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

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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 MnMe$_2$(dmpe)$_2$ and to MnMe$_4$(dmpe) whose *X*-ray structure has been determined; also synthesised from Mn(acac)$_3$ are MnMe$_4$(PMe$_3$)$_2$ and the green tetrahedral alkyl complexes MnR$_4$, R = CH$_2$SiMe$_3$ and CH$_2$CMe$_3$ which have been identified spectroscopically.

The only stable organomanganese(IV) compound,[1] the green tetrahedral tetranorbornylmanganese(IV) complex Mn(nor)$_4$, was obtained by action of the lithium alkyl on MnBr$_2$; the reaction pathway is not known. Green solutions, believed to contain the thermally unstable alkyl complexes MnR$_4$, R = CH$_2$SiMe$_3$ and CH$_2$CMe$_3$ on the basis of e.s.r. spectra, were obtained by controlled oxidation by dioxygen of the corresponding manganese(II) alkyl complexes.[2]

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 MnMe$_4$(dmpe)† can be obtained. Further concentration of the solutions gives dark orange crystals of MnMe$_2$(dmpe)$_2$.[3] We consider that the disproportionation reaction (1) is thus established. The trimethylphosphine analogue, MnMe$_4$(PMe$_3$)$_2$, may be obtained similarly although in this case the manganese(II) species[4] cannot be isolated.

$$2\mathrm{Mn^{III}} = \mathrm{Mn^{II}} + \mathrm{Mn^{IV}} \qquad (1)$$

The magnetic moment of MnMe$_4$(dmpe) in solution (3.87 μ_B) is consistent with Mn^{IV}, d^3. 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 $g_\perp = 4.55$ and a smaller, sharper feature at $g_{||} = 2.01$; neither feature showed evidence of ^{55}Mn or ^{31}P 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

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† M.p., 75 °C (decomp.); satisfactory analytical data were obtained.

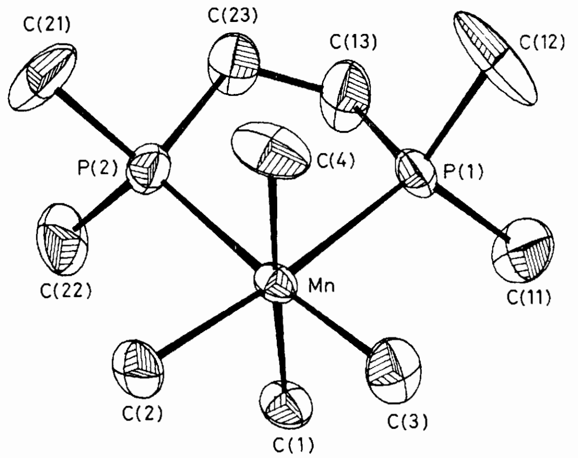

Figure 1. The molecular structure of $\mathrm{MnMe_4(dmpe)}$. Selected bond lengths (Å) and angles (°) are: Mn–C(1) 2.123(9), Mn–C(4) 2.123(11), Mn–C(2) 2.088(10), Mn–C(3) 2.060(11), Mn–P(1) 2.451(4), Mn–P(2) 2.447(4); P(1)–Mn–P(2) 80.2(2), C(2)–Mn–C(3) 93.6(5), P(1)–Mn–C(3) 95.4(4), P(2)–Mn–C(2) 90.9(4), 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).

electrode in tetrahydrofuran with $[\mathrm{Bu^n_4N}]\mathrm{ClO_4}$ as supporting electrolyte, no reduction was observed, but there was a broad irreversible oxidation wave at *ca.* 500 mV. An accurate determination of the potential was precluded evidently due to decomposition products coating the electrode.

A diagram of the structure‡ of $\mathrm{MnMe_4(dmpe)}$ 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 $\mathrm{Mn^{II}}$ and *ca.* 2.65 Å for high spin $\mathrm{Mn^{II}}$.[3–5]

Preliminary *X*-ray data for $\mathrm{MnMe_4(PMe_3)_2}$ confirm that the $\mathrm{PMe_3}$ groups are *cis*.

Interaction of $\mathrm{LiCH_2SiMe_3}$ or $\mathrm{LiCH_2CMe_3}$ with $\mathrm{Mn(acac)_3}$ in petroleum or toluene at 0 °C yields a pale orange precipitate of the manganese(II) dialkyl complex[2] 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 [$g_{\|} = 3.84$, $g_{\perp} = 2.02$, $A_{\|}$ (^{55}Mn) $= -0.0038$ cm^{-1}, $A_{\perp}$ (^{55}Mn) $= -0.0056$ cm^{-1}] at 77 K were identical with those for $\mathrm{Mn(nor)_4}$[1] and much better defined than those of the similar green species generated by oxidation.[2] Again, the disproportionation of $\mathrm{Mn^{III}}$ is confirmed.

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

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‡ *Crystal data:* monoclinic, space group $P2_1/n$ with $a = 13.986(2)$, $b = 13.112(2)$, $c = 8.677(1)$ Å, $\beta = 96.44(2)°$, $U = 1581$ Å^3, $Z = 4$, $R = 0.0667$ for 2130/3424 observed data [$F_o > 3\sigma(F_o)$] measured on a CAD4 diffractometer, Mo-K_α radiation, $\lambda = 0.71069$ Å, ω–2θ scan mode. 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.