

Tertiary Phosphine Adducts of Manganese(II) Dialkyls: Synthesis and X-Ray Crystal Structure of Bis(trimethylphosphine)bis(trimethylsilylmethyl)bis(μ -trimethylsilylmethyl)dimanganese(II)

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The interaction of PMe_3 with $[\text{Mn}(\text{CH}_2\text{SiMe}_3)_2]_n$ gives $\text{Mn}_2(\text{CH}_2\text{SiMe}_3)_4(\text{PMe}_3)_2$, the first crystallographically characterised unidentate phosphine complex of manganese(II).

Although tertiary phosphine alkyls are common for transition metals¹ manganese is an exception; the only compound is the phenyl, $\text{MnPh}_2[\text{P}(c\text{-C}_6\text{H}_{11})_3]$, but no structural data were given.² Adducts of manganese(II) alkyls with various oxygen and nitrogen ligands are however, known.³ We have isolated the air-sensitive orange complex of stoichiometry $\text{Mn}_2(\text{CH}_2\text{SiMe}_3)_4(\text{PMe}_3)_2$ by interaction of $[\text{Mn}(\text{CH}_2\text{SiMe}_3)_2]_n$ with PMe_3 in toluene. Crystals suitable for X-ray diffraction study were obtained from light petroleum.

Crystal data: triclinic, $a = 10.311(1)$, $b = 10.610(2)$, $c = 10.963(2)$ Å, $\alpha = 67.14(1)$, $\beta = 86.92(1)$, $\gamma = 61.52(1)^\circ$, $U = 958.5(3)$ Å³, space group $P\bar{1}$, $Z = 1$ dimeric unit. X-Ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an ω scan technique with graphite-monochromated Cu- K_α radiation. 2130 Independent reflections were measured (to $\theta = 50^\circ$), of which 187 were judged to be 'unobserved'. A combination of direct methods and difference Fourier synthesis yielded the structure, and least-

squares refinements has now reached $R = 0.034$.† The program system SHELXTL was used throughout the calculations.⁴

Figure 1 shows the centrosymmetric dimeric structure of the title compound. Each manganese atom is co-ordinated to a terminal PMe_3 group [Mn-P distance of 2.650(1) Å], a terminal CH_2SiMe_3 group, and to two bridging CH_2SiMe_3 groups. The co-ordination geometry about manganese is distorted tetrahedral, with bond angles in the range 99.8–125.0°. The methylene bridge is asymmetric with an Mn-C(1) distance of 2.369(5) Å and Mn'-C(1) distance of 2.208(3) Å. This can be compared with the Mn-C(2) distance of 2.111(3) Å. The Si-CH₂ distances in the two groups are also signifi-

†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.

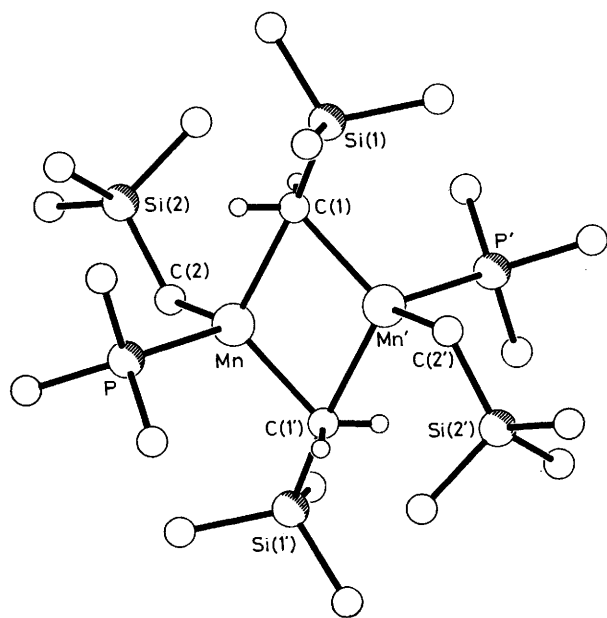


Figure 1. Molecular structure of the centrosymmetric dimer $\text{Mn}_2(\text{CH}_2\text{SiMe}_3)_4(\text{PMe}_3)_2$. Hydrogen atoms have been omitted, with the exception of those on the bridging CH_2 groups.

cantly different, with $\text{Si}(1)\text{-C}(1)$ 1.863(5) Å in the bridging group, and $\text{Si}(2)\text{-C}(2)$ 1.825(4) Å in the terminal group.

Given the tetrahedral geometry at the manganese atom, and the bridged dimeric nature of the molecule, the $\text{Mn} \dots \text{Mn}$ separation is inevitably short at 2.772(1) Å. The $\text{C}(1)\text{-Mn-C}(1')$ angle is $105.5(1)^\circ$, while the $\text{Mn-C}(1)\text{-Mn}'$ angle is $74.5(1)^\circ$. This geometry can be contrasted with that found in $\text{Nb}_2(\text{CSiMe}_3)_2(\text{CH}_2\text{SiMe}_3)_4$, where in the absence of hydrogen atoms on the bridging carbon the $\text{Nb-C-Nb}'$ angles are greater than the $\text{C-Nb-C}'$ angles, and the Nb-C (bridging) distance is appreciably shorter than the Nb-CH_2 (terminal) distance.⁵

The Mn-C-Mn-C segment is strictly planar by symmetry, but $\text{Si}(1)$ is 0.42 Å out of this plane. We have located both the hydrogen atoms of the bridging methylene groups. They are symmetrical with respect to $\text{Si}(1)$, but not with respect to Mn , so that one hydrogen atom is *ca.* 2.29 Å from Mn while the other is at *ca.* 2.57 Å. This suggests that there may be some $\text{C-H} \dots \text{Mn}$ interactions and there is a low i.r. stretching frequency at 2772 cm^{-1} , consistent with this. Other cases of $\text{C-H} \dots \text{M}$ interactions are known;⁶ for manganese(II), interaction with a C-H bond of the phenyl ring was observed in a

bridging manganese(II) dineophyl³ while, for manganese(I), interaction occurs in η^3 -cyclohexenylmanganese tricarbonyl.⁷

The complex is paramagnetic, having a magnetic moment in toluene (measured by the Evans' n.m.r. method) of $4.47 \mu_B$ per dimer ($3.16 \mu_B$ per Mn atom).

Although well known for manganese(I), tertiary phosphine complexes of manganese(II) have been recognised only recently.^{2,8,9} The halides⁸ $\text{MnX}_2(\text{PR}_3)_2$ are doubtless polymeric but no structural data have been published. For $\text{MnCl}_2(\text{diphos})_2$,⁹ where *diphos* = *o*-phenylenebis(dimethylphosphine) the structure is octahedral with *trans*-chlorines; the $\text{Mn-P}(\text{av.})$ distance of 2.625 Å is not strictly comparable with that of 2.650 Å for tetrahedral manganese(II) in the present complex.

Other trimethylsilylmethyl complexes with PMe_2Ph , PMePh_2 , and $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ as well as other manganese(II) trimethylphosphine compounds such as $\text{Mn}(\text{CH}_2\text{-CMe}_3)_2\text{PMe}_3$ or $(\eta^5\text{-C}_5\text{H}_5)_2\text{MnPMe}_3$ have been made.‡

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References

- 1 P. J. Davidson, M. F. Lappert, and R. Pearce, *Chem. Rev.*, 1976, **76**, 219; R. R. Schrock and G. W. Parshall, *Chem. Rev.*, 1976, **76**, 243; C. A. McAuliffe and W. Levason, 'Phosphine, Arsine and Stibine Complexes of the Transition Metals,' Elsevier, Amsterdam, 1979.
- 2 K. Maruyama, T. Ito, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 849.
- 3 R. A. Andersen, E. Carmona-Guzman, J. F. Gibson, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 2204.
- 4 G. M. Sheldrick, 'SHELXTL—an Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data,' Revision 3, July 1981, Nicolet Instruments Ltd., Warwick, England.
- 5 F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Commun.*, 1971, 1477.
- 6 See, R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 26; G. M. Dawkins, M. Green, A. G. Orpen, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1982, 41; C. P. Casey, P. J. Fagan, and W. H. Miles, *J. Am. Chem. Soc.*, 1982, **104**, 1134.
- 7 M. Brookhart, W. Lamanna, and M. B. Humphrey, *J. Am. Chem. Soc.*, 1982, **104**, 2117.
- 8 C. A. McAuliffe, *J. Organomet. Chem.*, 1982, **228**, 255 and references therein.
- 9 L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3127.

‡ Satisfactory microanalytical data for all new compounds were obtained.