Electron Addition to $[Mn_2(CO)_{10}]$ and $[Mn_2(CO)_8(PR_3)_2]$ induced by Ionizing Radiation: An Electron Spin Resonance Study †

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Exposure of dilute solutions of the title compounds to ^{60}Co γ-rays at 77 K gave the corresponding anions. Analyses of the e.s.r. spectra show that the excess electron is accommodated in the metal–metal σ* orbital. A small extra splitting for two equivalent ^{31}P nuclei for the $[Mn_2(CO)_8(PR_3)_2]^{\cdot -}$ anion shows that delocalisation of electron density onto the axial ligands is small (*ca.* 1%). This unexpectedly low value may account for the absence of any ^{13}C splitting for the anion derived from $[Mn_2(CO)_{10}]$ enriched with ^{13}C in the axial ligands. These results are compared with those for the cobalt anion, $[Co_2(CO)_6(PR_3)_2]^{\cdot -}$, which has been reported elsewhere to have a far higher spin density on the phosphine ligands (*ca.* 23%).

Although not widely appreciated, the use of ionising radiation is an excellent procedure for adding single electrons to molecules. We and others have established that by using dilute solutions of substrates in crystals or glasses at low temperatures, electron addition to the substrate is frequently remarkably selective.

We have recently shown that suitable compounds containing metal–metal bonds readily add electrons into the metal–metal σ* orbital, the resulting complexes being quite stable at 77 K. Such complexes which had not been previously studied by e.s.r. spectroscopy include $[(CO)_5Mn\dot{-}Mn(CO)_5]^-$ and $[(CO)_5Re\dot{-}Re(CO)_5]^-$.[2,3] In these and in our parallel studies on $[(CO)_5Mn\dot{-}X]^-$ anions, in which the excess electron is accommodated in the metal–halogen (Cl, Br, or I) σ* orbitals, a question arises regarding the axial ligands: to what extent are the excess electrons delocalised thereon, or are they lost on electron addition? In the hope of obtaining direct information, we have looked for ^{13}C hyperfine coupling in samples enriched in ^{13}CO and since this failed to give us positive information we have also studied $[Mn_2(CO)_8(PR_3)_2]$ (R = Bu^n or OEt) in the expectation that the two axial ^{31}P nuclei could give resolved hyperfine coupling. Since the work was completed a paper has appeared[4] which describes the e.s.r. spectrum of $[Co_2(CO)_6(PBu^n_3)_2]^{\cdot -}$. This result makes a most interesting comparison with those from our own work.

Experimental

The compounds $[Mn_2(CO)_8(PBu^n_3)_2]$ and $[Mn_2(CO)_8\{P(OEt)_3\}_2]$ were prepared and purified according to literature methods.[5] The ^{13}CO enrichment of $[Mn(CO)_5Cl]$ was by exchange with ^{13}CO in CH_2Cl_2.[6] The degree of enrichment was monitored by i.r. spectroscopy (*ca.* 20%). The complex $[Mn_2(CO)_{10}]$ was enriched by photolysis of hexane solutions saturated with ^{13}CO (*ca.* 50% enriched).

Samples were γ-irradiated as pure compounds, and as dilute solutions in 2-methyltetrahydrofuran (mthf). This solvent is used because it does not react with electrons and it gives good glasses on cooling to 77 K. Degassed solutions were frozen in liquid nitrogen as small glassy beads and then irradiated at 77 K in a Vickrad ^{60}Co γ-ray source with doses up to *ca.* 2 Mrad.

Electron spin resonance spectra were measured with a Varian E-109 spectrometer calibrated with a Hewlett-Packard 5246 L frequency counter and a Brucker B-H 12E field probe, standardised with a sample of diphenylpicrylhydrazyl. After measurements at 77 K, samples were annealed until significant changes were observed in their spectra and then re-cooled to 77 K for measurements.

Results and Discussion

$[Mn_2(CO)_8(PBu^n_3)_2]^{\cdot -}$.—The best results were obtained from irradiation of the phosphine derivative (Figure 1). The outer (parallel) features comprise well defined 1 : 2 : 1 triplets which can be assigned to hyperfine coupling to two equivalent ^{31}P nuclei (^{31}P has $I = \frac{1}{2}$). There are 11 parallel features as expected for two equivalent ^{55}Mn nuclei (^{55}Mn has $I = \frac{5}{2}$). Thus, since this species is formed in high yield in mthf, it must be the parent anion $[Mn_2(CO)_8(PBu^n_3)_2]^{\cdot -}$. The high- and low-field features are of comparable intensity, and analysis indicates almost no g anisotropy ($g_\perp = 2.002 \pm 0.001$ and $g_\parallel = 2.000 \pm 0.001$). Thus the orbital of the unpaired electron is remarkably isolated from neighbouring coupled levels, as was observed previously for $[Mn_2(CO)_{10}]^{\cdot -}$ anions.[2,3]

It is more difficult to extract the ^{55}Mn and ^{31}P perpendicular (x and y) coupling constants. The best fit is obtained using the stick diagram shown in Figure 1 and the parameters given in Table 1 but other interpretations cannot be ruled out. In arriving at the interpretation indicated, we fixed the locations of the first $I = \pm 5$ (^{55}Mn) perpendicular features unambiguously from the spectrum. Then, clearly, the (0) line is almost isotropic thus fixing the (0) components. Again the (±1) lines are fixed by the spectrum unambiguously. We then used these field values to estimate the positions for the remaining features. From the form of the central components we conclude that the ^{31}P splitting on the perpendicular features is in the range 6 ± 1 G. As often occurs in such spectra, the outer perpendicular features are broad and poorly defined, and are largely concealed under the relatively sharp parallel lines.

Structural considerations suggest that the ^{31}P hyperfine coupling components have like signs (see below). The fact that the coupling on the perpendicular features is less than that on the parallel features is in accord with expectations for the σ* structure shown in Figure 2, which comprises an antibonding combination of *sp* hybridised phosphorus lone-pair orbitals and manganese d_{z^2} orbitals. In this situation, the ^{31}P coupling constants should be principal values and the resulting isotropic (A) and anisotropic ($2B$) values can be used to give

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† Taken as Paramagnetic Transition-metal Carbonyls and Cyanides, Part 8.[1]

Non-S.I. units employed: 1 rad = 10^{-2} J kg^{-1}; 1 G = 10^{-4} T.

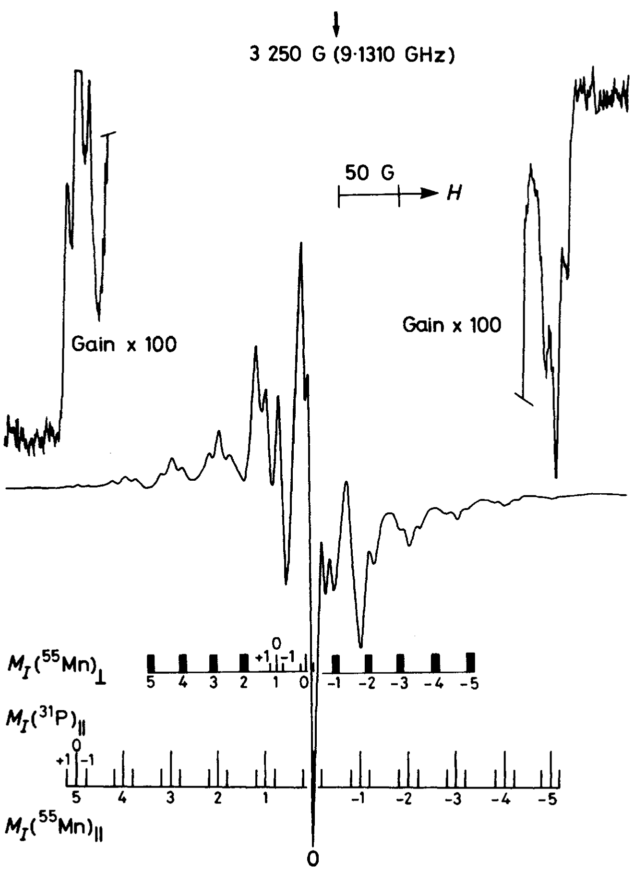

Figure 1. First-derivative *X*-band e.s.r. spectrum for a dilute solution of $[\mathrm{Mn_2(CO)_8(PBu^n_3)_2}]$ in mthf after exposure to ^{60}Co γ-rays at 77 K and slight annealing to remove signals from solvent radicals

Table 1. E.s.r. parameters for $[\mathrm{Mn_2(CO)_8(PBu^n_3)_2}]^{\cdot -}$ and related complexes

	Hyperfine coupling constants/G			
	Metal nuclei		^{31}P	
Complex	$A_\parallel$	$A_\perp$	$A_\parallel$	$A_\perp$
$[\mathrm{Mn_2(CO)_8(PBu^n_3)_2}]^-$	39.5	26.7	9.5	6
	±0.2	±0.5	±0.2	±1
$[\mathrm{Mn_2(CO)_{10}}]^{\cdot -}$ [a]	34.9	29.2		
$[\mathrm{Co_2(CO)_6(PBu^n_3)_2}]^{\cdot -}$ [b,c]	41.2	31.5	91.5	51.8
$[\mathrm{Rh_2(O_2CEt)_4(PPh_3)_2}]^{\cdot +}$ [d]	14.7		217	151

[a] Ref. 3. [b] Ref. 4. [c] Data reported as ^{59}Co: 38.5 × 10^{-4} ($A_\parallel$), 29.4 × 10^{-4} cm^{-1} ($A_\perp$); ^{31}P: 85.5 × 10^{-4} ($A_\parallel$), 48.4 × 10^{-4} cm^{-1} ($A_\perp$). [d] Ref. 9.

approximate 3*s* and 3*p* orbital populations in the usual manner (Table 2). However, because of the high spin density on the metal and very low density on phosphorus revealed by these results, it is necessary to allow for the indirect dipolar coupling from spin density on the metal. Using the point-dipole approximation, this coupling has a principal value of *ca.* 1 G. The corrected coupling to ^{31}P leads to the spin-density range given in Table 2. The $p:s$ ratio of *ca.* 3 : 1 is in the region expected for the hybridised phosphorus lone-pair orbitals. This result is discussed further below.

Comparison with Other Data.—The very small *g* shifts from the free spin value (2.0023) are comparable with earlier results for the $[(\mathrm{CO})_5\mathrm{Mn}\dot{-}\mathrm{Mn}(\mathrm{CO})_5]^-$ anion.[2,3] Also the ^{55}Mn hyperfine coupling constants for the two anions are almost equal which suggests that the extent of delocalisation of spin density onto the ligands is hardly changed on replacing the axial CO ligands by phosphine ligands, which is surprising. However, the ^{31}P hyperfine coupling, corresponding to a formal delocalisation of *ca.* 1% on each ligand, is no larger than is expected for spin polarisation of the σ electrons,[7] so that delocalisation is effectively zero. If this is the case for both anions, the almost equal coupling to ^{55}Mn is understandable.

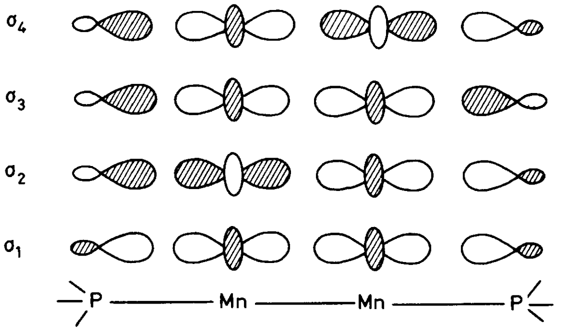

Figure 2. Sigma orbitals involved in the axial (*z*) bonding for $[\mathrm{Mn_2(CO)_8(PBu^n_3)_2}]$ and related complexes

Table 2. Estimated orbital populations (%)

	Phosphine ligands [a]		Metal [b]	
Complex	a_s^2	a_p^2	a_d^2	a_s^2
$[\mathrm{Mn_2(CO)_8(PBu^n_3)_2}]^{\cdot -}$	0.2 [c]	0.67 [c]	80	*ca.* 6 [d]
$[\mathrm{Mn_2(CO)_{10}}]^{\cdot -}$ [e]			78	*ca.* 6
$[\mathrm{Co_2(CO)_6(PBu^n_3)_2}]^{\cdot -}$ [f]	2.8	20	62	*ca.* 2.0
$[\mathrm{Rh_2(O_2CEt)_4(PPh_3)_2}]^{\cdot +}$ [g]	9.4	44		

[a] Total on both phosphorus atoms. [b] Total on both metal atoms. [c] After correction for indirect dipolar coupling: probably entirely due to spin polarisation. [d] Estimated from the isotropic coupling on the assumption that spin polarisation of inner *s* orbitals could give *ca.* −80 G for unit spin density. [e] Ref. 3. [f] Ref. 4. [g] Ref. 9.

It is tempting to argue that this situation arises because electron addition causes the metal–metal bond to stretch so as to reduce the σ* orbital energy and hence the unpaired electron is strongly confined to the Mn–Mn region of the orbital. However, the orbital involved (σ_4 in Figure 2) could equally well be stabilised by slight stretching of all three of the localised bond components. Comparison of our data with those of the dicobalt derivative[4] (Tables 1 and 2) shows that this is indeed, a reasonable alternative.

The estimated total spin density on phosphorus is decreased from *ca.* 23% in the cobalt derivative to *ca.* 1% in the manganese derivative. The trend is that expected for an antibonding orbital. Thus in an $\mathrm{A}\dot{-}\mathrm{B}$ σ* system, as the electronegativity of A increases relative to B, so the unpaired electron shifts towards B. However, the redistribution of spin density is quite remarkable, being far greater than the trends observed for σ* radicals involving only one localised bond.[7,8] Thus, for example, changes in spin distribution for various $\mathrm{V_k}$ centres ($\mathrm{X}\dot{-}\mathrm{X}^-$) (X = halogen) are much less drastic.

This greatly increased sensitivity to changes in metal electronegativity probably arises because there is a choice in the mode of deformation such that the electron is excluded from the metal ligand region if the elongation is confined to the metal–metal bond. Indeed, it may be valid to argue that in such cases, electron addition should lead to metal–metal bond breakage rather than loss of an axial ligand.

It is also interesting to compare these results for complexes having a $\sigma_4{}^1$ structure (Figure 2) with those for the complex $[Rh_2(O_2CEt)_4(PPh_3)_2]^{\cdot +}$ which is thought to have a $\sigma_3{}^1$ structure.[9] Hyperfine coupling to two equivalent ^{31}P nuclei is well defined in the powder spectrum of this complex, and analysis of the data (Tables 1 and 2) suggests that the total ligand spin density is *ca.* 53%. Perpendicular features for coupling to ^{103}Rh were not resolved so it is not possible to obtain good hyperfine coupling constants for these nuclei. Nevertheless, we can argue that the electron in this case is excluded from the central Rh–Rh bond and is largely confined to the outer Rh–P bonds. This interesting conclusion may reflect the fact that the σ_3 orbital is bonding in the Rh–Rh region, but antibonding in the Rh–P bonding region.

Phosphorus Orbital Hybridisation.—The ^{31}P hyperfine coupling constants lead to approximate 3*s* and 3*p* orbital populations (Table 2) and hence, if orbital following is a good approximation, to a measure of the bond angles in the PR_3 ligands. Our results are not very accurate but nevertheless the $p : s$ ratio must be in the region of $(3 \pm 1) : 1$. The result is close to our values of *ca.* 3.4 : 1 for the dimer σ* cations $[R_3P \dot{-} PR_3]^+$.[10] The ratio of 4.7 : 1 for the dirhodium cation $[Rh_2(O_2CEt)_4(PPh_3)_2]^{\cdot +}$ [9] suggests a slight flattening of the PR_3 groups whereas values in the region of 2 : 1, found by Labauze and Raynor [11] for various Co–PR_3 complexes, are surprisingly small, although they do reflect the small bond angles (in the 102—104° region) of most phosphine ligands in complexes.

The ratio of *ca.* 7 : 1 reported for the dicobalt anion $[Co_2(CO)_6(PBu^n{}_3)_2]^{\cdot -}$ [4] appears to be anomalously high for PR_3 ligands and we are unable to understand why this ratio should be so large.

Other Complexes.—We have also studied solutions of $[Mn_2(CO)_8\{P(OEt)_3\}_2]$ in mthf after irradiation at 77 K. The resulting e.s.r. spectra were almost indistinguishable from that for the $[Mn_2(CO)_{10}]^{\cdot -}$ anion [2,3] and we are therefore unable to state categorically that they are really due to the $P(OEt)_3$ derivative. However, the lines were unusually broad, and could possibly conceal weak ^{31}P coupling.

In view of the great similarity between the *g* and ^{55}Mn data for the $[Mn_2(CO)_{10}]^{\cdot -}$ and $[Mn_2(CO)_8(PBu^n{}_3)_2]^{\cdot -}$ anions and the very small ^{31}P coupling constants it does seem possible that we, in fact, prepared the $[Mn_2(CO)_8\{P(OEt)_3\}_2]^{\cdot -}$ anion.

Our results for ^{13}CO labelled $[Mn_2(CO)_{10}]$ also gave spectra which seemed identical with those for the ^{12}CO anion. Since the features in the spectrum of this anion are quite broad, we could have coupling to ^{13}C <4 G without being able to resolve it. It is, of course, possible that the two axial ligands were lost on electron addition, since loss of carbonyl is quite common, but it seems surprising that both axial ligands should be lost. (Loss of only one would be expected to make the two manganese atoms inequivalent which was not observed.) In view of the results for the phosphine substituted anion, we might expect that delocalisation onto the axial ligands should indeed be small. If spin polarisation is the major source of coupling we would expect a maximum coupling to ^{13}C of *ca.* 5 G which is close to the upper limit we have predicted above for this parameter. We conclude that once again it is the Mn–Mn bond that becomes stretched to accommodate the excess electron, which is thereby remarkably confined to this region.

We have also attempted to observe ^{13}C hyperfine coupling in the spectra for the anion prepared [12] from enriched $[Mn(CO)_5Cl]$. Again no coupling was detected. Whilst this may well be due to loss of CO on electron addition, it may also mean that the excess electron is largely confined to the Mn$\dot{-}$Cl region with virtually no delocalisation onto the axial carbonyl ligand.

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