Tertiary Phosphine Adducts of Manganese(II) Dihalides. The *X*-Ray Crystal Structure of Di-iodo(phenyldimethylphosphine)manganese(II)

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An *X*-ray crystal structure determination of $MnI_2(PPhMe_2)$ reveals iodide-bridged polymer chains consisting of alternating tetrahedral (MnI_4) and pseudo-octahedral (*trans*-MnP_2I_4) units.

Although phosphine complexes of manganese(I) are well known,[1] few complexes with the harder manganese(II) are known.[2—7] The diphosphine complex $MnCl_2(diphos)_2$,[3] where diphos = *o*-phenylenebis(dimethylphosphine), is octahedral with *trans* chlorines. Although Green, Mingos, and co-workers were unable to prepare the simple MnX_2(phosphine) complexes,[8] and cast doubt upon their existence, Hill and co-workers have recently reported the preparation of $MnBr_2(PMe_3)$,[9] and Wilkinson and co-workers have crystallographically characterised $[Mn(CH_2SiMe_3)_2(PMe_3)]_2$,[4] and $[Mn(CH_2CMe_3)_2(PMe_3)]_2$, $[Mn(CH_2Ph)_2(PMe_3)]_2$, and $[Mn(CH_2SiMe_3)_2(PPh_2Me)]_2$.[5] Wilkinson's complexes are dimers containing terminal phosphines, and terminal and bridging anions.

The $MnI_2(PPhMe_2)$ complex reversibly binds dioxygen in the solid state and in a 1:1 Mn:O_2 ratio in solution in a number of organic solvents. We obtained crystals suitable for *X*-ray analysis by synthesising the complex in absolutely dry diethyl ether under an argon atmosphere.

The material was characterised by a single-crystal *X*-ray

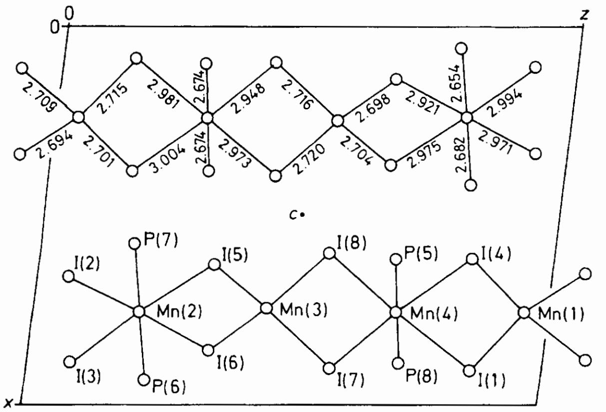

Figure 1. Structure of $MnI_2(PMe_2Ph)$. View down *y* showing centrosymmetrically related chains of alternating tetrahedrally and octahedrally co-ordinated Mn atoms (Me and Ph groups omitted). Adjacent chains shown are related by the centre of symmetry at *c*. Bond lengths (Å) have e.s.d.s *ca.* 0.004 Å (Mn–I) and 0.007 Å (Mn–P).

diffraction study employing the Hilger–Watts Y290 diffractometer at Nottingham.

Crystal data for $PhMe_2PMnI_2$: $(C_8H_{11}I_2MnP)_4$, M = 1787.6. triclinic, $P\bar{1}$, a = 11.389(2), b = 15.227(3), c = 15.228(3) Å, α = 89.10(1), β = 97.51(1), γ = 89.53(1)°, U = 2617.8 Å^3, D_c = 2.27 g cm^{-3}, Z = 2. Graphite monochromatized Mo-K_α radiation, λ = 0.710 69 Å, μ = 35.1 cm^{-1}. About 9300 unique reflections with $\theta < 25°$ measured; 5143 with $I \geqslant 3\sigma(I)$ used in refinement; R = 0.067.†

Using reflections with $\theta < 20°$, MULTAN revealed the 16 I atoms in the unit cell as two groups of eight related through a centre. The remaining atoms were found by Fourier methods. Refinement treated I, Mn, and P anisotropically, C isotropically, and included H atoms in calculated positions. The 4 $PhMe_2PMnI_2$ units in the asymmetric unit form part of an infinite chain of Mn atoms linked by pairs of I bridges. The chains possess the unique feature that the Mn atoms are alternatively tetrahedrally and octahedrally co-ordinated. The tetrahedral environments comprise four I atoms bridging to the adjacent octahedral Mn atoms which possess four equatorial I ligands and two axial phosphine P atoms (see Figure 1, which also gives bond lengths; e.s.d.s *ca.* 0.005 Å). The effect of a tetrahedral Mn site situated between two octahedral ones is to make alternate equatorial planes of I atoms approximately perpendicular to each other, so that there are 4 Mn atoms before the structure repeats. The packing of adjacent chains appears to be governed by the space requirements of the bulky phenylphosphine ligands, and also by the tendency for phenyl groups of adjacent chains to pack contiguously. Consequently, the centrosymmetric pairs of tetrahedral Mn sites of adjacent chains are situated astride comparatively empty regions.

The structure of this MnX_2(phosphine) complex is radically different from those of the first such complexes crystallographically analysed by Wilkinson and co-workers[4,5] and found to be dimeric.

In $MnI_2(PPhMe_2)$ the Mn–P bond lengths are equivalent for each phosphine bound to an individual manganese, but differ slightly from one octahedral unit to the next. The P–Mn–P angle is almost exactly 180°. The Mn–P bond lengths in this complex are very similar to that found for $[Mn(CH_2SiMe_3)_2(PMe_3)]_2$.[4] The Mn–I bond lengths for the octahedral units (Mn–I 2.973—3.004 Å) are much longer than those in the tetrahedral units (Mn–I 2.698—2.720 Å). This probably represents, firstly, the electronic effect of the bonding of the two phosphine ligands, causing increasing electron density at the O_h manganese centre, and, secondly, the expected shorter Mn–I bond lengths in a tetrahedral environment.

We have observed trends in the ability of these MnX_2(phosphine) complexes to bind small molecules in the solid state, *e.g.* $MnCl_2(PPhMe_2)$ will not bind dioxygen but will bind carbon monoxide,[10] $MnCl_2(PBu^n_3)$ will not bind sulphur dioxide but $MnI_2(PBu^n_3)$ will.[11] Although crystals of small molecule adducts suitable for crystallographic analysis have not yet been isolated, it is not unreasonable to expect that such binding occurs at the co-ordinatively unsaturated tetrahedral sites. The 'hole' at which such binding can occur is clearly susceptible to fine tuning by the size of bridging halide ligand [and hence the $Mn(O_h)$–X–$Mn(T_d)$–X–$Mn(O_h)$ distances] and by the steric demands of the phosphine ligand.

In general the behaviour of these $MnX_2(PR_3)$ complexes towards small molecule binding is mirrored in similar behaviour in toluene solution. The low solubility of the complexes in toluene suggests a polymeric or, at least, an oligomeric structure in this solvent. However, in co-ordinating solvents such as tetrahydrofuran (thf) the polymeric structure is broken on dissolution and e.s.r.[12] and molecular weight measurements strongly suggest that the species present is $MnX_2(PR_3)(thf)_3$. There must thus be phosphine transfer from one of the octahedral sites to a tetrahedral site on dissolution in tetrahydrofuran. At room temperature this phosphine lability results in oxidation of the phosphine to phosphine oxide on exposure of the solution to dioxygen. However, at low temperatures (−20 °C and below) this process occurs to a negligible degree.[7]

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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 Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.