

The Reaction of Coarse-grain Manganese Powder with Diiodotrimethylphosphorane to Form $[\text{Mn}(\text{PMe}_3)\text{I}_2]_n$, which Reacts with Trace Quantities of Molecular Oxygen to Form the Mixed (+2/+3) Oxidation State Complex $[\text{Mn}_2(\text{PMe}_3)_3\text{I}_5]\text{PMe}_3$

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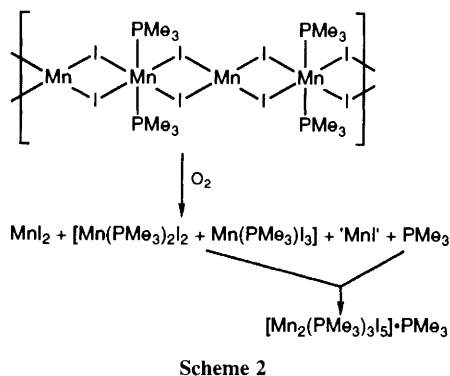
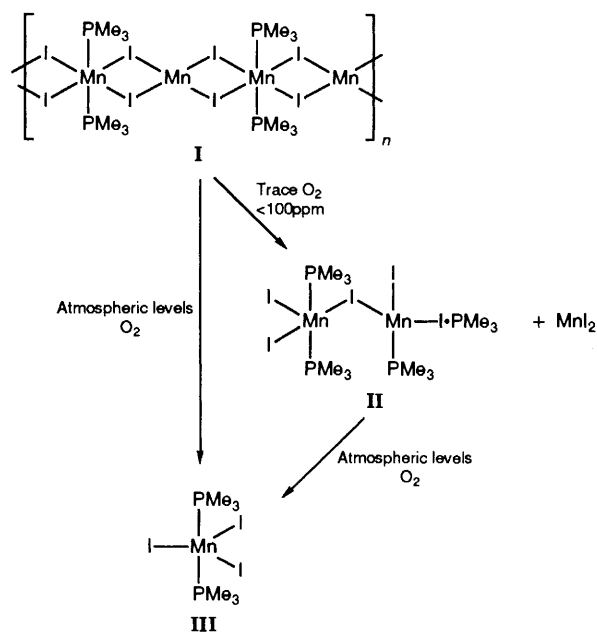
Coarse-grain unactivated manganese powder reacts with Me_3PI_2 in diethyl ether to form the polymeric $[\text{Mn}(\text{PMe}_3)\text{I}_2]_n$ complex, **I**, which reacts with trace quantities of dioxygen to form dinuclear $[\text{Mn}_2(\text{PMe}_3)_3\text{I}_5]\cdot\text{PMe}_3$, **II**, the first mixed oxidation state (+2/+3) manganese complex which contains phosphine ligands; both **I** and **II** react with an excess of dioxygen to form the monomeric $[\text{Mn}(\text{PMe}_3)_2\text{I}_3]$.

We have previously communicated a new synthetic method for transition metal complexes of tertiary phosphines from the reaction of unactivated coarse-grain metal powders with dihalogenophosphoranes.¹

This novel method has now been applied to the reaction of manganese powder with Me_3PI_2 . We chose these reagents because we have previously reported² the synthesis of $\text{Mn}(\text{PMe}_3)\text{I}_2$ from the conventional route: $\text{MnI}_2 + \text{PMe}_3$. This

complex is acutely sensitive to dioxygen, reacting irreversibly to form the monomeric trigonal bipyramidal $\text{Mn}(\text{PMe}_3)_2\text{I}_3$ plus other product(s) which are solely inorganic in nature.²

Coarse-grain (*ca.* 50 μ) manganese powder was reacted with diiodotrimethylphosphorane (1:1 mole ratio) in anhydrous diethyl ether under dry argon in a sealed tube for *ca.* 6 days at room temperature. Subsequently, after several days standing at room temperature, small cubic pale-pink crystals formed, **I**.



A sample of these was removed and then a trace quantity (<100 ppm) of dry dioxygen was admitted. An immediate dark-red colour formed and after *ca.* 4 days dark-red needles appeared, **II**, a sample of which was again removed. Both **I** and **II** have been crystallographically characterised.† Both **I** and **II** have also been exposed to atmospheric levels of a dry dioxygen and both form the trigonal bipyramidal $\text{Mn}(\text{PMe}_3)_2\text{I}_3$, **III**, a complex first synthesised and charac-

† *Crystal data* for **I**, $\text{C}_6\text{H}_{18}\text{I}_4\text{Mn}_2\text{P}_2$, $M = 769.65$, monoclinic, $P2_1/m$, $Z = 4$, $a = 11.001(8)$, $b = 14.108(4)$, $c = 13.443(7)$ Å, $\beta = 103.62(5)^\circ$, $V = 2028(2)$ Å³, $D_c = 2.520$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 7.36$ mm⁻¹. Rigaku AFC6S diffractometer, Mo-K α radiation ($\lambda = 0.71069$ Å) in ω - 2θ scan mode; 2933 reflections recorded ($0 < \theta < 25^\circ$). Lorentz-polarisation and absorption (max., min. transmission 1.15, 0.77) corrections applied. The structure was solved by direct methods and refined by full-matrix least-squares analysis to a final residual $R = 0.035$ for 2671 observed reflections with $I > 2\sigma(I)$.

Crystal data for **II**, $\text{C}_{12}\text{H}_{36}\text{I}_5\text{Mn}_2\text{P}_4$, $M = 1048.71$, orthorhombic, $Pnma$, $Z = 4$, $a = 24.143(8)$, $b = 10.982(7)$, $c = 13.920(9)$ Å, $V = 3691(3)$ Å³, $D_c = 1.887$ Mg m⁻³, $\mu(\text{Mo-K}\alpha) = 4.97$ mm⁻¹. A Rigaku AFC6S diffractometer, Mo-K α radiation ($\lambda = 0.71069$ Å) in ω - 2θ scan mode; 3680 reflections measured ($0 < \theta < 25^\circ$). Lorentz-polarisation, decomposition (4.4%) and absorption (max., min. transmission 1.5, 0.68) were applied. The structure was solved by direct methods and refined by full-matrix least-squares analysis to $R = 0.069$ for 1135 observed reflections with $I > 3\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

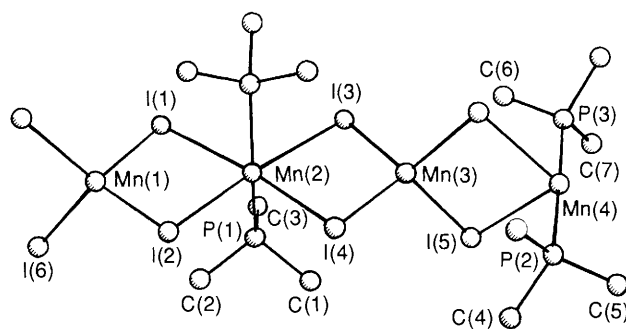


Fig. 1 The structure of part of $[\text{Mn}_2\text{I}_4(\text{PMe}_3)_2]_n$ polymeric chain. Selected interatomic distances (Å) and angles ($^\circ$): I(1)-Mn(1) 2.710(3), I(1)-Mn(2) 3.061(3), I(2)-Mn(1) 2.707(3), I(2)-Mn(2) 2.968(3), I(3)-Mn(2) 3.144(3), I(3)-Mn(3) 2.706(3), I(4)-Mn(3) 2.706(3), I(4)-Mn(2) 2.951(2), I(4)-Mn(3) 2.707(3), I(5)-Mn(3) 2.690(2), I(5)-Mn(4) 2.975(2), I(6)-Mn(1) 2.697(2), I(6)^a-Mn(4) 3.002(2), Mn(2)-P(1) 2.591(2), Mn(4)-P(2) 2.615(4), Mn(4)-P(3) 2.647(4); I(1)-Mn(1)-I(2) 100.97(8), I(1)-Mn(1)-I(6) 111.08(6), I(2)-Mn(1)-I(6) 114.33(6), I(6)-Mn(1)-I(6)^b 105.20(8), I(1)-Mn(2)-I(2) 87.74(7), I(1)-Mn(2)-I(3) 98.27(7), I(1)-Mn(2)-I(4) 173.57(6), I(1)-Mn(2)-P(1) 84.53(7), I(2)-Mn(2)-I(3) 173.99(7), I(2)-Mn(2)-I(4) 85.83(7), I(3)-Mn(2)-I(4) 88.16(7), I(3)-Mn(3)-I(4) 103.22(8), I(3)-Mn(3)-I(5) 112.98(6), I(4)-Mn(3)-I(5) 112.87(6), I(4)-I(5)-Mn(3)-I(5)^b 102.31(8), I(5)-Mn(4)-I(5)^b 89.50(7), I(5)^b-Mn(4)-I(6)^a 178.94(6), I(5)-Mn(4)P(2) 91.10(8), I(5)-Mn(4)-P(3) 88.29(8), I(5)-Mn(4)-I(6)^a 89.70(5), I(6)^c-Mn(4)-I(6)^a 91.08(7). Where ^a signifies $x, y, z + 1$, ^b signifies $x, \frac{1}{2} - y, z$, ^c signifies $x, \frac{1}{2} - y, z + 1$.

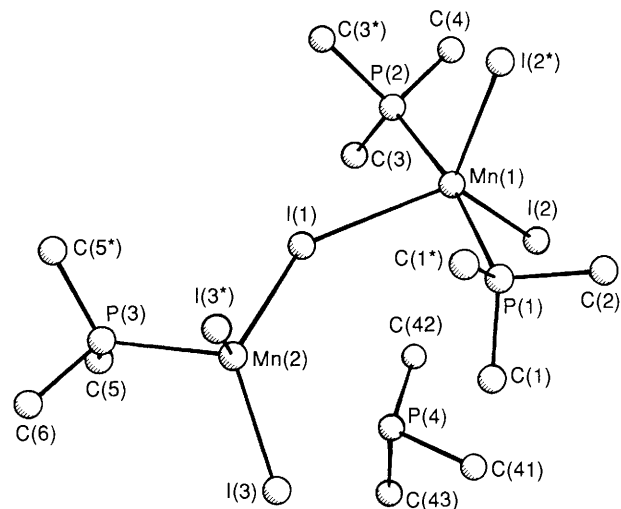


Fig. 2 Structure of $\text{Mn}_2\text{I}_5(\text{PMe}_3)_3$. PMe_3 disordered phosphine of crystallisation carbon atoms have been omitted for clarity: selected interatomic distances (Å) and angles ($^\circ$): I(1)-Mn(1) 2.991(8), I(1)-Mn(2) 2.727(6), I(2)-Mn(1) 2.738(4), I(3)-Mn(2) 2.655(4), Mn(1)-P(1) 2.59(1), Mn(1)-P(2) 2.55(1), Mn(2)-P(3) 2.53(1); Mn(1)-I(1)-Mn(2) 136.0(2), I(1)-Mn(1)-I(2) 120.2(1), I(1)-Mn(1)-P(1) 87.7(3), I(1)-Mn(1)-P(2) 84.5(3), I(2)-Mn(1)-I(2)^d 119.4(3), I(2)-Mn(1)-P(1) 92.5(2), I(2)-Mn(1)-P(2) 92.5(2), I(2)-Mn(1)-P(2) 91.5(2), P(1)-Mn(1)-P(2) 172.1(5), I(1)-Mn(2)-I(3) 114.1(1), I(1)-Mn(2)-P(3) 99.0(3), I(3)-Mn(2)-I(3)^d 116.4(2), I(3)-Mn(2)-P(3) 105.4(2). Where ^d denotes $x, \frac{3}{2} - y, z$.

terised by Minten and coworkers;² we observe identical electronic spectra for Minten's compound² and **III**.

Compound **I** is shown by X-ray crystallography to be a mirror-symmetric polymer $[\text{Mn}(\text{PMe}_3)_2\text{I}_2]_n$, and to have a $[6,4,6,4]_n$ structure, Fig. 1, such a structure having only one precedent, *viz.* the $[6,4,6,4]_n$ structure of $[\text{Mn}(\text{PPhMe}_2)_2\text{I}_2]_n$ characterised by King and coworkers.³

When **I** is exposed to trace levels of dioxygen the dinuclear species $[\text{Mn}_2(\text{PMe}_3)_3\text{I}_5]\cdot\text{PMe}_3$, **II**, is formed, Fig. 2. This complex, which is also mirror-symmetric, is unique in two

aspects: (i) although a few mixed oxidation state Mn^{II}/Mn^{III} complexes have been identified,⁴⁻⁷ there is no previous report of this occurring when 'soft' iodine or phosphine ligands are involved; (ii) there is no previous report of the highly reactive trimethylphosphine ligand occurring in a compound where it is not bound to a metal. The structural data, Fig. 2, clearly distinguishes the differing manganese oxidation states, showing the complex to be $[I_2(Me_3P)_2Mn^{II}-I-Mn^{III}(PMe_3)I_2] \cdot PMe_3$, the bridging iodine being 2.98 Å from the manganese(II) and 2.73 Å from the manganese(III).

Complex **II** almost certainly represents a transition state in the reaction of **I** with dioxygen to form **III**, as outlined in Scheme 1; it gives an insight into the mechanism of the oxidation of the manganese(II) centre and the degradation of the polymer chain of **I**. Further investigation has shown us that **II** is the major product of the reaction of **I** with trace quantities of dioxygen. The only other product from the partial oxidation of **I** is a pale-pink powder, identified by elemental analyses as essentially MnI_2 [% found (%cal.): Mn, 16.8(17.8); I, 79.9(82.2)]. The small, but significant, discrepancies between the found and calculated values point to the presence of a small quantity of a species such as MnO_2 or a mixed iodide/oxide species. Taken together, these observations lead

us to suggest how **I** fragments on reaction with O_2 to form **II**, Scheme 2.

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