Manganese(IV) Alkyl Complexes. Synthesis and Structure of Tetramethyl- 
[1,2-bis(dimethylphosphino)ethane]manganese(IV)

Christopher G. Howard,a Gregory S. Girolami,a Geoffrey Wilkinson,a Mark Thornton-Pett,b and Michael B. Hursthouseb

a Chemistry Department, Imperial College, London SW7 2AY, U.K.
b Chemistry Department, Queen Mary College, London E1 4NS, U.K.

The interaction of tris(acetylacetonato)manganese(III), Mn(acac)3, with methyl-lithium in the presence of 1,2-bis(dimethylphosphino)ethane (dmpe) in diethyl ether leads, in a disproportionation reaction, to MnMe2(dmpe)2 and to MnMe4(dmpe) whose X-ray structure has been determined; also synthesised from Mn(acac)3 are MnMe6(PMe3)2 and the green tetrahedral alkyl complexes MnR4, R = CH2SiMe3 and CH2CMe3 which have been identified spectroscopically.

The only stable organomanganese(IV) compound,t the green tetrahedral tetranorbornylmanganese(IV) complex Mn(nor)4, was obtained by action of the lithium alkyl on MnBr2; the reaction pathway is not known. Green solutions, believed to contain the thermally unstable alkyl complexes MnR4, R = CH2SiMe3 and CH2CMe3 on the basis of e.s.r. spectra, were obtained by controlled oxidation by dioxygen of the corresponding manganese(II) alkyl complexes.

The interaction of tris(acetylacetonato)manganese(III), Mn(acac)3, with 1,2-bis(dimethylphosphino)ethane (dmpe) and three equivalents of methyl-lithium in diethyl ether at −78 °C produces a clear yellow solution. After warming to room temperature, removing the solvent and extracting the residue with petroleum, yellow crystals of MnMe6(dmpe)" can be obtained. Further concentration of the solutions gives dark orange crystals of MnMe6(dmpe)6. We consider that the disproportionation reaction (1) is thus established. The tri-

2MnIII = MnII + MnIV  \hspace{1cm} (1)

methylphosphine analogue, MnMe6(PMe3)6, may be obtained similarly although in this case the manganese(II) species cannot be isolated.

The magnetic moment of MnMe6(dmpe) in solution (3.87 \mu_B) is consistent with MnIV, d5. The X-band e.s.r. spectrum in toluene at 77 K is consistent with an S = 3/2 species having a broad feature at g⊥ = 4.55 and a smaller, sharper feature at g∥ = 2.01; neither feature showed evidence of 55Mn or 31P hyperfine structure. The electronic spectrum had only an intense absorption rising toward shorter wavelengths beginning at 500 nm. In cyclic voltammetric studies at a glassy carbon
Figure 1. The molecular structure of MnMe₃(dmpe). Selected bond lengths (Å) and angles (°) are: Mn–C(1) 2.123(9), Mn–C(4) 2.123(11), Mn–C(2) 2.088(10), Mn–C(3) 2.060(11), Mn–P(1) 2.451(4), Mn–P(2) 2.447(4); P(1)–Mn–P(2) 80.2(2), C(2)–Mn–C(3) 93.6(5), P(1)–Mn–C(3) 95.4(4), P(2)–Mn–C(2) 90.9(4), P(1)–Mn–C(4) 88.8(4), P(2)–Mn–C(4) 87.4(5), P(1)–Mn–C(1) 85.9(3), P(2)–Mn–C(1) 89.1(4).

A diagram of the structure of MnMe₃(dmpe) is shown in Figure 1. The molecule has the expected octahedral structure. The average Mn–C distances are 2.07(1) Å trans to the phosphorus atoms and 2.12(1) Å trans to each other, the small differences indicating a trans influence for the alkyl groups greater than for the phosphine. The average Mn–P distance is 2.449(9) Å which compares with ca. 2.2 Å for low spin MnII and ca. 2.65 Å for high spin MnIII.

Preliminary X-ray data for MnMe₃(PMe₅) confirm that the PMe₅ groups are cis.

Interaction of LiCH₃SiMe₃ or LiCH₃CMe₃ with Mn(acac)₃ in petroleum or toluene at 0 °C yields a pale orange precipitate of the manganese(III) alkyl complex and a bright green solution. The green solutions can be stored at −78 °C for some hours but decompose at room temperature. The e.s.r. spectra [g∥ = 3.84, g⊥ = 2.02, A∥ (⁵⁵Mn) = −0.0038 cm⁻¹, A⊥ (⁵⁵Mn) = −0.0056 cm⁻¹] at 77 K were identical with those for Mn(nor)₃ and much better defined than those of the similar green species generated by oxidation. Again, the disproportionation of MnIII is confirmed.

The use of these manganese(III) alkyl complexes for synthesising other manganese(IV) compounds is under study.

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References