The *X*-Ray Crystal Structure of *trans*-Tri-iodobis(trimethylphosphine)manganese(III). The First Example of a Trigonal Bipyramidal Manganese(III) Tertiary Phosphine Complex

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The reaction of $MnI_2(PMe_3)$ with dioxygen leads to the formation of the trigonal bipyramidal bisphosphine manganese(III) complex, *trans*-$MnI_3(PMe_3)_2$; no phosphine oxidation is observed.

In our study of the MnX_2(phosphine) (X = Cl, Br, I, NCS) complexes which reversibly co-ordinate dioxygen[1—3] we have observed trends in the p_{50} values which can be related to the nature of the phosphine and of the halogen. Thus, in solution the ability to bind dioxygen is generally in the order Cl > Br > I and $PPhR_2 > PPh_2R \gg PPh_3$ (no ability);[2] even under high pressures the $MnX_2(PPh_3)$ complexes do not bind dioxygen. We have also observed another extreme: that represented by the $MnX_2(PMe_3)$ (X = Cl, Br, I) complexes, which react irreversibly with dioxygen to produce manganese(III) species and other products. Hill and co-workers[4] have also claimed to have observed reversible binding of O_2 by some MnX_2(phosphine) compounds but, like us, observed irreversible oxidation of $MnBr_2(PMe_3)$ when exposed to dioxygen. These workers also claim to observe $MnBr_2(OPMe_3)$ on thin films and have observed an intermediate exhibiting an i.r. band at 1132 cm^{-1}, suggesting a manganese(III)–superoxide complex.

We report here our own observations on the reaction of $MnX_2(PMe_3)$ (X = Cl, Br, I) with dioxygen in the solid state. There is a good deal of interest presently in the bonding of tertiary phosphines to manganese(II) and both we[5] and Wilkinson and co-workers[6,7] have reported *X*-ray crystal structures of $MnX_2(PR_3)$ species. Although Green, Mingos, and co-workers were unable to isolate $MnX_2(PR_3)$ compounds,[8] the manganese–phosphine bonds in such complexes must be quite stable since we observe that when the $MnX_2(PMe_3)$ complexes are exposed to dry dioxygen the colourless solids rapidly become highly coloured,† but in no case was evidence for oxidation of the phosphine found.

Our first indication that the reaction of dioxygen with the $MnX_2(PMe_3)$ complexes produces more than one product came from e.s.r. measurements. Although the intense $g = 2$ signal for the $MnX_2(PMe_3)$ complexes did rapidly become less intense over a 2—3 day period of exposure to dioxygen it did in no case entirely disappear. We thus concluded we were producing an e.s.r.-quiet species, e.g., manganese(III),[9] and an e.s.r.-active species.

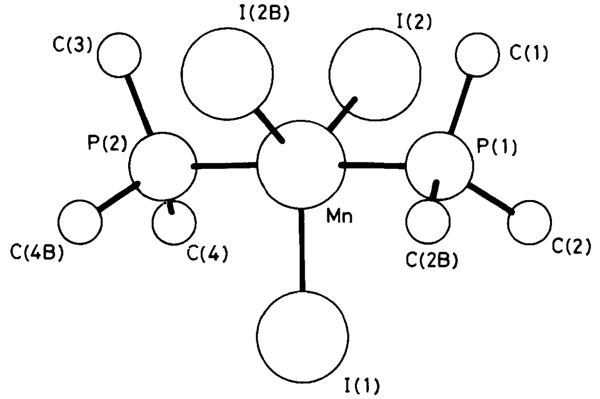

Figure 1. Structure of $MnI_3(PMe_3)_2$. [Interatomic distances (Å): Mn–I(1) 2.605(6), Mn–I(2) 2.635(3), Mn–P(1) 2.43(1), Mn–P(2) 2.44(1). Interatomic angles (°): I(1)–Mn–I(2) 121.3(1), I(2)–Mn–I(2B) 117.5(1), I(1)–Mn–P(1) 89.1(3), I(1)–Mn–P(2) 89.4(3), I(2)–Mn–P(1) 90.3(2), I(2)–Mn–P(2) 90.5(2). E.s.d.s in parentheses; mirror image atoms are labelled B.]

It proved possible to separate these compounds by vacuum sublimation in the $MnI_2(PMe_3) + O_2$ case. A dark green solid, $MnI_3(PMe_3)_2$, sublimed onto the cold finger leaving a flesh-coloured residue (which contained Mn and I, but no C or P). The $MnI_3(PMe_3)_2$ complex exhibits no e.s.r. signal and has a room temperature magnetic moment of 4.8 μ_B; these data are consistent with manganese(III). Moreover no ν(P=O) absorptions are present in the i.r. spectrum, and a single broad band at 192 cm^{-1} may be assigned to ν(Mn–I).

Crystals of $MnI_3(PMe_3)_2$ suitable for *X*-ray crystallographic study, but not of high quality, were grown from anhydrous diethyl ether.

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† However, the colours produced are different from those of, say, the $MnX_2(PPhMe_2)$ complexes which colour as the dioxygen adducts $MnX_2(PPhMe_2)(O_2)$ form. For example, $MnCl_2(PPhMe_2)(O_2)$ is purple, whereas exposure of $MnCl_2(PMe_3)$ to dioxygen produces a crimson solid.

Crystal data: $C_6H_{18}I_3MnP_2$, M = 587.81, orthorhombic, *Pnma*, a = 10.509(1), b = 11.167(8), c = 14.398(2) Å, U = 1689.7 Å^3, D_c = 2.31 g cm^{-3}, Z = 4. Graphite monochromatized Mo-K_α radiation, λ = 0.71069 Å; CAD4 diffractometer. Intensities measured in the range $0.01 < (\sin\theta)/\lambda < 0.6$ Å^{-1} were reduced to 671 unique reflections with $F > 3\sigma(F)$ and these were used for structure determination and refinement; R = 0.081.

A Patterson map revealed a triangle of iodine atoms and the remaining non-hydrogen atoms were found by Fourier methods. Refinement using SHELX[10] treated all non-hydrogen atoms anisotropically. Hydrogen atoms were not included owing to data limitations. The trigonal bipyramidal $MnI_3(PMe_3)_2$ molecule is situated with its axial P atoms, one equatorial I atom, two methyl C atoms, and Mn in a crystallographic mirror plane. A staggered arrangement of P–C and Mn–I bonds is adopted (see Figure 1). It is unusual for a metal in the 3+ oxidation state to have a less than octahedral co-ordination sphere and the pentaco-ordination may be favoured because the bulkiness of the five substituents can be relieved by the staggering. Bond lengths and angles are reported in the legend to Figure 1.‡ This compound represents a unique case of pentaco-ordinate Mn^{III} bound to tertiary phosphines. The Mn–P bonds are strong, being more than 0.2 Å shorter than the axial bonds (in octahedral co-ordination) found in $MnI_2(PPhMe_2)$.[5] In the latter, alternate Mn atoms (linked by pairs of iodine bridges) are tetrahedrally (MnI_4) and octahedrally (MnI_4P_2) co-ordinated, with the shortest Mn–I (bridge) bonds *ca.* 0.1 Å longer than the stronger Mn–I bonds in $MnI_3(PMe_3)_2$.

The work reported here directly contrasts with the reported observations of Hill and co-workers,[4] whose i.r. studies have led them to postulate manganese(III) trimethylphosphine oxide complexes resulting from the reaction of dioxygen with $MnBr_2(PMe_3)$ synthesised *in situ* on thin films.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.