

The Coordination of Small Molecules by Manganese(II) Phosphine Complexes. Part 12.* The Synthesis of some Tetrahydrofuran/Long Chain Tertiary Phosphine Complexes of Manganese(II) Halides, $MnX_2(\text{phosphine})(\text{THF})$, and their Reaction with Molecular Oxygen

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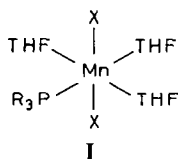
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Abstract

Manganese(II) complexes of long chain phosphines, $MnX_2(\text{phosphine})(\text{THF})$ $X = \text{Cl, Br, I}$; phosphine = $P(\text{C}_{12}\text{H}_{25})_3$, $P(\text{C}_{14}\text{H}_{29})_3$, $P(\text{C}_{16}\text{H}_{33})_3$, $\text{PPh}(\text{C}_{12}\text{H}_{25})_2$, $\text{PPh}(\text{C}_{14}\text{H}_{29})_2$, $\text{PPh}(\text{C}_{16}\text{H}_{33})_2$; THF = tetrahydrofuran have been prepared and characterised. These complexes react reversibly with molecular oxygen both in the solid state and in THF and toluene solution forming 1:1 $Mn:O_2$ adducts. These adducts are monomeric in toluene and THF and molecular weight measurements confirm that the THF ligand remains coordinated in toluene solution leading to the formation of $MnX_2(\text{phosphine})(\text{THF})(O_2)$ species. All the O_2 -adducts are highly coloured and binding curves have been constructed and K_{O_2} values calculated. Based on these K_{O_2} values the affinity for dioxygen is in the order $X = \text{Cl} > \text{Br} > \text{I}$ in toluene solution, with Hill coefficient, n , indicating cooperativity (1–1.5). In THF dioxygen binding does not appear to be cooperative.

Introduction

In our investigations of manganese(II) phosphine complexes, $MnX_2(\text{PR}_3)$ ($X = \text{Cl, Br, I, NCS}$), which can reversibly coordinate small molecules such as dioxygen [1–3], carbon monoxide [4], nitric oxide [5] and ethylene [6], and irreversibly coordinate carbon disulphide [7], sulphur dioxide [8] and tetracyanoethylene [9], we have suggested that the $MnX_2(\text{PR}_3)$ complexes may have structure I in tetrahydro-



*For Part 11, see ref. 1.

furan (THF) solution [3, 5], mainly from ESR evidence. However, on one previous occasion we have isolated species in which THF was bound to the manganese in addition to the small molecule, *viz.* $\{[MnX_2(\text{PR}_3)(\text{THF})_2]_2\text{CS}_2\}$ ($X = \text{Cl, Br, I}$; $R_3 = \text{Pr}_3^n, \text{Bu}_3^n, \text{PhMe}_2, \text{PhEt}_2, \text{PhPr}_2^n$) [7]. The THF ligands could be removed on heating to give $\{[MnX_2(\text{PR}_3)]_2\text{CS}_2\}$. These $\{[MnX_2(\text{PR}_3)(\text{THF})_2]\text{CS}_2\}$ complexes were generated *in situ* by mixing MnX_2 , PR_3 and CS_2 in tetrahydrofuran, and we have not previously been able to isolate simple $MnX_2(\text{PR}_3)(\text{THF})_x$ species.

Herewith we wish to report the isolation of a series of $MnX_2(\text{PR}_3)(\text{THF})$ complexes and their subsequent reaction with dioxygen. The phosphines involved in this study: $P(\text{C}_{12}\text{H}_{25})_3$ [$P(\text{C}_{12})_3$], $P(\text{C}_{14}\text{H}_{29})_3$ [$P(\text{C}_{14})_3$], $P(\text{C}_{16}\text{H}_{33})_3$ [$P(\text{C}_{16})_3$], $\text{PhP}(\text{C}_{12}\text{H}_{25})_2$ [$\text{PhP}(\text{C}_{12})_2$], $\text{PhP}(\text{C}_{14}\text{H}_{29})_2$ [$\text{PhP}(\text{C}_{14})_2$], $\text{PhP}(\text{C}_{16}\text{H}_{33})_2$ [$\text{PhP}(\text{C}_{16})_2$], contain long aliphatic chains. In using these long chain ligands the aim was to impart greater solubility to the manganese complexes in solution in organic solvents, especially non-coordinating solvents such as toluene. In addition to the $[MnX_2(\text{PR}_3)(\text{THF})]$ complexes reported here we also isolated some species which did not contain coordinated solvent, *viz.* the 'normal' $MnX_2(\text{PR}_3)$. The properties of the latter and their reaction with dioxygen are reported elsewhere [1].

Results and Discussion

Anhydrous manganese(II) salts, MnX_2 ($X = \text{Cl, Br, I}$) react with the long chain monodentate phosphines in tetrahydrofuran solution and from this were isolated products the stoichiometry of which correspond to $MnX_2(\text{PR}_3)(\text{THF})$, Table I. The reaction stoichiometry did not affect the stoichiometry of the resulting complex, inasmuch as we found that using an excess of the phosphine still resulted in complexes with a 1:1 Mn :phosphine ratio; any excess phosphine was either left in THF solution or could be removed

TABLE I. Physical and Analytical Data for $MnX_2(\text{phosphine})(\text{THF})$ Complexes^a

Complex	μ_{eff}	Melting point (°C)	Analysis: Found(calc.) (%)				
			C	H	P	X	Mn
$MnCl_2\{P(C_{12})_3\}(\text{THF})$	5.70	32	66.0(65.2)	11.5(11.3)	4.4(4.2)	9.0(9.6)	7.4(7.5)
$MnCl_2\{P(C_{14})_2\}(\text{THF})$	5.68	34	67.3(67.3)	11.7(11.6)	3.9(3.8)	8.6(8.7)	6.6(6.7)
$MnCl_2\{P(C_{16})_3\}(\text{THF})$	5.71	38	74.9(75.0)	13.1(12.9)	3.5(3.7)	8.6(8.5)	
$MnCl_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	5.65	48	63.2(63.4)	9.5(9.8)	4.5(4.8)	11.2(11.0)	8.9(8.5)
$MnCl_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	5.70	141	65.0(65.1)	11.0(11.3)		10.2(10.1)	
$MnCl_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	5.70	125	66.9(66.7)	10.1(10.4)		9.5(9.4)	
$MnBr_2\{P(C_{12})_3\}(\text{THF})$	5.59	47	58.0(58.2)	9.8(10.0)	4.0(3.8)	20.0(19.4)	6.5(6.7)
$MnBr_2\{P(C_{14})_3\}(\text{THF})$	5.60	33	60.6(60.7)	10.7(10.5)	3.5(3.4)	17.3(17.6)	6.0(6.1)
$MnBr_2\{P(C_{16})_3\}(\text{THF})$	5.65	44	68.0(67.8)	11.7(11.6)	3.4(3.4)	17.2(17.4)	
$MnBr_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	5.60	92	56.0(55.7)	8.8(8.6)	4.5(4.2)	22.0(21.8)	7.0(7.5)
$MnBr_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	5.65	116	58.0(57.8)	9.0(9.0)		20.0(20.3)	
$MnBr_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	5.60	102	60.0(59.7)	9.8(9.4)	4.0(3.7)	19.0(18.9)	6.0(6.5)
$MnI_2\{P(C_{12})_3\}(\text{THF})$	5.45	54	53.0(52.2)	10.0(9.0)	3.5(3.4)	27.0(27.6)	6.2(6.0)
$MnI_2\{P(C_{14})_3\}(\text{THF})$	5.40	45	54.7(55.0)	9.6(9.5)	3.0(3.1)	25.6(25.3)	5.5(5.4)
$MnI_2\{P(C_{16})_3\}(\text{THF})$	5.45	28	61.2(61.5)	10.6(10.5)	3.1(4.0)	25.2(25.0)	
$MnI_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	5.40	44	49.5(49.3)	8.0(7.6)	4.2(3.7)	31.0(30.7)	6.3(6.6)
$MnI_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	5.40	32	52.0(51.6)	8.1(8.0)		28.2(28.8)	
$MnI_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	5.40	58	54.0(53.7)	8.5(8.4)	3.0(3.3)	26.5(27.0)	6.0(5.9)

^aColours of the compounds are pale pink (X = Cl), pink (X = Br), pale orange (X = I).

TABLE II. ESR Data for $MnX_2(\text{phosphine})(\text{THF})$ Complexes

Complex	Line positions (G)
$MnCl_2\{P(C_{12})_3\}(\text{THF})$	900(w), 1500(w), 3300(s), 5400(w)
$MnCl_2\{P(C_{14})_2\}(\text{THF})$	900(w), 1500(w), 3350(s), 5500(w)
$MnCl_2\{P(C_{16})_3\}(\text{THF})$	850(m), 1500(w), 3350(s), 5400(w)
$MnCl_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	850(m), 1450(w), 3300(s), 5500(w)
$MnCl_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	900(m), 1550(w), 3300(s), 5450(w)
$MnCl_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	900(m), 1500(w), 3300(s), 5500(w)
$MnBr_2\{P(C_{12})_3\}(\text{THF})$	1100(m), 1400(w), 3250(s), 5350(w)
$MnBr_2\{P(C_{14})_3\}(\text{THF})$	1150(m), 1500(w), 3300(s), 5350(w)
$MnBr_2\{P(C_{16})_3\}(\text{THF})$	1100(m), 1450(w), 3300(s), 5400(w)
$MnBr_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	1050(w), 1500(w), 3350(s), 5400(w)
$MnBr_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	1100(w), 1450(w), 3350(s), 5450(w)
$MnBr_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	1050(w), 1500(w), 3300(s), 5350(w)
$MnI_2\{P(C_{12})_3\}(\text{THF})$	1000(m), 1400(w), 3300(s), 5400(w)
$MnI_2\{P(C_{14})_3\}(\text{THF})$	950(w), 1350(w), 3350(s), 5350(w)
$MnI_2\{P(C_{16})_3\}(\text{THF})$	1000(w), 1350(w), 3350(s), 5400(w)
$MnI_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	950(m), 1400(w), 3300(s), 5400(w)
$MnI_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	950(m), 1400(w), 3300(s), 5400(w)
$MnI_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	950(m), 1400(w), 3300(s), 5400(w)

by washing the solid product with n-pentane. As predicted by the use of long chain phosphine ligands the $MnX_2(PR_3)(\text{THF})$ species formed quite concentrated

solutions in THF and it was found that addition of diethylether was necessary in order to recover the products in reasonable yield. Alternatively, the THF

TABLE III. Infrared Data for $MnX_2(\text{phosphine})(\text{THF})$ Complexes (cm^{-1})

Complex	$\nu(\text{THF})^a$	$\nu(\text{Mn}-\text{O})$	$\nu(\text{Mn}-\text{P})$	$\nu(\text{Mn}-\text{X})$
$MnCl_2\{P(C_{12})_3\}(\text{THF})$	1040(s, sh) 880(m, sh)	425(m, sh)	380(m, sh)	295(s, sh)
$MnCl_2\{P(C_{14})_2\}(\text{THF})$	1040(s, sh) 880(m, sh)	420(m, sh)	385(m, sh)	300(s, sh)
$MnCl_2\{P(C_{16})_3\}(\text{THF})$	1040(s, sh) 880(m, sh)	425(m, sh)	380(m, sh)	300(s, sh)
$MnCl_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	1040(s, sh) 880(m, sh)	420(m, sh)	385(m, sh)	295(s, sh)
$MnCl_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	1040(s, sh) 880(m, sh)	425(m, sh)	390(m, sh)	300(s, br)
$MnCl_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	1040(s, sh) 880(m, sh)	425(m, sh)	390(m, sh)	295(s, sh)
$MnBr_2\{P(C_{12})_3\}(\text{THF})$	1042(s, sh) 878(m, sh)	430(m, sh)	390(m, sh)	240(s, br)
$MnBr_2\{P(C_{14})_3\}(\text{THF})$	1042(s, sh) 878(m, sh)	430(m, sh)	390(m, sh)	245(s, sh)
$MnBr_2\{P(C_{16})_3\}(\text{THF})$	1042(s, sh) 880(m, sh)	435(m, sh)	395(m, sh)	240(s, sh)
$MnBr_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	1040(s, sh) 878(m, sh)	435(m, sh)	400(m, sh)	235(s, sh)
$MnBr_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	1040(s, sh) 878(m, sh)	435(m, sh)	400(m, sh)	235(s, sh)
$MnBr_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	1040(s, sh) 878(m, sh)	435(m, sh)	400(m, sh)	235(s, sh)
$MnI_2\{P(C_{12})_3\}(\text{THF})$	1040(s, sh) 880(m, sh)	445(m, sh)	400(w, sh)	220(m, sh)
$MnI_2\{P(C_{14})_3\}(\text{THF})$	1040(s, sh) 880(m, sh)	445(m, sh)	400(w, sh)	210(m, br)
$MnI_2\{P(C_{16})_3\}(\text{THF})$	1040(s, sh) 880(m, sh)	440(m, sh)	400(w, br)	210(m, br)
$MnI_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	1040(s, sh) 880(m, sh)	445(m, sh)	405(m, sh)	210(m, sh)
$MnI_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	1040(s, sh) 880(m, sh)	445(m, sh)	405(m, sh)	210(s, sh)
$MnI_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	1040(s, sh) 880(m, sh)	450(m, sh)	410(m, sh)	205(s, sh)

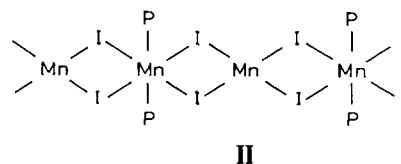
^aUncoordinated THF absorbs at 1060 and 900 cm^{-1} .

solvent could be removed from the solution by application of a vacuum and the mixture pumped almost to dryness. Addition of ether or n-pentane followed by filtration of the resultant slurry gave the $MnX_2(PR_3)(\text{THF})$ complexes in good yield.

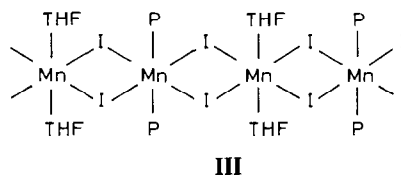
The solid state ESR spectra of the $MnX_2(PR_3)(\text{THF})$ complexes are listed in Table II. The spectra show a strong, broad absorption at $g_{\text{eff}} = 2$, together with other, much weaker bands; no hyperfine coupling was observed in any of the spectra. The spectra appear to indicate a mixture of species: the strong $g_{\text{eff}} = 2$ band being due to a highly symmetric, or more probably polymeric species, with the weak bands being due to the presence of a manganese species of low symmetry. Some infrared spectral data for the complexes as mulls are listed in Table III. These clearly show the presence of coordinated THF (bands *ca.* 1040 and 880 cm^{-1}) [12] and terminal $\nu(\text{Mn}-\text{X})$ bands [13, 14] (the far infrared spectra were not recorded in the bridging $\nu(\text{Mn}-\text{X})$ region) [15]. In addition a band lying between 380–410 cm^{-1} is assignable to $\nu(\text{Mn}-\text{P})$ [14], and the energy of this band increases in the order $X = \text{Cl} < \text{Br} < \text{I}$ indicating that the Mn–P bond is strongest in the $MnI_2(\text{phosphine})$ complexes. The room temperature magnetic moments, Table I, lie in the range 5.40–5.71 μ_B , somewhat lower than the spin-only value for a d^5 metal ion in a high-spin environment, and lend further support to a halide bridged structure. In general the μ_{eff} values fall in the order $X = \text{Cl} > \text{Br} >$

I, reflecting the proximity of adjacent Mn atoms in the Mn–X–Mn bridged systems.

In view of the X-ray crystal structure of $MnI_2(\text{PPhMe}_2)$ [16], shown schematically in II, which



consists of an infinite array of MnI_2 , every alternate Mn also being coordinated by two PPhMe_2 groups, it is tempting to suggest that the THF ligands occupy the coordinatively unsaturated t_d sites to yield the infinite polymer, III, which has the stoichiometry

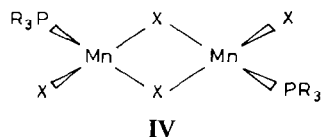


$MnX_2(PR_3)(\text{THF})$. This would certainly not be inconsistent with the ESR and the magnetic susceptibility, but the presence of terminal $\nu(\text{Mn}-\text{X})$ and the solubility of the complexes point towards a short chain polymeric structure.

TABLE IV. ESR Data for $MnX_2(\text{phosphine})(\text{THF})$ Complexes in Toluene Glasses at -160°C

Complex	Line position (G)
$MnCl_2\{P(C_{12})_3\}(\text{THF})$	900(m), 1500(w), 3300(s), 5000(w), 8500(w)
$MnCl_2\{P(C_{14})_2\}(\text{THF})$	900(m), 1500(w), 3300(s), 5000(w), 8000(w)
$MnCl_2\{P(C_{16})_3\}(\text{THF})$	900(m), 1500(w), 3300(s), 5000(w), 8000(w)
$MnCl_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	850(m), 1550(w), 3300(s), 5200(w), 8200(w)
$MnCl_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	850(m), 1550(w), 3300(s), 5200(w), 8200(w)
$MnCl_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	850(m), 1550(w), 3300(s), 5200(w), 8200(w)
$MnBr_2\{P(C_{12})_3\}(\text{THF})$	1100(m), 1400(w), 3300(s), 5400(w), 8500(w)
$MnBr_2\{P(C_{14})_3\}(\text{THF})$	1100(m), 1400(w), 3300(s), 5400(w), 8500(w)
$MnBr_2\{P(C_{16})_3\}(\text{THF})$	1100(m), 1400(w), 3300(s), 5400(w), 8500(w)
$MnBr_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	1000(m), 1500(w), 3350(s), 5300(w), 8000(w)
$MnBr_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	1000(m), 1500(w), 3300(s), 5200(w), 8200(w)
$MnBr_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	1000(m), 1500(w), 3350(s), 5250(w), 8200(w)
$MnI_2\{P(C_{12})_3\}(\text{THF})$	1000(m), 1400(w), 3300(s), 5500(w)
$MnI_2\{P(C_{14})_3\}(\text{THF})$	1000(m), 1450(w), 3300(s), 5500(w)
$MnI_2\{P(C_{16})_3\}(\text{THF})$	1000(m), 1450(w), 3300(s), 5500(w)
$MnI_2\{\text{PhP}(C_{12})_2\}(\text{THF})$	900(m), 1350(w), 3350(s), 5400(w)
$MnI_2\{\text{PhP}(C_{14})_2\}(\text{THF})$	950(m), 1350(w), 3350(s), 5400(w)
$MnI_2\{\text{PhP}(C_{16})_2\}(\text{THF})$	950(m), 1350(w), 3300(s), 5450(s)

For the non-solvento complexes of these long chain phosphines, $MnX_2(PR_3)$, we have already assigned a dimeric pseudotetrahedral structure, **IV**



[1]. There are precedents for this type of structure in manganese(II) phosphine complexes, as evidenced by the X-ray crystal structures of Wilkinson and co-workers for $MnR_2(P)_2$ ($R = \text{alkyl}$) complexes [17]. We thus tentatively assign the THF complexes, $MnX_2(PR_3)(\text{THF})$, the dimeric structure **V**. Penta-coordination is almost unknown for manganese(II), but we propose that it exists in these $MnX_2(PR_3)(\text{THF})$ species and in their dioxygen adducts (see below).

Solution Studies

All of the complexes react with dioxygen in the solid state, but also in toluene or THF solutions. The toluene solution ESR spectra of the complexes were recorded as frozen glasses at -160°C . Data is given in Table IV and a typical spectrum is shown in Fig. 1. In fact, the spectra in toluene glasses are almost identical to those in the solid state. When dissolved in THF the complexes exhibit a strong $g_{\text{eff}} = 6$ band with coupling to ^{55}Mn ($I = 5/2$) splitting the band into six lines. The spectra are very similar to those reported

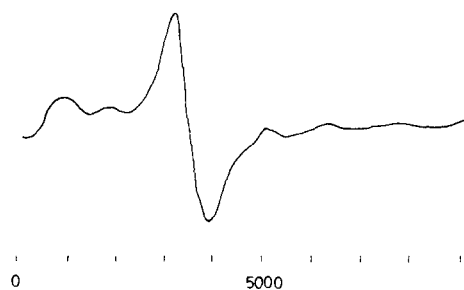


Fig. 1. Typical ESR spectrum of $MnX_2(\text{phosphine})(\text{THF})$ complexes recorded as toluene glasses at 77 K.

for the MnX_2 (short chain phosphine) complexes and thus may be assigned a similar structure in THF solution, **VI**.

As already stated the complexes reported here react rapidly with dioxygen in toluene and THF solutions; the amount of dioxygen absorbed was determined by the gas burette technique [2] under strictly thermostated conditions and also by concentration plots for a number of the complexes, see, for example, Fig. 2. From many of these graphs [18] and data such as in Table V it is evident that each complex reported here binds one mole of dioxygen per mole of Mn at 20°C in toluene solution, and we have similar data [17] for THF solution at -78°C . At 20°C it was found that 100 cm^3 toluene alone (the blank) absorbed 1.18×10^{-3} mol O_2 and that at -78°C 100 cm^3 THF alone absorbed 1.27×10^{-3} mol O_2 .

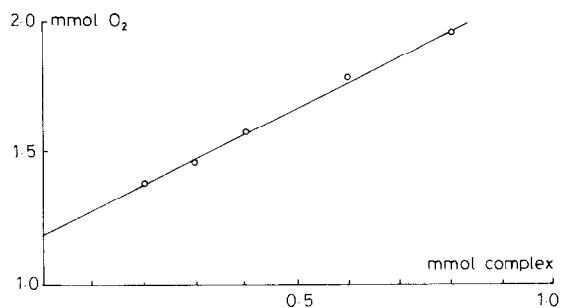


Fig. 2. Plot of mmol O_2 absorbed vs. mmol $MnBr_2\{PhP(C_{16})_2\}(THF)$ in toluene solution at $20^\circ C$.

TABLE V. Data from Plots of Dioxygen Uptake at $20^\circ C$ as a Function of Complex Concentration in Toluene Solution

Complex	Slope	Intercept ($\times 10^{-3}$)
$MnCl_2\{PhP(C_{16})_2\}(THF)$	0.89	1.21
$MnBr_2\{PhP(C_{16})_2\}(THF)$	0.99	1.20
$MnI_2\{PhP(C_{16})_2\}(THF)$	0.98	1.18

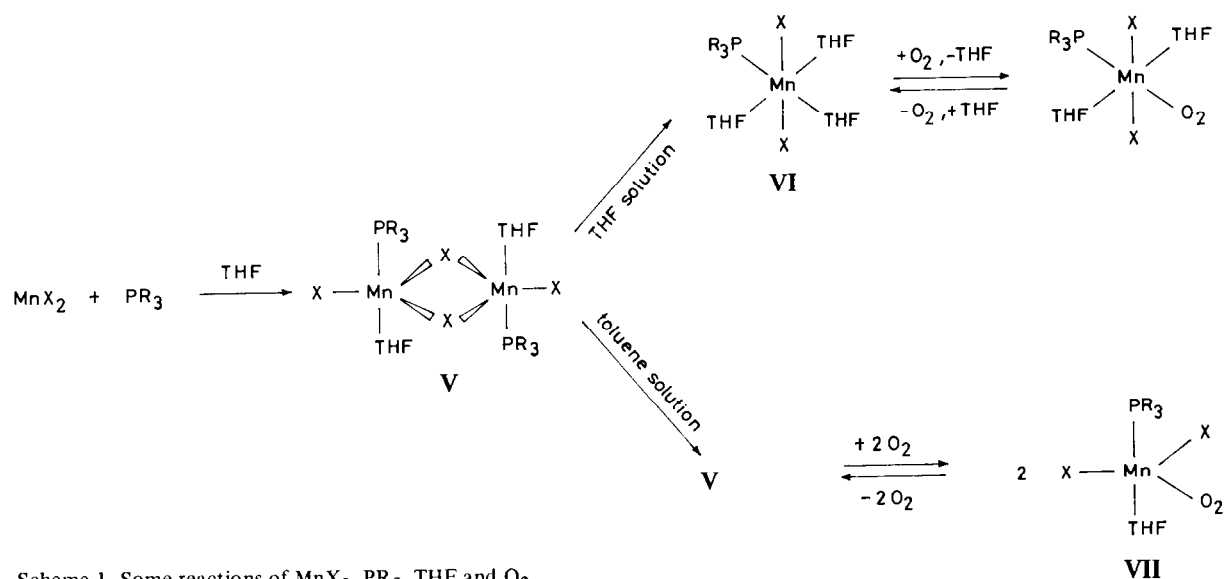
From concentration plots it is seen that the intercepts for each complex (*i.e.* the amount of O_2 absorbed at zero concentration) are in good agreement with the independently measured amounts.

The 1:1 Mn: O_2 stoichiometry is further substantiated by molecular weight measurements in toluene solution: for $MnBr_2\{P(C_{14})_3\}(THF)(O_2)$ (found 934; calc. for monomer 941) and for $MnBr_2\{PhP(C_{16})_2\}(THF)(O_2)$ (found 890; calc. for monomer 878). It is thus clear that, on dissolution in toluene

the Mn-THF bond is not broken and that, further, addition of O_2 is not by a substitution at the Mn-THF site, Scheme 1. Since the reaction with O_2 appears to be very similar for manganese complexes of long chain and short chain phosphines then in THF substitution the $Mn-THF + O_2 \rightarrow Mn-O_2 + THF$ substitution mechanism [3] obtains, as shown in Scheme 1, whereas in toluene solution all data presented here strongly indicate a purely addition mechanism whereby two O_2 molecules insert between the two Mn-X-Mn moieties after the bridge breaks, Scheme 1.

Solutions of all the complexes rapidly develop deep colours on exposure to air or dioxygen, the colour being much more dependent on the nature of X than of PR_3 , *viz.* X = Cl (purple), Br (blue), I (red-brown). Typical spectra of the complexes in toluene solution are shown in Fig. 3. The positions of the band maxima for each halide series showed only small variations with change in phosphine ligand, usually only by 5–10 nm.

By following the increase in intensity of the electronic spectra with increasing partial pressure of O_2 , P_{O_2} , it has been possible to construct dioxygen binding curves ('isotherms') for the complexes both in toluene and THF solution. Some typical isotherms are shown: for example, Fig. 4 illustrates one trend which has been previously observed for the MnX_2 (short chain phosphine) complexes in their isotherms [2], *i.e.* substitution of a phenyl group for an alkyl group in the coordinated phosphine causes a shift of the isotherm to the right (*i.e.* the complex has less affinity for dioxygen); Fig. 5 shows another previously observed trend [2], *i.e.* that for any phosphine the affinity for dioxygen varies as X = Cl > Br; Fig. 6 illustrates behaviour towards dioxygen of a group of iodo complexes in tetrahydrofuran. Once again it is



Scheme 1. Some reactions of MnX_2 , PR_3 , THF and O_2 .

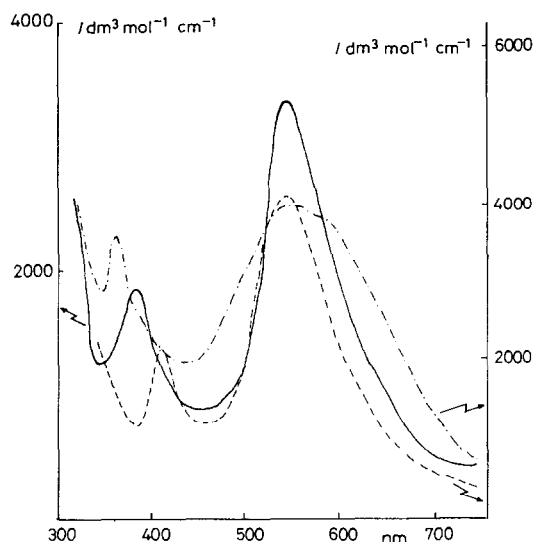


Fig. 3. Electronic spectra of dioxygen adducts of the manganese complexes, $\text{MnX}_2(\text{PR}_3)(\text{O}_2)$ ($\text{X} = \text{Cl}$, —; $\text{X} = \text{Br}$, - - -; $\text{X} = \text{I}$, - · -) in toluene solution.

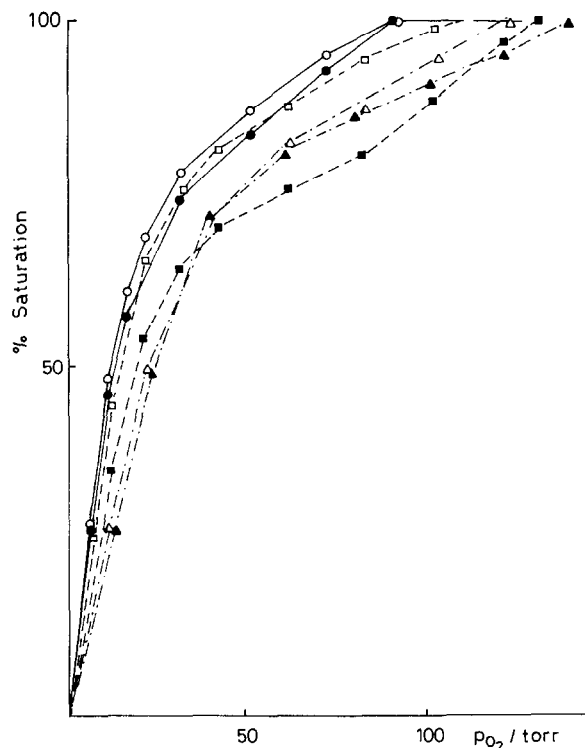


Fig. 4. Dioxygen binding curves for $\text{MnX}_2[\text{P}(\text{C}_{16})_3](\text{THF})$ (\circ , \square , \triangle) and $\text{MnX}_2[\text{PhP}(\text{C}_{16})_2](\text{THF})$ (\bullet , \blacksquare , \blacktriangle) in toluene solution at 20 °C ($\text{X} = \text{Cl}$, —; $\text{X} = \text{Br}$, - - -; $\text{X} = \text{I}$, - · -).

seen that there is a trend in affinity for dioxygen $\text{P}(\text{alkyl})_3 > \text{PhP}(\text{alkyl})_2$, but it is seen that for the two particular types of phosphine small changes in the length of the alkyl chain cause negligible effects on the isotherm.

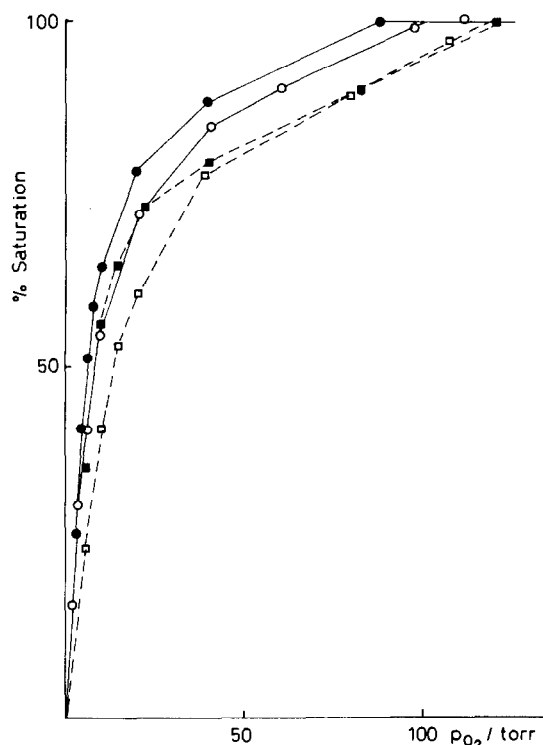


Fig. 5. Dioxygen binding curves for $\text{MnX}_2[\text{P}(\text{C}_{12})_3](\text{THF})$ (\bullet , \blacksquare) and $\text{MnX}_2[\text{PhP}(\text{C}_{12})_2](\text{THF})$ (\circ , \square) in tetrahydrofuran solution at 20 °C ($\text{X} = \text{Cl}$, —; $\text{X} = \text{Br}$, - - -).

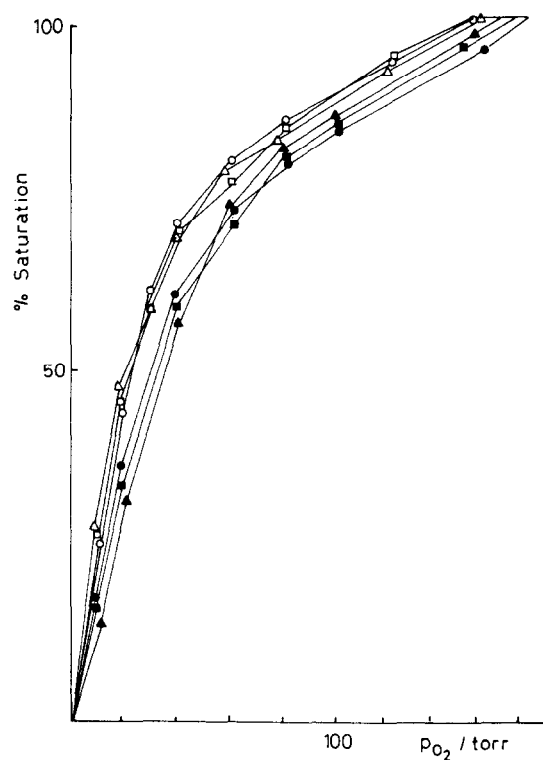


Fig. 6. Dioxygen binding curves for $\text{MnI}_2[\text{PR}_3](\text{THF})$ ($\text{R} = \text{C}_{12}$, \circ ; C_{14} , \square ; C_{16} , \triangle) complexes in tetrahydrofuran solution at -40 °C.

Isotherms in toluene solution were obtained at 20 °C, whereas in tetrahydrofuran solution isotherms for the chloro and bromo complexes were also obtained at 20 °C but the iodo complexes were run at -40 °C. It was found necessary to perform measurements at -40 °C because at higher temperatures the dioxygen adduct decomposed before equilibrium was reached (it was observed that there was a slow decay in the intensity of the electronic absorption bands after exposure to dioxygen at temperatures >0 °C, and phosphine oxides could be isolated eventually).

We can make some generalities about dioxygen affinities in both solvents, but since our initial aim in employing long chain phosphines in the $MnX_2(PR_3)$ system was to increase solubility in non-coordinating solvents, we will discuss in some detail the toluene isotherms.

$MnX_2(\text{phosphine})(THF)$ Complexes in Toluene Solution

$MnX_2[P(C_{12})_3](THF)$

The affinity of the complexes for O_2 is in the order $X = Cl > Br > I$, with 100% saturation occurring at 73, 82 and 114 torr, respectively.

$MnX_2[P(C_{14})_3](THF)$

At low P_{O_2} , the chloro and bromo complexes have similar affinities, the chloro complex reaching 100% saturation at the lowest P_{O_2} of 91 torr. The isotherms for $X = Br$ and I cross at 60 torr, 100% saturation being reached at 111(Br) and 102(I) torr.

$MnX_2[P(C_{16})_3](THF)$

The affinities are in the order $X = Cl > Br > I$, Fig. 4, with 100% saturation being reached at 86(Cl), 107(Br) and 113(I) torr.

$MnX_2[PhP(C_{12})_2](THF)$

The chloro complex has the highest affinity, reaching 100% saturation at 128 torr. A most unusual phenomenon is observed for the bromo and iodo complexes in that the isotherms cross at two points, 52 and 120 torr, Fig. 7, the bromo complex being 100% saturated at 182 torr.

$MnX_2[PhP(C_{14})_2](THF)$

The dioxygen affinities are in the order $X = Cl > Br > I$, with 100% saturation being reached at 111(Cl), 118(Br) and 131(I) torr.

$MnX_2[PhP(C_{16})_2](THF)$

The chloro complex reaches 100% saturation at 89 torr. Once again, the bromo and iodo complex isotherms cross at two points, Fig. 8, and between 48 and 106 torr the affinity is thus $X = I > Br$.

The equilibrium constants for the binding of dioxygen by the manganese complexes

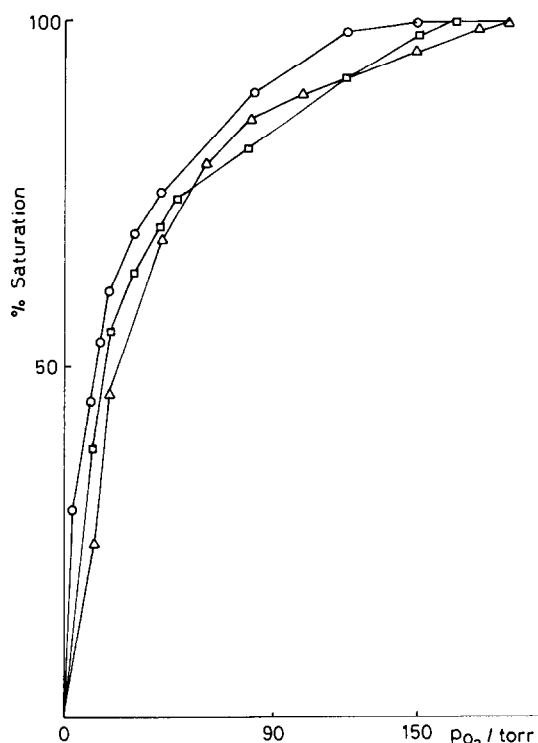


Fig. 7. Dioxygen binding curves for $MnX_2[PhP(C_{16})_2](THF)$ toluene solution at 20 °C ($X = Cl, \circ; Br, \square; I, \triangle$).

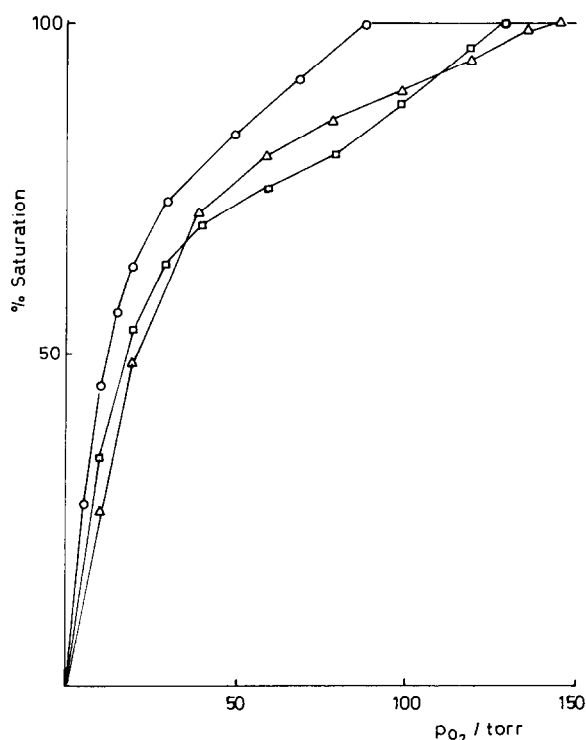


Fig. 8. Dioxygen binding curves for $MnX_2[PhP(C_{16})_2](THF)$ complexes in toluene solution at 20 °C ($X = Cl, \circ; Br, \square; I, \triangle$).

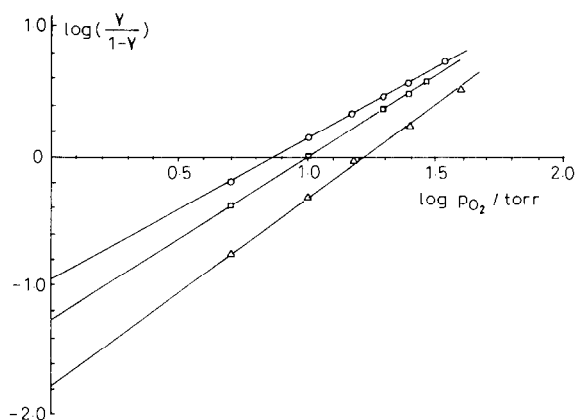


Fig. 9. Hill plots for $\text{MnX}_2\{\text{P}(\text{C}_{12})_2\}(\text{THF})$ complexes in toluene solution at 20 °C ($\text{X} = \text{Cl}, \circ; \text{Br}, \square; \text{I}, \triangle$).

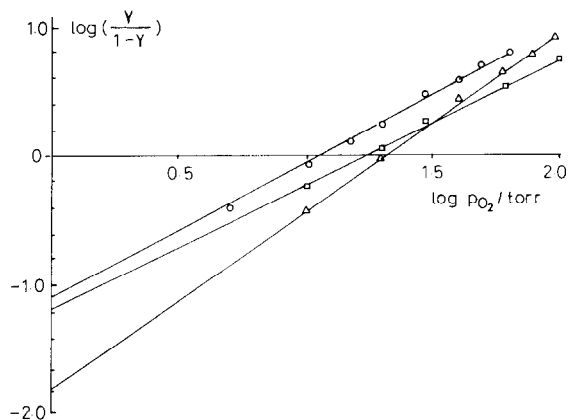
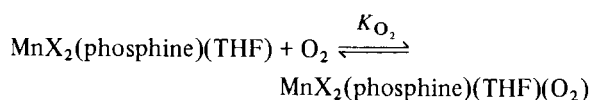


Fig. 10. Hill plots for $\text{MnX}_2\{\text{PhP}(\text{C}_{16})_2\}(\text{THF})$ complexes in toluene solution at 20 °C ($\text{X} = \text{Cl}, \circ; \text{Br}, \square; \text{I}, \triangle$).

TABLE VI. Equilibrium Data for $\text{MnX}_2(\text{phosphine})(\text{THF})$ Complexes in Toluene at 20 °C

Complex	P_{50} (torr)	n	$\log K_{\text{O}_2}$	$K_{\text{O}_2} (\times 10^{-3})$
$\text{MnCl}_2\{\text{P}(\text{C}_{12})_3\}(\text{THF})$	7.5	1.10	-0.9625	109.0
$\text{MnBr}_2\{\text{P}(\text{C}_{12})_3\}(\text{THF})$	10.0	1.25	-1.2500	56.2
$\text{MnI}_2\{\text{P}(\text{C}_{12})_3\}(\text{THF})$	17.0	1.45	-1.7842	16.4
$\text{MnCl}_2\{\text{P}(\text{C}_{14})_3\}(\text{THF})$	10.2	1.15	-1.1599	69.2
$\text{MnBr}_2\{\text{P}(\text{C}_{14})_3\}(\text{THF})$	12.0	1.30	-1.4029	39.5
$\text{MnI}_2\{\text{P}(\text{C}_{14})_3\}(\text{THF})$	19.0	1.50	-1.9181	12.1
$\text{MnCl}_2\{\text{P}(\text{C}_{16})_3\}(\text{THF})$	10.5	1.20	-1.2254	59.5
$\text{MnBr}_2\{\text{P}(\text{C}_{16})_3\}(\text{THF})$	12.0	1.25	-1.3489	44.8
$\text{MnI}_2\{\text{P}(\text{C}_{16})_3\}(\text{THF})$	20.0	1.40	-1.8214	15.0
$\text{MnCl}_2\{\text{PhP}(\text{C}_{12})_2\}(\text{THF})$	12.5	0.95	-1.0421	90.8
$\text{MnBr}_2\{\text{PhP}(\text{C}_{12})_2\}(\text{THF})$	16.0	0.95	-1.1439	71.8
$\text{MnI}_2\{\text{PhP}(\text{C}_{12})_2\}(\text{THF})$	22.0	1.40	-1.8794	13.2
$\text{MnCl}_2\{\text{PhP}(\text{C}_{14})_2\}(\text{THF})$	10.2	1.00	-1.0086	98.0
$\text{MnBr}_2\{\text{PhP}(\text{C}_{14})_2\}(\text{THF})$	14.0	1.15	-1.3180	48.0
$\text{MnI}_2\{\text{PhP}(\text{C}_{14})_2\}(\text{THF})$	24.0	1.50	-2.0703	8.50
$\text{MnCl}_2\{\text{PhP}(\text{C}_{16})_2\}(\text{THF})$	12.0	1.10	-1.1871	64.9
$\text{MnBr}_2\{\text{PhP}(\text{C}_{16})_2\}(\text{THF})$	17.0	1.05	-1.2919	51.0
$\text{MnI}_2\{\text{PhP}(\text{C}_{16})_2\}(\text{THF})$	21.0	1.35	-1.7849	16.4



were calculated from the isotherms by use of the Hill equation [19, 20] where Y = fraction of dioxygenated sites, K_{O_2} = equilibrium constant for the reaction, $P_{50} = P_{\text{O}_2}$ at which 50% of the sites are dioxygenated.

A plot of $\log(Y/1 - Y)$ versus $\log P_{\text{O}_2}$ yields Hill plots, see for example Figs. 9 and 10, with slope n known as the Hill coefficient. The values of $\log K_{\text{O}_2}$ were obtained from the intercept of the best straight lines.

The data derived from the Hill plots are summarised in Tables VI–VIII, and an example of the data used for such a plot is contained in Table IX. From these data we can make the following generalisations:

MnX₂(phosphine)(THF) Complexes in Toluene

From the K_{O_2} values the dioxygen affinity is in the order $\text{X} = \text{Cl} > \text{Br} > \text{I}$. For $\text{X} = \text{Cl}$, the relative affinity as the phosphine is varied is: $\text{P}(\text{C}_{12})_3 > \text{PhP}(\text{C}_{14})_2 > \text{PhP}(\text{C}_{16})_2 > \text{P}(\text{C}_{14})_3 > \text{PhP}(\text{C}_{12})_2 > \text{P}(\text{C}_{16})_3$; for $\text{X} = \text{Br}$, the relative dioxygen affinity

TABLE VII. Equilibrium Data for $MnX_2(\text{phosphine})(\text{THF})$ Complexes in Tetrahydrofuran Solution at 20 °C

Complex	P_{50} (torr)	n	$\log K_{O_2}$	$K_{O_2} (\times 10^{-3})$
$MnCl_2\{P(C_{12})_3\}(\text{THF})$	5.7	1.00	-0.7404	182.0
$MnBr_2\{P(C_{12})_3\}(\text{THF})$	8.4	1.10	-1.0168	96.3
$MnCl_2\{P(C_{14})_3\}(\text{THF})$	6.6	1.06	-0.8536	140.2
$MnBr_2\{P(C_{14})_3\}(\text{THF})$	9.1	1.14	-1.1086	80.0
$MnCl_2\{P(C_{16})_3\}(\text{THF})$	6.8	1.05	-0.8740	133.5
$MnBr_2\{P(C_{16})_3\}(\text{THF})$	9.6	1.05	-1.0266	94.0
$MnCl_2\{PhP(C_{12})_2\}(\text{THF})$	7.5	1.10	0.9626	120.5
$MnBr_2\{PhP(C_{12})_2\}(\text{THF})$	11.9	1.20	-1.2996	50.4
$MnCl_2\{PhP(C_{14})_2\}(\text{THF})$	7.9	1.15	-1.0323	92.8
$MnBr_2\{PhP(C_{14})_2\}(\text{THF})$	12.0	1.15	-1.2370	58.0
$MnCl_2\{PhP(C_{16})_2\}(\text{THF})$	8.4	1.11	-1.0167	96.2
$MnBr_2\{PhP(C_{16})_2\}(\text{THF})$	13.2	1.17	-1.2888	51.5

TABLE VIII. Equilibrium Data for $MnI_2(\text{phosphine})(\text{THF})$ Complexes in Tetrahydrofuran Solution at -40 °C

Complex	P_{50} (torr)	n	$\log K_{O_2}$	$\log K_{O_2} (\times 10^{-3})$
$P(C_{12})_3$	21.7	1.40	-1.8684	13.5
$P(C_{14})_3$	20.5	1.30	-1.7054	19.8
$P(C_{16})_3$	22.5	1.35	-1.8204	15.3
$PhP(C_{12})_2$	29.7	1.46	-2.1294	7.6
$PhP(C_{14})_2$	31.4	1.48	-2.2454	5.7
$PhP(C_{16})_2$	31.1	1.53	-2.3119	5.0

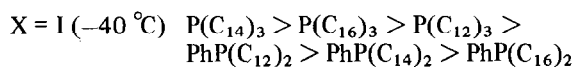
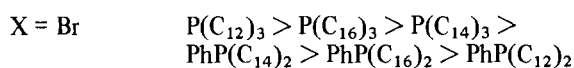
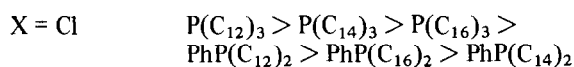
TABLE IX. Hill Plot Data for $MnX_2\{PhP(C_{16})_2\}(\text{THF})$ in Toluene at 20 °C

	P_{O_2}	%	$\log P_{O_2}$	$\log\left(\frac{Y}{1-Y}\right)$
Cl	5	27.5	0.6989	-0.4183
	10	45.0	1.0000	-0.0872
	15	56.2	1.1762	0.1067
	20	63.6	1.3010	0.2439
	30	73.3	1.4771	0.4377
	40	78.9	1.6030	0.5751
Br	50	82.7	1.6989	0.6818
	10	36.3	1.0000	-0.2419
	20	54.3	1.3010	0.0741
	30	64.5	1.4771	0.2590
	40	71.0	1.6020	0.3902
	60	75.8	1.7782	0.4963
I	80	80.3	1.9030	0.6111
	100	83.6	2.0000	0.7081
	10	27.0	1.0000	-0.4349
	20	48.4	1.3010	-0.0286
	40	72.5	1.6020	0.4197
	60	80.5	1.7782	0.6156
	80	85.8	1.9030	0.7841
	100	89.2	2.0000	0.9150
	120	95.4	2.3010	1.3214

varies as $PhP(C_{12})_2 > P(C_{12})_3 > PhP(C_{16})_2 > PhP(C_{14})_2 > P(C_{16})_3 > P(C_{14})_3$, and for the iodo complexes the order is $P(C_{12})_3 > PhP(C_{16})_2 > P(C_{16})_3 > PhP(C_{12})_2 > P(C_{14})_3 > PhP(C_{14})_2$.

$MnX_2(\text{phosphine})(\text{THF})$ Complexes in Tetrahydrofuran

Lower P_{50} values and larger K_{O_2} values are found for the chloro complexes than for the bromo complexes, and all the Hill coefficients are close to unity. The relative dioxygen affinities are:



Comparing Tables VI and VII it can be seen that in toluene solution the $MnX_2(\text{phosphine})(\text{THF})$ ($X = \text{Cl}, \text{Br}$) complexes have larger Hill coefficients, n , than in tetrahydrofuran solution, suggesting a degree of cooperativity in binding in the former solvent. This is in keeping with the structures suggested for these species in solution, Scheme 1. In tetrahydrofuran a

monomeric structure VI, would not be expected to act cooperatively regarding dioxygen binding, whereas the dimeric structure V might be expected to show some cooperativity as bridging Mn–X–Mn moieties are broken on dioxygenation.

Experimental

All solvents, other reagents and phosphines were obtained and manipulated as previously described [1, 2]. All physical measurements were performed as previously described [1, 2].

Complex Preparation

This is typified by the preparation of $\text{MnCl}_2 \cdot \text{P}(\text{C}_{16})_3(\text{THF})$: a round bottom flask (250 cm³) with side arm, ground glass tap and magnetic stirrer bar was flame dried, and then charged with anhydrous MnCl_2 (0.63 g; 5.0 mmol) and solid $\text{P}(\text{C}_{16})_3$ (3.53 g; 5.0 mmol). Dry tetrahydrofuran (approx. 50 cm³) was then distilled into the flask under argon and the mixture was allowed to stir under argon for 10 d. After this time the THF was removed by application of a vacuum, dry n-pentane (50 cm³) was added and the mixture stirred for 1 h. The resulting slurry was then filtered in a Schlenk apparatus and the solid complex dried *in vacuo* for 6 h (yield 97%).

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