Tertiary Phosphine Adducts of Manganese(II) Dialkyls. Part 1. Synthesis, Properties and Structures of Alkyl-bridged Dimers †

Christopher G. Howard and Geoffrey Wilkinson *
Chemistry Department, Imperial College of Science and Technology, London SW7 2AY
Mark Thornton-Pett and Michael B. Hursthouse *
Chemistry Department, Queen Mary College, London E1 4NS

The reactions of manganese(II) dialkyls with tertiary phosphines or of $MnCl_2$ with magnesium dialkyls in the presence of phosphines leads to dimeric complexes of stoicheiometry $Mn_2R_4(PMe_3)_2$ (R = CH_2SiMe_3, CH_2CMe_3, and CH_2Ph) and $Mn_2(CH_2SiMe_3)_4(PR_3)_2$ [R_3 = Et_3, Me_2Ph, $MePh_2$, and $(cyclo\text{-}C_6H_{11})_3$]. The *X*-ray crystal structures of $Mn_2(CH_2CMe_3)_4(PMe_3)_2$, $Mn_2(CH_2Ph)_4(PMe_3)_2$, and $Mn_2(CH_2SiMe_3)_4(PMePh_2)_2$ have been determined. In the dimers there are two asymmetrically bridging alkyl groups with one additional terminal alkyl and one phosphine per manganese. The structures show a variation in bond lengths probably due to steric effects, with Mn–Mn distances of 2.667(1)—2.828(1) Å, and long Mn–P distances [2.562(1)—2.684(1) Å]. There is a close contact between one hydrogen atom on each of the bridging methylene groups and the manganese atom (Mn ··· H–C 2.15—2.29 Å). Infrared and e.s.r. spectra of the compounds are discussed.

The first transition metal compounds with bridging alkyl groups to be characterised were the manganese(II) dialkyls, $(MnR_2)_n$ R = CH_2SiMe_3 ($n = \infty$), CH_2CMe_3 (n = 4), and CH_2CMe_2Ph (n = 2).[1] These compounds are of interest because of the potential for interaction between the metal and hydrogen atoms on the bridging carbon. Such interactions[2] may be involved in the activation of C–H bonds in many heterogeneous and homogeneous catalytic processes. Additionally, the compounds possess Mn–Mn distances similar to the separation found in the manganese-containing proteins which oxidise water to dioxygen in photosystem II.[3]

We now describe a series of unidentate tertiary phosphine adducts of manganese(II) dialkyls of formula $Mn_2R_4(PR'_3)_2$ which retain the bridging alkyl groups;[4] these dimeric compounds are the first structurally characterised complexes of manganese(II) that contain unidentate phosphines. In a subsequent paper, monomeric species of the type $MnR_2(PR'_3)_2$ will be described.

Results and Discussion

Synthesis and Properties.—The dimeric complexes $Mn_2R_4(PR'_3)_2$ can be made either by interaction of the phosphine with a toluene solution of the manganese(II) dialkyl when this is available, or, more conveniently, by a single-step reaction of manganese(II) chloride, the appropriate dialkylmagnesium reagent, and the phosphine in diethyl ether. The second method was used for synthesis of $Mn_2(CH_2Ph)_4(PMe_3)_2$ as dibenzylmanganese is unknown, although the dioxane adduct has been reported.[5]

The only other similar phosphine adduct is $MnPh_2[P(cyclo\text{-}C_6H_{11})_3]$, but the structure is not known.[6] There are numerous tertiary phosphine adducts of manganese halides[7] of stoicheiometry $MnX_2(PR_3)$, but only the structure of $MnI_2(PMe_2Ph)$ has been determined.[8] The latter is an iodide-bridged polymer with both tetrahedral and octahedral Mn^{II}, the latter bearing *trans* phosphines. By contrast, the chelate phosphine complex $MnCl_2(P\text{–}P)_2$ [P–P = *o*-phenylenebis(dimethylphosphine)] is an octahedral monomer with *trans* chlorine atoms.[9]

The complexes and some of their properties are listed in Table 1. All are soluble in hydrocarbon and ether solvents, except for the benzyl derivative, which dissolves only in presence of excess PMe_3. The magnetic moments in the solid state or in solution are, like those of the dialkyls,[1] considerably below the value expected for high-spin manganese(II), and this can be attributed to antiferromagnetic interactions in the dimeric species, probably *via* the carbon bridge atoms.

Even bulky phosphines, *e.g.* $P(cyclo\text{-}C_6H_{11})_3$, and weakly basic phosphines, *e.g.* $PMePh_2$, form quite stable adducts. Although $[Mn(CH_2SiMe_3)_2]_n$ is almost totally insoluble in cold toluene, it readily dissolves on addition of other phosphorus ligands, notably PPh_3, $P(OMe)_3$, and $P(SiMe_3)_3$, but crystalline adducts could not be isolated in these cases.

Compounds (1) and (2) do not react with hydrogen (*ca.* 10^6 Pa) either in the presence or absence of excess phosphine. There is also no reaction with butadiene or 1-hexene. Carbon monoxide gives a mixture of carbonyl–phosphine complexes of manganese as judged by ^{31}P n.m.r. and i.r. spectroscopy.

The reaction of the phosphine complexes with small amounts of oxygen gives bright red solutions (*cf.* ref. 7) except for the benzyl derivative, which turns deep blue. With an excess of oxygen these colourations are rapidly discharged of and brown, insoluble manganese oxides are precipitated.

Structures.—The structure of $Mn_2(CH_2SiMe_3)_4(PMe_3)_2$ (1) has been reported.[4] Three other structures have now been determined to assess the effects of size and electronic factors on the molecular geometry: $Mn_2(CH_2CMe_3)_4(PMe_3)_2$ (2), $Mn_2(CH_2Ph)_4(PMe_3)_2$ (3), and $Mn_2(CH_2SiMe_3)_4(PMePh_2)_2$ (5). The structures are similar to that of (1), *i.e.* bis-alkyl-bridged dimers with one phosphine ligand bound to each metal atom. The molecules of (3) and (5), like that of (1), are crystallographically centrosymmetric, while molecules of (2), although lying in general positions in the unit cell, have a structure that is very close to centrosymmetric. The basic features of the molecular geometries are given in Table 2, which includes data[4] for compound (1). Diagrams of the structures are shown in Figures 1—3. Although the structures are all very similar at first sight, detailed examination shows many significant and interesting differences.

First, the Mn–Mn distances vary over the range 2.667(1)—2.828(1) Å. These distances seem to depend on the degree of steric congestion in the molecule with the shorter Mn–Mn distances occurring with the smaller ligands. The Mn–P

---

† *Supplementary data available* (No. SUP 23658, 53 pp.): isotropic and anisotropic thermal parameters, observed and calculated structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Properties and analytical data for manganese dialkyl-phosphine complexes

Compound	Colour	M.p. (θ_c/°C)	Analysis [a] (%) C	H	P	I.r.[b] (cm^{-1})
(1) $Mn_2(CH_2SiMe_3)_4(PMe_3)_2$	Orange	80	43.2 (43.3)	10.1 (10.2)	9.8 (10.1)	2 772
(2) $Mn_2(CH_2CMe_3)_4(PMe_3)_2$	Orange	86	56.1 (57.1)	11.4 (11.4)	11.3 (11.4)	2 700
(3) $Mn_2(CH_2Ph)_4(PMe_3)_2$	Yellow	157 decomp.	64.3 (65.2)	7.3 (7.4)	9.5 (9.9)	2 760
(4) $Mn_2(CH_2SiMe_3)_4(PMe_2Ph)_2$	Orange	76	51.1 (52.3)	9.0 (9.0)	8.8 (8.4)	2 755
(5) $Mn_2(CH_2SiMe_3)_4(PMePh_2)_2$	Orange	80—100	58.3 (58.7)	8.2 (8.2)	7.8 (7.2)	2 762
(6) $Mn_2(CH_2SiMe_3)_4(PEt_3)_2$	Orange	71—72	47.9 (48.4)	10.7 (10.7)	8.9 (8.9)	2 760
(7) $Mn_2(CH_2SiMe_3)_4[P(cyclo\text{-}C_6H_{11})_3]_2$	Orange	80—82	60.9 (61.2)	10.8 (10.9)	6.5 (6.1)	

[a] Calculated values are in parentheses; for (1), Si, 17.7 (18.3)%. [b] Lowest band attributed to M $\cdots$ H–C in bridge.

Table 2. Selected molecular geometry parameters for the dimeric phosphine complexes, $Mn_2R_4(PR'_3)_2$

Parameter	Compound (1) *	Compound (2)	Compound (3)	Compound (5)
(*a*) Distances (Å)				
Mn $\cdots$ Mn	2.772(1)	2.718(3)	2.667(1)	2.828(1)
Mn–C_t	2.111(3)	2.14, 2.19(3)	2.127(3)	2.117(5)
Mn–C_b	2.208(3)	2.23, 2.31(2)	2.236(3)	2.193(5)
Mn–C_b'	2.369(5)	2.45, 2.44(2)	2.391(3)	2.389(5)
Mn–P	2.650(1)	2.67, 2.67(1)	2.562(1)	2.684(1)
Mn $\cdots$ H	2.29(6)		2.20(6)	2.15(6)
(*b*) Angles (°)				
Mn–C_b–Mn	74.5(1)	69.6, 71.0(6)	70.3(2)	76.1(4)
C_b–Mn–C_b'	105.5(1)	111, 108(1)	109.7(2)	103.9(2)
C_t–Mn–P		123, 123(1)	119.2(2)	107.4(4)
C_t–Mn–C_b		109, 106(1)	112.8(2)	122.4(3)
C_t–Mn–C_b'		112, 117(1)	108.6(2)	113.7(3)
C_b–Mn–P		114, 115(1)	113.5(2)	102.8(3)
C_b'–Mn–P		85, 86(1)	90.4(2)	104.7(3)

* Data taken from ref. 4.

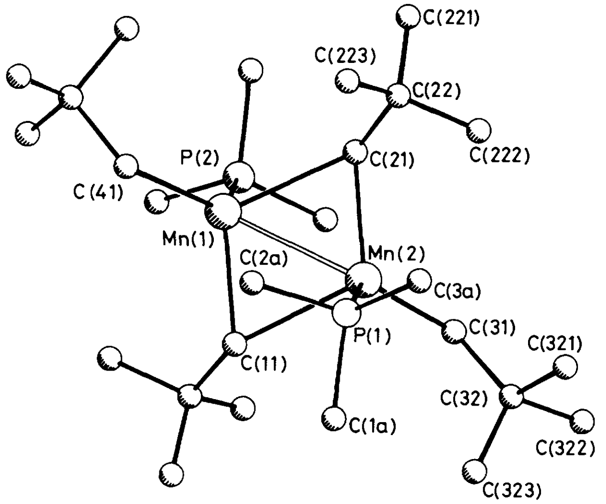


Figure 1. Structure of $Mn_2(CH_2CMe_3)_4(PMe_3)_2$

distances vary over the range 2.562(1)—2.684(1) Å, and also reflect the same trend. Thus, compound (3) with relatively small ligands has the shortest Mn–Mn and Mn–P distances, whereas compound (5), with relatively bulky ligands, has the longest in the series.

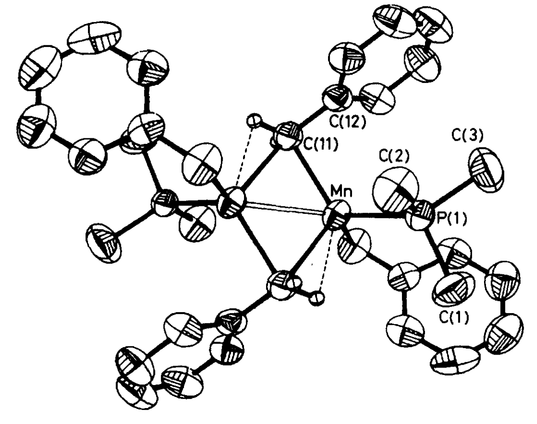


Figure 2. Structure of $Mn_2(CH_2Ph)_4(PMe_3)_2$

A detailed discussion of these differences and their possible origin will be given separately after completion of a quantitative analysis of the steric factors present.[10]

The Mn–C_t distances to the terminal alkyl groups are equal, within limits of experimental error, and serve to

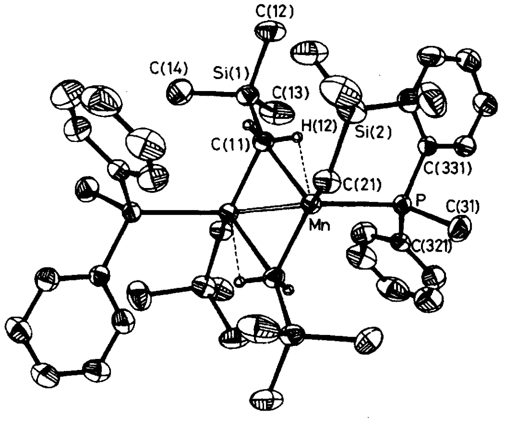
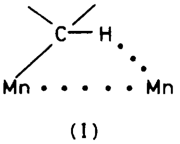


Figure 3. Structure of $Mn_2(CH_2SiMe_3)_4(PMePh_2)_2$

establish a common manganese(II) radius for these complexes. All the compounds show asymmetry in the carbon bridges with all $Mn-C_b$ distances longer than the $Mn-C_t$ distances. The long and short $Mn-C_b$ distances themselves show small, but seemingly significant differences [even when the less reliable values for compound (2) are disregarded]. Thus, the short $Mn-C_b$ distances varies from 2.193(5) to 2.236(3) Å and the long bonds from 2.369(5) to 2.391(3) Å. Moreover, the asymmetry of the bridge also seems to vary, with differences of *ca.* 0.16 Å for (1) and (3), and *ca.* 0.2 Å for (2) and (5). One hydrogen atom from each of the bridging methylene groups has a close approach to the metal atoms with $Mn \cdots H$ distances of 2.15(6)—2.29(6) Å. It is of note that in the three structures for which the CH_2 hydrogens were located, the orientations of the C–H bonds involving the interacting hydrogens are all similar and lie approximately along the direction of the Mn–Mn vector. This suggests that the common bridging function is the system (I). A similar bonding situation was once proposed for Al_2Me_6[11] but this interesting suggestion was not confirmed when the structure was accurately redetermined at low temperature.[12]



(I)

Any direct Mn–Mn interactions in these dimers are likely to be weak since the Mn^{II} centres have tetrahedral ligand coordination and the molecules have appreciable magnetic moments. This situation is quite different from that in the analogous *diamagnetic* chromium(II) complex[13] $Cr_2(CH_2SiMe_3)_4(PMe_3)_2$ where the ligand arrangement around the Cr^{II} centres can be described as square planar and the Cr–Cr distance, 2.201 Å, is consistent with the presence of a bent quadruple bond. Nevertheless, the alkyl bridges in this chromium complex were also found to be asymmetric and close $Cr \cdots H$ contacts were also observed. Asymmetric Mn–C–Mn bridges were also noted in our previous studies of the binary manganese(II) alkyls,[1] although the quality of the data recorded for these compounds[14] did not allow the location of the hydrogen atoms with any certainty. However, a recent re-examination[10] of certain of these alkyls has confirmed that short $Mn \cdots H$ contacts are indeed present.

The $M \cdots H$ interactions in all these manganese and chromium compounds are most likely attributable to the electron deficient nature of the metal centres which have electron counts far fewer than 18. This electronic unsaturation also explains why the bridging benzyl groups in (3) are bent over towards the manganese atoms so that the $Mn \cdots C(12)$ distance is 2.798(4) Å and the angle Mn(1)–C(11)–C(12) is 96.0(1)°. A similar effect was also observed[1,10,14] in the neophyl, $[Mn(CH_2CMe_2Ph)_2]_2$, where the closest approach of the phenyl ring to the manganese is a $Mn \cdots C$ contact of 2.690(4) Å.

Spectroscopic Studies.—Infrared. The i.r. spectra of the dimers show C–H stretching frequencies between 2 800 and 2 700 cm^{-1} that are lower than is commonly observed for transition metal alkyls. These absorptions can be reasonably assigned to the distorted bridging methylene groups. The small variation in the C–H stretches of compounds (1)—(6) (Table 1) does not appear to be related to the steric bulk of the alkyl or the phosphine ligands but does appear to show a relation with the $Mn \cdots H$ distances determined crystallographically, being in the expected direction, despite the uncertainty in the exact location of the H atoms. Thus, comparing compounds (1) and (5) the i.r. frequency decreases from 2 772 to 2 762 cm^{-1} and the $Mn \cdots H$ distance decreases from 2.29 to 2.15 Å.

Electron spin resonance. The e.s.r. spectra of the dimers were recorded in toluene or methylcyclohexane glasses at 77 K. These showed major features at *g ca.* 9 and *ca.* 4 with additional weaker, broader features also evident. The *g ca.* 9 and *ca.* 4 features are characteristic of near-tetrahedral high-spin d^5 manganese monomers of the type MnA_2B_2.[15] The present spectra can be accounted for by partial disproportionation in solution, reaction (i). By analogy with the spectra

$$Mn_2R_4(PR'_3)_2 \longrightarrow MnR_2(PR'_3)_2 + (MnR_2)_n \qquad \text{(i)}$$

observed[1] for the parent alkyls, $(MnR_2)_n$ the e.s.r. spectra of the dimers presumably consist of weak broad bands which are obscured by the stronger signals due to the monomeric tetrahedral species, even though the extent of disproportionation may be small. The addition of an excess of the tertiary phosphine would be expected to convert the dimers to $MnR_2(PR'_3)_2$, and, as expected, the intensity of the bands assigned to these species increases by a factor of about four. The e.s.r. spectra of the monomeric tertiary phosphine species will be discussed separately in a paper on mononuclear manganese(II) phosphine complexes.

Experimental

Microanalyses were performed by Pascher, Bonn. The following spectrometers were used: n.m.r., Perkin-Elmer R32 (90 MHz); e.s.r., Varian E12 (*X*-Band); i.r., Perkin-Elmer 683. Magnetic moments on solids were obtained by the Gouy method, and in solution by a modification of the Evans method.

All operations were carried out *in vacuo* or under purified argon. Solvents were distilled from sodium or sodium benzophenone under nitrogen. The petroleum used had b.p. 40—60 °C. Dialkylmagnesium compounds were prepared as before.[16] Anhydrous $MnCl_2$ was made by action of $SOCl_2$ on the hydrate followed by vacuum pumping at 200 °C.

(*A*) *Trimethylsilylmethyl Compounds.*—These were all prepared from the isolated dialkyl[1] using essentially the same procedure given below for the trimethylphosphine complex.

To a suspension of $[Mn(CH_2SiMe_3)_2]_n$ (1.5 g, 6.55 mmol) in toluene (50 cm^3) at room temperature was added PMe_3 (1.4

Table 3. Crystal data and details of the structure analysis

	Compound (2)	Compound (3)	Compound (5)
(*a*) Crystal data			
Formula	$C_{26}H_{62}Mn_2P_2$	$C_{34}H_{46}Mn_2P_2$	$C_{42}H_{70}Mn_2P_2Si_4$
M	546.58	626.21	859.16
Crystal system	Orthorhombic	Monoclinic	Monoclinic
a/Å	20.672(5)	12.096(2)	11.551(1)
b/Å	9.345(4)	10.089(3)	10.829(5)
c/Å	17.868(2)	15.144(3)	20.964(3)
β/°		112.63(3)	104.52(1)
U/Å^3	3 451	1 706	2 538
T/K	295	295	295
Space group	$Pna2_1$	$P2_1/c$	$P2_1/c$
Z	4	2	2
D_c/g cm^{-3}	1.05	1.22	1.12
(*b*) Data collection			
ω scan width/°	←0.8 + 0.35 tanθ→		
θ_{min}, θ_{max}/°	2.0—25.0	1.5—28.0	2.0—22.0
Total data	3 565	4 685	3 623
Total unique data	3 219	4 095	3 106
Total observed data $[F_o > 3\sigma(F_o)]$	1 950	2 754	2 150
(*c*) Refinement			
Number of parameters	274	264	366
Weights	Unit weights	$[\sigma^2(F_o) + 0.0005\ F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.000\ 85F_o^2]^{-1}$
Final R	0.073	0.046	0.042
Final R'	0.073	0.045	0.041

Table 4. Atomic co-ordinates (× 10^4) for compound (2)

Atom	x	y	z	Atom	x	y	z
Mn(1)	877(1)	210(3)	2 500	C(22)	1 820(10)	−2 286(18)	1 913(12)
Mn(2)	1 684(1)	−176(3)	3 684(2)	C(221)	2 527(13)	−2 567(29)	1 693(24)
P(1)	2 691(3)	1 561(6)	3 462(4)	C(222)	1 569(12)	−3 553(24)	2 376(15)
C(1a)	2 619(16)	2 929(32)	2 720(21)	C(223)	1 374(14)	−2 123(31)	1 228(14)
C(2a)	2 980(14)	2 656(27)	4 249(19)	C(31)	1 690(10)	−1 868(27)	4 529(15)
C(3a)	3 430(8)	605(24)	3 197(18)	C(32)	2 290(10)	−2 420(19)	4 934(14)
P(2)	−120(3)	−1 553(6)	2 743(4)	C(331)	2 485(22)	−1 090(26)	5 378(17)
C(1b)	−387(16)	−2 834(28)	2 029(13)	C(332)	2 761(14)	−2 872(36)	4 312(17)
C(2b)	−70(14)	−2 719(25)	3 570(18)	C(333)	2 094(13)	−3 750(28)	5 388(16)
C(3b)	−859(12)	−611(28)	3 020(21)	C(41)	838(10)	1 964(29)	1 736(13)
C(11)	695(10)	964(21)	3 795(13)	C(42)	231(10)	2 427(16)	1 310(12)
C(12)	730(9)	2 319(19)	4 275(11)	C(421)	284(16)	3 555(22)	689(13)
C(121)	980(15)	3 560(20)	3 794(14)	C(422)	3(18)	1 236(25)	783(18)
C(122)	47(10)	2 646(25)	4 574(17)	C(423)	−372(15)	2 773(39)	1 770(19)
C(123)	1 192(13)	2 120(29)	4 948(14)	C(1S)	808(14)	4 755(30)	2 523(22)
C(21)	1 825(9)	−905(17)	2 382(10)				

cm^3, 14 mmol). The yellow solution was stirred for 1 h, then evaporated *in vacuo* and the residue extracted with light petroleum (2 × 40 cm^3). This solution was filtered and reduced to 20 cm^3, when cooling at −20 °C gave orange prisms. Yield 1.6 g, 80%.

In a similar way, complexes from PMe_2Ph, $PMePh_2$, and PEt_3 were obtained; for $P(cyclo\text{-}C_6H_{11})_3$ the ligand was added in toluene and the solution stirred for *ca.* 12 h at room temperature before work-up.

(*B*) *Bis*(μ-*2,2-dimethylpropyl*)-*bis*(*2,2-dimethylpropyl*)*bis*(*trimethylphosphine*)*dimanganese*(II).—To a suspension of $MnCl_2$ (0.59 g, 4.68 mmol) and PMe_3 (1.4 cm^3, 14 mmol) in toluene at −78 °C was added $Mg(CH_2CMe_3)_2$ (10.8 cm^3 of a 0.43 mol dm^{-3} solution in diethyl ether, 4.64 mmol). After warming to and stirring at room temperature for *ca.* 12 h, the red-brown solution was filtered from the white precipitate and evaporated. The residue was extracted with light petroleum (2 × 50 cm^3), the extract filtered and reduced to 20 cm^3. Cooling at −20 °C gave orange crystals which were recrystallised from light petroleum. Yield 0.57 g, 45%.

(*C*) *Bis*(μ-*benzyl*)-*bis*(*benzyl*)*bis*(*trimethylphosphine*)*dimanganese*(II).—To a suspension of $MnCl_2$ (1.86 g, 14.7 mmol) and PMe_3 (3 cm^3, 30 mmol) in diethyl ether (50 cm^3) was added $Mg(CH_2Ph)_2$ (130 cm^3 of a 0.11 mol dm^{-3} solution in diethyl ether, 14.3 mmol). After 6 h, the filtered solution was concentrated to 40 cm^3 and cooled to −20 °C to give orange prisms that can be recrystallised from diethyl ether only in the presence of excess PMe_3. The solid is insoluble in light petroleum but will dissolve in toluene in the presence of PMe_3. On exposure to air the solid rapidly turns black while the solution turns a deep blue. Yield 2.32 g, 50%.

Crystallographic Studies.—Crystals of all three compounds were sealed under argon in Lindemann capillaries. All crystal-

Table 5. Atomic co-ordinates (× 10^4) for compound (3)

Atom	x	y	z
Mn(1)	3 983	−635	−129
P(1)	3 097(1)	247(1)	1 045(1)
C(1)	3 289(6)	−873(5)	2 024(3)
C(2)	3 825(6)	1 750(4)	1 653(4)
C(3)	1 526(4)	629(8)	600(4)
C(11)	4 109(3)	898(4)	−1 152(2)
C(12)	2 912(3)	1 487(3)	−1 354(2)
C(13)	1 861(3)	783(3)	−1 850(2)
C(14)	741(3)	1 336(4)	−2 052(3)
C(15)	647(4)	2 598(5)	−1 748(3)
C(16)	1 662(4)	3 308(4)	−1 251(3)
C(17)	2 770(3)	2 767(3)	−1 058(3)
C(21)	3 413(4)	−2 512(4)	−787(3)
C(22)	2 805(3)	−3 175(3)	−242(2)
C(23)	1 604(3)	−2 959(3)	−424(3)
C(24)	1 015(4)	−3 533(5)	79(4)
C(25)	1 598(5)	−4 340(5)	810(4)
C(26)	2 787(6)	−4 613(4)	1 055(3)
C(27)	3 397(4)	−4 028(4)	519(3)
H(1a)	2 872(79)	−1 874(91)	1 778(66)
H(1b)	3 001(50)	−592(49)	2 455(41)
H(1c)	4 114(45)	−1 106(48)	2 366(36)
H(2a)	3 604(40)	2 438(51)	1 182(38)
H(2b)	3 585(39)	1 945(45)	2 153(35)
H(2c)	4 600(47)	1 743(50)	1 967(37)
H(3a)	1 429(34)	1 153(43)	1 187(30)
H(3b)	1 321(44)	1 398(59)	163(38)
H(3c)	1 087(58)	−39(81)	550(51)
H(11a)	4 133(31)	371(36)	−1 595(27)
H(11b)	4 665(37)	1 543(44)	−1 157(30)
H(13)	1 929(32)	−49(41)	−2 092(26)
H(14)	−16(39)	799(41)	−2 378(31)
H(15)	−103(48)	2 928(58)	−1 845(41)
H(16)	1 546(36)	4 122(43)	−980(30)
H(17)	3 460(26)	3 186(29)	−702(22)
H(21a)	2 799(37)	−2 326(41)	−1 421(32)
H(21b)	4 081(33)	−2 967(38)	−760(27)
H(23)	1 123(35)	−2 418(41)	−972(31)
H(24)	205(72)	−3 465(85)	66(61)
H(25)	1 320(41)	−4 851(53)	1 215(35)
H(26)	3 197(42)	−5 060(51)	1 455(37)
H(27)	4 097(41)	−4 218(42)	561(31)

Table 6. Atomic co-ordinates (× 10^4) for compound (5)

Atom	x	y	z
Mn	547(1)	1 103(1)	288
Si(1)	1 857(1)	−2 517(1)	625(1)
C(11)	1 284(5)	−964(5)	331(3)
C(12)	3 462(6)	−2 487(7)	1 089(4)
C(13)	1 024(8)	−3 140(10)	1 204(5)
C(14)	1 677(10)	−3 631(7)	−72(4)
Si(2)	3 382(1)	2 511(1)	518(1)
C(21)	1 773(5)	2 444(5)	122(3)
C(22)	4 230(7)	3 522(8)	65(4)
C(23)	4 105(6)	950(7)	557(5)
C(24)	3 667(8)	3 160(10)	1 371(4)
P	287(1)	1 454(1)	1 512(1)
C(31)	349(7)	3 077(6)	1 735(3)
C(321)	−1 105(5)	883(5)	1 654(2)
C(322)	−1 890(6)	1 579(8)	1 904(3)
C(323)	−2 920(8)	1 042(12)	2 004(5)
C(324)	−3 188(8)	−159(13)	1 856(5)
C(325)	−2 424(8)	−846(8)	1 600(4)
C(326)	−1 394(6)	−332(6)	1 498(3)
C(331)	1 416(4)	820(4)	2 213(2)
C(332)	2 485(6)	403(6)	2 129(3)
C(333)	3 389(6)	28(8)	2 671(4)
C(334)	3 203(6)	57(7)	3 279(3)
C(335)	2 143(6)	442(6)	3 374(3)
C(336)	1 250(5)	817(5)	2 840(3)
H(11a)	1 856(44)	−755(42)	97(24)
H(11b)	1 484(54)	−532(57)	701(30)
H(12a)	4 047(52)	−2 010(65)	897(35)
H(12b)	3 762(57)	−3 331(27)	1 253(30)
H(12c)	3 610(64)	−1 896(57)	1 473(25)
H(13a)	1 387(59)	−3 916(38)	1 435(32)
H(13b)	152(22)	−3 238(78)	973(33)
H(13c)	1 152(86)	−2 450(57)	1 538(34)
H(14a)	2 295(40)	−3 171(51)	−247(27)
H(14b)	2 287(56)	−4 312(50)	63(40)
H(14c)	807(29)	−3 700(96)	−323(46)
H(21a)	1 650(47)	2 378(46)	−372(28)
H(21b)	1 402(45)	3 311(55)	164(25)
H(22a)	5 099(18)	3 567(55)	309(25)
H(22b)	3 898(69)	4 385(30)	37(42)
H(22c)	3 966(56)	3 408(64)	−427(8)
H(23a)	3 639(63)	343(62)	761(37)
H(23b)	4 991(16)	1 068(61)	756(30)
H(23c)	3 915(80)	551(77)	108(21)
H(24a)	4 553(18)	3 003(44)	1 571(22)
H(24b)	3 303(60)	2 691(72)	1 701(32)
H(24c)	3 564(99)	4 075(19)	1 477(60)
H(31a)	−299(37)	3 579(45)	1 433(23)
H(31b)	181(52)	3 192(60)	2 182(15)
H(31c)	1 136(40)	3 425(71)	1 683(37)
H(322)	−1 588(47)	2 422(24)	2 072(26)
H(323)	−3 525(54)	1 518(53)	2 186(32)
H(324)	−3 842(48)	−552(66)	2 031(36)
H(325)	−2 721(55)	−1 709(23)	1 481(30)
H(326)	−950(54)	−901(52)	1 265(30)
H(332)	2 674(47)	396(52)	1 684(13)
H(333)	4 159(38)	−218(69)	2 559(36)
H(334)	3 830(35)	−270(47)	3 670(17)
H(335)	1 924(50)	555(54)	3 806(15)
H(336)	488(22)	1 117(38)	2 935(21)

lographic measurements were made using a CAD4 diffractometer in the $\omega/2\theta$ scan mode with monochromated Mo-K_α radiation (λ = 0.710 69 Å), in a manner previously described in detail;[17] the intensity data were all corrected for absorption empirically.[18] Structures were determined using standard heavy-atom procedures and refined by full-matrix least-squares methods with all non-hydrogen atoms refined anisotropically. For compounds (3) and (5), all hydrogen atoms were located experimentally and refined with isotropic thermal parameters. For compound (2), disorder in the orientations of both PMe_3 and CMe_3 groups limited the precision to which the atomic co-ordinates could be determined, since the only way in which stable refinement could be achieved was by restricting P–C and C–C bond lengths to standard values, 1.84 ± 0.02 and 1.54 ± 0.03 Å respectively. As a result, it proved impossible to locate any of the hydrogen atoms, including those on the methylene groups. Details of crystal data, intensity measurements and refinement procedures are summarised in Table 3. Computers, programs and sources of scattering factor data are as given previously.[17] Final fractional atomic co-ordinates are given in Tables 4—6.

Acknowledgements

We thank the S.E.R.C. for provision of the diffractometer and Drs. J. F. Gibson and G. S. Girolami for helpful discussions.

References

1 R. A. Andersen, E. Carmona-Guzman, J. F. Gibson, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 2204.

2 R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 26; Z. Dawoodi, M. L. H. Green, V. S. B. Mtetwa, and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 802, 1411; M. Brookhart, W. Lamanna, and M. B. Humphrey, *J. Am. Chem. Soc.*, 1982, **104**, 2117.

3 J. A. Kirby, A. S. Robertson, J. P. Smith, A. C. Thompson, S. R. Cooper, and M. P. Klein, *J. Am. Chem. Soc.*, 1981, **103**, 5529; G. C. Dismukes and Y. Siderer, *Proc. Natl. Acad. Sci., USA*, 1981, **78**, 274.

4 J. I. Davies, C. G. Howard, A. C. Skapski, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1982, 1077.

5 K. Jacob and K.-H. Thiele, *Z. Anorg. Allg. Chem.*, 1979, **455**, 3.

6 K. Maruyama, T. Ito, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 849.

7 C. A. McAuliffe, *J. Organomet. Chem.*, 1982, **228**, 225 and refs. therein.

8 C. A. McAuliffe, personal communication; structure by T. J. King, Nottingham University.

9 L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3127.

10 M. B. Hursthouse, P. R. Raithby, and M. A. Thornton-Pett, unpublished work.

11 S. K. Bryan, J. K. Fawcett, S. C. Nyburg, and R. J. O'Brien, *Chem. Commun.*, 1970, 16.

12 J. C. Huffman and W. E. Streib, *Chem. Commun.*, 1971, 911.

13 R. A. Andersen, R. A. Jones, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1978, 446; M. B. Hursthouse, K. M. A. Malik, and K. D. Sales, *J. Chem. Soc., Dalton Trans.*, 1978, 1314.

14 P. R. Raithby, Ph.D. Thesis, University of London, 1976.

15 R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, M. Goodgame, and P. J. Hayward, *J. Chem. Soc. A*, 1969, 1242.

16 R. A. Andersen and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1977, 809.

17 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.

18 A. C. T. North, D. C. Phillips, and F. J. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

Received 9th February 1983; *Paper* 3/206