The Reaction of Bromo- and Iodo-phosphoranes with Unactivated Coarse Grain Manganese Metal Powder to Yield $[MnI_2(phosphine)_2]$ and $[\{MnX_2(phosphine)\}_n]$ (X = Br or I) by Insertion of Mn into the P–X Bond. The Crystal Structure of $[MnI_2(PPh_3)_2]$†

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The novel reaction of crude manganese metal powder with dibromo- and diiodo-phosphoranes, R_3PX_2, has been studied. Reaction of the phosphoranes R_3PI_2 (R = phenyl or substituted aryl) with manganese allows insertion of the metal into P–X bonds and gives the monomeric tetrahedral complexes $[MnI_2(PR_3)_2]$ and MnI_2. However, reaction of R_3PX_2 (R_3 = mixed aryl/alkyl, trialkyl; X = Br or I) with manganese, whilst once again proceeding *via* insertion into P–X bonds, now leads to the quantitative isolation of the polymeric complexes $[\{MnX_2(PR_3)\}_n]$, thus illustrating the subtle nature of these reactions. Examples of both types of complex have been crystallographically characterised and represent rare examples of such. There is some evidence that where $R_3 = Ph_2Me$ an equilibrium exists and both types of complex, $[MnI_2(PPh_2Me)_2]$ and $[\{MnI_2(PPh_2Me)\}_n]$ can be detected from the same reaction.

The insertion of metallic reagents into carbon–halogen bonds was pioneered in the middle of the nineteenth century by Frankland who produced dialkylzinc complexes from the reaction of alkyl iodides with zinc powder. However, perhaps a more successful example of this type of chemistry has arisen from the work of Grignard at the beginning of this century, equation (1).

$$RX + Mg \longrightarrow RMgX \qquad (1)$$

We have recently begun to develop[1–4] the chemistry of the reactions of crude metal powders with dihalogenophosphoranes which involves the insertion of a metal into a phosphorus–halogen bond, equation (2). This type of reaction may be seen

$$\text{‘P–X’} + M \longrightarrow \text{‘P–M–X’} \qquad (2)$$

as an inorganic analogue of the Grignard reaction.

Here we wish to report our studies involving unactivated manganese powder with a range of dibromo- and diiodo-phosphoranes, preliminary reports of which have been published.[1,2]

In 1979 we[5] first reported the synthesis of polymeric $[MnX_2(PR_3)]$ complexes (X = Cl, Br, I or NCS; PR_3 = tertiary alkyl- or aryl-phosphine). The remarkable ability of these complexes to bind molecular oxygen as well as other small molecules was also communicated in subsequent reports.[6] The first crystallographically characterised complex of this stoichiometry $[MnI_2(PPhMe_2)]$ was reported in 1984 by King and co-workers.[7] The structure consists of a polymeric chain of MnI_2 with alternating tetrahedral (MnI_4) and pseudo-octahedral (*trans*-MnI_4P_2) units (the 6,4,6,4 structure). A further example of a crystallographically characterised complex of stoichiometry $[MnX_2(phosphine)]$ is the dimeric pseudo-tetrahedral $[\{Mn(CH_2SiMe_3)_2(PMe_3)\}_2]$ complex synthesised by Wilkinson and co-workers.[8]

In addition to the complexes of stoichiometry $MnX_2(PR_3)$, a second type of manganese(II) phosphine complex has been recognised which has the stoichiometry $[MnI_2(PR_3)_2]$. These compounds may be isolated from diethyl ether solutions of $[MnI_2(PR_3)]$ complexes upon the addition of a further mole equivalent of PR_3. The only crystallographically characterised example of a complex of this type was reported in 1984 by Kohler and co-workers[9] who characterised $[MnI_2(PEt_3)_2]$ which they synthesised from the direct reaction of anhydrous MnI_2 and an excess of PEt_3.

Despite the emphasis placed on the solvent dependence of the reaction and the need for strictly anhydrous and oxygen-free conditions, confusion has been generated by the difficulties encountered when other workers attempted to repeat the work.[10,11] However, further complexes of manganese(II) tertiary phosphines have subsequently been crystallographically characterised.[12–14] Nevertheless, in view of these difficulties encountered by other workers, an alternative method for synthesising $[MnX_2(PR_3)]$ (X = Br or I) and $[MnI_2(PR_3)_2]$ complexes is highly desirable.

We have recently reported the novel reaction of unactivated coarse grain metal powders with phosphoranes of stoichiometry R_3PX_2 (X = Br or I). We have found that this is a general synthetic route for the production of transition-metal[1–3] and main-group[4] metal phosphine complexes. Furthermore not only has this method of synthesis yielded known complexes but also novel isomers of existing complexes[1] and complexes in rare oxidation states.[1,2]

Results and Discussion

Reactions with Triarylphosphoranes.—Following our preliminary reports concerning $[MnI_2(PPhMe_2)]$,[1] $[MnI_2(PMe_3)]$ and $[Mn_2I_5(PMe_3)_3]{\cdot}PMe_3$[2] we now report an extensive study of the reaction of unactivated manganese metal powder with

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

Table 1 Analytical data for the complexes $[MnI_2(PR_3)_2]$ (R = aryl)

			Analytical data[a] (%)		
Compound	Colour	M.p./°C	C	H	I
$[MnI_2(PPh_3)_2]$	Pink	238	50.1 (51.9)	3.5 (3.6)	30.6 (30.5)
$[MnI_2\{PPh_2(C_6H_4Me\text{-}2)\}_2]$	Pink	225	52.0 (53.0)	4.0 (3.9)	28.6 (29.5)
$[MnI_2\{PPh_2(C_6H_4Me\text{-}3)\}_2]$	Pink	211	53.1 (53.0)	3.9 (3.9)	29.1 (29.5)
$[MnI_2\{PPh_2(C_6H_4Me\text{-}4)\}_2]$	Pink	198	53.1 (53.0)	3.7 (3.9)	29.4 (29.5)
$[MnI_2\{P(C_6H_4F\text{-}4)_3\}_2]$	Orange	172	47.7 (48.7)	5.4 (2.7)	30.6 (28.6)
$[MnI_2\{P(C_6H_4Cl\text{-}4)_3\}_2]$	Orange	189	40.1 (41.5)	2.2 (2.3)	23.7 (24.4) 20.8 (20.5)[b]
$[MnI_2\{PPh_2(C_6H_4SMe\text{-}4)\}_2]$	Pink	166	49.0 (49.3)	3.7 (3.7)	28.0 (27.5)

[a] Required values are given in parentheses. [b] For Cl.

Table 2 Selected bond lengths (Å) and angles (°) in the complex $[MnI_2(PPh_3)_2]$

I(1)–Mn	2.670(6)	I(1)–Mn–I(2)	118.2(2)
I(2)–Mn	2.638(6)	I(1)–Mn–P(1)	108.7(3)
Mn–P(1)	2.75(2)	I(1)–Mn–P(2)	111.6(3)
Mn–P(2)	2.74(1)	I(2)–Mn–P(1)	109.4(3)
P(1)–C(1)	1.79(4)	I(2)–Mn–P(2)	104.3(3)
P(1)–C(7)	1.82(3)	P(1)–Mn–P(2)	103.5(4)
P(1)–C(13)	1.65(4)	Mn–P(1)–C(1)	114(1)
P(2)–C(19)	1.72(3)	Mn–P(2)–C(19)	111(1)
P(2)–C(25)	1.67(4)	C(1)–P(1)–C(7)	102(2)
P(2)–C(31)	1.77(3)	C(19)–P(2)–C(25)	106(2)

dibromo- and diiodo-phosphoranes. Two reaction schemes have been identified both giving quantitative yields of different products. The nature of these products, *i.e.* which reaction scheme is followed, is determined by the nature of the R and X groups on the phosphorane.

In the case of the reaction of Mn with the phosphoranes R_3PI_2 (R = phenyl or substituted aryl) reaction scheme 1, equation (3), gives $[MnI_2(PR_3)_2]$.

$$2R_3PI_2 + 2Mn \longrightarrow \underset{\mathbf{I}}{[MnI_2(PR_3)_2]} + MnI_2 \qquad (3)$$

The lower solubility of the $[MnI_2(PR_3)_2]$ species compared with MnI_2 in diethyl ether means that careful removal of solvent in an inert atmosphere leads to an almost quantitative yield of **I**. Almost pure MnI_2 may be isolated by removal of the remaining solvent, although it is difficult to isolate a sample of MnI_2 without trace contamination from $[MnI_2(PR_3)_2]$, and pure MnI_2 was only isolated for the reaction of Ph_3PI_2 with Mn.

Analytical data for the complexes $[MnI_2(PR_3)_2]$ are shown in Table 1. In the case of the reaction Ph_3PI_2 + Mn, careful removal of the solvent under vacuum yielded a pale pink microcrystalline product. Recrystallisation of this product from diethyl ether yielded pale pink block crystals suitable for single-crystal X-ray analysis. The structure of $[MnI_2(PPh_3)_2]$ is shown in Fig. 1. The complex exists as a monomeric tetrahedral species, and the bond lengths and angles, Table 2, are similar to those reported for $[MnI_2(PEt_3)_2]$ by Kohler and co-workers.[9] The only exception to this is the considerably longer Mn–P bond lengths for $[MnI_2(PPh_3)_2]$ compared to $[MnI_2(PEt_3)_2]$ [2.75(2) and 2.74(1) compared to 2.53(4) and 2.54(4) Å]. The notable differences in these bond lengths are probably due to two factors, namely the reduced basicity of PPh_3 compared to PEt_3 and also the greater steric bulk of the PPh_3 ligand, both factors combining to weaken considerably the Mn–P bond. Fractional atomic coordinates for the non-hydrogen atoms of $[MnI_2(PPh_3)_2]$ are displayed in Table 3. This structure represents only the second example of a compound of this stoichiometry to be crystallographically characterised.

Although equation (3) obtains for the diiodophosphoranes the subtlety of this type of synthesis is illustrated by the reaction of Ph_3PBr_2 with Mn. This, surprisingly, does not yield the bis(phosphine) complex; instead polymeric $[MnBr_2(PPh_3)]$ is produced, Table 4.

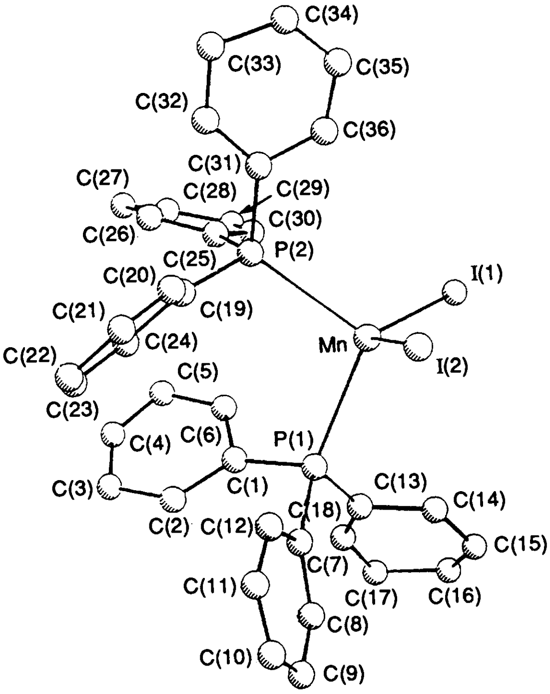

Fig. 1 The X-ray crystal structure of $[MnI_2(PPh_3)_2]$. Hydrogen atoms are omitted for clarity

Reactions with Other Phosphoranes.—Interestingly, when X = Br or I and R = mixed aryl/alkyl or trialkyl, no evidence for the formation of the complexes $[MnX_2(PR_3)_2]$ is observed; instead the highly oxygen-sensitive $[MnX_2(PR_3)]$ complexes are obtained in quantitative yield, reaction scheme 2, equation (4) (X = I, $R_3 \neq (aryl)_3$; X = Br, R_3 = trialkyl, mixed alkyl/aryl or triphenyl).

$$R_3PX_2 + Mn \xrightarrow[Et_2O]{N_2, 3\,d} [MnX_2(PR_3)] \qquad (4)$$

The products from these reactions are listed in Table 4 together with analytical data. As has previously been reported,[6,15] upon exposure to dioxygen, the intensely coloured dioxygen adducts $[MnX_2(PR_3)(O_2)]$ are formed. Where R ≠ Me, the dioxygen is reversibly bound and is lost by the application of a vacuum. Where R = Me, metal oxidation occurs to form the manganese(III) complex $[MnX_3(PMe_3)_2]$.[16] The intense colouration of these $[MnX_2(PR_3)(O_2)]$ adducts means that they may be characterised by their distinctive electronic spectra. The electronic transitions, together with the

Table 3 Fractional atomic coordinates for the non-hydrogen atoms in $[MnI_2(PPh_3)_2]$

Atom	*x*	*y*	*z*
I(1)	0.8431(2)	0.8212(3)	0.4302(2)
I(2)	0.5961(2)	0.7524(3)	0.3881(2)
Mn	0.7337(2)	0.6595(6)	0.4295(3)
P(1)	0.7734(6)	0.546(1)	0.5718(8)
P(2)	0.7207(5)	0.453(1)	0.3331(6)
C(1)	0.814(2)	0.388(4)	0.578(2)
C(2)	0.787(2)	0.274(5)	0.603(2)
C(3)	0.818(3)	0.146(4)	0.600(2)
C(4)	0.869(3)	0.145(4)	0.568(2)
C(5)	0.902(2)	0.240(5)	0.541(2)
C(6)	0.870(2)	0.363(4)	0.547(2)
C(7)	0.703(2)	0.518(3)	0.614(2)
C(8)	0.713(2)	0.532(3)	0.693(2)
C(9)	0.653(2)	0.514(3)	0.720(2)
C(10)	0.587(2)	0.471(4)	0.666(3)
C(11)	0.577(2)	0.451(4)	0.594(2)
C(12)	0.630(2)	0.473(3)	0.564(2)
C(13)	0.837(2)	0.622(4)	0.644(3)
C(14)	0.840(2)	0.761(5)	0.653(2)
C(15)	0.884(2)	0.835(4)	0.714(3)
C(16)	0.944(2)	0.780(4)	0.766(2)
C(17)	0.956(2)	0.637(5)	0.770(2)
C(18)	0.900(2)	0.581(3)	0.704(3)
C(19)	0.664(2)	0.335(4)	0.348(2)
C(20)	0.584(2)	0.334(4)	0.315(2)
C(21)	0.538(2)	0.255(5)	0.333(2)
C(22)	0.566(2)	0.150(4)	0.385(2)
C(23)	0.641(2)	0.136(3)	0.420(2)
C(24)	0.688(2)	0.225(4)	0.403(2)
C(25)	0.800(2)	0.377(4)	0.339(2)
C(26)	0.814(2)	0.253(5)	0.323(2)
C(27)	0.884(3)	0.187(4)	0.332(2)
C(28)	0.947(3)	0.260(6)	0.361(2)
C(29)	0.940(3)	0.387(5)	0.377(2)
C(30)	0.866(3)	0.437(3)	0.363(2)
C(31)	0.677(2)	0.483(3)	0.234(2)
C(32)	0.642(2)	0.397(3)	0.176(2)
C(33)	0.608(2)	0.419(4)	0.097(3)
C(34)	0.608(2)	0.553(4)	0.077(2)
C(35)	0.641(2)	0.639(3)	0.129(2)
C(36)	0.670(2)	0.607(4)	0.203(3)

Table 4 Analytical data for the complexes $[MnX_2(PR_3)]$ (X = Br or I, R_3 = trialkyl or mixed alkyl/aryl)

		Analytical data (%)		
Compound	Colour	C	H	Br
$[MnBr_2(PPh_3)]$	White	44.7 (45.3)	3.0 (3.1)	33.2 (33.5)
$[MnBr_2(PPhMe_2)]$	White	26.6 (27.2)	3.0 (3.1)	45.3 (45.3)
$[MnBr_2(PBu_3)]$	White	34.4 (34.5)	6.4 (6.5)	37.1 (38.4)
$[MnBr_2(PPr_3)]$	White	28.8 (28.8)	5.6 (5.6)	44.3 (42.7)
$[MnBr_2(PEt_3)]$	White	21.3 (21.6)	4.2 (4.5)	49.4 (48.0)
$[MnBr_2(PMe_3)]$	White	14.7 (16.1)	3.8 (4.0)	54.8 (55.0)
$[MnI_2(PPhMe_2)]$	Pink	21.2 (21.5)	2.7 (2.5)	51.5 (51.3)
$[MnI_2(PBu_3)]$	Pink	30.0 (28.2)	2.0 (5.3)	51.5 (49.7)
$[MnI_2(PPr_3)]$	Orange	24.5 (23.0)	4.6 (4.5)	53.0 (54.1)
$[MnI_2(PEt_3)]$	Pink	16.8 (16.9)	3.2 (3.5)	59.2 (59.5)
$[MnI_2(PMe_3)]$	Pale pink	9.6 (9.4)	2.5 (2.3)	68.2 (66.0)

* Required values are given in parentheses.

absorption coefficient maxima, for the adducts $[MnBr_2(PR_3)(O_2)]$ are displayed in Table 5. Unfortunately the corresponding iodo complexes decomposed with such rapidity at room temperature that an accurate determination of their absorption coefficients was not possible. However, the spectra were recorded at arbitrary concentration and the band positions in the visible spectra are displayed in Table 5.

We have previously reported[2] a preliminary study into the interaction of $[MnI_2(PMe_3)]$ with molecular oxygen at trace (< 100 ppm) and atmospheric levels. At trace levels of dioxygen, the mixed oxidation state complex $[I_2(Me_3P)_2Mn^{II}–I–Mn^{III}(PMe_3)I_2]·PMe_3$ was formed, together with MnI_2,[2] thus giving an insight into how fracture of the polymer chain of $[MnI_2(PMe_3)]$ upon exposure to dioxygen might occur. Exposure of this intermediate complex, or unreacted $[MnI_2(PMe_3)]$ to atmospheric levels of dioxygen results[2] in the formation of the manganese(III) complex $[MnI_3(PMe_3)_2]$, first reported by Minten and co-workers.[16]

In contrast, the complexes $[MnX_2(PR_3)]$ (R ≠ Me) form adducts with dioxygen in which it is reversibly bound, $[MnX_2(PR_3)(O_2)]$. These dioxygen adducts all exhibit similar features in the electronic spectrum, the intense colour being halide dependent. Thus the adducts $[MnBr_2(PR_3)(O_2)]$ are blue whereas the adducts $[MnI_2(PR_3)(O_2)]$ are green. All the spectra exhibit two peaks in the visible region of the electronic spectrum, *viz.* a sharp spike at shorter wavelengths and a much broader peak at longer wavelengths. The nature of the complexes $[MnX_2(PR_3)(O_2)]$ has been the subject of a number of previous studies[6] and although their preparation directly from metallic manganese has not been reported prior to the work presented, the aim in this study was to establish the complexes $[MnX_2(PR_3)(O_2)]$ reported here to be identical to those previously reported. A comparison of the electronic spectral data of the complexes reported here, Table 5, and those previously reported by McAuliffe *et al.*[15] shows excellent agreement.

The X-ray crystal structures of the complexes $[MnI_2(PMe_3)]$ and $[MnI_2(PPhMe_2)]$ formed directly from the reaction of manganese metal and phosphorane have been reported in preliminary communications.[1,2] A schematic representation of both structures is shown in Figs. 2 and 3. Clearly two isomeric forms of complexes of stoichiometry $[MnX_2(PR_3)]$ are available *via* this new synthetic route: $[MnI_2(PPhMe_2)]$, Fig. 3, consists of an infinite chain of MnI_2 onto which one tertiary phosphine ligand is syndiotactically bound to each manganese, creating a trigonal-bipyramidal geometry at the manganese centre. This complex is interesting for two reasons. First, complexes which contain manganese in a trigonal-bipyramidal geometry are rare, especially with monodentate ligands, and few examples have been crystallographically characterised.[17–21] Secondly, and more importantly, a complex of this stoichiometry, $[MnI_2(PPhMe_2]$, has previously been crystallographically characterised.[7] This complex, synthesised by Minten and co-workers,[7] was prepared from the stoichiometric reaction of anhydrous MnI_2 and dimethylphenylphosphine. The structure of this complex was shown to be an infinite ribbon of MnI_2 with alternating tetrahedral (MnI_4) and pseudo-octahedral (*trans*-MnI_4P_2) units (the 6,4,6,4 structure), *i.e.* a different isomeric form of the complex described here (the 5,5,5,5 structure) which was prepared directly from manganese metal.[1] Reinvestigation of the reaction of MnI_2 with $PPhMe_2$ first described by Minten[7] has revealed, from unit-cell measurements, that the 6,4,6,4 structure is invariably formed. Therefore the synthesis of the novel 5,5,5,5 structure must arise from the new synthetic route of treating metal powder with the diiodophosphorane.

In contrast, however, the structure of $[MnI_2(PMe_3)]$, Fig. 2, which was prepared from the direct reaction of equimolar quantities of Me_3PI_2 and manganese metal powder[2] adopts the 6,4,6,4 structure previously exemplified by the isomer of $[MnI_2(PPhMe_2)]$ which was prepared from the metal salt.[7] The reason for this is unclear, but it illustrates that both types of isomer are available from this new synthetic route.

The synthesis of the complexes $[MnX_2(PR_3)]$ directly from metallic manganese illustrates the self assembling nature of the manganese halide chain, since both the phosphoranes and metallic manganese are discrete species. Presumably, discrete molecules of MnI_2 form in solution which then link to form the polymeric MnI_2 ribbon, and conceivably the tertiary phosphine ligands could co-ordinate to the manganese during the polymer

Table 5 Band positions (λ/nm) with absorption coefficients (ε/dm³ mol⁻¹ cm⁻¹) in parentheses of the dioxygenated products of the $[MnX_2(PR_3)]$ complexes (X = Br or I)

Product	Band 1	Band 2	Band 3
$[MnBr_2(PPhMe_2)(O_2)]$	543 (3.19×10^3)	413	—
$[MnBr_2(PBu_3)(O_2)]$	574 (1.72×10^4)	419	—
$[MnBr_2(PPr_3)(O_2)]$	607 (1.89×10^4)	418	—
$[MnBr_2(PEt_3)(O_2)]$	562 (2.11×10^4)	412	—
$[MnBr_2(PMe_3) + O_2]$	607 (sh)	514 (1.91×10^5)	407
$[MnI_2(PPh_2Me)(O_2)]$*	630	460	—
$[MnI_2(PPhMe_2)(O_2)]$	626	458	—
$[MnI_2(PBu_3)(O_2)]$	652	464	—
$[MnI_2(PPr_3)(O_2)]$	641	459	—
$[MnI_2(PEt_3)(O_2)]$	629	457	—
$[MnI_2(PEt_2Me)(O_2)]$	620	456	—
$[MnI_2(PMe_3) + O_2]$	696	578 (1.47×10^5)	450

* Not isolated, see text.

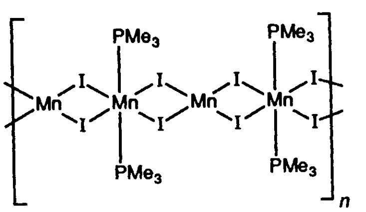

Fig. 2 Schematic representation of a section of the polymer chain of $[MnI_2(PMe_3)]$, the 6,4,6,4 structure

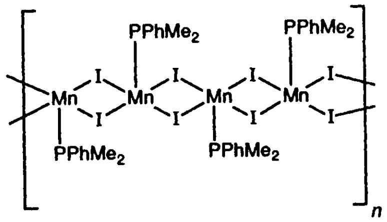

Fig. 3 Schematic representation of a section of the polymer chain of $[MnI_2(PPhMe_2)]$, the 5,5,5,5 structure

assembling process. This provides a speculative explanation why the $[MnI_2(PPhMe_2)]$ complex prepared here has the five-co-ordinate 5,5,5,5 structure rather than the previously characterised 6,4,6,4 structure of $[MnI_2(PPhMe_2)]$ synthesised from the reaction of tertiary phosphine with anhydrous MnI_2 which contains the manganese iodide polymeric chain already assembled. The presence of this 'ready assembled' polymer chain of MnI_2 at the start of the reaction means that the reaction of MnI_2 and PR_3 and the reaction of R_3PI_2 and Mn cannot proceed by the same mechanism. However, exposure of both isomers of $[MnI_2(PPhMe_2)]$ in diethyl ether solution to atmospheric levels of dry dioxygen resulted in identical electronic spectra for the dioxygen adducts,[4,5] $[MnI_2(PPhMe_2)(O_2)]$, indicating no significant difference in the nature of dioxygen binding to either isomer.

There is some evidence that the reaction of 1 equivalent of diiodomethyldiphenylphosphorane, Ph_2MePI_2, with manganese produces both the monomeric tetrahedral complex $[MnI_2(PPh_2Me)_2]$ and the polymeric complex $[MnI_2(PPh_2Me)]$ *i.e.* products from both reaction schemes [equations (3) and (4)]. A pink crystalline solid was isolated from this reaction in poor yield (*ca.* 15% based on the weight of manganese) {Found: C, 42.8; H, 3.6. $[MnI_2(PPh_2Me)_2]$ requires C, 44.0; H, 3.7%)}. However, exposure of the filtrate from the reaction to dioxygen indicated the presence of the polymeric complex $[MnI_2(PPh_2Me)(O_2)]$, Table 5. These results suggest that for the reaction of Ph_2MePI_2 with manganese an equilibrium is set up and both types of complex are formed [equation (5)], by

$$3Ph_2MePI_2 + 3Mn \longrightarrow [MnI_2(PPh_2Me)_2] + [MnI_2(PPh_2Me)] + MnI_2 \quad (5)$$

analogy to reaction scheme 1, the equation being balanced by the formation of MnI_2; however, this was not isolated.

Conclusion

The reaction of manganese metal powder with dibromo- and diiodo-phosphoranes of stoichiometry R_3PX_2 clearly provides an alternative method for the synthesis of the complexes $[MnI_2(PR_3)_2]$ and $[MnX_2(PR_3)]$ (X = Br or I; R = aryl). An important advantage of using this new reaction route is that the necessity of rigorous drying of the manganese(II) salts is obviated. Of course, the synthesis of the phosphoranes requires anhydrous conditions but even considering this the technique is more straightforward.

However, synthesis of the complexes $[MnI_2(PR)_2]$ by this reaction route is, in fact, problematical. Separation of the complex $[MnI_2(PR_3)_2]$ from an equimolar quantity of MnI_2 in diethyl ether is not easy and complete separation of the two products can be difficult and rather time-consuming. The reasons for this are, first, the similar solubilities of the two products and, secondly, the great moisture sensitivity of the two components. Nevertheless, isolation of a sufficient quantity of the pure complex $[MnI_2(PR_3)_2]$ for characterisation is easily achieved by removal of approximately half of the solvent from which uncontaminated $[MnI_2(PR_3)_2]$ can then be obtained. Removal of more solvent tends to lead to the precipitation of some MnI_2.

Synthesis of the polymeric complexes $[MnX_2(PR_3)]$ by the direct reaction of manganese metal powder and phosphorane, R_3PX_2, provides an excellent, even favourable, alternative synthetic route. Reaction times are faster (typically 3–4 d) than using normal methods *viz.* the reaction of anhydrous MnX_2 with tertiary phosphine (which typically takes two weeks and involves the prior drying of the salt), and yields the manganese complex $[MnX_2(PR_3)]$ in quantitative yield. The fact that the novel isomer of $[MnI_2(PPhMe_2)]$ is accessible from this new reaction route suggests that the products from this reaction may be novel in some cases. Isolation of $[MnI_2(PPh_2Me)_2]$ and detection of $[MnI_2(PPh_2Me)]$ from the same reaction vessel in the reaction Mn + Ph_2MePI_2 indicates that where $R_3 = Ph_2Me$ an equilibrium exists and the products from both reaction schemes [equations (3) and (4)] (see above) can be observed.

Experimental

For the successful synthesis of all the manganese phosphine complexes described here it is essential that strictly anaerobic

Table 6 Crystal data and details of refinement for the complex $[MnI_2(PPh_3)_2]$

Empirical formula	$C_{36}H_{30}I_2MnP_2$
Formula weight	833.33
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
a/Å	19.135(2)
b/Å	10.286(2)
c/Å	18.690(2)
U/Å^3	3425(2)
Z	4
D_c/g cm^{-3}	1.616
F(000)	1628
μ/cm^{-1}	22.69
Crystal size/mm	0.25 × 0.15 × 0.15
Total data measured (θ_{max} = 24°)	5967
No. of unique reflections	5706
No of observed reflections [$F_o > 3\sigma(F_o)$]	957
No. of parameters	190
Minimum, maximum/e Å^{-3}	−0.64, 0.67
Maximum least-squares shift to error ratio	<0.01
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.03
Final R	0.069
Final R'	0.045

and anhydrous conditions are adhered to during synthesis. The synthesis of the phosphoranes R_3PI_2 has been described elsewhere[22] and the bromophosphoranes, R_3PBr_2, are prepared in an analogous manner. Diethyl ether was obtained from BDH, dried over sodium wire for *ca.* 1 d and then distilled over CaH_2 in an inert atmosphere prior to use. The diethyl ether was then distilled directly into the reaction vessel and degassed with a nitrogen sparge. Standard reagent grade coarse-grain manganese metal powder was obtained from Aldrich and used as received. After isolation, any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glove-box.

Synthesis of the Complexes $[MnI_2(PR_3)_2]$.—All the complexes $[MnI_2(PR_3)_2]$ were synthesised in a similar way, the synthesis of $[MnI_2(PPh_3)_2]$ being typical. Diiodotriphenylphosphorane (1.430 g, 2.77 mmol) was dissolved in diethyl ether (*ca.* 100 cm^3) and subsequently manganese powder (0.152 g, 2.77 mmol) was added. After *ca.* 4 d, a small quantity of pale pink solid formed which was isolated by standard Schlenk techniques and dried *in vacuo*. Concentration of the filtrate from the reaction to *ca.* half its original volume resulted in the isolation of more of the complex. Further concentration tends to precipitate some MnI_2. Very careful and gradual reduction in the volume of the filtrate yielded all of the complex $[MnI_2(PPh_3)_2]$. Evaporation of the remaining solvent *in vacuo* yielded MnI_2. The products from the reaction were then transferred to pre-dried argon-filled ampoules which were subsequently sealed in a flame.

Synthesis of the Complexes $[MnX_2(PR_3)]$.—The extreme oxygen sensitivity of the complexes $[MnX_2(PR_3)]$ means that considerable care must be taken in their synthesis and subsequent manipulation to ensure they are not exposed to oxygen or moisture. All the complexes $[MnX_2(PR_3)]$ were synthesised in a similar way, that of $[MnBr_2(PPhMe_2)]$ being typical. Dibromodimethylphenylphosphorane (0.872 g, 2.93 mmol) was dissolved in diethyl ether (*ca.* 100 cm^3) and subsequently manganese powder (0.161 g, 2.93 mmol) was added. After *ca.* 4 d, the resultant white solid was isolated by standard Schlenk techniques and dried *in vacuo*. The dry solid was then transferred to pre-dried argon-filled ampoules which were subsequently sealed in a flame.

Elemental analyses were performed by the analytical laboratory of this department, and the results are displayed in Tables 1 and 4. Electronic spectra were recorded on a Varian Cary 610 spectrophotometer or a Cecil 6000 spectrophotometer.

Single-crystal X-Ray Study.—Crystals of $[MnI_2(PPh_3)_2]$ were sealed under argon in thin-walled glass capillaries. Cell dimensions and intensity data were recorded as previously described[23] using a CAD4 diffractometer. Lorentz and polarisation corrections were applied, but not for absorption. The structure was solved and developed *via* the heavy-atom method and refined by full-matrix least squares. The I, Mn and P atoms were refined anisotropically and the remainder isotropically. Hydrogens were included in idealised positions. Crystal data and experimental details are given in Table 6. Final fractional atomic coordinates for non-hydrogen atoms are given in Table 3.

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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References

1 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1447.

2 S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 483.

3 C. A. McAuliffe, S. M. Godfrey, A. G. Mackie and R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 919.

4 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1992, 944.

5 C. A. McAuliffe, H. Al-Khateeb, M. H. Jones, W. Levason, K. Minten and F. P. McCullough, *J. Chem. Soc., Chem. Commun.*, 1979, 737.

6 C. A. McAuliffe, *J. Mol. Cat.*, 1988, **44**, 35 and refs. therein.

7 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.

8 J. I. Davies, C. G. Howard, A. C. Skapski and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1982, 2025; C. G. Howard, G. Wilkinson, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1983, 2025.

9 N. Hebendanz, F. H. Kohler and G. Muller, *Inorg. Chem.*, 1984, **23**, 3044.

10 R. M. Brown, R. E. Bill, M. L. H. Green, P. D. Grebenck, J. J. Martin-Polo and D. M. P. Mingos, *J. Organomet. Chem.*, 1980, **201**, 437.

11 C. A. McAuliffe, *J. Organomet. Chem.*, 1980, **228**, 255.

12 C. G. Howard, G. S. Girolami, G. Wilkinson, M. Thornton-Pett and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1983, 2631.

13 P. T. Ndifon, Ph.D. Thesis, Victoria University of Manchester, 1989.

14 D. G. Kelly, Ph.D. Thesis, Victoria University of Manchester, 1990.

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

16 B. Beagley, C. A. McAuliffe, K. Minten and R. G. Pritchard, *J. Chem. Soc., Chem. Commun.*, 1984, 658; *J. Chem. Soc., Dalton Trans.*, 1987, 1999.

17 J. Delauney, C. Kappenstein and R. J. Jugel, *J. Chem. Soc., Chem. Commun.*, 1980, 679.

18 F. L. Phillips, F. M. Shreeve and A. C. Skapski, *Acta Crystallogr., Sect. B*, 1976, **32**, 887.

19 P. Stolz and S. Pohl, *Z. Naturforsch., Teil B*, 1988, **43**, 175.

20 M. D. Vaira and F. Mani, *J. Chem. Soc., Dalton Trans.*, 1990, 191.

21 F. Cecconi, C. A. Ghilardi, S. Midollini and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1992, 33.

22 N. Bricklebank, S. M. Godfrey, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and P. J. Kobryn, *J. Chem. Soc., Dalton Trans.*, 1993, 101.

23 S. M. Godfrey, D. G. Kelly, A. G. Mackie, C. A. McAuliffe, R. G. Pritchard and S. M. Watson, *J. Chem. Soc., Chem. Commun.*, 1991, 1163.

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