

Controlled Reaction of Molecular Oxygen with $[\text{MnI}_2(\text{PPh}_2\text{Me})_2]$ to form the Mixed Phosphine–Phosphine Oxide Complex $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ and the Bis(phosphine oxide) Complex $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$ †

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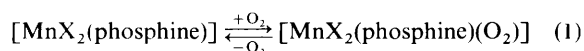
When a preformed solution of $[\text{MnI}_2(\text{PPh}_2\text{Me})_2(\text{O}_2)]$ in pentane at -40°C under argon was allowed to warm to room temperature, specific oxidation of one phosphine occurred and an almost quantitative yield of the mixed phosphine–phosphine oxide complex $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ was obtained; when the same procedure is followed under dry dioxygen the oxidation of both phosphines occurs and $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$ is obtained in almost quantitative yield. X-Ray crystallography showed both of these complexes to be pseudo-tetrahedral monomers, and $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ represents the first example of a mixed phosphine–phosphine oxide complex of manganese to be reported.

Although examples of transition-metal complexes containing both tertiary phosphine and tertiary phosphine oxide ligands are known they are rare. Moreover, their methods of synthesis are both varied and intriguing. They range from the straightforward use of mixed phosphine–phosphine oxides, $\text{Ph}_2\text{P}(\text{O})\text{CHRPPH}_2$ ($\text{R} = \text{H, Me or Pr}^n$), to produce metal(0) ($\text{M} = \text{Cr, Mo or W}$) and metal(II) ($\text{M} = \text{Cd or Hg}$) complexes,¹ to the quite exotic, as exemplified the synthesis by McCleverty and co-workers² of $[\text{Pd}(\text{NO}_3)_2(\text{OPPh}_3)(\text{PPh}_3)]$ from the reaction of $[\text{Pd}(\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{I}(\text{PPh}_3)_2]$ with NO_2 . Again, the straightforward displacement of perchlorate in $[\text{Pt}(\text{ClO}_4)(\text{C}_6\text{F}_5)(\text{PEt}_3)_2]$ by OPPh_3 to yield $[\text{Pt}(\text{C}_6\text{F}_5)(\text{OPPh}_3)(\text{PEt}_3)_2]\text{ClO}_4$ ³ contrasts with the isolation of small quantities of $[\text{MoI}_3(\text{OPPhMe}_2)(\text{PPhMe}_2)_2]$ from attempts to crystallise $[\text{Mo}_2\text{I}_4(\text{PPhMe}_2)_4]$.⁴ Collman and co-workers⁵ discovered that an unco-ordinated phosphine group of the tripodal ligand 1,1,1-tris(diphenylphosphinomethyl)ethane(L) in $[\text{RhCl}(\text{CO})_2\text{L}]$ can be oxidised *in situ* with cumene (1-methyl-1-phenylethyl) hydroperoxide. Recently, Abram and co-workers⁶ have isolated $[\text{Tc}(\text{NS})\text{Cl}_3(\text{PPhMe}_2)(\text{OPPhMe}_2)]$ from the reaction of $[\text{TcNCl}_2(\text{PPhMe}_2)_3]$ with an excess of S_2Cl_2 .

We report here the synthesis and crystal structures of $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ and $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$ from $[\text{MnI}_2(\text{PPh}_2\text{Me})_2]$. We also discuss the ability to isolate both the mixed phosphine–phosphine oxide complex and the bis(phosphine oxide) complex in the light of our observations of the reaction of $[\text{MnI}_2(\text{PPh}_2\text{Me})_n]$ ($n = 1$ or 2) with dioxygen.

Results and Discussion

Most of our investigations on manganese(II) phosphine complexes have been on the monophosphine species $[\text{MnX}_2(\text{PR}_3)]$ ($\text{X} = \text{Cl, Br, I or NCS}$; $\text{R} = \text{alkyl or aryl}$).^{7–9} In this series of complexes we have studied the ability of the materials reversibly to bind molecular oxygen^{10–13} [equation (1)].



Equilibrium data indicate that the affinity for dioxygen generally varies with X and with phosphine, *viz.* $\text{Cl} > \text{Br} > \text{I}$ and $\text{PR}_3 > \text{PPhR}_2 > \text{PPh}_2\text{R} > \text{PPh}_3$ ($\text{R} = \text{alkyl}$). In fact the PPh_2R ligand systems constitute the borderline. In the solid state, for example, $[\text{MnI}_2(\text{PPh}_2\text{Me})]$ does not bind dioxygen under ambient conditions, but a toluene solution of this complex immediately becomes deep green in the presence of air, forming $[\text{MnI}_2(\text{PPh}_2\text{Me})(\text{O}_2)]$. In contrast to the complexes $[\text{MnX}_2(\text{PR}_3)]$, the corresponding bis(phosphine) complexes, $[\text{MnX}_2(\text{PR}_3)_2]$, have received very little attention; $[\text{MnI}_2(\text{PEt}_3)_2]$ has been crystallographically characterised¹⁴ and we have recently reported the synthesis of some complexes of stoichiometry $[\text{MnI}_2(\text{PR}_3)_2]$ ($\text{R} = \text{Ph}$ or substituted aryl) from the reaction of manganese powder with triaryldiiodo-phosphorus compounds, R_3PI_2 .¹³

There is some evidence¹⁵ that pseudo-tetrahedral monomeric $[\text{MnI}_2(\text{phosphine})_2]$ complexes also interact with dioxygen both at low temperatures and under ambient conditions. Once again the PPh_2Me complex appears to represent a borderline situation as we now report that $[\text{MnI}_2(\text{PPh}_2\text{Me})_2]$ does not react with O_2 in the solid state, but does in toluene solution to form the 1:1 adduct $[\text{MnI}_2(\text{PPh}_2\text{Me})_2(\text{O}_2)]$. This adduct is stable at *ca.* -40°C , and applying a vacuum causes rapid desorption of the bound O_2 . We find that this absorption/desorption occurs quantitatively over the five cycles examined.

Additionally, we observe that an anhydrous solution of $[\text{MnI}_2(\text{PPh}_2\text{Me})_2(\text{O}_2)]$ in pentane under argon, formed at -40°C , but allowed to warm to room temperature and stand for 2 weeks gradually deposits pale pink crystals of $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ in almost quantitative yield. However, if dioxygen is admitted to a flask containing a pentane solution of $[\text{MnI}_2(\text{PPh}_2\text{Me})_2]$ under ambient conditions, after *ca.* 2 weeks pale yellow crystals of $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$ form in essentially quantitative yield.

These observations thus confirm earlier studies which indicate that when O_2 is co-ordinated to $[\text{MnX}_2(\text{phosphine})]$ complexes it is activated. Thus, we have previously isolated $[\text{MnI}_2(\text{OPBu}^n)_3]$ from a $[\text{MnI}_2(\text{PBu}^n)_3(\text{O}_2)]$ solution in tetrahydrofuran¹⁰ and under very low concentrations of dioxygen have isolated such species as $[\text{Mn}_4\text{I}_6(\mu_4\text{-O})(\text{PPr}^n)_4]$ formed by O=O bond cleavage.¹⁶

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

We have also reported the reaction of $[\text{MnI}_2(\text{PMe}_3)]$ with both trace and atmospheric levels of molecular oxygen. At atmospheric levels of dioxygen the manganese(III) complex $[\text{MnI}_3(\text{PMe}_3)_2]$ is formed. However, when the dioxygen concentration is low (< 100 ppm) the unusual mixed-oxidation-state dinuclear complex $[\text{Mn}_2\text{I}_5(\text{PMe}_3)_3] \cdot \text{PMe}_3$ is formed.¹⁷

Crystal-structure Determinations.—Fig. 1 shows the crystal structure of $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ together with the atom labelling used in the list of selected bond parameters (Table 1). The molecule consists of a distorted-tetrahedral arrangement of ligands about the manganese(II) centre with P–Mn–O and I–Mn–I bond angles of 97.3 and 117.7° respectively. The phosphine oxide is co-ordinated to the metal

centre *via* the oxygen atom to give Mn–O and P–O bond lengths of 1.99 and 1.47 Å, respectively, with a bond angle of 150.9° at the oxygen atom.

The phosphine ligand is co-ordinated *via* the phosphorus atom giving an Mn–P bond length of 2.601 Å and I–Mn–P bond angles of 104.3 and 113.9°. These and other bond parameters are within the range observed for other pseudo-tetrahedral manganese(II)–tertiary phosphine complexes.^{13,14}

The molecular structure together with the atom labelling scheme for $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$ is shown in Fig. 2. The molecule is a distorted-tetrahedral monomer with the manganese atom co-ordinated to the two terminal iodide atoms and the oxygen atoms of the two methyldiphenylphosphine oxide ligands. The bond angles at the manganese centre lie in the

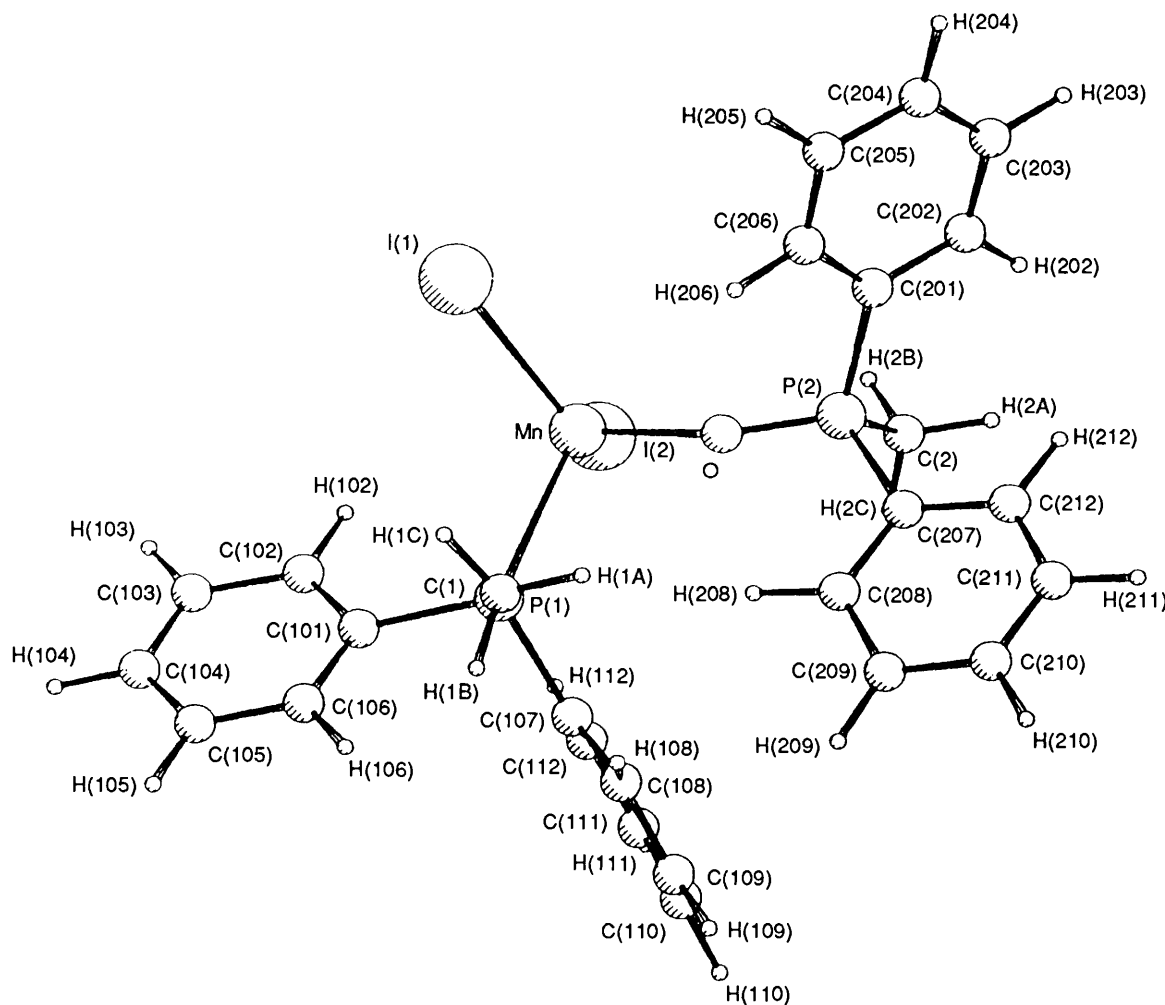


Fig. 1 The molecular structure of $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ showing the crystallographic numbering scheme

Table 1 Selected bond lengths (Å) and angles (°) for the complex $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$

Mn–I(1)	2.654(3)	P(1)–C(101)	1.80(2)
Mn–I(2)	2.634(3)	P(1)–C(107)	1.82(2)
Mn–P(1)	2.601(5)	P(2)–O	1.47(1)
Mn–O	1.99(1)	P(2)–C(2)	1.82(2)
P(1)–C(1)	1.80(2)	P(2)–C(201)	1.78(2)
I(1)–Mn–I(2)	117.7(1)	I(2)–Mn–O	112.6(3)
I(1)–Mn–P(1)	104.3(1)	P(1)–Mn–O	97.3(4)
I(2)–Mn–P(1)	113.9(1)	Mn–O–P(2)	150.9(7)
I(1)–Mn–O	109.0(3)		

Table 2 Selected bond lengths (Å) and angles (°) for the complex $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$

Mn–I(1)	2.679(1)	P(1)–C(1)	1.77(1)
Mn–I(2)	2.677(1)	P(1)–C(7)	1.781(9)
Mn–O(1)	1.996(7)	P(1)–C(13)	1.80(1)
Mn–O(2)	2.009(7)	P(2)–C(14)	1.79(1)
P(1)–O(1)	1.503(8)	P(2)–C(20)	1.793(9)
P(2)–O(2)	1.499(7)	P(2)–C(26)	1.80(1)
I(2)–Mn–I(1)	113.4(1)	O(2)–Mn–I(2)	111.1(2)
O(1)–Mn–I(1)	113.1(2)	O(2)–Mn–I(1)	109.6(2)
O(1)–Mn–I(2)	109.0(2)	O(2)–Mn–O(1)	100.0(3)

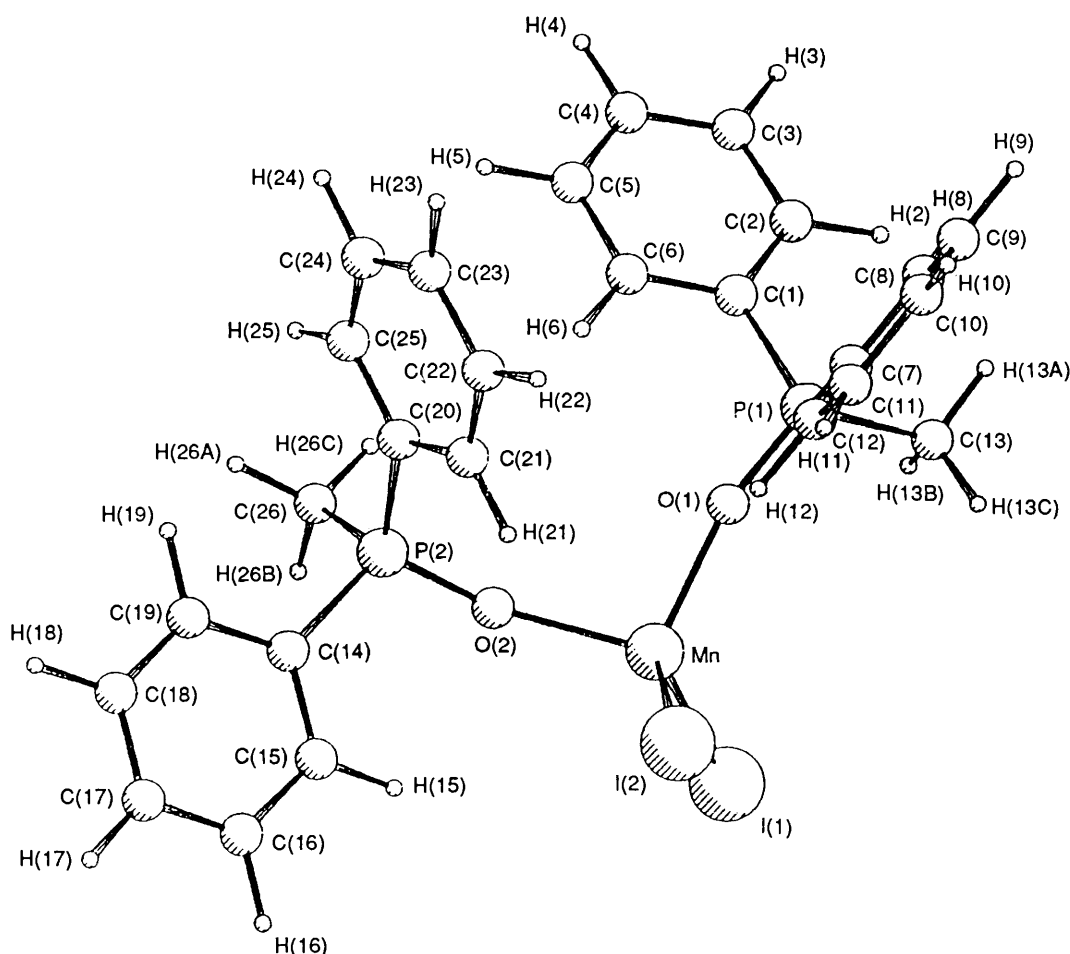


Fig. 2 The molecular structure of $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$ showing the crystallographic numbering scheme

Table 3 Crystal data and details of refinement

Formula	$\text{C}_{26}\text{H}_{26}\text{I}_2\text{MnOP}_2$	$\text{C}_{26}\text{H}_{26}\text{I}_2\text{MnO}_2\text{P}_2$
<i>M</i>	725.19	741.19
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
<i>a</i> /Å	16.568(6)	10.552(4)
<i>b</i> /Å	18.728(6)	12.832(2)
<i>c</i> /Å	9.343(3)	11.129(3)
β /°	102.04(4)	92.92(3)
<i>U</i> /Å ³	2835	1505
<i>Z</i>	4	2
<i>D_c</i> /g cm ⁻³	1.70	1.64
<i>F</i> (000)	1404	718
μ /cm ⁻¹	25.88	24.41
Scan speed/° min ⁻¹	1–5	4–10
Scan range/°	$0.85 + 0.35 \tan \theta$	$2.0 + \alpha_1 - \alpha_2$
Crystal size/mm	$0.3 \times 0.2 \times 0.2$	$0.3 \times 0.3 \times 0.2$
Maximum 2θ /°	50	50
Total data measured	6748	3469
No. of unique reflections	2877	3203
No. of observed reflections [$F_o > 3\sigma(F_o)$]	1763	2614
No. of parameters	291	300
$\rho_{\text{min}}, \rho_{\text{max}}$ /e Å ⁻³	–0.7, 1.2	–0.5, 0.6
Maximum least-squares shift-to-error ratio	0.06	0.1
Weighting scheme parameter <i>g</i> in $w = 1/[\sigma^2(F) + gF^2]$	0.0006	0.0002

range 100.0–113.4° (Table 2). The Mn–O bond distances are 1.996 and 2.009 Å, which is comparable to 1.99 Å found for $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$. The Mn–I bond lengths are 2.677 and 2.679 Å.

Experimental

All materials were handled under an argon atmosphere in a glove box. $[\text{MnI}_2(\text{PPh}_2\text{Me})_2]$ was prepared by stirring a mixture of pre-dried MnI_2 (1.2 g, 3.9 mmol) and PPh_2Me (1.6 g,

Table 4 Fractional atomic coordinates for non-hydrogen atoms in $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$

Atom	x	y	z
Mn	0.254 8(2)	0.432 2(1)	0.732 4(3)
I(1)	0.365 2(1)	0.476 43(6)	0.963 4(1)
I(2)	0.158 8(1)	0.529 04(8)	0.578 3(2)
P(1)	0.174 8(3)	0.331 2(2)	0.834 3(4)
P(2)	0.342 5(3)	0.358 5(2)	0.475 3(4)
C(1)	0.244(1)	0.262 3(9)	0.922(2)
C(101)	0.119(1)	0.355 8(8)	0.973(2)
C(102)	0.110(1)	0.425(1)	1.005(2)
C(103)	0.069(1)	0.447(1)	1.116(2)
C(104)	0.037(1)	0.396(1)	1.192(2)
C(105)	0.048(2)	0.326(1)	1.160(2)
C(106)	0.089(1)	0.306(1)	1.051(2)
C(107)	0.097(1)	0.285 9(9)	0.698(2)
C(108)	0.099(2)	0.213(1)	0.671(2)
C(109)	0.037(2)	0.181(1)	0.567(2)
C(110)	-0.025(1)	0.222 4(9)	0.488(2)
C(111)	-0.025(2)	0.296 2(9)	0.509(2)
C(112)	0.037(1)	0.324 8(9)	0.612(2)
O	0.310 9(8)	0.370 6(6)	0.609(1)
C(2)	0.282(1)	0.404 7(9)	0.318(2)
C(201)	0.448(1)	0.384 1(7)	0.501(2)
C(202)	0.483(1)	0.408(1)	0.388(2)
C(203)	0.567(1)	0.422(1)	0.411(2)
C(204)	0.615(1)	0.413(1)	0.550(2)
C(205)	0.578(1)	0.393(1)	0.665(2)
C(206)	0.499(1)	0.374 7(9)	0.640(2)
C(207)	0.334 0(9)	0.263 9(8)	0.434(1)
C(208)	0.287(1)	0.223(1)	0.508(2)
C(209)	0.271(2)	0.152(1)	0.471(2)
C(210)	0.311(1)	0.123(1)	0.371(2)
C(211)	0.356(1)	0.163(1)	0.300(2)
C(212)	0.370(1)	0.233(8)	0.332(2)

8.0 mmol) in pentane (*ca.* 80 cm³) for 7d in an argon-filled sealed tube. The pale pink product was isolated by standard Schlenk techniques, dried *in vacuo* and stored in argon-filled sealed ampoules (Found: C, 43.7; H, 3.6; I, 36.0; P, 8.7. $\text{C}_{26}\text{H}_{26}\text{I}_2\text{MnP}_2$ requires C, 44.0; H, 3.7; I, 35.8; P, 8.7%).

An anhydrous solution of $[\text{MnI}_2(\text{PPh}_2\text{Me})]$ in pentane was cooled to -40 °C and an argon-O₂ (90:10) mixture admitted while stirring. When the green dioxygen adduct $[\text{MnI}_2(\text{PPh}_2\text{Me})_2(\text{O}_2)]$ was allowed to gradually warm to room temperature and stand for 2 weeks, pale pink crystals of $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ were gradually deposited in almost quantitative yield (Found: C, 43.1; H, 3.7; I, 35.6; P, 8.8. $\text{C}_{26}\text{H}_{26}\text{I}_2\text{MnO}_2\text{P}_2$ requires C, 43.0; H, 3.6; I, 35.0; P, 8.6%). The complex $[\text{MnI}_2(\text{OPPh}_2\text{Me})]$ was prepared by admitting molecular oxygen to a flask containing a pentane solution of $[\text{MnI}_2(\text{PPh}_2\text{Me})_2]$ and allowing to stand at ambient conditions. After 2 weeks, pale yellow crystals of $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$ were observed to have formed.

Crystallography.—A crystal of $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ (0.2 × 0.2 × 0.3 mm) was sealed in a Lindemann tube under argon and the X-ray diffraction data collected on an Enraf-Nonius CAD4 diffractometer using graphite-mo-chromatised Mo-K α radiation ($\lambda = 0.710 69 \text{ \AA}$). 1763 Unique reflections with $F \geq 3\sigma(F)$ were measured and the structure solved by standard heavy-atom techniques followed by blocked-matrix least-squares refinement to give a final $R = 0.065$ ($R' = 0.067$). All non-hydrogen atoms were treated anisotropically and hydrogen atoms constrained to chemically reasonable positions with a common overall isotropic vibration parameter. Computations were carried out on the joint CDC 7600/Amdahl 470 system of the University of Manchester Regional Computing Centre using the SHELX 76 program.¹⁸ Full details of structure refinement are given in Table 3, fixed atomic coordinates in Table 4.

Table 5 Fractional atomic coordinates for non-hydrogen atoms in $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$

Atom	x	y	z
I(1)	0.317 87(6)	0.489 52	0.235 55(7)
I(2)	0.705 71(6)	0.347 95(7)	0.238 25(8)
Mn	0.566 9(1)	0.516 4(1)	0.284 8(1)
P(1)	0.670 3(2)	0.724 6(3)	0.115 6(2)
O(1)	0.637 5(7)	0.639 1(6)	0.200 6(7)
C(1)	0.687 8(9)	0.845(1)	0.191 6(9)
C(2)	0.651(1)	0.939(1)	0.140(1)
C(3)	0.670(1)	1.034(1)	0.203(1)
C(4)	0.725(2)	1.033(1)	0.311(2)
C(5)	0.762(2)	0.943(2)	0.363(2)
C(6)	0.743(2)	0.849(1)	0.303(1)
C(7)	0.816 7(8)	0.697 3(9)	0.049 4(8)
C(8)	0.866(1)	0.767(1)	-0.032(1)
C(9)	0.979(1)	0.748(1)	-0.084(1)
C(10)	1.045(1)	0.659(2)	-0.054(1)
C(11)	0.997(1)	0.588(2)	0.026(2)
C(12)	0.882(1)	0.609(1)	0.078(1)
C(13)	0.550 2(9)	0.739(1)	-0.004(1)
P(2)	0.676 8(2)	0.590 9(3)	0.566 5(2)
O(2)	0.596 3(6)	0.562 1(6)	0.456 6(6)
C(14)	0.699(1)	0.479(1)	0.660 9(9)
C(15)	0.633(1)	0.392(1)	0.636(1)
C(16)	0.656(2)	0.305(1)	0.711(2)
C(17)	0.740(2)	0.307(2)	0.805(2)
C(18)	0.802(2)	0.395(2)	0.829(2)
C(19)	0.784(2)	0.481(2)	0.758(1)
C(20)	0.829 1(9)	0.641 5(9)	0.532 2(8)
C(21)	0.894 9(9)	0.585(1)	0.449(1)
C(22)	1.011(1)	0.623(1)	0.419(1)
C(23)	1.061(1)	0.712(2)	0.473(2)
C(24)	0.990(2)	0.765(2)	0.554(2)
C(25)	0.876(1)	0.731(1)	0.583(1)
C(26)	0.598(1)	0.688(1)	0.651(1)

The complex $[\text{MnI}_2(\text{OPPh}_2\text{Me})_2]$ was obtained as pale yellow crystals from a pentane solution of $[\text{MnI}_2(\text{PPh}_2\text{Me})_2]$ to which dry dioxygen was added and allowed to stand at room temperature for about 2 weeks. A suitable crystal (0.2 × 0.3 × 0.3 mm) was sealed in a Lindemann tube and X-ray diffraction data collected on a Nicolet R3m/V diffractometer. The unit-cell constants were determined from the setting angles of 25 accurately centred reflections ($8.2 \leq \theta \leq 12.4^\circ$). 3469 Reflections were measured, corrected for Lorentz polarisation and absorption effects and averaged to give 3203 unique reflections of which 2614 with $F \geq 3\sigma(F)$ were used in the refinement. The structure was solved and refined^{19, 21} as for $[\text{MnI}_2(\text{OPPh}_2\text{Me})(\text{PPh}_2\text{Me})]$ to give a final $R = 0.048$ ($R' = 0.037$). Full details of the structure refinement are given in Table 3, final atomic coordinates in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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