The Co-ordination of Small Molecules by Manganese(II) Phosphine Complexes. Part 3.† The Dependence on the Nature of the Halogen in $[MnX_2(PR_3)]$ (X = Cl, Br, or I; R_3 = $PhMe_2$, $PhEt_2$, $PhPr^n{}_2$, $PhBu^n{}_2$, $PhBu^i{}_2$, $Pr^n{}_3$, $Bu^n{}_3$, or Ph_3) on Adduct Formation with Sulphur Dioxide in the Solid State and in Tetrahydrofuran Solution‡

David S. Barratt, Christopher G. Benson, George A. Gott, Charles A. McAuliffe,* and S. Peter Tanner
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The reaction of the complexes $[MnX_2(PR_3)]$ (X = Cl, Br, or I; R_3 = $PhMe_2$, $PhEt_2$, $PhPr^n{}_2$, $PhBu^n{}_2$, $PhBu^i{}_2$, $Pr^n{}_3$, $Bu^n{}_3$, or Ph_3) with sulphur dioxide in the solid state, in toluene slurries and in tetrahydrofuran (thf) has been studied. In all three systems a strong dependence on the nature of the halide is observed. For X = Cl, no reaction takes place; for X = I, all complexes irreversibly absorb SO_2; for X = Br a borderline exists and the nature of the phosphine is important, *viz.* trialkylphosphines promote SO_2 binding, whereas complexes containing phenyl-substituted phosphines (except $PPhMe_2$) are inactive towards SO_2. The reaction stoicheiometry is unusual, $[MnX_2(PR_3)(SO_2)_x]$ (for measurements in the solid state $x = 0.66$, for thf solution $x = 0.65$—0.76). Although $[MnI_2(PPh_3)]$ does not bind dioxygen it forms an adduct with sulphur dioxide in the solid state and in thf.

We have shown that the complexes [MnX$_2$(phosphine)] (X = Cl, Br, I, or NCS)[1] are capable of reversibly co-ordinating a number of small molecules, *e.g.* dioxygen,[2] carbon monoxide,[3] or nitric oxide.[4] Structure/reactivity relationships are emerging from which it is seen that the binding of the small molecule is dependent on both the nature of the phosphine and the halogen or pseudohalogen.

There is much interest in the co-ordination of sulphur dioxide by transition-metal complexes,[5] arising originally for purely academic factors, but more recently because of pressing environmental considerations. We have recently shown[6] that sulphur dioxide can insert into a manganese–iodide bond to form the unusual complex $[Mn(OPPh_3)_4(O_2SI)_2]$; one of the sulphur dioxide molecules is lost by heating to 129 °C, and this reaction may be reversed by addition of further sulphur dioxide [equation (1)].

$$[Mn(OPPh_3)_4(O_2SI)_2] \underset{+SO_2}{\overset{129\,^\circ C}{\rightleftharpoons}} [Mn(OPPh_3)_4(O_2SI)I] + SO_2 \quad (1)$$

Here we report our studies of the reaction of sulphur dioxide with some $[MnX_2(PR_3)]$ (X = Cl, Br, or I; R_3 = $PhMe_2$, $PhEt_2$, $PhPr^n{}_2$, $PhBu^n{}_2$, $PhBu^i{}_2$, $Pr^n{}_3$, $Bu^n{}_3$, or Ph_3) complexes in the solid state and in tetrahydrofuran (thf) solution. In both phases, for reaction to occur there is a strong dependence on the nature of the halide and, where reaction occurs, the stoicheiometry of the products is unusual.

Results and Discussion

Solid-state Studies.—The complexes $[MnX_2(PR_3)]$ were synthesised by published methods[7] and the sulphur dioxide adducts were prepared by exposing toluene slurries of these complexes to an atmosphere of dry sulphur dioxide. The yellow $[MnI_2(PPh_3)(SO_2)_{0.66}]$ and $[MnI_2(PPhMe_2)(SO_2)_{0.66}]$ were readily isolated as solids; the remaining adducts formed as yellow oils which solidified slowly over a period of months. In all cases elemental analyses, Table 1, indicated the stoicheiometry of the adducts to be $[MnX_2(PR_3)(SO_2)_{0.66}]$. This contrasts with the 1:1 $[MnX_2(PR_3)L]$ (L = O_2,[2] CO,[3] or NO[4]) adducts found for other small molecules. {There is a precedent for this rare M:SO_2 ratio of 3:2, *viz.* $[Pd_3(Bu^tNC)_5(SO_2)_2]$.[8]} Moreover, although all the iodo-complexes studied do form adducts with sulphur dioxide, none of the chloro-complexes appears to react. The bromo-complexes represent a borderline of SO_2 activity; for the trialkylphosphine complexes sulphur dioxide adducts form readily but for the phenyl-substituted tertiary phosphine complexes only the complex $[MnBr_2(PPhMe_2)]$ is active. Of particular interest is the fact that $[MnI_2(PPh_3)]$, which shows no tendency to co-ordinate dioxygen under ambient conditions or even at P_{O_2} = 20 atm,[9] or carbon monoxide,[10] does form an adduct with sulphur dioxide.

In addition to the isolation of the complexes $[MnX_2(PR_3)(SO_2)_{0.66}]$ by the above method we have also studied sulphur dioxide absorption of two complexes, $[MnBr_2(PPhMe_2)]$ and $[MnBr_2(PPr^n{}_3)]$, by monitoring the weight increase on an analytical balance when these complexes were exposed to one atmosphere of sulphur dioxide. As can be seen from the results, Table 2, the final weight change (after there is no further gain in weight) corresponds to the formation of the species $[MnBr_2(PR_3)(SO_2)_{0.66}]$.

The sulphur dioxide adducts all exhibit an i.r. absorption, ν(SO), in the range 1 140—1 112 cm^{-1}, Table 1, which is absent in the spectra of the $[MnX_2(PR_3)]$ complexes. This observation is consistent with manganese–sulphur dioxide co-ordination but is not, on its own, sufficient to suggest a mode of binding. We have not been able to obtain sufficient solubility of the complexes in solvents for which we could obtain molecular-weight measurements; but solutions in thf exhibited non-electrolyte behaviour. The complexes are recovered unchanged from thf.

---

† Part 2 is ref. 3.

‡ *Supplementary data available* (No. SUP 56350, 11 pp.): derivation of equations (2) and (3) by Dr. J. Lee (U.M.I.S.T.). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix.

Non-S.I. units employed: Torr = (101 325/760) Pa, atm = 101 325 Pa, G = 10^{-4} T.

Table 1. Infrared and analytical data for the SO_2 adducts

Complex	$\nu(SO)/cm^{-1}$	Analysis[a] (%) C	H	Halogen	S
$[MnBr_2(PPhMe_2)(SO_2)_{0.66}]$	1 112m	24.0 (24.2)	3.1 (2.8)	39.8 (40.4)	5.6 (5.3)
$[MnBr_2(PPr^n{}_3)(SO_2)_{0.66}]$	1 120m	25.6 (25.8)	5.3 (5.0)	38.5 (38.3)	5.5 (5.0)
$[MnBr_2(PBu^n{}_3)(SO_2)_{0.66}]$	1 120m	31.3 (31.3)	5.9 (5.9)	34.4 (34.8)	4.8 (4.5)
$[MnI_2(PPhMe_2)(SO_2)_{0.66}]$	1 140m	20.7 (20.6)	2.7 (2.4)	55.0 (54.6)	4.8 (4.5)
$[MnI_2(PPhEt_2)(SO_2)_{0.66}]$	1 135s	23.0 (23.2)	2.9 (2.9)	49.2 (49.0)	4.3 (4.0)
$[MnI_2(PPhBu^n{}_2)(SO_2)_{0.66}]$	1 130s	29.6 (29.3)	4.2 (4.0)	44.0 (44.3)	4.0 (3.6)
$[MnI_2(PPhBu^i{}_2)(SO_2)_{0.66}]$	1 135s	29.4 (29.3)	4.3 (4.0)	44.7 (44.3)	3.9 (3.6)
$[MnI_2(PBu^n{}_3)(SO_2)_{0.66}]$	1 130m	26.0 (26.0)	4.8 (4.9)	46.1 (45.8)	3.9 (3.7)
$[MnI_2(PPh_3)(SO_2)_{0.66}]$	1 119m	35.3 (35.1)	2.7 (2.4)	40.7 (41.4)	3.6 (3.4)
$[MnI_2(PPr^n{}_3)(SO_2)_{0.66}]$	1 130s	21.4 (21.1)	4.4 (4.1)	49.6 (49.6)	4.3 (4.0)

[a] Calculated values in parentheses.

Table 2. Solid-state SO_2 uptake data for $[MnBr_2(PPhMe_2)]$ and $[MnBr_2(PPr^n{}_3)]$

Complex	Mass (g)	Amount (10^{-4} mol)	Mass SO_2 absorbed (g)	Amount SO_2 absorbed (10^{-4} mol)	Mole ratio (SO_2/Mn)
$[MnBr_2(PPhMe_2)]$	0.3475	9.85	0.0423	6.61	0.67
$[MnBr_2(PPr^n{}_3)]$	0.2850	7.60	0.0318	4.97	0.65

Table 3. Blank absorption of SO_2–Ar mixtures by 100 cm^3 thf at 0 °C

P_{SO_2}/Torr	Total volume absorbed (cm^3)
0	12.2
50	15.4
100	20.2
120	24.6
150	46.8
170	49.4

Solution Studies in Tetrahydrofuran.—The solubility of sulphur dioxide in organic solvents is known to be extremely high. Thus, because of the large blank solvent absorption of SO_2 few, if any, studies on the uptake of SO_2 by solutions of transition-metal complexes have been reported.

We have studied the uptake of other small molecules by solutions of $[MnX_2(PR_3)]$ by using a thermostatted gas burette system,[2–4] and thus we have developed a technique to use such a system to investigate SO_2 absorption by thf solutions of the $[MnX_2(PR_3)]$ complexes (see Experimental section).

First, a series of blank uptakes was performed using (SO_2 + Ar) gas mixtures containing different partial pressures of SO_2. The results, Table 3, are shown graphically in Figure 1.

An initial partial pressure of 80 Torr SO_2 was chosen for the solution uptakes. Because of the constantly changing composition of the gas mixture it was not possible to follow the uptakes as a function of time, and thus only the total uptake was measured.

The SO_2 absorption data for a series of $[MnX_2(PR_3)]$ complexes in thf (100 cm^3) solution at 0 °C are contained in Table 4. An example of the method used to calculate the volume of SO_2 absorbed by the complexes is given below for a $[MnBr_2(PBu^n{}_3)]$ solution.*

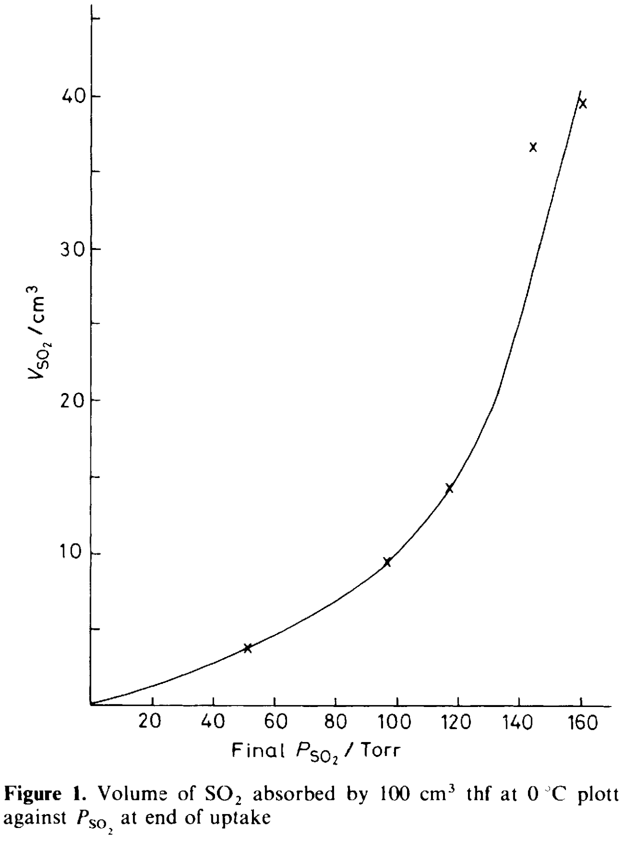

Figure 1. Volume of SO_2 absorbed by 100 cm^3 thf at 0 °C plotted against P_{SO_2} at end of uptake

For the uptake $x_{Ar} = 0.89$ and the total gas uptake for the solution is 33.0 cm^3. The final partial pressure of SO_2 in the mixture is given by equation (2). For $[MnBr_2(PBu^n{}_3)]$: $P =$

$$P_{SO_2} = P\{1 - [(x_{Ar}V')/(V + V^{\circ\prime} - V^{\circ})]\} \qquad (2)$$

760 Torr, $V' = 2\,300\ cm^3$, $V^{\circ\prime} = 2\,300\ cm^3$, and $V^{\circ} = 2\,287.8\ cm^3$; therefore giving $P_{SO_2} = 77.4$ Torr. From Figure 1 this corresponds to a blank absorption by the thf of 6.8 cm^3 SO_2.

---

* In equations (2) and (3) x_i is the mole fraction of component i, V' is the initial volume of the gas mixture, V is the final volume of the gas mixture (= V' − measured volume of gas absorbed by solution), P is the atmospheric pressure and V° and $V^{\circ\prime}$ correspond to V and V' respectively when $x_{SO_2} = 0$. These equations were derived assuming that SO_2 is an ideal gas and that Ar obeys Henry's law. The derivation of the equations is available on request (SUP 56350).

Table 4. Sulphur dioxide absorption data for 100-cm^3 aliquots of [$MnX_2(PR_3)$] in thf

Complex	Concentration (10^{-3} mol dm^{-3})	Total gas volume absorbed by solution (cm^3)	Volume of SO_2 absorbed by complex (cm^3)	Mol ratio
[$MnCl_2(PPhMe_2)$]	4.54	19.8	0	0
[$MnCl_2(PPhEt_2)$]	4.48	19.6	0	0
[$MnCl_2(PPhPr^n{}_2)$]	4.69	19.0	0	0
[$MnCl_2(PPhBu^n{}_2)$]	4.41	18.6	0	0
[$MnCl_2(PPhBu^i{}_2)$]	4.46	18.8	0	0
[$MnCl_2(PPr^n{}_3)$]	4.41	18.9	0	0
[$MnCl_2(PBu^n{}_3)$]	4.47	19.8	0	0
[$MnBr_2(PPhMe_2)$]	8.50	31.0	13.2	0.69
[$MnBr_2(PPhEt_2)$]	8.97	19.0	0	0
[$MnBr_2(PPhPr^n{}_2)$]	8.98	20.0	0	0
[$MnBr_2(PPhBu^n{}_2)$]	8.93	19.2	0	0
[$MnBr_2(PPhBu^i{}_2)$]	5.26	19.4	0	0
[$MnBr_2(PPr^n{}_3)$]	8.73	31.9	14.2	0.73
[$MnBr_2(PBu^n{}_3)$]	8.96	33.0	15.2	0.76
[$MnI_2(PPhMe_2)$]	12.10	38.2	20.4	0.75
[$MnI_2(PPhEt_2)$]	15.70	41.4	23.9	0.68
[$MnI_2(PPhPr^n{}_2)$]	15.70	41.8	24.3	0.69
[$MnI_2(PPhBu^n{}_2)$]	15.80	43.8	26.4	0.75
[$MnI_2(PPhBu^i{}_2)$]	9.53	32.0	14.3	0.67
[$MnI_2(PPr^n{}_3)$]	15.40	40.0	22.5	0.65
[$MnI_2(PBu^n{}_3)$]	15.60	43.0	25.6	0.73
[$MnI_2(PPh_3)$]	15.60	43.0	25.6	0.73

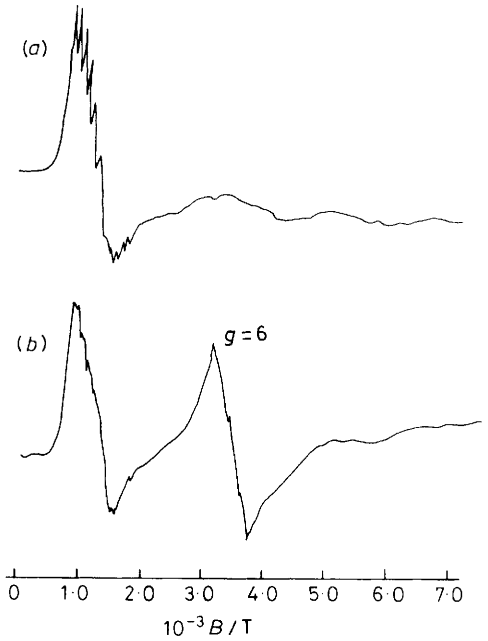

Figure 2. X-Band e.s.r. spectra of (*a*) [$MnBr_2(PR_3)$] and (*b*) [$MnBr_2(PR_3)$] + SO_2 in frozen thf at 93 K. Spectrum is illustrated for PR_3 = $PPr^n{}_3$

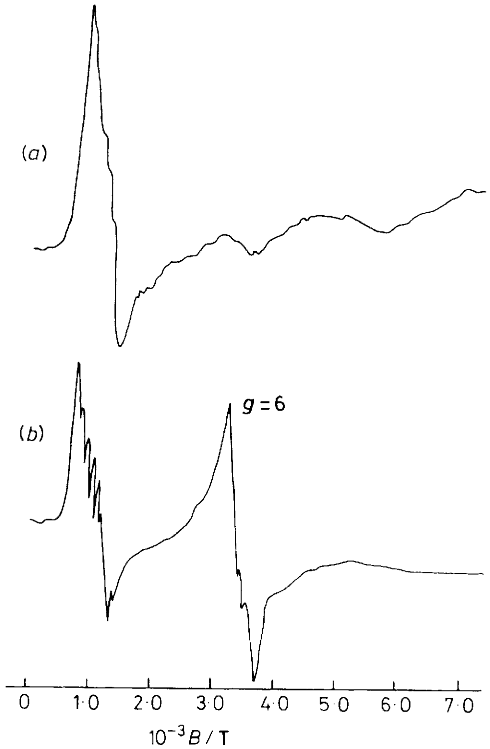

Figure 3. X-Band e.s.r. spectra of (*a*) [$MnI_2(PR_3)$] and (*b*) [$MnI_2(PR_3)$] + SO_2 in frozen thf at 93 K. Spectrum illustrated for PR_3 = $PBu^n{}_3$

The total volume of SO_2 absorbed by the solution may be calculated from equation (3). Thus for [$MnBr_2(PBu^n{}_3)$],

$$V_{SO_2} = x_{SO_2}V' - V + [(x_{Ar}VV')/(V + V^{\circ\prime} - V^{\circ})] \qquad (3)$$

V_{SO_2} = 22.0 cm^3. Hence the volume of SO_2 absorbed by the complex is 15.2 cm^3, giving a Mn:SO_2 ratio of 4:3.

From the data contained in Table 4 two points emerge. (*i*) The SO_2:Mn ratio is in the region 0.65—0.76 which corresponds well with the ratio found for uptake in the solid state. Both sets of data confirm that the reaction of SO_2 with the complexes in either phase results in adducts of unusual stoicheiometry and not in the 1:1 stoicheiometry expected by analogy with previous work.[2-4] (*ii*) Here, once again, for reaction a clear dependence on the nature of the halide in [$MnX_2(PR_3)$] is observed; for X = I, all complexes react, for X = Cl no reaction is observed, and for X = Br a borderline of activity exists (only trialkyl- or phenyldimethyl-phosphine complexes react).

E.s.r. measurements have been made on frozen thf solutions of the $[MnX_2(PR_3)]$ complexes before and after exposure to sulphur dioxide. The spectra of the $[MnCl_2(PR_3)]$ complexes show no change after prolonged exposure to SO_2. However the e.s.r. spectra of all the $[MnI_2(PR_3)]$ complexes and some of the $[MnBr_2(PR_3)]$ (R_3 = trialkyl or $PhMe_2$) complexes show an increase in the $g = 2$ peak together with concomitant changes in the fine structure, Figures 2 and 3. The peak at $g = 6$ is suggestive of a structure with axial symmetry.[11]

None of the $[MnX_2(PR_3)]$ complexes studied was found to co-ordinate SO_2 reversibly. Neither heating for *ca.* 3 h at 50 °C, nor exposing solutions to a static vacuum for *ca.* 3 h was effective for the removal of the SO_2. Solutions treated this way showed identical e.s.r. spectra to those run immediately after a SO_2 uptake had been performed. In addition, solutions to which desorption procedures had been applied showed a subsequent SO_2 absorption equivalent to the thf blank value.

Experimental

Unless otherwise stated, all manipulations involving air-sensitive materials were performed under a dry argon atmosphere. Solvents were dried by the published procedures and $[MnX_2(PR_3)]$ complexes synthesised by published methods.[2,7] The approach taken by Green and co-workers[12] to the synthesis of these complexes should be avoided.[13]

Measurement of SO_2 *Uptake by thf Solutions.*—The apparatus employed has been described elsewhere.[2] The entire apparatus was evacuated and then filled with the appropriate gas mixture of SO_2 and Ar (usually initial P_{SO_2} = 80 Torr). The gaseous mixture was allowed to equilibrate for *ca.* 3 h before cooling to the appropriate temperature. The solution was then degassed and connected to the gas mixture, the zero reading on the burette taken and the uptake begun. Once the uptake was complete, the final reading on the burette was taken and the volume absorbed calculated.

Solid-state Uptake of Sulphur Dioxide by $[MnBr_2(PR_3)]$ ($PR_3 = PPr^n{}_3$ or $PPhMe_2$).—Approximately 0.3 g of the relevant $[MnBr_2(PR_3)]$ complex ($PR_3 = PPhMe_2$ or $PPr^n{}_3$) was placed in a dry 10-mm (o.d.) tube fitted with a greaseless polytetrafluoroethylene seal and a 3-mm high-vacuum tap. The complex was then placed under 1 atm of dry SO_2 by evacuating the tube and slowly filling it with dry SO_2. The sample was weighed on an analytical balance accurate to 4 decimal places. Before each successive weighing, the sample was made up to 1 atm of SO_2 to compensate for the SO_2 absorbed by the complex. The sample was weighed at intervals until the mass of the sample had stopped changing.

Synthesis of $[MnX_2(PR_3)(SO_2)_{0.66}]$ (X = Br *or* I).—The procedure used in the synthesis of the complexes $[MnX_2(PR_3)(SO_2)_{0.66}]$ (X = Br or I; $PR_3 = PPr^n{}_3$ or $PPhMe_2$; X = I; $PR_3 = PPhEt_2$, $PPhBu^n{}_2$, $PPhBu^i{}_2$, or PPh_3) was essentially the same in each case. However, only $[MnI_2(PPh_3)(SO_2)_{0.66}]$ and $[MnI_2(PPhMe_2)(SO_2)_{0.66}]$ were obtained readily as solids, the remaining complexes being isolated initially as yellow oils, but which subsequently solidified on standing. The procedure for $[MnI_2(PPh_3)(SO_2)_{0.66}]$ is outlined here.

To dry toluene (60 cm^3) in a dry flask (250 cm^3) with a side-arm was added $[MnI_2(PPh_3)]$ (0.55 g, 1.0 mmol). The flask was evacuated and then filled with dry sulphur dioxide (P_{SO_2} = 760 Torr) and the mixture stirred for 48 h. The resulting solid was filtered off using a Schlenk apparatus and dried *in vacuo.*

Acknowledgements

We are grateful to U.M.I.S.T. (Part-time Teaching Assistantship to D. S. B.), the S.E.R.C. (Studentship to G. A. G.), the Central Electricity Generating Board Laboratories, Leatherhead (CASE Award to C. G. B.), and to the Board of Regents of the University of West Florida (sabbatical leave for S. P. T.). A special acknowledgement is made to Dr. Joe Lee (U.M.I.S.T.) who gave such helpful advice on data handling after an initial suggestion by a referee.

References

1 B. Beagley, J. C. Briggs, A. Hosseiny, W. E. Hill, T. J. King, C. A. McAuliffe, and K. Minten, *J. Chem. Soc., Chem. Commun.*, 1984, 305.

2 C. A. McAuliffe, H. F. Al-Khateeb, D. S. Barratt, J. C. Briggs, A. Challita, A. Hosseiny, M. G. Little, A. G. Mackie, and K. Minten, *J. Chem. Soc., Dalton Trans.*, 1983, 2147.

3 C. A. McAuliffe, D. S. Barratt, C. G. Benson, A. Hosseiny, M. G. Little, and K. Minten, *J. Organomet. Chem.*, 1983, **258**, 35.

4 D. S. Barratt and C. A. McAuliffe, *J. Chem. Soc., Chem. Commun.*, 1984, 594.

5 R. R. Ryan, G. J. Kubas, D. C. Moody, and P. G. Eller, *Struct. Bonding (Berlin)*, 1981, **46**, 47.

6 G. A. Gott, J. Fawcett, C. A. McAuliffe, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1984, 1283.

7 A. Hosseiny, C. A. McAuliffe, A. G. Mackie, and K. L. Minten, *Inorg. Chim. Acta*, 1981, **49**, 99.

8 S. Otsuka, Y. Tatsuno, M. Miki, T. Aoki, M. Matsumato, H. Yashioka, and K. Nakatsu, *J. Chem. Soc., Chem. Commun.*, 1973, 445.

9 A. G. Mackie and C. A. McAuliffe, unpublished work.

10 A. Hosseiny, Ph.D. Thesis, University of Manchester, 1980.

11 J. F. Gibson, 'ESR and NMR of Paramagnetic Species in Biological and Related Systems,' NATO Advanced Study Institute Series, eds. I. Bertini and R. S. Drago, D. Reidel Publ. Co., Dordrecht, 1979, p. 225 and refs. therein.

12 R. M. Brown, R. E. Bull, M. L. H. Green, P. D. Grebenik, J. J. Martin-Polo, and D. M. P. Mingos, *J. Organomet. Chem.*, 1980, **201**, 437.

13 C. A. McAuliffe, *J. Organomet. Chem.*, 1982, **228**, 225.

Received 12*th March* 1985; *Paper* 5/799