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PARAMAGNETIC TRANSITION METAL CARBONYLS

IV *. ESR STUDY OF ANIONS DERIVED FROM $(CO)_5MnPbPh_3$ AND $(CO)_4CoPbPh_3$ BY HIGH ENERGY RADIATION

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Summary

Exposure of $(CO)_5MnPbPh_3$ to ^{60}Co γ-rays at 77 K gave one major paramagnetic species detectable by ESR spectroscopy. This exhibited an anisotropic hyperfine interaction with ^{55}Mn, near free-spin g-values, and a small, almost isotropic coupling to ^{207}Pb. The form of the $A(^{55}Mn)$ and g-tensor components suggest an orbital of d_{z^2} symmetry on manganese for the unpaired electron, but this cannot be directed along the Mn—Pb bond since the ^{207}Pb hyperfine coupling indicates a very low spin-density on lead. We suggest that the centre is formed by electron addition to manganese to give a formal d^7 centre, with concomitant loss of one equatorial carbonyl ligand. We define z as the direction of the lost ligand. A second centre, detected at high gain, having a large hyperfine coupling to ^{207}Pb and a 30 G coupling to ^{55}Mn is tentatively identified as the parent cation.

In marked contrast, the molecule $(CO)_4CoPbPh_3$ gave a single centre having comparable ^{59}Co hyperfine and g-tensor components, but also a very large hyperfine coupling to ^{207}Pb (ca. 3300 G). Thus, in this case, an electron gain centre (d^9) has been formed, the electron being accommodated in the highest MO having a large d_{z^2} component on cobalt (z being now the Co—Pb direction).

Reasons for the adoption of these different structures are discussed.

Introduction

Since the great majority of transition metal compounds containing metal—carbon bonds are diamagnetic, the technique of ESR spectroscopy has not been

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widely used despite the fact that it is a powerful tool for structural studies. There have been several recent experimental approaches to the preparation of paramagnetic species, especially in the metal carbonyl field. For example, Matheson et al. obtained a liquid-phase ESR spectrum for a range of radical anions $YCCo_3(CO)_9^-$ (when Y = alkyl, aryl, halogen, etc.), formed by sodium reduction of ethereal solutions of the neutral molecules [1]. Similar anions with the YC group replaced S, Se or Te were previously studied by Strouse and Dahl [2]. Apart from establishing identity and the equivalence of the three cobalt nuclei the ESR data are not structurally very informative. This is also true of the results for various new radical anions such as $Fe(CO)_5^-$, $Fe_2(CO)_9^-$, $Fe_3(CO)_{12}^-$ etc. [3] formed either by alkali metal or electrochemical reduction and the results for vanadium hexacarbonyl, studied by Pratt and Myers [4]. Curiously, $V(CO)_6$ even in solution, gave no ^{51}V hyperfine structure even at 4.2 K. Nevertheless, from the form of the g-tensor components the presence of a small tetragonal distortion was inferred [4].

In an interesting new development, Hudson et al. [5] used the spin-trapping technique to trap both components of the ultraviolet induced homolyses (eq. 1).

$$RMn(CO)_5 \rightarrow R^{\cdot} + {}^{\cdot}Mn(CO)_5 \qquad (1)$$

Again, these studies have mainly diagnostic value and the data only give structural information pertaining to the adducts, $Ar\dot{N}O(ML_5)$, the results for which can be compared with those for similar transition metal nitroxides [6,7].

The paramagnetic carbonyl $Co(CO)_4$ has been studied in the solid-state by ESR spectroscopy [8,9] with more success, in that the results strongly suggest that the unpaired electron is in the $3d_{z^2}$ orbital, which in turn favours the C_{3v} structure deduced from infrared studies [10]. However, our results are not in agreement with the alternative D_{2d} structure proposed by Ozin and Vander Voet [11] and deduced by Burdett to be slightly more stable than the C_{3v} structures [12]. However, the molecule $Mn(CO)_5$ has probably not been detected by ESR methods. A paramagnetic species detected after subliming the dimer $Mn_2(CO)_{10}$ [13] seems to have been the peroxy derivative $(CO)_5MnO_2$ [9] since, in the complete absence of molecular oxygen, no ESR signal was detected. We have also found that electron capture by the molecules $(CO)_5MnX$ (X = Cl, Br, I) gives the paramagnetic anions $Mn(CO)_5X^-$ but when these decompose, probably to give $Mn(CO)_5 + X^-$, only a very broad ESR spectrum remains, which does not become narrower even at 4.2 K [14]. A recent report that $Mn(CO)_5$ in tetrahydrofuran gives an isotryic sextet with $A(^{55}Mn)$ 93 G [15] can probably be discounted since the solid-state spectrum is characteristic of an S 5/2 state typical of manganese(II), as was stressed by Hudson et al. [5]. It seems possible that there is an efficient spin-relaxation process operative for $Mn(CO)_5$, making the spectrum very broad. This is not expected for the C_{4v} ($^2A_1$) state predicted by Burdett to be the gound-state, but could be true for the alternative $D_{3h}(^2E')$ state [12].

The aim of the present study was to extend our radiation experiments which were successful with the halides $(CO)_5MnX$ [14,16] to other similar materials. After screening a range of possible substrates, we found that the two lead derivatives $(CO)_5MnPbPh_3$ and $(CO)_4CoPbPh_3$ gave well defined paramagnetic centres which make an interesting contrast with each other.

Results

The X-band ESR powder spectra are shown in Figs. 1 and 2, together with our suggested interpretations. The parameters derived thereby are listed in Table 1.

The central ($g = 2$) region for the cobalt derivative shows three octets which lead to an axial hyperfine coupling and non-axial g-tensor components. The high and low field octets arise from radicals containing ^{207}Pb (^{207}Pb has a natural abundance of 21.11% and $I\ \frac{1}{2}$). The set of lines just to low field of the main set may be due to a second radical, but was always so much obscured by the stronger features that we have been unable to derive significant information. The form of the normal doublet features for ^{207}Pb is similar to the central features except that the low field set appear to be isotropic and have a relative intensity (ca. 15%) slightly greater than that predicted (10.56%) whilst the high field set show the x and y features but, unfortunately, no well-defined z-features. However, the relative intensities of the $x + y$ features is ca. 7% which is so close to the predicted value that the z-features cannot be far removed. All we can say is that $A(^{207}\text{Pb})$ is nearly isotropic, but that $A_{\parallel} > A_{\perp}$, as required for an admixture of some $6p_z$ character into the orbital.

A very weak set at even higher fields (Fig. 1) cannot be the undetected z-features since they are far too remote and are of the wrong shape. They may possibly be associated with a second species but, if so, this has to be remarkably similar to the major magnetic centre.

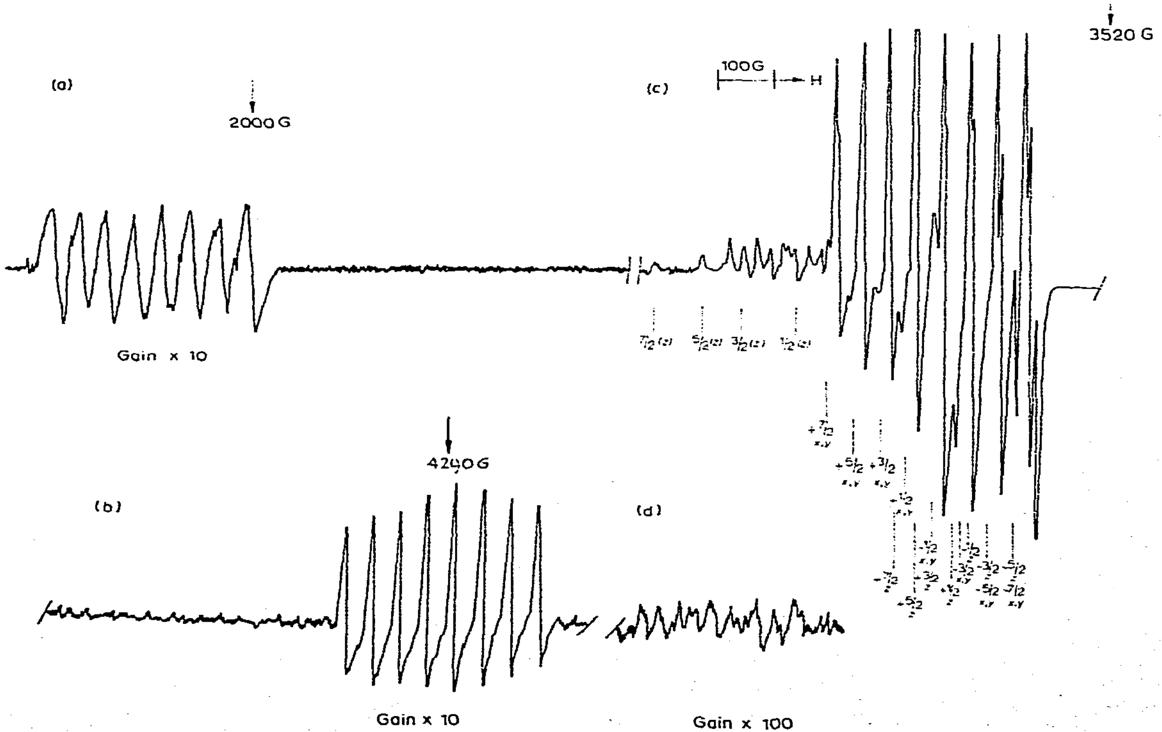

Fig. 1. First derivative X-band ESR spectrum for $(CO)_4CoPbPh_3$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $[(CO)_4CoPbPh_3]^-$ including the ^{207}Pb satellite lines (a and b) and unidentified features (c and d).

TABLE 1

ESR PARAMETERS FOR PARAMAGNETIC CENTRES IN γ-IRRADIATED $(CO)_5MnPbPh_3$ and $(CO)_4CoPbPh_3$

Host	Centre	^{55}Mn/^{59}Co hyperfine coupling (G) [a]			^{207}Pb hyperfine coupling (G) [a,b]	g-Tensor components		
		A_x	A_y	A_z		g_x	g_y	g_z
$(CO)_5MnPbPh_3$	A	−43.5	−43.5	+52.5 [c]	+90 ± 3	2.025	2.025	2.000
	B	ca. −30	−30	+30 [c]	3600 ± 10	ca. 2.00		
$(CO)_4CoPbPh_3$	$[(CO)_4CoPbPh_3]^-$	−48	−48	+37	3300 ± 10	2.020	2.017	1.996

[a] G = 10^{-4} T. [b] Calculated when necessary using the Briet–Rabi equation. [c] Signs chosen as indicated in text.

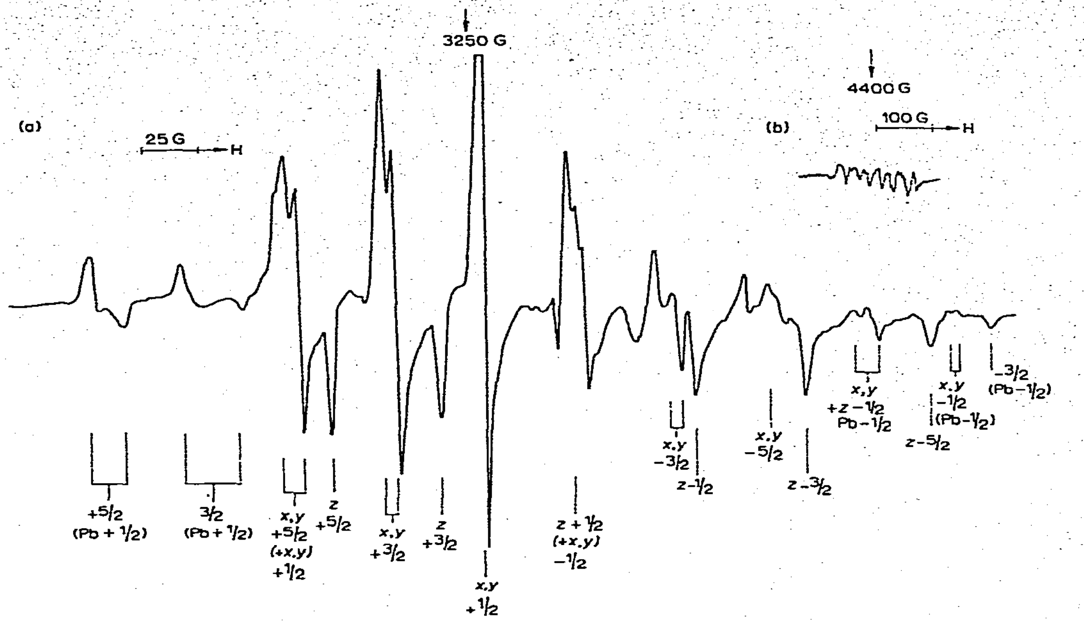

Fig. 2. First derivative X-band ESR spectrum for $(CO)_5MnPhPh_3$ after exposure to ^{60}Co γ-rays at 77 K, showing (a) features assigned to centre A, possibly $[(CO)_4MnPbPh_3]^-$, including the ^{207}Pb satellite lines (a and b of Fig. 1) and (b) high-field features assigned to centre B, possibly $[(CO)_5MnPbPh_3]^+$ containing ^{207}Pb.

The ESR spectrum for the manganese derivative (A) shows no high or low field features similar to those for the cobalt compound. However, the main set of lines from ^{55}Mn hyperfine interaction is flanked on each side by weaker features having ca. 10% relative intensity as required for complexes containing ^{207}Pb (Fig. 2). The manganese features are difficult to interpret precisely because each set display an uneven distribution indicative of a minor quadrupole effect. This can be seen, in particular, in the convergence of the x and y features in the M_I +1/2 line relative to, say, the M_I ±5/2 lines. The effects are small and too poorly defined to warrant an estimate of the quadrupole term. Again, the ^{207}Pb coupling is not quite isotropic, but the extra anisotropy is not well enough defined for us to say more than $A(^{207}Pb) = 90 \pm 3$ G.

If the power and gain are increased considerably, it is just possible to detect a weak sextet of lines in the 4400 G region (Fig. 2b). These were still detectable after slight annealing, and a sextet of poorly defined central lines having $A(^{55}Mn) \approx 30$ G could then be seen overriding the reduced spectrum of A. This new centre, B, is in relatively low abundance and was never observed in the absence of A. By analogy with our results for the cobalt complex and for the $Mn_2(CO)_{10}^-$ anion [16] we suggest the parameters given in Table 1 for centre B.

Discussion

The cobalt centre

The ^{59}Co hyperfine coupling appears to be axial. If this is accepted then there are only four possibilities for the signs, namely $A_\parallel$ ±37 G and $A_\perp$ ±48 or ∓48 G.

Taking all positive or all negative gives an anisotropy that is far too small for an electron that is expected to have considerable $3d$-character. Taking $A_\parallel$ —37 G and $A_\perp$ +48 G gives A_{iso} +19.7 G and $2B$ —56.7 G ($2B$ is the parallel component of the dipolar hyperfine coupling). Since the calculated $2B^\circ$ value for unit occupancy of the $d_{x^2-y^2}$ orbital is —152.3 G * this is quite reasonable. However, the usual value for A_{iso} for cobalt complexes is ca. —100 G, which is an indirect value stemming largely from spin-polarisation of inner s electrons. To achieve a value of +19.7 G requires considerable admixture of the outer, $4s$ orbital, which is forbidden by symmetry. We therefore favour the choice of sign given in Table 1, which leads to A_{iso} —19.7 G and $2B$ +56.7 G. This corresponds, uniquely, to an orbital with d_{z^2} symmetry, with a population of ca. 37%. If the spin-polarisation value is taken as ca. —50 G, then a very approximate $4s$ population of 2.3% is required to give A_{iso} —19.7 G, using the calculated value of 1320 G for 100% population *. In this case, admixture of the $4s$ orbital is symmetry allowed.

The very large value of $A(^{207}\text{Pb})$ can also be used to give an approximate spin-density on lead. Since the calculated value for A° is subject to large errors, we prefer to use the experimental value for solvated Pb^{3+} ions of ca. 10 000 G [19]. This will be too large for the formally neutral system under consideration and so the value of 33% $6s$-character is probably an under-estimate. In addition, there must be some $6p_z$-character also, but we have not been able to obtain a reliable estimate of the small hyperfine anisotropy and, hence, this is unknown. It seems fair to conclude that there is a rather even distribution of the unpaired electron between the two metal atoms.

The major primary effect of high energy radiation can be taken to be electron-ejection followed by electron capture for these systems. Thus, unless secondary reactions are involved, we expect to have $(\text{CO})_4\text{CoPbPh}_3^+$ and $(\text{CO})_4\text{CoPbPh}_3^-$ ions trapped in the parent compound at 77 K. In fact, only one major centre seems to have been detected and we need to decide if this is the primary cation or anion.

The parent molecule has a trigonal bipyramidal structure and is formally $3d^8$ on cobalt. The upper filled MOs are probably the degenerate $3d_{xy}$, $3d_{x^2-y^2}$ pair (when z is the Co—Pb direction). Loss of an electron from this level should lead to a Jahn—Teller distortion but, if this is not large, we would expect a large Δg_z which is not observed. This structure could lead to an efficient electron-spin relaxation (spin lattice) which could lead to severe line-broadening.

However, electron capture must lead to an electron in the antibonding orbital comprising $3d_{z^2}$ on cobalt and $6s$ and $6p_z$ on lead. This should have g_z close to the free-spin value, as observed, and g_x and g_y values greater than $g = 2$. (The small splitting between the x and y values probably reflects a crystal field effect possibly leading to a small deviation from the ideal angle of 120° between the equatorial carbonyl ligands.) The hyperfine parameters for ^{59}Co and ^{207}Pb agree satisfactorily with this model and we conclude that the centre is the parent anion $(\text{CO})_4\text{Co-Pb(Ph)}_3^-$.

The manganese centres

Two centres were observed. The major centre (A; Fig. 2) seems to have the

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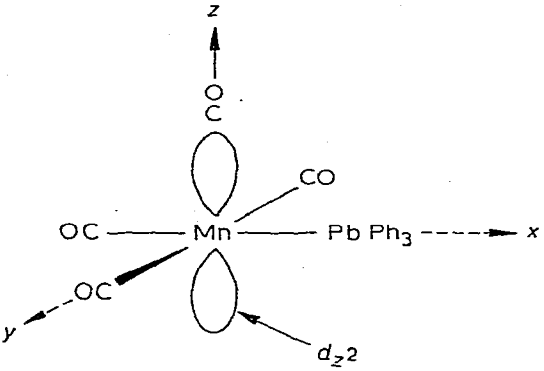
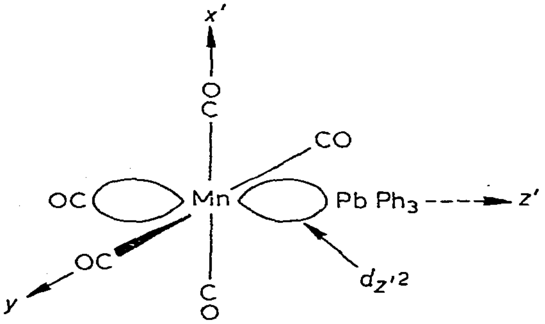
* Calculated from the data of Froese [17].

unpaired electron also in an orbital of $3d_{z^2}$ symmetry, using the same arguments as those used for the cobalt centre. However, absence of a large coupling to ^{207}Pb means that this orbital is not directed along the Mn—Pb bond (see below). In that case, we need to postulate a drastic change in symmetry and suggest that one of the four equatorial carbonyl ligands has been lost. If we define this as the z-direction, then, since x and y are no longer equivalent, we should not observe clear axial symmetry. We expect g_z to be close to the free-spin value, and g_x and $g_y > 2.0$, as observed. The coupling to ^{207}Pb should be small, but the value observed (ca. 1% spin density in the 6s orbital leading to, say, 4% on lead), is extremely small for this structure, which should still give rise to real delocalisation. Possibly there is a negative term from spin polarisation that largely cancels this contribution.



(I)



(II)

The structure envisaged (I) might change towards II on relaxing, but this may not be complete since II would have the unpaired electron in the degenerate $3d_{xy}$, $3d_{x^2-y^2}$ level and should distort. No clear change of this type was observed during the annealing process.

The other centre, B, is clearly very similar to the cobalt centre, and we can argue firmly that the unpaired electron must be in a σ^* orbital comprising largely the $3d_{z'^2}$(Mn) and $6s$(Pb) orbitals. (Here z' relates to the Mn—Pb direction: we could write this as, say, d_{x^2}, but prefer to retain the conventional use of z for orbitals of this symmetry.)

We now need to assign structures to centres A and B. Electron loss from the molecule $(CO)_5MnPbPh_3$, which is formally $3d^6$ on manganese, will probably be from the Mn—Pb σ-orbital. This would lead directly to a species with an ESR spectrum resembling B. This centre is certainly a primary product, so this assignment could be correct.

Electron capture is expected to be in the $d_{x'^2-y'^2}$ or $d_{z'^2}$ orbitals on manganese. The latter would again give a centre like B and, hence, B can be either the the primary cation or anion. One possible method of choice rests upon comparison with the analogous cobalt centre. For this, and for $(CO)_5MnPbPh_3^-$, the electron is in a σ^* orbital, so on going from Mn to Co the spin should move towards the Pb atom. In fact, there is a small shift in the opposite direction, which leads us to favour the cationic representation for B.

As stressed above, centre A can only result by loss of symmetry, most easily attained by loss of an equatorial carbonyl ligand. This would lead to electron capture in the $3d_{z^2}$ orbital, if we revert to the original x, y and z axes, as required. We therefore tentatively conclude that A is formed by electron capture coupled with loss of an equatorial carbonyl ligand with little distortion from the resulting asymmetric structure, and that B is formed directly by electron loss.

One remote alternative for centre A should be considered. It is known that, in the solid-state, dissociative electron capture by alkyl halides can lead to alkyl radicals that still exhibit a weak "charge-transfer" interaction with the ejected halide ions [19-21]. If this were to occur in the present case (eg. 2) the results for centre A could be explained. However, for the alkyl halides there

$$(CO)_5Mn{-}PbPh_3 + e^- \rightarrow (CO)_5Mn \cdots PbPh_3^- \qquad (2)$$

is no low-lying σ^* orbital available, and the alkyl radicals undergo a large change in shape as they are formed, which is not necessary for the manganese pentacarbonyl residue. Also, since such total ejection was not observed for the cobalt complex or the corresponding chloride, bromide or iodide complexes [15], it is difficult to see why it should be favoured for $(CO)_5MnPbPh_3$.

These results can be compared with those reported for $Mn_2(CO)_{10}$ and $Mn(CO)_5X$ (X = halogen). The former gave a centre having two equivalent manganese nuclei and was identified as the anion [17]. This is possible but, according to our present arguments, it might also have been the cation, $Mn_2(CO)_{10}^+$. The manganese halides (Cl, Br, I) [14] gave two centres, the electron-capture centre having the excess electron in a σ^* orbital having considerable $3d_{z^2}$(Mn) character. Since the halide ligands have considerable anionic character this is a reasonable conclusion which is not at variance with the present results except that, in these cases, there was no evidence for loss of an equatorial carbonyl ligand. However, the electron-loss centres are thought to have five unpaired electrons with a large, nearly axial, zero-field splitting [14]. We do not understand the drastic changes that this represents and no such dramatic modification is evident in any of the centres detected in the present study.

Experimental

Materials

Triphenyl(tetracarbonylcobalt)lead(IV) was prepared from triphenyllead chloride and octacarbonyldicobalt in methanol and triphenyl(pentacarbonylmanganese)lead(IV) from triphenyllead chloride and sodium pentacarbonylmanganate (−1) in diethyl ether according to the published procedures [22,23]. Subsequent manipulations of these materials were performed in a nitrogen glove bag. Other materials were of the highest grade available.

Samples were cooled to 77 K as fine powders or small beads, or in evacuated quartz tubes. They were irradiated in a Vickrad ^{60}Co γ-ray cell at a dose-rate of 1.7 MRad h^{-1} for up to 2h.

ESR spectra were measured with a Varian E3 spectrometer at 77 K. Samples were either annealed using a variable temperature Dewar tube, or by allowing the samples to warm slowly in the insert Dewar, with addition of liquid nitrogen whenever significant changes were observed in the ESR spectra.

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References

1 T.W. Matheson, B.M. Peake, B.H. Robinson, J. Simpson and D.J. Watson, J. Chem. Soc. Chem. Commun., (1973) 894.
2 C.E. Strouse and L.F. Dahl, Discuss. Faraday Soc., 47 (1969) 93.
3 B.M. Peake, B.H. Robinson, J. Simpson and D.J. Watson, J. Chem. Soc. Chem. Commun., (1974) 945.
4 D.W. Pratt and R.J. Myers, J. Amer. Chem. Soc., 89 (1967) 6470.
5 A. Hudson, M.F. Lappert, P.W. Lednor and B.K. Nicholson, J. Chem. Soc. Chem. Comm., (1974) 966.
6 D. Mulvey and W.A. Waters, J. Chem. Soc. Perkin II., (1974) 666.
7 M.C.R. Symons, D.X. West and J.G. Wilkinson, Inorg. Nuclear Chem. Letters, 10, (1974) 243.
8 H.J. Keller and H. Wawersik, Z. Naturforsch. B, 20 (1965) 938
9 S.A. Fieldhouse, B.W. Fullam, G.W. Neilson and M.C.R. Symons, J. Chem. Soc. Dalton, (1974) 567.
10 O. Crichton, M. Poliakoff, A.J. Rest and J.J. Turner, J. Chem. Soc. Dalton, (1973) 1321.
11 G.A. Ozin and A. Vander Voet, Acc. Chem. Res., 6, (1973) 313.
12 J.K. Burdett, Trans. Faraday Soc. II., (1974) 1599.
13 E.O. Fischer, E. Offhaus, J. Muller and D. Nothe, Chem. Ber., 105 (1972) 3027.
14 O. Anderson, S.A. Fieldhouse, C.E. Forbes and M.C.R. Symons, J. Chem. Soc. Dalton, in press.
15 S.A. Hallock and A. Wojcicki, J. Organometal. Chem., 54 (1973) C27.
16 O. Anderson and M.C.R. Symons, J. Chem. Soc. Chem. Commun., (1972) 1020.
17 C. Froese, J. Chem. Phys., 45 (1966) 1417.
18 R.J. Booth, H.C. Starkie and M.C.R. Symons, J. Chem. Soc. Dalton, (1973) 2233.
19 E.D. Sprague and F. Williams, J. Chem. Phys., 54 (1971) 5425.
20 S.P. Mishra and M.C.R. Symons, J. Chem. Soc. Perkin II., (1973) 391.
21 A.R. Lyons, M.C.R. Symons and S.P. Mishra, Nature, 249 (1974) 341.
22 D.J. Patmore and W.A.G. Graham, Inorg. Chem., 7 (1968) 771.
23 W. Jetz, P.B. Simmons, J.A.J. Thompson and W.A.G. Graham, Inorg. Chem., 5 (1966) 2217