*, is very large, but we cannot deduce anything about the extent to which CO ligands have been lost. Since CO groups invariably stabilize low-spin configurations, however, we consider that some loss of CO from the paramagnetic manganese atom is possible. This is also suggested by the rhombic distortion indicated by the difference between g_x and g_y, which is small but significant, and would also explain why two manganese atoms have become completely inequivalent.

The small hyperfine coupling to the second ^{55}Mn was barely resolved. Resolution on the $M_I = \frac{5}{2}$ (*x*) feature is shown in Figure 1(*c*), and although this is close to noise level it was quite reproducible and comparable inflections appeared on all the other features. Unfortunately, the receiver gain was very high and the noise could not be eliminated. The splitting (*ca.* 5 G) appeared to be equal on the *x* and *y* features. If the high-spin d^5 configuration is correct, then there is a three-electron σ bond between the two manganese atoms, and the weakly interacting atom must receive spin density *via* this bond. Also the unpaired electron in the d_{xz} and d_{yz} orbitals will delocalize on to the second manganese *via* π overlap. It is unfortunate that the *z* features are unobtainable, since they might well help to shed more light on the structure of these most interesting centres. The magnitude suggests a spin-polarization effect rather than any major delocalization.

We were unable to obtain a similar species from $[Re_2(CO)_{10}]$, nor have we been able to detect the formation of any electron-loss centre from this compound.

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