Electron Spin Resonance Investigations of the Photo-oxidation of Decacarbonyldimanganese and Related Complexes

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An e.s.r. study has been made of the photolytic reactions of decacarbonyldimanganese derivatives in the presence of air or dioxygen in solution at low temperatures. E.s.r. parameters for the species $[Mn(CO)_4L(O_2)]$ [L = CO, PPh_3, PBu^n_3, or $P(OEt)_3$] are presented and oxygen-17 labelling of the species where L = CO has given isotropic coupling constants for the two atoms of the dioxygen moiety of 2.2 ± 0.1 and 2.05 ± 0.1 mT. Frozen-solution spectra of $[Mn(CO)_5(O_2)]$ have been analysed and the results are discussed in terms of the bonding in the complex. Related photo-oxidation studies of other binuclear carbonyl complexes are reported and a species which is probably $[Fe(\eta\text{-}C_5H_5)(CO)_2(O_2)]$ has been identified by e.s.r. spectroscopy.

THE nature of species arising during the photolysis of decacarbonyldimanganese in solution has caused controversy.[1-4] The six-line e.s.r. signal [$A_{iso.}(^{55}Mn)$ 9.3 mT] produced in tetrahydrofuran (thf) was originally assigned [1] to $[Mn(CO)_5]$ but later studies have definitely shown that it arises from a d^5 manganese(II) species.[2] When photolysis is carried out at <173 K in hydrocarbon solvents a different six-line e.s.r. spectrum [$A_{iso.}(^{55}Mn)$ 1.2 mT] has been observed and this is dependent on the presence of dioxygen so it has been assigned to $[Mn(CO)_5(O_2)]$.[4] However, the relationship between this complex and the species {also assigned to $[Mn(CO)_5(O_2)]$ but with differing e.s.r. parameters} formed during the sublimation of $[Mn_2(CO)_{10}]$ in the presence of dioxygen [5] has not been established. Also, there is a discrepancy between the solid-state e.s.r. spectrum of the latter species and that of the paramagnetic material produced during sublimation of the carbene complex $[Mn_2(CO)_9\{C(OMe)Ph\}]$,[6] although this was also reassigned, in a later paper,[5] to $[Mn(CO)_5(O_2)]$.

Since dioxygen–metal complexes are currently of much interest,[7] the aim of the present work was to investigate in more detail the nature of the photo-oxidation products of decacarbonyldimanganese and related complexes using e.s.r. spectroscopy.

EXPERIMENTAL

The complexes $[Mn_2(CO)_{10}]$,[8] $[Mn_2(CO)_8L_2]$ (L = PPh_3, or $AsPh_3$),[9] $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$,[10] $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$,[10] $[Ni_3(\eta\text{-}C_5H_5)_3(CO)_2]$,[11] and $[Co_2(CO)_6\{P(OEt)_3\}_2]$ [12] were prepared by literature methods; $[Mn_2(CO)_{10}]$ was freshly sublimed before use and the other complexes were purified by chromatography and recrystallisation or by sublimation as appropriate. Commercially obtained (Strem Chemicals) $[Co_2(CO)_8]$ and $[Re_2(CO)_{10}]$ were purified by sublimation and $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$ by chromatography. 2-Methyl-2-nitrosopropane and $^{17}O_2$ (64.08 atom %) were purchased from Aldrich Chemicals and Miles Laboratories Inc., respectively. Organic solvents were dried by routine procedures and $^{17}O_2$ gas was handled in a conventional vacuum system.

E.s.r. experiments were carried out on *ca.* 10^{-2} mol dm^{-3} solutions of organometallic complexes using a JEOL PE1 *X*-band spectrometer equipped with a variable-temperature facility. Temperatures were monitored with a thermocouple to within ±10 °C. Samples were subjected to u.v. irradiation in the e.s.r. cavity by a 100-W medium-pressure mercury lamp *via* a light guide, focusing lens, and Pyrex filter. Spectra were calibrated with diphenylpicrylhydrazyl and Fremy's salt.

RESULTS AND DISCUSSION

Photolysis of $[Mn_2(CO)_{10}]$ *and Derivatives.*—(*a*) *Solution studies.* It has been established by synthetic and physical studies that near-u.v. photolysis of $[Mn_2(CO)_{10}]$ in solution results in the homolytic fission of the Mn–Mn bond to produce $[Mn(CO)_5]$ [13] and that a similar homolysis occurs under thermal reaction conditions.[14] This 17-electron radical has been trapped using nitroso-compounds and species $[Mn(CO)_5(NOR)]$ have been characterised by e.s.r. spectroscopy.[4,15,16] We have confirmed these results under the conditions of our experiments and the spin adduct $[Mn(CO)_5(ONBu^t)]$ forms in the presence of 2-methyl-2-nitrosopropane [e.s.r. parameters in toluene at 203 K: $g_{iso.}$ 2.006 5, $A_{iso.}(^{55}Mn)$ 6.5×10^{-4} cm^{-1}, $A_{iso.}(^{14}N)$ 15.3×10^{-4} cm^{-1}].

No e.s.r. signal is observed when a degassed solution of $[Mn_2(CO)_{10}]$ in toluene is subjected to near-u.v. irradiation in the range 173—230 K, but when air or dioxygen is admitted a six-line signal rapidly develops [$A_{iso.}(^{55}Mn)$ 11.9×10^{-4} cm^{-1}, see Table]. This signal is also observed under the same conditions during photolysis in the presence of air in n-hexane, n-pentane, 1- and 2-bromobutane, dichloromethane, and thf [although prolonged photolysis, especially in the latter solvent, produces spectra characteristic of manganese(II) species [2,4]]. There are minor changes in the A_{iso} (^{55}Mn) values which appear to increase with increasing solvent polarity (Table).

In toluene solution the spectrum of this species decays in the dark with a half-life of *ca.* 10 min at 203 K and decays completely within 2 min at 223 K. Degassing of a photolytically produced sample of the paramagnetic species at low temperatures indicated that its existence and thermal decomposition are essentially independent of the presence of excess of free dioxygen. The half-width of the e.s.r. lines is *ca.* 0.1 mT in the presence of 150 Torr O_2 (or air) but increases to 0.5—0.6 mT in the presence of 760 Torr O_2.†

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† Throughout this paper: 1 Torr = (101 325/760) Pa.

E.s.r. data for dioxygen complexes of manganese in solution [a]

Species	Solvent	T/K	$g_{iso.}$	$A_{iso.}(^{55}Mn)$ [b]	$A_{iso.}(^{31}P)$ [b]
$[Mn(CO)_5(O_2)]$	n-Hexane	203	2.017	11.6	
	n-Pentane	203	2.017	11.6	
	Toluene	203	2.017	11.9	
	2-Bromobutane	193	2.017	11.9	
	Dichloromethane	210	2.017	12.1	
	thf	193	2.017	12.2	
$[Mn(CO)_4(PPh_3)(O_2)]$	Toluene	233	2.020	13.8	7.4
$[Mn(CO)_4(PBu^n_3)(O_2)]$	Toluene	233	2.0205	14.1	7.4
$[Mn(CO)_4\{P(OEt)_3\}(O_2)]$	Toluene	203	2.020	13.9	8.9

[a] Estimated errors: $g < \pm 0.001$; A, $\pm 0.1 \times 10^{-4}$ cm^{-1}. [b] Values in 10^{-4} cm^{-1}.

In view of the earlier proposals[4] and the above evidence, it may be assumed that $[Mn(CO)_5(O_2)]$ is formed. Attempts to trap this dioxygen species by formation of an adduct in the presence of 2-methyl-2-nitrosopropane, however, were unsuccessful and led only to the observation of spectra attributable to the nitroxides Bu^t_2NO and $[Mn(CO)_5(ONBu^t)]$ and a radical which is probably $Bu^tNO(OBu^t)$.[17]

Photolysis of $[Mn_2(CO)_8(PPh_3)_2]$ in toluene at 203 K in the presence of dioxygen produces an e.s.r. spectrum with ^{31}P hyperfine splitting (see Table) which may be assigned to $[Mn(CO)_4(PPh_3)(O_2)]$. An identical spectrum can be produced from a 1 : 2 mixture of $[Mn_2(CO)_{10}]$ and PPh_3 in solution so that the substituted derivative can be formed *in situ*. Similar *in situ* experiments give e.s.r. spectra for the species $[Mn(CO)_4L(O_2)][L = P(OEt)_3$ or PBu^n_3, see Figure 1 and Table].

Photolysis of $[Mn_2(CO)_8(AsPh_3)_2]$ in aerated toluene in the range 173—233 K gives a broad e.s.r. spectrum, $g_{iso.} = 2.026$ (total width *ca.* 11 mT), from which hyperfine splitting parameters cannot be obtained. Experiments conducted on mixtures of $[Mn_2(CO)_{10}]$ and $AsPh_3$ in solution give complex e.s.r. signals indicating the presence of more than one paramagnetic species.

(*b*) *Frozen-solution spectra.* When solutions containing photolytically produced $[Mn(CO)_5(O_2)]$ are frozen *in situ* in the e.s.r. cavity at 113—133 K spectra characteristic of polycrystalline samples are obtained.

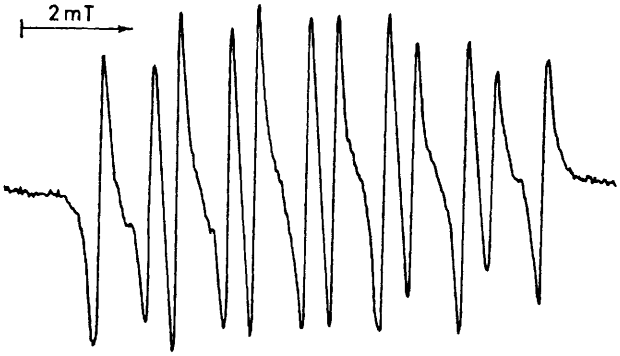


FIGURE 1 E.s.r. spectrum of $[Mn(CO)_4\{P(OEt)_3\}(O_2)]$ in toluene solution at 203 K. Microwave frequency = 9.34 GHz

The main features of these solid-state spectra are the same in n-pentane, methylcyclohexane, toluene, and 1- or 2-bromobutane, although minor variations in linewidths and resolution do occur. These spectra appear to correspond to those obtained by Fischer *et al.*[6] from sublimation of $[Mn_2(CO)_9\{C(OMe)Ph\}]$. Computer simulation using a program based on equations of Pilbrow and Winfield[18] and developed by Lund and Raynor[19] yields the following e.s.r. parameters for the best fit, assuming an orthorhombic model with coincident axes for g and A tensors (see Figure 2): $g_1 = 2.007$, $A_1 = 6 \times 10^{-4}$ cm^{-1}; $g_2 = 2.013$, $A_2 = 20 \times 10^{-4}$ cm^{-1}; $g_3 = 2.031$, $A_3 = 10 \times 10^{-4}$ cm^{-1}. Agreement between the computed and experimental spectra and between the mean g and A values and the isotropic solution parameters is quite good. Attempts were made to improve the fitting by introduction of an angle (α) between the axes of the g and A tensors in one plane while keeping the third axis common,[18] but variations of α in intervals of 10° using various sets of values for A tensors consistent with the isotropic spectrum give poorer simulations. It is interesting that Pilbrow and his co-workers[20] have attributed such a non-coincidence in axes in paramagnetic dioxygen–cobalt complexes to the angle of the Co–O–O system although the deviation is only 10—15° in several cases.

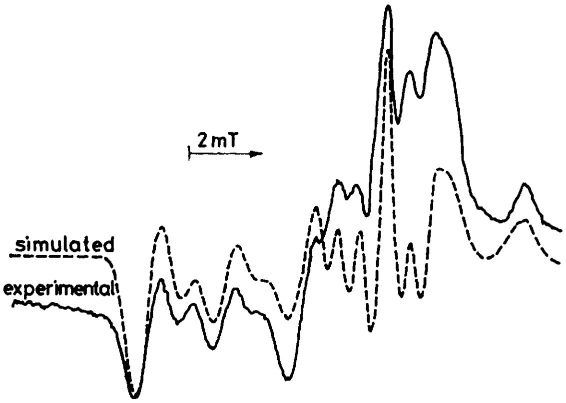


FIGURE 2 E.s.r. spectrum of $[Mn(CO)_5(O_2)]$ in frozen solution of n-pentane at 113 K: (——) experimental spectra, 9.34 GHz; (– – – –) simulated spectrum using $g_1 = 2.007$, $A_1 = 6 \times 10^{-4}$ cm^{-1}, $\sigma_1 = 0.15$ mT, $g_2 = 2.013$, $A_2 = 20 \times 10^{-4}$ cm^{-1}, $\sigma_2 = 0.4$ mT, $g_3 = 2.031$, $A_3 = 10 \times 10^{-4}$ cm^{-1}, and $\sigma_3 = 0.4$ mT (σ = linewidth)

(*c*) *Experiments with* $^{17}O_2$. To demonstrate the incorporation of oxygen in the species produced by photo-oxidation of $[Mn_2(CO)_{10}]$ $^{17}O_2$ was employed. Using *ca.* 150 Torr $^{17}O_2$, an e.s.r. spectrum from toluene solution at 203 K showed hyperfine splitting due to ^{17}O (see Figure 3). It was impossible to improve the spectrum in terms of intensity or resolution using a variety of concentrations of $[Mn_2(CO)_{10}]$, $^{17}O_2$ pressures, or temperatures so that the weakest outer lines expected from a species $[Mn(CO)_5(^{17}O\text{–}^{17}O)]$ could not be resolved.

Surprisingly, it was also found that at higher pressures of $^{17}O_2$ (*ca.* 500 Torr) no signal could be obtained at 203 K under conditions in which the normal $^{16}O_2$ species was observed; this phenomenon may be due to broadening of the signal by interaction with the nuclear quadrupole of $^{17}O_2$. Simulation in terms of a mixture of species $[Mn(CO)_5(^{16}O-^{16}O)]$, $[Mn(CO)_5(^{17}O-^{16}O)]$, $[Mn(CO)_5(^{16}O-^{17}O)]$, and $[Mn(CO)_5(^{17}O-^{17}O)]$ in relative concentration 1 : 1.78 : 1.78 : 3.18 and assuming different $A_{iso.}(^{17}O)$ values for the two oxygen atoms gives the best-fit parameters $A_{iso.}(^{17}O) = 2.2 \pm 0.1$ (20.7×10^{-4}) and 2.05 ± 0.1 mT $(19.3 \times 10^{-4}$ cm$^{-1})$, see Figure 3. The rather poor resolution of the spectrum and the resulting experimental error do not conclusively rule out equivalence of the two oxygen atoms, but the overall fit for a symmetrical species is not completely satisfactory.

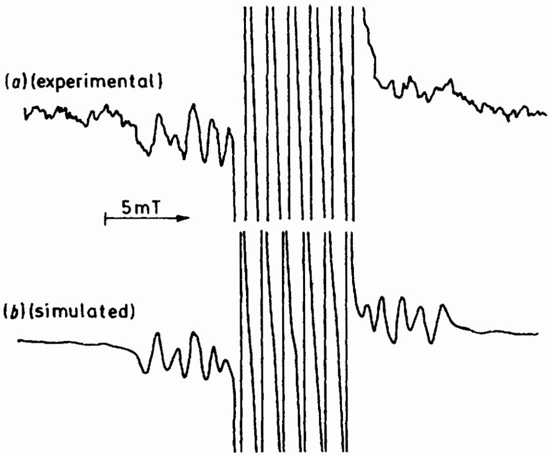
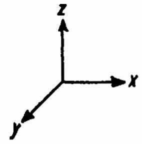


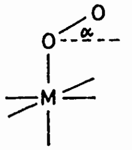
FIGURE 3 E.s.r. spectrum of $[Mn(CO)_5(^*O_2)]$ with ^{17}O(64.08%)-labelled O_2 in toluene at 203 K: (*a*) experimental (9.30 GHz), (*b*) simulated spectrum for a mixture of $Mn-^{16}O-^{16}O$, $Mn-^{17}O-^{16}O$, $Mn-^{16}O-^{17}O$, and $Mn-^{17}O-^{17}O$ in concentration ratio 1 : 1.78 : 1.78 : 3.18 with respective linewidths 0.25 : 0.5 : 0.5 : 1.0 mT and using $g = 2.017$, $A_{iso.}(^{55}Mn) = 1.26$ mT, $A_{iso.}(^{17}O) = 2.05$ and 2.2 mT

These data confirm that O_2 is incorporated into the species formed by photolysis of $[Mn_2(CO)_{10}]$ in air or dioxygen. Spectra of this $^{17}O_2$-containing species in frozen solutions are complex so that analysis was impossible.

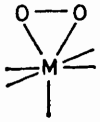
(*d*) *Comments on structure and bonding.* The data presented above provide good evidence for the formation of species $[Mn(CO)_4L(O_2)]$. Dioxygen in metal complexes has been shown to bond in a σ-bent, (A), or a η^2-side-on (π-bonded) manner, (B).[7] When the metal is in a low oxidation state it might be presumed that the O_2 ligand would favour the π-bonded geometry. However, calculations on isoelectronic cobalt complexes [21] or on the general transition-metal interaction with diatomic ligands [22] suggest that $[ML_5(O_2)]$ systems with a total of nine metal $3d$ and ligand $\pi_g{}^*$ electrons should contain a bent bonding arrangement with the unpaired electron in an orbital comprising mainly dioxygen $\pi_y{}^*$ character with little metal d_{yz}. The bent model seems consistent with the e.s.r. data presented here.

The low $A_{iso.}(^{55}Mn)$ value, $\mp 11.9 \times 10^{-4}$ cm^{-1}, and the anisotropic coupling constants $(A_{aniso.} = A_i - A_{iso.})$, $\pm 5.9 \times 10^{-4}$, $\pm 1.9 \times 10^{-4}$, $\mp 8.1 \times 10^{-4}$ cm^{-1}, indicate low electron-spin density at the Mn atom.





(A)



(B)

Assuming only *s* and *d* contributions to $A_{iso.}$ and $A_{aniso.}$, the ' apparent ' 4*s* and 3*d* spin densities at the manganese are *ca.* 0.01 and 0.09 respectively (principal values from ref. 23), but must arise at least in part from a spin-polarisation mechanism (*cf.* refs. 5 and 24). The ^{17}O coupling constants are consistent with essentially one unpaired electron localised on the two atoms of the O_2 unit in a p_π orbital [the relationship $A_{iso.}(^{17}O) = Q_{OO}{}^{O}\rho_{O}$, where $Q_{OO}{}^{O} = \pm 4.1 \pm 0.3$ mT, has been proposed [25]]. These conclusions are comparable to those made for $[Co(bzacen)(py)(^{17}O_2)]$ [py = pyridine, bzacen = *NN'*-ethylenebis(benzoylacetonieminate)] which in the crystal has a bent bond with α = 36°, although in solution both oxygen atoms appeared equivalent in the e.s.r. spectrum so that a dynamic equilibrium involving interchange $A \rightleftharpoons B$ was proposed.[26] The small difference in $A_{iso.}(^{17}O)$ values in $[Mn(CO)_5(^{17}O_2)]$ supports a rigid model for this complex with magnetically inequivalent oxygen atoms, but a dynamic process cannot be conclusively ruled out in light of the experimental error. It should be noted that anisotropic ^{17}O data for the cobalt complex confirmed the inequivalent oxygen atoms[26b] and it is unfortunate that such data could not be obtained for the manganese complex. The fact that the best simulations of the frozen-solution spectra of $[Mn(CO)_5(^{16}O_2)]$ are obtained when the *g* and *A* tensors have coincident axes supports a small or zero value for α or (90 − α).[20] The absence of axial symmetry $(g_1 \neq g_2 \neq g_3)$ is inconsistent with a linearly bonded C_{4v} structure (α 90°) so that it seems reasonable to propose that α is less than 10°.

The increase in $A_{iso.}(^{55}Mn)$ in the phosphorus-substituted derivatives $[Mn(CO)_4L(O_2)]$[L = PR_3 or $P(OEt)_3$] compared to the case where L = CO may reflect the poorer π-acceptor abilities of the former ligands and hence an increasing π interaction between $Mn(d_{yz})$ and $O_2(\pi_y{}^*)$ causing greater *s*-orbital polarisation at Mn.

Photolysis of Other Binuclear Carbonyl Complexes.—It is known that photolysis of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ in solution in the presence of nitroso-compounds produces spin adducts $[Fe(\eta\text{-}C_5H_5)(CO)_2(ONR)]$ [15] (R = aryl) and that the 17-electron radical $[Fe(\eta\text{-}C_5H_5)(CO)_2]$ is probably an intermediate. When $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ is irradiated in degassed toluene at 203 K no e.s.r. signals are obtained, but in the presence of air or dioxygen a singlet with $g_{iso.} = 2.025 \pm 0.001$ is observed which decays rapidly in the dark. Similar results occur in 2-bromobutane solutions. Frozen solutions give spectra typical of an axially symmetric species, $g_{\parallel} = 2.067 \pm 0.003$ and $g_{\perp} = 2.007 \pm 0.001$. On prolonged irradiation in solution at 203 K a second, broader, signal develops with $g_{iso.} = 2.04$. Using $^{17}O_2$ gas (150 Torr), incorporation of oxygen in the primary photolysis product is confirmed by the appearance of extra hyperfine structure in the e.s.r. spectrum. The analysis of this complex spectrum of mixed $^{17}O-^{16}O$ species is difficult since the signal intensity is low and the lines are broad. It is complicated by formation of the second signal on attempts to increase intensity by prolonged photolysis, and at higher pressures of $^{17}O_2$(500 Torr) the signals are broadened beyond detection. However, the maximum value for $A_{iso.}(^{17}O)$ is $(21 \pm 2) \times 10^{-4}$ cm^{-1} and the complexity and spread of the signals indicates the presence of another ^{17}O atom with a lower coupling constant. Thus we suggest that the species is $[Fe(\eta\text{-}C_5H_5)(CO)_2(O_2)]$.

Photo-oxidation in toluene solution of $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$, which also produces a 17-electron radical by metal–metal bond fission,[15,27] gives two broad e.s.r. signals at 193 K, $g_{iso.} = 1.967 \pm 0.002$ and 1.926 ± 0.005, which are stable to decomposition in the dark at this temperature over several hours, although the former signal decays on warming. These species are probably oxygenated products.

Despite several attempts to purify $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$ by chromatography and recrystallisation, solutions of our sample of this complex in toluene exhibited a single e.s.r. line with $g_{iso.} = 2.052 \pm 0.001$ and, in frozen solutions, $g_{\parallel} = 2.103 \pm 0.003$ and $g_{\perp} = 2.026 \pm 0.002$. These parameters are characteristic of the known [28] paramagnetic trinuclear species $[Ni_3(\eta\text{-}C_5H_5)_3(CO)_2]$ and this was confirmed by preparation of a pure sample of the latter complex. No additional e.s.r. signals are observed on photolysis of $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$ in the presence of air at low temperatures. Similarly, photo-oxidation of $[Re_2(CO)_{10}]$ or $[Co_2(CO)_6\{P(OEt)_3\}_2]$ in toluene in the range 183—273 K or $[Co_2(CO)_8]$ in toluene at 203 K or 2-methylbutane at 143—163 K produces no e.s.r. signals in spite of the fact that 17-electron radicals of the former two complexes are formed on photolysis and these may be spin trapped.[13,15] It is also of interest here that $[Re(CO)_5(O_2)]$ has been discussed as an intermediate in the oxygen inhibition of reactions of rhenium carbonyls.[29]

We thank Dr. J. A. Hunter for his assistance with the computer simulations, and Mr. B. D'Arcy for help in running e.s.r. spectra.

[8/1479 *Received*, 11*th August*, 1978]

REFERENCES

[1] S. A. Hallock and A. Wojcicki, *J. Organometallic Chem.*, 1973, **54**, C27.

[2] A. Hudson, M. F. Lappert, and B. K. Nicholson, *J. Organometallic Chem.*, 1975, **92**, C11; 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, *ibid.*, 1976, **110**, C5.

[3] C. L. Kwan and J. K. Kochi, *J. Organometallic Chem.*, 1975, **101**, C9.

[4] A. S. Huffadine, B. M. Peake, B. H. Robinson, J. Simpson, and P. A. Dawson, *J. Organometallic Chem.*, 1976, **121**, 391.

[5] S. A. Fieldhouse, B. W. Fullam, G. W. Neilson, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 567.

[6] E. O. Fischer, E. Offhaus, J. Müller, and D. Nöthe, *Chem. Ber.*, 1972, **105**, 3027.

[7] L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175; G. McLendon and A. E. Martell, *Co-ordination Chem. Rev.*, 1976, **19**, 1, and refs. therein.

[8] R. B. King, J. C. Stokes, and T. F. Korenowski, *J. Organometallic Chem.*, 1968, **11**, 641.

[9] J. Lewis, A. R. Manning, and J. R. Miller, *J. Chem. Soc. (A)*, 1966, 845.

[10] R. B. King, 'Organometallic Synthesis,' vol. 1, eds. J. J. Eisch and R. B. King, Academic Press, New York, 1965.

[11] E. O. Fischer and C. Palm, *Chem. Ber.*, 1958, **91**, 1725.

[12] A. Sacco, *Ann. Chim. (Italy)*, 1953, **43**, 495.

[13] M. S. Wrighton and D. S. Ginley, *J. Amer. Chem. Soc.*, 1975, **97**, 2065.

[14] J. P. Fawcett, A. Poë, and K. R. Sharma, *J. Amer. Chem. Soc.*, 1976, **98**, 1401.

[15] A. Hudson, M. F. Lappert, and B. K. Nicholson, *J.C.S. Dalton*, 1977, 551.

[16] L. S. Benner and A. L. Balch, *J. Organometallic Chem.*, 1977, **134**, 121.

[17] J. Pfab, *Tetrahedron Letters*, 1978, 843.

[18] J. R. Pilbrow and M. E. Winfield, *Mol. Phys.*, 1973, **25**, 1073.

[19] G. E. Herberich, T. Lund, and J. B. Raynor, *J.C.S. Dalton*, 1975, 985.

[20] J. A. de Bolfo, T. D. Smith, J. F. Boas, and J. R. Pilbrow, *J.C.S. Dalton*, 1976, 1495; D. J. Cookson, T. D. Smith, J. F. Boas, P. R. Hicks, and J. R. Pilbrow, *ibid.*, 1977, 109; M. F. Corrigan, K. S. Murray, B. O. West, P. R. Hicks, and J. R. Pilbrow, *ibid.*, p. 1478.

[21] B.-K. Teo and W.-K. Li, *Inorg. Chem.*, 1976, **15**, 2005; A. Dedieu, M.-M. Rohmer, and A. Veillard, *J. Amer. Chem. Soc.*, 1976, **98**, 5789.

[22] R. Hoffmann, M. M. L. Chen, and D. L. Thorn, *Inorg. Chem.*, 1977, **16**, 503.

[23] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 155.

[24] B. S. Tovrog, D. J. Kitko, and R. S. Drago, *J. Amer. Chem. Soc.*, 1976, **98**, 5144.

[25] E. Melamud and B. L. Silver, *J. Phys. Chem.*, 1973, **77**, 1896.

[26] (*a*) E. Melamud, B. L. Silver, and Z. Dori, *J. Amer. Chem. Soc.*, 1974, **96**, 4689; (*b*) D. Getz, E. Melamud, B. L. Silver, and Z. Dori, *ibid.*, 1975, **97**, 3846.

[27] M. S. Wrighton and D. S. Ginley, *J. Amer. Chem. Soc.*, 1975, **97**, 4246.

[28] H. C. Longuet-Higgins and A. J. Stone, *Mol. Phys.*, 1962, **5**, 417; R. E. Dessy, R. B. King, and M. Waldrop, *J. Amer. Chem. Soc.*, 1966, **88**, 5112.

[29] B. H. Byers and T. L. Brown, *J. Amer. Chem. Soc.*, 1977, **99**, 2527.