The Co-ordination of Small Molecules by Manganese(II) Phosphine Complexes. Part 11.[1] The Co-ordination of Dioxygen by Manganese(II) Complexes containing Long-chain Phosphine Ligands*

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Manganese(II) complexes of long-chain phosphines, [MnX_2(phosphine)] [X = Cl, Br, or I; phosphine = $P(C_{12}H_{25})_3$, $P(C_{14}H_{29})_3$, $P(C_{16}H_{33})_3$, $PPh(C_{12}H_{25})_2$, $PPh(C_{14}H_{29})_2$, or $PPh(C_{16}H_{33})_2$], have been prepared. They form highly coloured 1 : 1 adducts with dioxygen, [MnX_2(phosphine)(O_2)], in both toluene and tetrahydrofuran (thf) solution. Infrared and e.s.r. spectra strongly suggest that these [MnX_2(phosphine)] complexes are pseudotetrahedral dimers in the solid state and in toluene, contrasting vividly with the previously reported structure of [$MnI_2(PPhMe_2)$]. Some molecular weight data indicate the product of dioxygenation in toluene to be the monomeric [MnX_2(phosphine)(O_2)] species. Dioxygen-binding curves for toluene and thf solutions have been obtained and equilibrium constants, K_{O_2}, for the dioxygenation reaction have been deduced. The general observation that K_{O_2} increases and P_{50}, the partial pressure when 50% of sites are deoxygenated, decreases for changes in halide ligand from Cl to Br to I in both solvents mirrors earlier observations with complexes of short-chain phosphines. The affinity of the complexes for O_2 in thf is in the order phenyldialkylphosphines < trialkylphosphines. Hill coefficients, *n*, are approximately 1 for thf solutions of the chloride and bromide complexes, but for the iodides in thf and all of the complexes in toluene *n* lies in the range 1.10—1.64 indicating co-operativity for O_2 binding, which may be related to the dimeric structure proposed for the complexes in toluene.

The group of complexes [$MnX_2(PR_3)$] are proving to be an intriguing chemical system in their ability to bind small molecules, often reversibly, in a discriminating manner. For example, in their reaction with sulphur dioxide to form [$MnX_2(PR_3)(SO_2)_{0.66}$], reaction occurs for all phosphines studied when X = I, but when X = Cl no phosphine complexes are active and for X = Br the reactivity depends upon the nature of the phosphine.[2] On the other hand many [$MnCl_2(PR_3)$] complexes form 1:1 adducts with ethylene, but for X = I no reaction occurs and again X = Br represents an intermediate system.[3] In addition we have examined the binding of carbon monoxide,[4] nitric oxide,[1,5] carbon disulphide,[6] and tetracyanoethylene[7] by these complexes.

However, it is the interaction of dioxygen with these [$MnX_2(PR_3)$] (X = Cl, Br, I, or NCS; R_3 = Bu^n_3 or $PhBu^n_2$) complexes that we have studied most.[8–10] The relative insolubility of the complexes in non-co-ordinating organic solvents, such as toluene or dichloromethane, has led us to prepare analogous species containing phosphines with long alkyl chains, effectively encapsulating the manganese centre in a hydrocarbon 'pocket' in the hope that improved solubility would result. We hereby report the preparation of [$MnX_2(PR_3)$] [X = Cl, Br, or I; R_3 = $(C_{12}H_{25})_3$, $(C_{14}H_{29})_3$, $(C_{16}H_{33})_3$, $Ph(C_{12}H_{25})_2$, $Ph(C_{14}H_{29})_2$, or $Ph(C_{16}H_{33})_2$], their characterisation, and observations of dioxygen binding in solution.

Results and Discussion

Anhydrous manganese(II) salts react with long-chain monodentate phosphine ligands in non-co-ordinating or weakly co-ordinating solvents (toluene–dichloromethane, diethyl ether, or pentane) to form [MnX_2(phosphine)] complexes, Table 1. The stoicheiometry of the final product was found to be independent of the quantity of the phosphine ligand employed. When the products were thoroughly washed with toluene and/or n-pentane any excess of phosphine was removed and could be recovered from the washings (identity confirmed by i.r. spectra). The complexes thus formed were found to be appreciably soluble in toluene–dichloromethane (1:1) (*ca.* 10^{-3} mol dm^{-3}) and when using this solvent mixture it was found necessary to precipitate the product by addition of diethyl ether. However, when either diethyl ether or pentane was used as the reaction media the resulting [MnX_2(phosphine)] species were only sparingly soluble and could be recovered by filtration only.

The solid-state e.s.r. spectra of the complexes all exhibit three bands at 1 550—1 600m-w, 3 300—3 350s, and 4 400—4 500w G consistent with high-spin manganese(II) in a pseudotetrahedral environment,[11] each of the spectra comprising only broad bands with no hyperfine coupling to ^{55}Mn. Far-i.r. spectra of the complexes show bands assignable to both terminal Mn–X and bridging Mn–X–Mn linkages as shown in Table 2.[12–14] The characteristic ν(Mn–P) vibration occurs in the region 380—405 cm^{-1}, increasing in energy in the order X = Cl < Br < I, suggesting that the Mn–P bond is strongest in the [MnI_2(phosphine)] complexes. The room-temperature magnetic moments, Table 1, are somewhat lower than expected for a d^5 high-spin system, and this can be attributed to the spin pairing resulting from the Mn–X–Mn bridges. All of the complexes rapidly react with even small amounts of dioxygen, and this high reactivity precluded obtaining reliable molecular weight measurements for the unoxygenated complexes.

However, from the available evidence (e.s.r. and i.r.) the complexes are best assigned structure (**I**). Such a structure has been shown to occur for [$\{Mn(CH_2SiMe_3)_2(PMe_3)\}_2$] by *X*-

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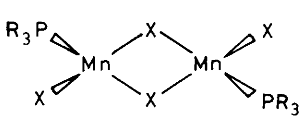
* *Non-S.I. units employed:* G = 10^{-4} T, Torr ≈ 133 Pa.

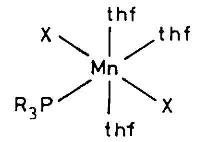
Table 1. Physical and analytical data for $[MnX_2(phosphine)]^a$ complexes

Complex	$\mu_{eff.}$	M.p./°C	Analysis^b/% C	H	P	X	Mn
$[MnCl_2\{P(C_{12}H_{25})_3)]$	5.75	49	65.4 (65.0)	11.5 (11.3)	5.0 (4.7)	10.2 (10.7)	8.0 (8.3)
$[MnCl_2\{P(C_{14}H_{29})_3\}]$	5.80	82	67.0 (67.4)	12.0 (11.6)	4.0 (4.2)	9.8 (9.5)	7.0 (7.4)
$[MnCl_2\{P(C_{16}H_{33})_3)]$	5.80	92	70.0 (69.2)	12.2 (11.9)	4.0 (3.7)	8.0 (8.5)	6.4 (6.6)
$[MnCl_2\{PPh(C_{12}H_{25})_2\}]$	5.75	124	63.2 (62.9)	10.0 (9.6)	5.0 (5.4)	12.5 (12.4)	9.0 (9.6)
$[MnCl_2\{PPh(C_{14}H_{29})_2\}]$	5.75	124	64.0 (63.6)	11.0 (10.4)	5.4 (5.1)	11.0 (11.8)	9.5 (9.1)
$[MnCl_2\{PPh(C_{16}H_{33})_2\}]$	5.80	105	67.0 (66.7)	10.5 (10.4)	4.0 (4.5)	10.0 (10.4)	8.2 (8.0)
$[MnBr_2\{P(C_{12}H_{25})_3\}]$	5.70	38	57.0 (57.4)	10.0 (10.0)	4.0 (4.1)	21.5 (21.5)	7.0 (7.3)
$[MnBr_2\{P(C_{14}H_{29})_3\}]$	5.70	88	60.5 (60.2)	10.5 (10.4)	3.5 (3.7)	19.3 (19.1)	6.2 (6.6)
$[MnBr_2\{P(C_{16}H_{33})_3\}]$	5.65	58	63.0 (62.6)	11.0 (10.8)	3.0 (3.4)	17.5 (17.4)	6.0 (5.9)
$[MnBr_2\{PPh(C_{12}H_{25})_2\}]$	5.70	104	55.0 (54.5)	8.5 (8.3)	5.0 (4.7)	24.0 (24.2)	8.0 (8.3)
$[MnBr_2\{PPh(C_{14}H_{29})_2)]$	5.65	100	56.0 (55.4)	9.8 (9.1)	4.0 (4.5)	22.5 (23.1)	8.2 (7.9)
$[MnBr_2\{PPh(C_{16}H_{33})_2\}]$	5.65	92	60.0 (59.0)	10.0 (9.2)	4.2 (4.0)	20.5 (20.7)	6.8 (7.1)
$[MnI_2\{P(C_{12}H_{25})_3\}]$	5.45	42	50.5 (51.0)	9.2 (8.9)	3.5 (3.7)	31.0 (30.0)	6.0 (6.5)
$[MnI_2\{P(C_{14}H_{29})_3\}]$	5.40	91	53.8 (54.1)	9.0 (9.3)	3.0 (3.3)	27.8 (27.5)	6.2 (5.9)
$[MnI_2\{P(C_{16}H_{33})_3\}]$	5.45	52	57.0 (56.8)	10.0 (9.8)	3.2 (3.1)	24.5 (25.0)	5.5 (5.4)
$[MnI_2\{PPh(C_{12}H_{25})_2\}]$	5.40	64	48.0 (47.7)	7.5 (7.3)	3.5 (4.1)	34.0 (33.6)	6.8 (7.3)
$[MnI_2\{PPh(C_{14}H_{29})_2\}]$	5.40	86	49.5 (48.8)	8.8 (8.0)	4.0 (3.9)	31.5 (32.3)	6.8 (7.0)
$[MnI_2\{PPh(C_{16}H_{33})_2\}]$	5.40	58	53.0 (52.6)	8.5 (8.2)	3.0 (3.6)	30.0 (29.3)	6.0 (6.3)

[a] For X = Cl all complexes are pale pink; X = Br (pink); X = I (pink-orange). [b] Calculated values are given in parentheses.



(I)



(II)

ray crystallographic data.[15,16] Moreover, the far-i.r. spectra of these complexes are very similar to those of $[\{MnX_2[P(CH_2CH_2CN)_3]\}_2]$ for which molecular weight data indicated a dimeric structure.[14] Structure (**I**) contrasts vividly with the structure of $[MnI_2(PPhMe_2)]$; *X*-ray crystallography has shown this to consist of an infinite MnI_2 chain with two phosphine ligands co-ordinated to each alternate Mn atom.[17]

Solution Studies.—The toluene solution e.s.r. spectra of the complexes were recorded as frozen glasses at −160 °C. These (Table 3) show that the spectra in the solid state are essentially the same as those in toluene glasses, implying that the dimeric structure (**I**) is retained in toluene solution. When dissolved in tetrahydrofuran (thf), the complexes exhibit a strong band at $g_{eff.} = 6$ with coupling to ^{55}Mn ($I = \frac{5}{2}$) splitting the band into six lines. The spectra are very similar to those reported for complexes of short-chain phosphines in thf solution.[9] These observations suggest a similar structure in thf, (**II**), to that previously reported.[9]

The $[MnX_2(phosphine)]$ complexes react rapidly with dioxygen in toluene or thf solution. The amount of dioxygen absorbed was determined by the gas burette technique[8] and concentration plots, Figure 1 and Table 4. From these, and much other data,[18,*] it is clear for all the complexes reported here that 1 mol O_2 is bound per Mn atom in both toluene and thf solution. Under the conditions employed it was found that the solvent blanks (100 cm³) absorbed 1.18 (toluene, 20 °C) and 1.27 mmol O_2 (thf), and it can be seen from Figure 1 and Table 4 that the intercepts (*i.e.* amount of O_2 absorbed at zero concentration) are in good agreement with the independently measured blanks. The 1:1 stoicheiometry of the reaction was further substantiated by molecular weight measurements in toluene, *viz*. $[MnCl_2\{P(C_{12}H_{25})_3\}(O_2)]$ 708 (calc. for monomer 696) and $[MnI_2\{PPh(C_{14}H_{29})_2](O_2)]$ 850 (calc. for monomer 843). The process (1) thus occurs in solution.

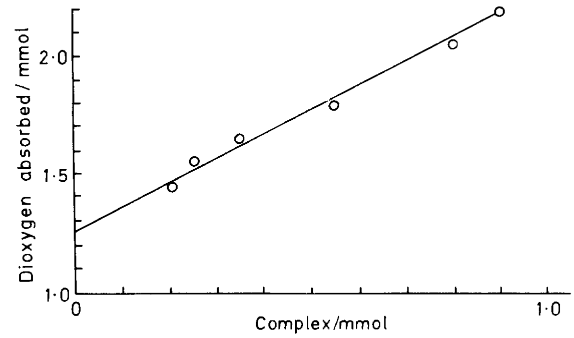
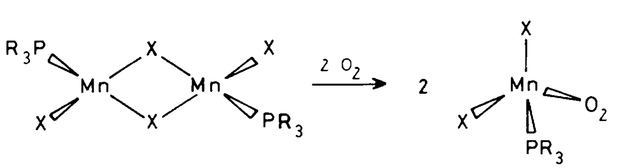


Figure 1. Plot of dioxygen absorbed *versus* concentration of $[MnI_2\{PPh(C_{14}H_{29})_2\}]$ in thf solution at −78 °C



(1)

Solutions of all the manganese complexes rapidly develop deep colours upon contact with dioxygen, and these colours appear to depend more upon the nature of the halide than that of the phosphine, and also to some extent on the solvent. The dioxygenated complexes are purple (X = Cl), blue (X = Br), green (X = I, toluene), or red-brown (X = I, thf). Typical spectra are illustrated in Figures 2—4. The positions of the band maxima for each halide series showed only small variations with change in phosphine ligand, usually by 5—10 nm. The average positions of the band maxima and their molar absorption coefficients are listed in Table 5.

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[*] We have measured O_2 uptake as a function of concentration for all the complexes described and found the slope of the plots of uptake *vs.* concentration to be 1, the intercept close to the value for O_2 uptake for the solvent alone, in all cases.

Table 2. Far-i.r. data for the complexes [MnX_2(phosphine)]

X	ν(MnX)/cm^{-1}	ν(X-Mn-X)/cm^{-1}
Cl	289—300	220—230
Br	235—245	195—205
I	205—220	165—170

Table 3. E.s.r. data for [MnX_2(phosphine)] complexes in toluene glasses at −160 °C

Complex	Line positions/G
[$MnCl_2\{P(C_{12}H_{25})_3\}$]	1 500m, 3 300s, 4 800w, 5 400w
[$MnCl_2\{P(C_{14}H_{29})_3\}$]	1 500m, 3 300s, 4 750w, 5 400w
[$MnCl_2\{P(C_{16}H_{33})_3\}$]	1 500m, 3 300s, 4 900w, 5 500w
[$MnCl_2\{PPh(C_{12}H_{25})_2\}$]	1 500m, 3 300s, 4 850w
[$MnCl_2\{PPh(C_{14}H_{29})_2\}$]	1 550m, 3 350s, 4 900w
[$MnCl_2\{PPh(C_{16}H_{33})_2\}$]	1 550m, 3 350s, 5 000w
[$MnBr_2\{P(C_{12}H_{25})_3\}$]	1 600m, 3 300s, 4 300w, 5 500w
[$MnBr_2\{P(C_{14}H_{29})_3\}$]	1 600m, 3 300s, 4 350w, 5 500w
[$MnBr_2\{P(C_{16}H_{33})_3\}$]	1 600m, 3 300s, 4 350w, 5 500w
[$MnBr_2\{PPh(C_{12}H_{25})_2\}$]	1 550m, 3 350s, 5 100w
[$MnBr_2\{PPh(C_{14}H_{29})_2\}$]	1 540m, 3 350s, 5 100w
[$MnBr_2\{PPh(C_{16}H_{33})_2\}$]	1 550m, 3 350s, 5 100w
[$MnI_2\{P(C_{12}H_{25})_3\}$]	1 450m, 3 350s, 4 200w, 5 400m
[$MnI_2\{P(C_{14}H_{29})_3\}$]	1 450m, 3 350s, 4 200w, 5 400m
[$MnI_2\{P(C_{16}H_{33})_3\}$]	1 500m, 3 350s, 4 200w, 5 400m
[$MnI_2\{PPh(C_{12}H_{25})_2\}$]	1 550m, 3 300s, 5 000w, 6 000m
[$MnI_2\{PPh(C_{14}H_{29})_2\}$]	1 550m, 3 300s, 5 000w, 6 000w
[$MnI_2\{PPh(C_{16}H_{33})_2\}$]	1 550m, 3 300s, 5 000w, 6 000w

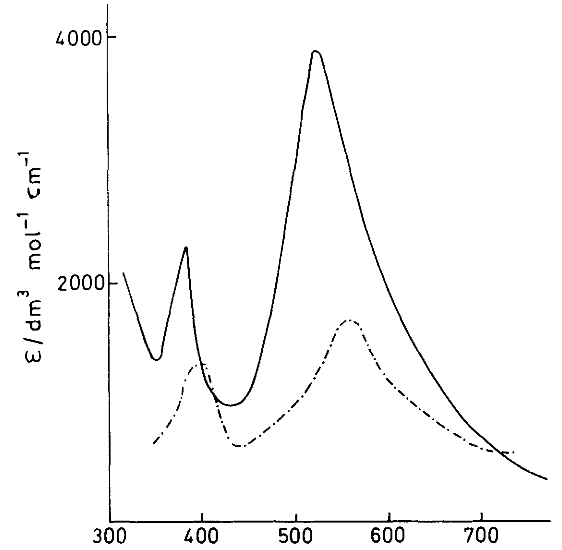

Figure 2. Typical electronic spectrum of dioxygen adducts of [$MnCl_2$(phosphine)] complexes in toluene (———) and thf (-·-·-)

Table 4. Data from plots of O_2-uptake as a function of complex concentration

Complex	Slope	Intercept (× 10^{-3})	Solvent	Temperature (°C)
[$MnCl_2\{P(C_{12}H_{25})_3\}$]	0.98	1.17	Toluene	20
[$MnBr_2\{P(C_{12}H_{25})_3\}$]	1.04	1.15	Toluene	20
[$MnI_2\{P(C_{12}H_{25})_3\}$]	0.93	1.21	Toluene	20
[$MnCl_2\{PPh(C_{14}H_{29})_2\}$]	1.00	1.26	thf	−78
[$MnBr_2\{PPh(C_{14}H_{29})_2\}$]	1.05	1.27	thf	−78
[$MnI_2\{PPh(C_{14}H_{29})_2\}$]	1.05	1.27	thf	−78

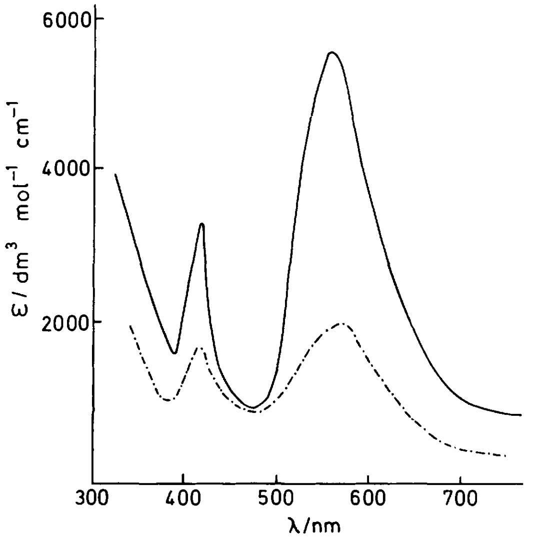

Figure 3. Typical electronic spectrum of dioxygen adducts of [$MnBr_2$(phosphine)] complexes in toluene (———) and thf (-·-·-)

By following the increase in intensity of the electronic spectra with increasing partial pressure of dioxygen it has been possible to construct dioxygen-binding isotherms for the complexes, both in toluene and thf solution. Some isotherms are shown in Figures 5—7. For the iodo complexes in thf solution, measurements were made at −40 °C since at higher temperatures the dioxygen adduct decomposed before equilibrium was reached (this was observable as a slow decay in the intensity of electronic absorption bands after exposure to dioxygen at >0 °C, and phosphine oxides were isolable from solution). An interesting feature which appears in many isotherms, and is shown in Figures 5 and 6, is that for a series of [MnX_2(phosphine)] complexes (X = Br or I), at low p_{O_2}, the affinity for O_2 is Br > I, but at around 80—90% dioxygenation the affinity changes to I > Br.

The equilibrium constants for the binding of dioxygen [equation (2)] were calculated from the isotherms by use of the

$$[MnX_2(phosphine)] + O_2 \rightleftharpoons [MnX_2(phosphine)(O_2)] \quad (2)$$

$$\frac{Y}{1 - Y} = \frac{[MnX_2(phosphine)(O_2)]}{[MnX_2(phosphine)]} = K_{O_2} p_{O_2}{}^{n}$$

$$= p_{O_2,50}{}^{1} p_{O_2} \quad (3)$$

Hill equation[19,20] (3) where Y is the fraction of dioxygenated sites, K_{O_2} the equilibrium constant for the reaction, and $p_{O_2,50}$ (p_{50}), the partial pressure at which 50% of the sites are dioxygenated. A plot of log [$Y/(1 - Y)$] *versus* log p_{O_2} yields a Hill plot (Figure 8 is a representative plot) with slope n, the Hill coefficient. The data derived from the Hill plots are summarised in Tables 6—8.

Toluene solution. From the K_{O_2} values it is clear that the chloro complexes have the highest affinity (and lowest p_{50} values) for dioxygen. The bromo complexes have similar Hill coefficients to their chloro analogues but have higher p_{50} values and lower dioxygen affinities. The iodo complexes have much lower dioxygen affinities (a factor of *ca.* 10) and higher p_{50}

Table 5. Average positions and molar absorption coefficients in electronic spectra of $[MnX_2(phosphine)]$ complexes

X	Solvent	λ/nm(ε/dm^3 mol^{-1} cm^{-1})
Cl	Toluene	520 ± 10 (3 800 ± 500), 380 ± 10 (220 ± 400)
	thf	540 ± 10 (1 600 ± 300), 400 ± 5 (1 200 ± 100)
Br	Toluene	545 ± 10 (5 700 ± 500), 410 ± 5 (3 200 ± 400)
	thf	560 ± 10 (1 800 ± 300), 415 ± 5 (1 600 ± 100)
I	Toluene	545 ± 20 (4 100 ± 400), 390 ± 10 (5 700 ± 500), 370 ± 5 (440 ± 400)
	thf	620 ± 10 (2 800 ± 300), 520 ± 20 (2 700 ± 200)

Table 6. Equilibrium data for $[MnX_2(phosphine)]$ complexes in toluene at 20 °C

Complex	p_{50}/Torr	n	K_{O_2} ($\times 10^{-3}$)/ Torr^{-1}
$[MnCl_2\{P(C_{12}H_{25})_3\}]$	12.1	1.25 ± 0.03	4.4 ± 2
$[MnBr_2\{P(C_{12}H_{25})_3\}]$	1.96	1.24 ± 0.04	25 ± 2
$[MnI_2\{P(C_{12}H_{25})_3\}]$	29.7	1.64 ± 0.04	3.8 ± 0.2
$[MnCl_2\{P(C_{14}H_{29})_3\}]$	13.4	1.15 ± 0.04	50 ± 3
$[MnBr_2\{P(C_{14}H_{29})_3\}]$	21.4	1.17 ± 0.04	28 ± 2
$[MnI_2\{P(C_{14}H_{29})_3\}]$	31.1	1.59 ± 0.09	4 ± 1
$[MnCl_2\{P(C_{16}H_{33})_3\}]$	11.9	1.30 ± 0.04	39.5 ± 2.5
$[MnBr_2\{P(C_{16}H_{33})_3\}]$	17.5	1.36 ± 0.03	20 ± 1
$[MnI_2\{P(C_{16}H_{33})_3\}]$	34.8	1.48 ± 0.11	5.0 ± 1.0
$[MnCl_2\{PPh(C_{12}H_{25})_2\}]$	14.2	1.20 ± 0.04	42 ± 3
$[MnBr_2\{PPh(C_{12}H_{25})_2\}]$	22.8	1.10 ± 0.05	32 ± 3
$[MnI_2\{PPh(C_{12}H_{25})_2\}]$	32.6	1.39 ± 0.07	7.9 ± 1.0
$[MnCl_2\{PPh(C_{14}H_{29})_2\}]$	12.6	1.30 ± 0.05	37 ± 3
$[MnBr_2\{PPh(C_{14}H_{29})_2\}]$	20.4	1.40 ± 0.04	15 ± 1
$[MnI_2\{PPh(C_{14}H_{29})_2\}]$	37.4	1.25 ± 0.08	10.5 ± 1.5
$[MnCl_2\{PPh(C_{16}H_{33})_2\}]$	18.8	1.10 ± 0.06	39 ± 4
$[MnBr_2\{PPh(C_{16}H_{33})_2\}]$	21.9	1.28 ± 0.04	19 ± 2
$[MnI_2\{PPh(C_{16}H_{33})_2\}]$	39.4	1.43 ± 0.09	5.3 ± 1.4

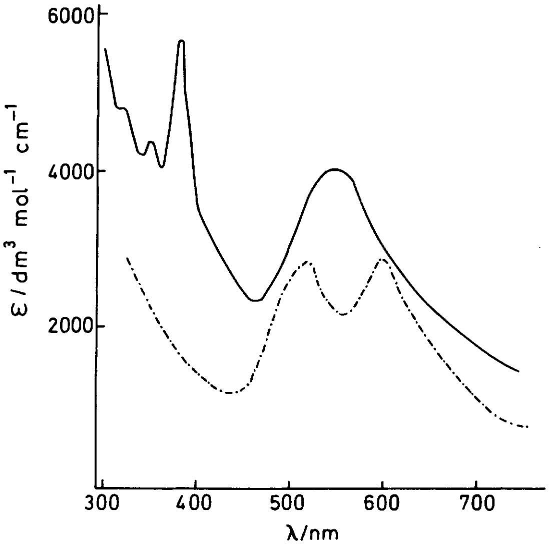

Figure 4. Typical electronic spectrum of dioxygen adducts of $[MnI_2(phosphine)]$ complexes in toluene (———) and thf (–·–·–)

Table 7. Equilibrium data for $[MnX_2(phosphine)]$ complexes in thf solution at 20 °C

Complex	p_{50}/Torr	n	K_{O_2} ($\times 10^{-3}$)/ Torr^{-1}
$[MnCl_2\{P(C_{12}H_{25})_3\}]$	5.5	1.00 ± 0.03	182 ± 9
$[MnBr_2\{P(C_{12}H_{25})_3\}]$	8.4	0.91 ± 0.17	146 ± 16
$[MnCl_2\{P(C_{14}H_{29})_3\}]$	6.5	1.05 ± 0.09	141 ± 17
$[MnBr_2\{P(C_{14}H_{29})_3\}]$	9.2	1.15 ± 0.07	78 ± 9
$[MnCl_2\{P(C_{16}H_{33})_3\}]$	6.8	0.98 ± 0.04	152 ± 12
$[MnBr_2\{P(C_{16}H_{33})_3\}]$	9.5	1.05 ± 0.17	95 ± 11
$[MnCl_2\{PPh(C_{12}H_{25})_2\}]$	7.5	1.10 ± 0.08	108 ± 14
$[MnBr_2\{PPh(C_{12}H_{25})_2\}]$	12.5	1.20 ± 0.11	57 ± 6
$[MnCl_2\{PPh(C_{14}H_{29})_2\}]$	7.9	1.15 ± 0.11	93 ± 18
$[MnBr_2\{PPh(C_{14}H_{29})_2\}]$	11.9	1.15 ± 0.13	58 ± 8
$[MnCl_2\{PPh(C_{16}H_{33})_2\}]$	8.4	1.10 ± 0.11	96 ± 17
$[MnBr_2\{PPh(C_{16}H_{33})_2\}]$	13.2	1.15 ± 0.10	52 ± 9

Table 8. Equilibrium data for $[MnI_2(phosphine)]$ complexes in thf solution at −40 °C

Phosphine	p_{50}/Torr	n	K_{O_2} ($\times 10^{-3}$)/ Torr^{-1}
$P(C_{12}H_{25})_3$	21.6	1.40 ± 0.10	14 ± 3
$P(C_{14}H_{29})_3$	20.5	1.30 ± 0.08	20 ± 3
$P(C_{16}H_{33})_3$	22.3	1.35 ± 0.09	15.5 ± 2.5
$PPh(C_{12}H_{25})_2$	29.4	1.43 ± 0.11	8 ± 2
$PPh(C_{14}H_{29})_2$	31.4	1.50 ± 0.11	6 ± 1
$PPh(C_{16}H_{33})_2$	31.0	1.55 ± 0.12	5 ± 1

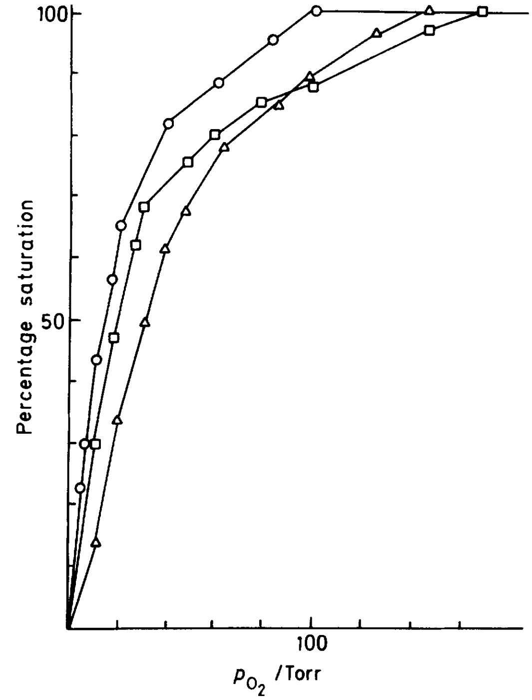

Figure 5. Dioxygen-binding isotherms for $[MnX_2\{P(C_{12}H_{25})_3\}]$ complexes in toluene solution at 20 °C: X = Cl (○), Br (□), or I (△)

values and greater Hill coefficients than either the chloro or bromo complexes. The fact that $n > 1$ indicates some co-operativity in dioxygen binding, which may be due to the dimeric nature of the complex in toluene solution.

Tetrahydrofuran solution. As for the toluene solutions of the complexes, the order of dioxygen affinity is Cl > Br > I. The values of K_{O_2} measured indicate that the complexes of trialkylphosphine have a greater dioxygen affinity than the phenyldialkylphosphine complexes by a factor of *ca.* 2. The Hill coefficient, n, for the chloride and bromide complexes is *ca.* 1 indicating no co-operativity in dioxygen binding, whereas for the iodide complexes n lies in the range 1.30—1.55 indicating some co-operativity, although the reason for this is unclear.

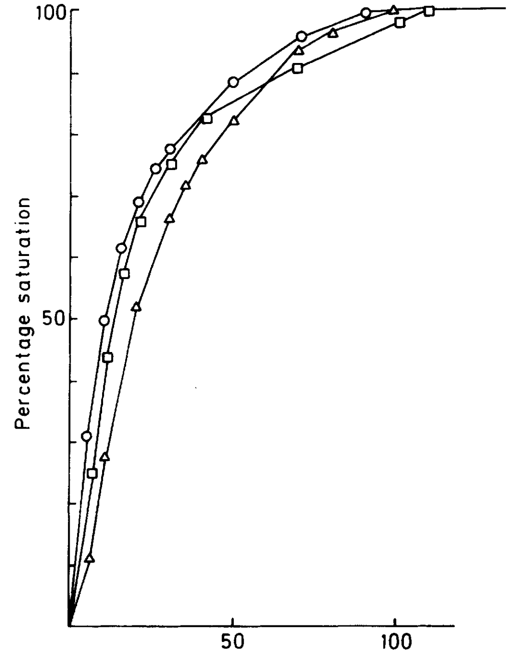

Figure 6. Dioxygen-binding isotherms for $[MnX_2\{P(C_{14}H_{29})_3\}]$ complexes in toluene at 20 °C; details as in Figure 5

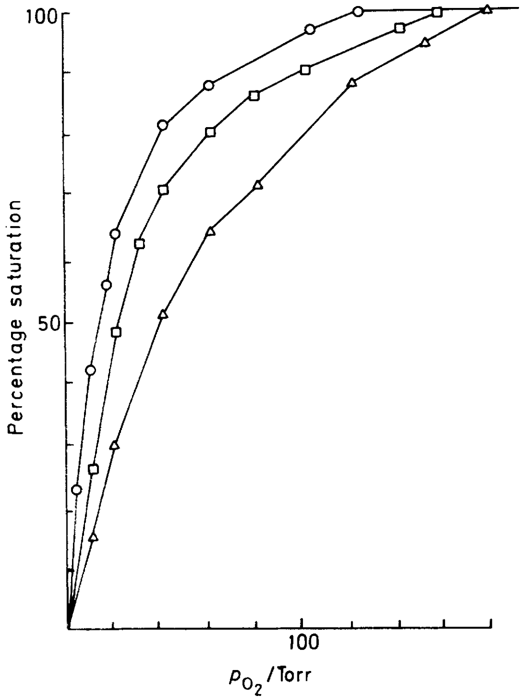

Figure 7. Dioxygen-binding isotherms for $[MnX_2\{PPh(C_{14}H_{29})_2\}]$ complexes in toluene at 20 °C; details as in Figure 5

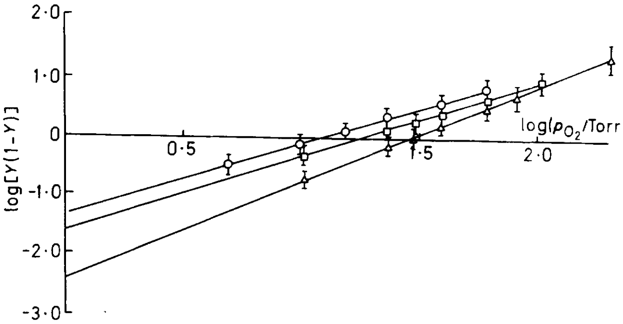

Figure 8. Hill plots for $[MnX_2\{P(C_{12}H_{25})_3\}]$ complexes in toluene solution at 20 °C; X = Cl (○), Br (□), or I (△)

Conclusions

Manganese(II) complexes of long-chain phosphines, $[MnX_2(phosphine)]$, bind dioxygen in a 1:1 ratio in toluene or thf solution to form highly coloured $[MnX_2(phosphine)(O_2)]$ species. There are similarities between these complexes and their short-chain phosphine analogues in that the affinity for dioxygen varies for X = Cl > Br > I in both solvents, that the affinity is greater in thf than in toluene, and that in thf the trialkylphosphine complexes have a greater affinity than do the phenyldialkylphosphine complexes.

In general the magnitudes of the equilibrium constants for O_2 binding by long- and short-chain[8] phosphine complexes are similar. The Hill coefficients, n, for the reactions of the chloride and bromide complexes with O_2 in thf are close to unity, indicating no co-operative effects in binding, which is in keeping with the monomeric structure proposed, (**II**). On the other hand, in toluene solution n lies in the range 1.10—1.64, indicating co-operativity, which may well be due to the effect of the dimeric structure proposed, (**I**).

Experimental

All manipulations involving air-sensitive materials were performed under a dry argon atmosphere. Solvents and manganese salts were dried by published procedures. The apparatus and method of measuring gas uptakes have been fully described.[8] Physical measurements were performed as described elsewhere.

Preparation of Manganese(II) *Phosphine Complexes*.—We have developed three methods for the preparation of the $[MnX_2(phosphine)]$ complexes reported here. Some general comments may be made, however, about the attraction of each method in view of the synthetic failure of others.[21,22] The use of toluene–dichloromethane as a medium is, in our experience, well suited to the synthesis of complexes of short-chain phosphines such as PPr^n_3, PBu^n_3, $PPhMe_2$, *etc.*[23] We have also had excellent results with diethyl ether as a medium for synthesising $[MnX_2\{PPh_{3-n}(CH_2CH_2CN)_n\}]$ (n = 1—3) complexes.[14] For the long-chain phosphine complexes reported here we have found that n-pentane gave the best results and describe the preparation of $[MnBr_2\{PPh(C_{16}H_{33})_2\}]$ as a typical example.

A round-bottom flask (250 cm³) equipped with a ground-glass tap and magnetic stirring bar was flame dried and then charged with anhydrous manganese(II) bromide (1.07 g, 5.0 mmol) and solid $PPh(C_{16}H_{33})_2$ (2.79 g, 5.0 mmol). Dry n-pentane (*ca.* 75 cm³) was then distilled into the flask under dry argon. The flask was then equipped with a condenser, placed in an oil-bath, heated to 40 °C under a slow stream of argon and maintained at this temperature for 5 d. The oil-bath and condenser were then removed and the mixture allowed to cool under argon to room temperature. The solid complex was then isolated by Schlenk techniques, washed with dry n-pentane (5 × 50 cm³), and finally dried *in vacuo* for 6 h (yield 96%).

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