Alkyl, Hydrido, and Tetrahydroaluminato Complexes of Manganese with 1,2-Bis(dimethylphosphino)ethane (dmpe). *X*-Ray Crystal Structures of $Mn_2(\mu\text{-}C_6H_{11})_2(C_6H_{11})_2(\mu\text{-dmpe})$, $(dmpe)_2Mn(\mu\text{-}H)_2AlH(\mu\text{-}H)_2AlH(\mu\text{-}H)_2\text{-}Mn(dmpe)_2$, and $Li_4\{MnH(C_2H_4)[CH_2(Me)PCH_2CH_2PMe_2]_2\}_2\cdot 2Et_2O$†

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Alkylation of $MnBr_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] with $MgBu^t_2$ leads to the t-butyl complex $MnBu^t_2(dmpe)$; alkylation with $Mg(C_6H_{11})_2$ gives the cyclohexyl-bridged dimer $Mn_2(\mu\text{-}C_6H_{11})_2(C_6H_{11})_2(\mu\text{-dmpe})$ (**2**). By contrast, alkylation with $MgEt_2$ leads to the diamagnetic manganese(I) species, *trans*-$MnH(C_2H_4)(dmpe)_2$. Interaction of the latter with $LiBu^t$ leads to deprotonation of the dmpe ligand and formation of a complex, (**4**), of stoicheiometry $Li_2\{MnH(C_2H_4)[CH_2(Me)PCH_2CH_2PMe_2]_2\}\cdot Et_2O$. A reduction of Mn^{II} to Mn^I also occurs in the interaction of $MnBr_2(dmpe)_2$ with $LiAlH_4$ when the tetrahydroaluminate complex $[Mn(AlH_4)(dmpe)_2]_2$ (**5**) is formed. Hydrolysis of (**5**) gives the volatile diamagnetic hydride $MnH_3(dmpe)_2$. The *X*-ray crystal structures of the complexes (**2**), (**4**), and (**5**) have been determined. In (**2**), the molecule, which has two-fold symmetry, has two manganese atoms each bound to one terminal related cyclohexyl group [Mn–C = 2.118(10) Å] and bridged asymmetrically by two symmetry related cyclohexyls [Mn–C = 2.256(9), 2.327(9) Å]. The Mn ··· Mn distance is quite short at 2.616(5) Å and the manganese atoms have a distorted tetrahedral co-ordination. In complex (**4**), two $MnH(C_2H_4)(dmpe)_2$ units [Mn–H 1.44(4), Mn–C (av.) 2.121(5), Mn–P 2.213(3)—2.274(3) Å] have each lost two hydrogen atoms, one from each of two dmpe methyls, and the resulting four CH_2 groups form multicentre alkyl bridges to a central Li_4 tetrahedron [C ··· Li 2.20—2.36(1), Li ··· Li 2.46(1)—2.69(1) Å]. Two of the lithiums are co-ordinated by diethyl ether [Li–O 2.053(8) Å]. The complex as a whole has C_2 symmetry and the manganese(I) centre has a pseudo-octahedral geometry, although pentagonal bipyramidal is an alternative description if the ethylene is considered to occupy two co-ordination sites. Complex (**5**) is a centrosymmetric dimer in which two *cis*-octahedral $MnH_2(dmpe)_2$ units are bridged by a $AlH(\mu\text{-}H)_2AlH$ moiety *via* $Al(\mu\text{-}H)_2Mn$ linkages. The two H atoms in the AlH_2Mn bridge are closer to the Mn atoms [Mn–H = 1.61(3), 1.63(3) Å] than to the Al atoms [Al–H = 1.81(3), 1.81(3) Å]. The Al–H distances in the AlH_2Al unit are 1.64(3) and 1.80(3) Å, while the terminal Al–H distance is 1.51(3) Å. The aluminium has trigonal bipyramidal co-ordination with one terminal hydrogen in an equatorial position.

In previous papers,[1,2] we have described several monomeric and dimeric maganese(II) alkyls containing tertiary phosphine ligands. Details of further studies on alkyls, hydrides, and an AlH_4 complex derived from $MnBr_2(dmpe)_2$ [dmpe = 1,2-bis(dimethylphosphino)ethane] are now given; some of this work was reported in a preliminary note.[3]

Results and Discussion

1. *[1,2-Bis(dimethylphosphino)ethane]bis(t-butyl)-manganese*(II).—Alkylation of $MnBr_2(dmpe)_2$ with $MnBu^t_2$ in diethyl ether produces the yellow complex $MnBu^t_2(dmpe)$ (**1**), which may also be obtained directly from $MnCl_2$ by alkylation in the presence of dmpe.

This 13-electron species is high-spin in solution (μ = 5.8 B.M.); the e.s.r. spectrum is similar to those of other four-co-ordinate $S = \frac{5}{2}$ $MnR_2(PR'_3)_2$ complexes with rhombically distorted tetrahedral geometries.[2] The spectrum can be analysed in terms of the Hamiltonian given by equation (i),

$$\mathscr{H} = \beta B\cdot g\cdot S + D[S_z^2 - \tfrac{1}{3}S(S+1) + \lambda(S_x^2 - S_y^2)] + I\cdot A\cdot S \quad \text{(i)}$$

assuming that g is isotropic and equal to 2.0, as is typical of $^6S_{\frac{5}{2}}$ ground states.[4] Computer fitting of the spectrum of (**1**) gives a zero-field splitting parameter $D = 0.63$ cm^{-1}, a symmetry parameter $\lambda = 0.295$, and an isotropic hyperfine coupling $A(^{55}Mn) = 0.0030$ cm^{-1}. All these values are near those of other $MnR_2(PR'_3)_2$ complexes,[2] with the symmetry parameter λ being slightly closer to $\frac{1}{3}$, the limit for maximum possible rhombic symmetry.[4] Observed field strengths for the individual e.s.r. resonances and their assignments are included in the Experimental section.

The i.r. spectrum of $MnBu^t_2(dmpe)$ (**1**) shows a strong C–H stretching mode at 2 760 cm^{-1} and several weaker features to lower frequency that are probably overtone or combination

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† μ-[1,2-Bis(dimethylphosphino)ethane-*P,P'*]-di-μ-cyclohexyl-dicyclohexyldimanganese(II), 1,1,4,4-tetrakis[1,2-bis(dimethylphosphino)ethane-*P,P'*]-1,2;1,2;2,3;2,3;3,4;3,4-hexa-μ-hydrido-2,3-dihydrido-1,4-dimanganese-2,3-dialuminium, and bis[bis{1-dimethylphosphino-2-[lithiomethyl(methyl)]phosphinoethane-*P,P'*}(ethylene)hydridomanganese(I)]–diethyl ether (1/2) respectively.

Supplementary data available (No. SUP 56166, 8 pp.): anisotropic and isotropic thermal parameters, H-atom co-ordinates for (**2**). See Instructions for Authors, *J. Chem. Soc., Dalton Trans*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: atm = 101 325 N m^{-2}, B.M. = 0.927 × 10^{-23} A m^2.

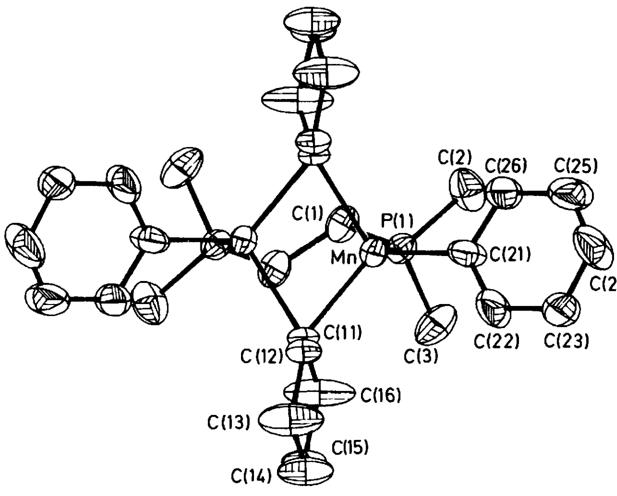

Figure 1. The structure of $Mn_2(C_6H_{11})_4$(dmpe) (**2**)

bands of C–C stretching and C–H bending modes. Absorptions in the region 2 700—2 800 cm^{-1} are attributable in some cases to M $\cdots$ H–C interactions, but vibrations associated with such interactions are commonly weak; although low-frequency bands were observed in bridged manganese alkyls[1] they were not observed in the monomeric species.[2] Since the i.r. spectrum of liquid $ZnBu^t_2$ has a strong band at 2 817 cm^{-1} assigned as a C–H stretch,[5] we consider that the band at 2 760 cm^{-1} in the manganese complex (**1**) is probably similarly attributable to a C–H fundamental. The lower frequency could be due either to the different symmetries adopted by the two molecules or to the differences in metal–alkyl bonding due to greater ionic character in (**1**) arising from the greater electropositive character of the metal, thereby inducing a shift to lower energy.

The general similarity of the spectra of the Zn and Mn compounds indicates that the t-butyl groups in the manganese complex (**1**) have not undergone rearrangement to n-, i-, or s-butyl analogues. Indeed, attempts to prepare such manganese alkyls by alkylation with the corresponding dialkylmagnesium reagents have not given tractable products.

Although $MnBu^t_2$(dmpe) is quite air- and moisture-sensitive, it is thermally stable at room temperature for days in solution and indefinitely in the solid state. As for other $MnR_2(PR'_3)_2$ compounds,[2] e.s.r. spectra indicate that reversible dissociation of the dmpe ligand occurs in solution consistent with the long Mn–P distances found for such species.[1,2] The compound does not react with H_2 (10 atm) and its preparation may be carried out under hydrogen with no reduction in yield.

Few t-butyl complexes of transition metals have been described; examples include $Fe(CO)_2Bu^t(\eta^5\text{-}C_5H_5)_2$,[6] $CrBu^t_4$,[7] and various gold(I) and gold(III) species.[8] It is of interest that the species believed to be 'manganese dialkyls' (but more likely manganese analogues of Grignard reagents) prepared *in situ* by alkylation of $MnCl_2$ with Grignard reagents[9] provided some of the first evidence that alkyls lacking β-hydrogen atoms showed enhanced thermal stability. It was also noted by Tamura and Kochi[9] that the decomposition rate of '$MnBu^t_2$' was slowed by the addition of triphenylphosphine although no explanation was provided.

2. [1,2-*Bis(dimethylphosphino)ethane*)]*tetrakis(cyclohexyl)-dimanganese*(II).—Examples of transition-metal cyclohexyl complexes are relatively rare, including $Re_3Cl_3(C_6H_{11})_6(PMe_2Ph)_3$,[10] $Zr(C_6H_{11})Cl(\eta^5\text{-}C_5H_5)_2$,[11] $Ti(C_6H_{11})_4$,[12] $Re_2(\mu\text{-}H)_2(\mu\text{-}C_6H_{10})(C_6H_6)$,[13] and some iridium(III) species of the form $Ir(C_6H_{11})H(L)(\eta^5\text{-}C_5R_5)$.[14]

Table 1. Selected bond lengths (Å) and angles (°) for $Mn_2(C_6H_{11})_4$(dmpe) (**2**)

Mn–Mn^{I}	2.616(5)	Mn–P(1)	2.579(5)
Mn–C(11)	2.256(9)	Mn–C(12)	2.118(10)
Mn–C(11^{I})	2.327(9)	C(1)–P(1)	1.811(10)
C(2)–P(1)	1.813(10)	C(3)–P(1)	1.800(11)
C(1)–C(1^{I})	1.619(18)	C(12)–C(11)	1.541(11)
C(16)–C(11)	1.417(12)	C(13)–C(12)	1.452(12)
C(14)–C(13)	1.336(14)	C(15)–C(14)	1.509(14)
C(16)–C(15)	1.471(13)	C(22)–C(21)	1.374(13)
C(26)–C(21)	1.429(12)	C(23)–C(22)	1.516(13)
C(24)–C(23)	1.422(13)	C(25)–C(24)	1.315(14)
C(26)–C(25)	1.519(14)		

P(1)–Mn–Mn^{I}	102.0(3)	C(11)–Mn–Mn^{I}	56.5(3)
C(21)–Mn–Mn^{I}	152.3(3)	C(11^{I})–Mn–Mn^{I}	53.9(4)
C(11)–Mn–P(1)	109.5(3)	C(21)–Mn–P(1)	105.1(4)
C(21)–Mn–C(11)	117.6(4)	P(1)–Mn–C(11^{I})	104.8(4)
C(11)–Mn–C(11^{I})	106.5(4)	C(21)–Mn–C(11^{I})	112.6(5)
C(1)–P(1)–Mn	124.7(4)	C(2)–P(1)–Mn	110.0(4)
C(3)–P(1)–Mn	113.5(4)	C(2)–P(1)–C(1)	100.3(5)
C(3)–P(1)–C(1)	103.1(5)	C(3)–P(1)–C(2)	102.4(6)
P(1)–C(1)–C(1^{I})	113.4(5)	Mn–C(11)–Mn^{I}	69.6(4)
C(12)–C(11)–Mn	108.3(5)	C(16)–C(11)–Mn	110.5(8)
C(12)–C(11)–Mn^{I}	108.9(5)	C(16)–C(11)–Mn^{I}	134.0(7)
C(16)–C(11)–C(12)	113.8(7)	C(13)–C(12)–C(11)	115.1(7)
C(14)–C(13)–C(12)	124.4(10)	C(15)–C(14)–C(13)	117.5(9)
C(16)–C(15)–C(14)	113.4(8)	C(15)–C(16)–C(11)	112.2(10)
C(22)–C(21)–Mn	122.7(8)	C(26)–C(21)–Mn	118.7(7)
C(26)–C(21)–C(22)	118.4(9)	C(23)–C(22)–C(21)	123.1(10)
C(24)–C(23)–C(22)	115.2(9)	C(25)–C(24)–C(23)	123.6(10)
C(26)–C(25)–C(24)	120.7(10)	C(25)–C(26)–C(21)	118.5(9)

Key to symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*): I, 0.5 − *x*, 0.5 − *y*, *z*.

Interaction of cyclohexylmagnesium chloride with $MnCl_2$ and dmpe leads to an orange crystalline species whose structure has been determined by *X*-ray diffraction. The compound is identified as $Mn_2(C_6H_{11})_4$(dmpe) (**2**), in which the two Mn atoms are bridged by the bidentate dmpe ligand and by two cyclohexyl groups; the other cyclohexyl groups are terminal, one to each metal (Figure 1). The complex is thus closely related to the previously described[1] dimeric species $[MnR_2(PR'_3)]_2$, although structurally there is one very significant difference. In all the dimers studied crystallographically the molecules are centrosymmetric, or nearly so, with a *trans* disposition of the two unidentate phosphines. In the present molecule the use of the bidentate dmpe ligand has produced a *cis* arrangement, and a molecule with crystallographic C_2 symmetry. In most other respects, the structure shows similarities to those of the $[MnR_2(PR'_3)]_2$ dimers.[1] Thus, the Mn–P bond is fairly long and the alkyl bridges are asymmetric (Table 1). Both these features correlate with the apparent ease of dissociation of the molecules in solution. Unfortunately high thermal motion or disorder in the cyclohexyl groups (see Experimental section) made it impossible to locate the hydrogens attached to the σ-bonded carbons, and it is thus not possible to say whether the C–H $\cdots$ Mn interactions consistently found in the dimers[1] are also present here. The geometry around the Mn atoms is distorted tetrahedral, with interligand angles in the range 104.8(4)—117.6(4)°. The Mn–C(terminal) bond length of 2.118(10) Å agrees very closely with values found previously.[1]

Complex (**2**) is thermally stable in the solid state but decomposes slowly at room temperature in solution. The e.s.r. spectrum of the dimer could not be observed at 77 K due to dissociation to the monomer. This resulted in a spectrum consistent with a high-spin tetrahedral Mn^{II} monomeric species

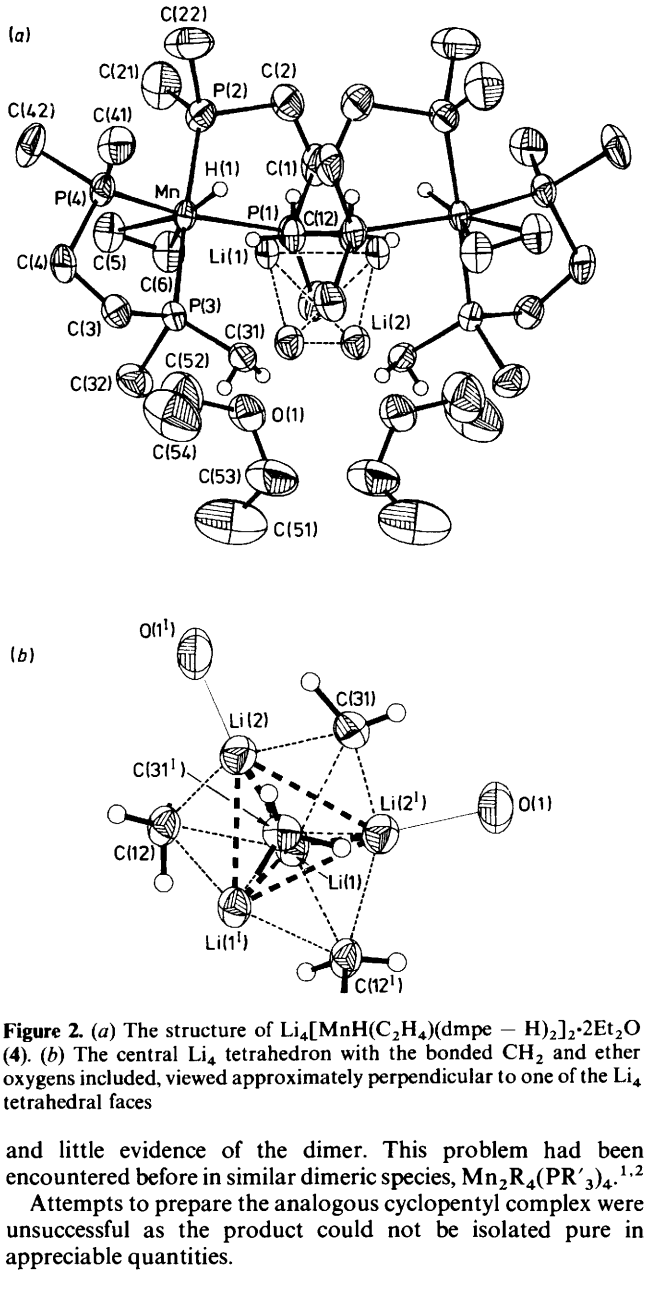

Figure 2. (*a*) The structure of $Li_4[MnH(C_2H_4)(dmpe - H)_2]_2{\cdot}2Et_2O$ (**4**). (*b*) The central Li_4 tetrahedron with the bonded CH_2 and ether oxygens included, viewed approximately perpendicular to one of the Li_4 tetrahedral faces

and little evidence of the dimer. This problem had been encountered before in similar dimeric species, $Mn_2R_4(PR'_3)_4$.[1,2]

Attempts to prepare the analogous cyclopentyl complex were unsuccessful as the product could not be isolated pure in appreciable quantities.

3. *Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*](*ethylene*)*hydridomanganese*(I).—Alkylation of $MnBr_2(dmpe)_2$ with $MgEt_2$ yields the diamagnetic species $MnH(CH_2{=}CH_2)(dmpe)_2$ (**3**) which has a Mn–H stretch in the i.r. at 1 725 cm^{-1} and absorptions due to co-ordinated etheylene at 3 020, 3 005, and 1 175 cm^{-1}. The ^1H n.m.r. spectrum shows a binomial quintet at δ −11.89 due to the hydride [J(P–H) = 56.5 Hz].

The resonance of the C_2H_4 moiety is a quintet at δ 0.87 [J(P–H) = 4.4 Hz] indicating that rotation of the bound ethylene is rapid on the n.m.r. time-scale at room temperature. The proton-coupled ^{13}C n.m.r. spectrum for C_2H_4 is a triplet with the ^1J(C–H) coupling constant of 150 Hz being typical for co-ordinated alkenes;[15] no phosphorus coupling to the ethylene carbon atoms is observed even in the proton-decoupled spectrum. The $^{31}P\text{-}\{^1H\}$ spectrum is a singlet broadened by quadrupolar effects of the $I = \frac{5}{2}$ ^{55}Mn nucleus. The n.m.r. data are consistent with an octahedral structure with H and C_2H_4 in *trans* positions. Only two other ethylene complexes of manganese are known, both being carbonyl species.[16]

Complex (**3**) does not react with H_2 (10 atm), and as for complex (**1**) above, the preparation of $MnH(CH_2{=}CH_2)(dmpe)_2$ may be conducted under H_2 (10 atm) without affecting the yield. Photolysis of (**3**) under a hydrogen atmosphere leads to an intractable mixture of several hydride-containing products.

We were unable to obtain crystals suitable for X-ray study. It is difficult to see how complex (**3**) arises if *trans*-$MnBr_2(dmpe)_2$ is fully alkylated to $Mn(C_2H_5)_2(dmpe)_2$; successive β-hydride transfers would be expected to lead to $Mn(C_2H_4)(dmpe)_2$. It seems more likely that $MnBr(dmpe)_2$ is an intermediate; this could be formed in a one-electron reduction by the Grignard reagent possibly *via* a bridged manganese(II) alkyl eliminating butane. The monobromide, on alkylation followed by β-hydride transfer should then give the *cis*-hydrido–ethylene complex which would be expected to isomerise to the more stable *trans* isomer isolated.

4. *Lithiation of* $MnH(C_2H_4)(dmpe)_2$ (**3**).—Treatment of $MnH(C_2H_4)(dmpe)_2$ (**3**) with $LiBu^t$ in light petroleum followed by diethyl ether extraction of the resulting solid leads to a yellow crystalline complex, (**4**), of stoicheiometry $Li_2[MnH(C_2H_4)(dmpe - H)_2]{\cdot}Et_2O$. Since the i.r. spectrum indicated that the Mn–H and $Mn(C_2H_4)$ groups were still present in the molecule it was evident that hydrogen atoms must have been removed from the dmpe ligand (dmpe − H = monoanion of dmpe). The structure of compound (**4**) has been confirmed by X-ray study [Figure 2(*a*)]. The manganese co-ordination comprises two chelating dmpe − H ligands in which two Mn–P bonds are mutually *trans* and two *cis*. The latter form part of a pentagonal equatorial girdle which also contains the hydride and the two carbons of the ethylene. Selected bond lengths and angles are given in Table 2. The differences in Mn–P bond lengths do not correlate with the axial or equatorial position, and it is perhaps best to consider the complex to have a pseudo-octahedral geometry, with a 'unidentate' ethylene co-ordination. The ethyl C–C distance [1.41(1) Å] is only slightly longer than a C=C bond, although the hydrogens are bent away from the metal in the usual fashion [the angle sums at C(5) and C(6) are 351.8 and 354.0° respectively], and a significant contribution from the metallacyclopropane form is possible. The interaction between the manganese complex and the two independent lithium atoms is the most interesting feature of the complex. The two lithiums lie close to a crystallographic two-fold axis and together with their symmetry relatives form a slightly distorted Li_4 tetrahedron (see Table 2). On each of two Mn complex systems, related by the same symmetry element, two dmpe methyl groups, one on each of two dmpe ligands, have lost one hydrogen, with the resulting CH_2 groups acting as face-capping alkyls to the Li_4 tetrahedron, see Figure 2(*b*). The C $\cdots$ Li interactions are unsymmetrical (Table 2) and one of the independent lithiums is bonded to the oxygen of a diethyl ether molecule.

Relatively few hydrido–ethylene complexes are known; in the structure of *cis*-$[MoH(C_2H_4)_2(Ph_2PCH{=}CHPPh_2)_2]^+$ the hydride was not located.[17]

We have been unable to find a previous example of lithiation of a co-ordinated phosphine ligand in a transition-metal complex of the type described here, although lithiation of methyl groups on tertiary phosphines is well known.[18]

There are several examples of reactions involving $LiN(SiMe_3)_2$ or lithium alkyls[19,20] that have led to deprotonation of co-ordinated PMe_3 or other phosphines in transition-metal complexes and the formation, commonly, of cyclometallated products; however these reactions doubtless involve initial displacement of halide or carboxylate from the metal complex followed by intramolecular hydride transfer from the phosphine. They are thus similar to reductions of phosphine–halide or –carboxylate complexes by sodium or other reducing

Table 2. Selected bond lengths (Å) and angles (°) for $Li_4[MnH(C_2H_4)(dmpe - H)_2]_2 \cdot 2Et_2O$ (**4**)

H(1)–Mn	1.442(41)	P(1)–Mn	2.274(3)
P(2)–Mn	2.221(3)	P(3)–Mn	2.267(3)
P(4)–Mn	2.213(3)	C(5)–Mn	2.127(5)
C(6)–Mn	2.116(6)		
C(1)–P(1)	1.863(6)	C(11)–P(1)	1.835(6)
C(12)–P(1)	1.816(5)	C(2)–P(2)	1.849(6)
C(21)–P(2)	1.851(7)	C(22)–P(2)	1.839(8)
C(3)–P(3)	1.861(6)	C(31)–P(3)	1.813(5)
C(32)–P(3)	1.857(6)	C(4)–P(4)	1.853(6)
C(41)–P(4)	1.834(7)	C(42)–P(4)	1.838(6)
C(2)–C(1)	1.510(8)	C(4)–C(3)	1.512(7)
C(6)–C(5)	1.406(6)	H(121)–C(12)	0.960(37)
H(122)–C(12)	0.926(40)	H(311)–C(31)	0.821(40)
H(312)–C(31)	1.054(41)		
C(52)–O(1)	1.492(8)	C(53)–O(1)	1.442(7)
C(53)–C(51)	1.480(10)	C(54)–C(52)	1.415(9)
Li(1) ··· C(12)	2.200(8)	Li(2) ··· C(12)	2.293(9)
Li(1) ··· C(31)	2.253(9)	Li(2) ··· C(31)	2.360(9)
Li(1$^{\mathrm{I}}$) ··· C(12)	2.348(10)	Li(2$^{\mathrm{I}}$) ··· C(31)	2.263(9)
Li(2) ··· Li(1)	2.685(11)	Li(1) ··· Li(2$^{\mathrm{I}}$)	2.464(12)
Li(2) ··· Li(2$^{\mathrm{I}}$)	2.676(15)	Li(2) ··· Li(1$^{\mathrm{I}}$)	2.509(12)
Li(2) ··· O(1)	2.053(8)		

P(1)–Mn–H(1)	77.3(17)	P(2)–Mn–H(1)	81.3(17)
P(2)–Mn–P(1)	84.80(5)	P(3)–Mn–H(1)	94.5(17)
P(3)–Mn–P(1)	93.40(4)	P(3)–Mn–P(2)	175.70(5)
P(4)–Mn–H(1)	80.5(17)	P(4)–Mn–P(1)	157.50(5)
P(4)–Mn–P(2)	95.30(5)	P(4)–Mn–P(3)	84.80(5)
C(5)–Mn–H(1)	160.1(16)	C(5)–Mn–P(1)	121.2(2)
C(5)–Mn–P(2)	92.4(2)	C(5)–Mn–P(3)	91.9(2)
C(5)–Mn–P(4)	81.3(2)	C(6)–Mn–H(1)	159.3(16)
C(6)–Mn–P(1)	82.6(2)	C(6)–Mn–P(2)	92.3(2)
C(6)–Mn–P(3)	91.4(2)	C(6)–Mn–P(4)	119.8(2)
C(6)–Mn–C(5)	38.7(1)		
C(1)–P(1)–Mn	107.8(2)	C(11)–P(1)–Mn	120.7(3)
C(11)–P(1)–C(1)	98.9(3)	C(12)–P(1)–Mn	118.7(2)
C(12)–P(1)–C(1)	106.9(3)	C(12)–P(1)–C(11)	101.5(3)
C(2)–P(2)–Mn	110.9(2)	C(21)–P(2)–Mn	121.8(3)
C(21)–P(2)–C(2)	100.7(3)	C(22)–P(2)–Mn	122.8(3)
C(22)–P(2)–C(2)	98.0(4)	C(22)–P(2)–C(21)	98.2(5)
C(3)–P(3)–Mn	108.7(2)	C(31)–P(3)–Mn	121.1(2)
C(31)–P(3)–C(3)	101.4(3)	C(32)–P(3)–Mn	119.0(3)
C(32)–P(3)–C(3)	99.4(3)	C(32)–P(3)–C(31)	103.9(3)
C(4)–P(4)–Mn	110.7(2)	C(41)–P(4)–Mn	119.0(3)
C(41)–P(4)–C(4)	99.5(3)	C(42)–P(4)–Mn	123.9(3)
C(42)–P(2)–C(4)	99.9(3)	C(42)–P(4)–C(41)	99.7(4)
C(2)–C(1)–P(1)	108.1(4)	C(1)–C(2)–P(2)	108.9(4)
C(4)–C(3)–P(3)	108.9(4)	C(3)–C(4)–P(4)	107.6(3)
C(6)–C(5)–Mn	70.3(3)	C(5)–C(6)–Mn	71.0(3)
H(121)–C(12)–P(1)	112.3(22)	H(122)–C(12)–P(1)	107.8(23)
H(122)–C(12)–H(121)	107.8(31)	H(311)–C(31)–P(3)	101.0(28)
H(312)–C(31)–P(3)	96.4(21)	H(312)–C(31)–H(311)	105.7(34)
C(53)–O(1)–C(52)	121.6(5)	C(54)–C(52)–O(1)	114.3(7)
C(51)–C(53)–O(1)	111.7(7)		

Key to symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*): I, 1.5 − *x*, *y*, 1.0 − *z*.

agents[21] in which complexes with groups such as $\overline{MCH_2P}Me_2$ or $H\overline{MCH_2P}Me_2$ are generated. The first example[22] of such a reaction involved dmpe, although the product was later shown[23] to be a dimer containing the bridged unit $Ru(CH_2{-}P{<})_2Ru$.

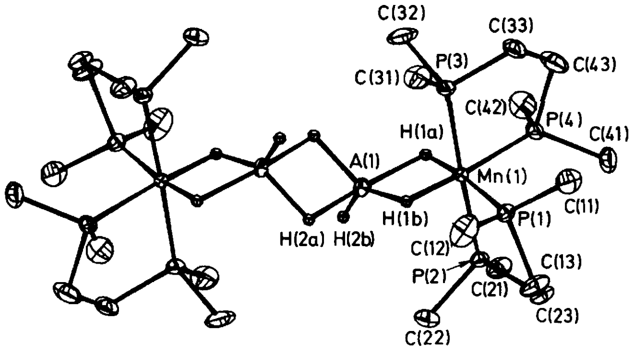

Figure 3. The structure of $[Mn(AlH_4)(dmpe)_2]_2$ (**5**)

It should be possible to lithiate neutral dmpe, PMe_3, similar phosphine complexes such as $Ni(dmpe)_2$,[18] or phosphine complexes such as the present one with ligands less readily lithiated than the phosphine, to give new types of lithium alkyls, which in turn should be able to alkylate metal halides, complex halides *etc.*

5. *Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*](*tetrahydroaluminato*)*manganese*(I).—In an effort to prepare other examples of manganese hydride complexes, the interaction of $MnBr_2(dmpe)_2$ with $LiAlH_4$ was investigated; in toluene a yellow solution is obtained from which the diamagnetic complex (**5**), of stoicheiometry $Mn(AlH_4)(dmpe)_2$, may be isolated. This compound has i.r. absorptions at 1 740, 1 610, and 970 cm^{-1} that may be assigned to various Al–H and Mn–H–Al modes. In the ^1H n.m.r. spectrum, a Mn–H–Al hydride resonance occurs at δ −15.02 that is broadened due to the quadrupole moments of manganese and aluminium. A terminal Al–H signal at δ 5.05 is similarly broadened, although to a lesser extent; the ratio of bridging to non-bridging hydrides is 1 : 1 by integration. The ^1H and ^{13}C-{^1H} n.m.r. resonances of dmpe indicate a *cis*-octahedral arrangement about manganese, while the ^{31}P-{^1H} spectrum is again uninformative due to quadrupolar effects.

In the solid state, compound (**5**) exists as a centrosymmetric dimer, $[Mn(AlH_4)(dmpe)_2]_2$, due to the formation of a $Mn(\mu\text{-}H)_2AlH(\mu\text{-}H)_2AlH(\mu\text{-}H)_2Mn$ bridge (Figure 3). The aluminium atoms adopt distorted trigonal bipyramidal geometries, with the terminal hydride on each aluminium atom occupying an equatorial position. The Mn–H distances in the $Mn(\mu\text{-}H)_2Al$ units are equal, and are shorter than the two Al–H distances by 0.2 Å, indicating a strong affinity of these hydrides for the manganese atom, Table 3. The geometries about Mn are *cis*-octahedral, as deduced by n.m.r., with the Mn–P distances *trans* to the hydrides being slightly *shorter* than the Mn–P distances *trans* to each other. Evidently, the *trans*-effect of bridging hydrides is reduced relative to that of terminal hydrides. The central $Al(\mu\text{-}H)_2Al$ unit is asymmetric, with the long and short Al–H distances differing by *ca.* 0.2 Å so that the molecule may be thought of as a loosely bound dimer.

The structural data indicate three different hydride environments, but the room temperature ^1H n.m.r. spectrum shows only two. Low-temperature studies (by Barron and co-workers[24]) show that on cooling to 193 K the peak due to the Al–H groups (δ + 5.05) splits into two peaks of equal intensity (δ + 5.34 and 4.76, T_c = 210 K). Hence there is a fluxional process involving the $HAl(\mu\text{-}H)_2AlH$ unit; fluxionality of this type has been observed in several other related AlH_4^- systems.[24] The activation energy, calculated from the n.m.r. data ($\Delta G_a^{\ddagger}$ = 40 kJ mol^{-1}) is comparable with that found in other cases.[24]

Table 3. Selected bond lengths (Å) and angles (°) for $[MnAlH_4(dmpe)_2]_2$ (**5**)

H(1a)–Mn(1)	1.610(26)	H(1b)–Mn(1)	1.631(28)
Al(1)–Mn(1)	2.393(4)	P(1)–Mn(1)	2.206(3)
P(2)–Mn(1)	2.218(3)	P(3)–Mn(1)	2.218(3)
P(4)–Mn(1)	2.215(3)		
Al(1)–H(1a)	1.809(27)	Al(1)–H(1b)	1.809(28)
H(2a)–Al(1)	1.804(28)	H(2b)–Al(1)	1.510(30)
Al(1)–Al(1a)	2.728(6)	H(2a)–Al(1a)	1.642(32)
C(11)–P(1)	1.835(9)	C(12)–P(1)	1.831(9)
C(13)–P(1)	1.852(8)	C(23)–C(13)	1.494(10)
C(21)–P(2)	1.826(8)	C(22)–P(2)	1.836(8)
C(23)–P(2)	1.857(8)		
C(31)–P(3)	1.821(8)	C(32)–P(3)	1.806(9)
C(33)–P(3)	1.847(9)	C(43)–C(33)	1.503(12)
C(41)–P(4)	1.837(8)	C(42)–P(4)	1.822(9)
C(43)–P(4)	1.869(9)		
H(1b)–Mn(1)–H(1a)	97.9(14)	Al(1)–Mn(1)–H(1a)	49.1(9)
Al(1)–Mn(1)–H(1b)	49.1(9)	P(1)–Mn(1)–H(1a)	173.6(8)
P(1)–Mn(1)–H(1b)	78.5(10)	P(1)–Mn(1)–Al(1)	126.7(2)
P(2)–Mn(1)–H(1a)	90.7(10)	P(2)–Mn(1)–H(1b)	91.2(10)
P(2)–Mn(1)–Al(1)	87.8(2)	P(2)–Mn(1)–P(1)	84.0(2)
P(3)–Mn(1)–H(1a)	89.6(10)	P(3)–Mn(1)–H(1b)	91.4(10)
P(3)–Mn(1)–Al(1)	94.5(2)	P(3)–Mn(1)–P(1)	95.8(2)
P(3)–Mn(1)–P(2)	177.3(1)	P(4)–Mn(1)–H(1a)	84.0(10)
P(4)–Mn(1)–H(1b)	174.1(10)	P(4)–Mn(1)–Al(1)	133.1(1)
P(4)–Mn(1)–P(1)	100.0(2)	P(4)–Mn(1)–P(2)	94.3(2)
P(4)–Mn(1)–P(3)	83.1(2)		
Al(1)–H(1a)–Mn(1)	88.7(12)	Al(1)–H(1b)–Mn(1)	88.0(12)
Al(1)–H(2a)–Al(1$^{\mathrm{I}}$)	104.6(11)		
H(1a)–Al(1)–Mn(1)	42.3(8)	H(1a)–Al(1)–H(2a$^{\mathrm{I}}$)	107.8(13)
H(1b)–Al(1)–Mn(1)	42.9(8)	H(1b)–Al(1)–H(1a)	85.0(12)
H(1b)–Al(1)–H(2a$^{\mathrm{I}}$)	111.6(12)	H(2a)–Al(1)–Mn(1)	123.2(9)
H(2a)–Al(1)–H(1a)	164.9(12)	H(2a)–Al(1)–H(1b)	80.2(13)
H(2a)–Al(1)–H(2a$^{\mathrm{I}}$)	75.4(13)	H(2b)–Al(1)–Mn(1)	122.5(12)
H(2a)–Al(1)–H(1a)	95.7(14)	H(2b)–Al(1)–H(1b)	138.4(12)
H(2b)–Al(1)–H(2a)	97.5(14)		
C(11)–P(1)–Mn(1)	125.0(3)	C(12)–P(1)–Mn(1)	119.5(4)
C(12)–P(1)–C(11)	97.6(5)	C(13)–P(1)–Mn(1)	111.7(3)
C(13)–P(1)–C(11)	100.1(4)	C(13)–P(1)–C(12)	98.2(5)
C(23)–C(13)–P(1)	111.7(5)		
C(21)–P(2)–Mn(1)	123.2(3)	C(22)–P(2)–Mn(1)	120.4(3)
C(22)–P(2)–C(21)	99.0(4)	C(23)–P(2)–Mn(1)	109.9(3)
C(23)–P(2)–C(21)	101.4(4)	C(23)–P(2)–C(22)	98.9(4)
P(2)–C(23)–C(13)	107.2(5)		
C(31)–P(3)–Mn(1)	123.7(3)	C(32)–P(3)–Mn(1)	119.4(4)
C(32)–P(3)–C(31)	98.0(5)	C(33)–P(3)–Mn(1)	110.7(3)
C(33)–P(3)–C(31)	100.8(4)	C(33)–P(3)–C(32)	100.5(5)
C(43)–C(33)–P(3)	111.6(6)		
C(41)–P(4)–Mn(1)	126.5(3)	C(42)–P(4)–Mn(1)	116.6(4)
C(42)–P(4)–C(41)	98.5(4)	C(43)–P(4)–Mn(1)	112.7(3)
C(43)–P(4)–C(41)	97.6(4)	C(43)–P(4)–C(42)	100.6(5)
P(4)–C(43)–C(33)	112.1(5)		

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z): I $2.0 - x, -y, -z$.

Although many BH_4^- complexes of transition metals are known, mostly with bidentate BH_4^- groups, it was noted that few AlH_4^- derivatives were known;[25] some have been described as black solids or oils, some characterised spectroscopically, but none structurally characterised.[26] The present complex was the first to be structurally determined[3] but recently Russian workers[27] have described the structure of $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}H)_2AlH_2$, where the molecules are linked by *NNN'N'*-tetramethylethylenediamine with N co-ordinated to Al, and of $[(\eta\text{-}C_5H_5)_2YAlH_4\cdot C_4H_8O]_2$; additionally we have determined the structure of $[WH_3\{AlH_3(OBu^n)\}(PMe_3)_3]_2$.[24] Other species with M–H–Al bridges are however characterised;[28] the structure of $[TaAlH_2(OCH_2CH_2OMe)_2(dmpe)_2]_2$[28d] is similar to the manganese molecule now described, but the hydrogen atoms were not located. We have also spectroscopically characterised two related molecules $[WH_3(AlH_4)(PMe_3)_3]_2$ and $[ReH_2\{AlH_3(OBu^n)\}(PMe_2Ph)_3]_2$.[24]

For aluminium, as distinct from boron, presumably due to the larger radius of Al, the formation of Al_2H_8 or related bridging Al_2 units may prove to be common.

6. *Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*trihydridomanganese*(III).—Hydrolysis of complex (**5**) in ether gives a high yield of a yellow crystalline complex $MnH_3(dmpe)_2$ (**6**) that is readily volatile in high vacuum at 50 °C. The i.r. spectrum shows a single Mn–H stretch at 1 680 cm^{-1} while the ^1H n.m.r. spectrum has a binomial quintet at δ −12.67 due to the hydrides, J(P–H) = 28.6 Hz. The spectrum is unchanged on cooling to −60 °C as is the $^{31}P\text{-}\{^1H\}$ spectrum which is a broad singlet at δ 88.0. Although the molecule is thus non-rigid down to −60 °C, a pentagonal bipyramidal structure could be expected by analogy with the structure of $ReH_3(Ph_2PCH_2CH_2PPh_2)_2$.[29]

This hydride extends the series $MH_n(dmpe)_2$ known for other first-row transition metals: Cr (n = 4),[30] Fe (n = 2),[31] Co (n = 1),[32] and Ni (n = 0).[33] The only other neutral manganese(III) hydrides reported are complexes of the type $Mn(CO)_2H(SiR_3)(\eta\text{-}C_5H_5)$ (R = alkyl), but these are unusual in that there appear to be significant interactions between the hydrides and the trialkylsilyl ligands.[34]

Complex (**6**) reacts with CO in refluxing toluene to give mixtures of various hydrido–carbonyl–phosphine species. Photolysis in the presence of ethylene gave $MnH(C_2H_4)(dmpe)_2$ in high yield.

Experimental

Microanalyses were by Pascher, Bonn. All operations were carried out under vacuum and under purified nitrogen or argon. Solvents were distilled from sodium or sodium benzophenone under nitrogen. The light petroleum used had b.p. 40—60 °C.

Literature routes were used for the preparation of 1,2-bis(dimethylphosphino)ethane,[35] dialkylmagnesium reagents,[36] and $MnBr_2(dmpe)_2$.[3] Anhydrous $MnCl_2$ was prepared by the action of $SOCl_2$ on the hydrate followed by evacuation at 200 °C; commercial $LiAlH_4$ was used without purification.

Analytical and physical data for the new compounds are given in Table 4.

Spectrometers.—N.m.r.: Bruker WM 250, JEOL FX90Q; spectra in deuteriobenzene at 25 °C unless otherwise specified, with positive chemical shifts (δ/p.p.m.) downfield of $SiMe_4$ (^1H, ^{13}C), external 85% H_3PO_4 (^{31}P), or external $[Al(H_2O)_6]^{3+}$ in D_2O (^{27}Al); e.s.r.: Varian E-12 (X-band, 9 200 MHz); i.r.: Perkin-Elmer 683, spectra in cm^{-1} as Nujol mulls.

1. [1,2-*Bis*(*dimethylphosphino*)*ethane*]*bis*(*t-butyl*)*manganese*(II) (1).—(a) *From* $MnBr_2(dmpe)_2$. To $MnBr_2(dmpe)_2$ (0.63 g, 1.22 mmol) in diethyl ether (50 cm^3) at −78 °C was added $MgBu^t_2$ (2.25 cm^3 of a 0.56 mol dm^{-3} solution in diethyl

Table 4. Properties and analytical data for manganese compounds

Compound	Colour	M.p. (θ_c/°C)	Analysis[a] (%) C	H	P
(**1**) $MnBu^t_2(dmpe)$	Yellow	140	51.7 (52.7)	10.5 (10.7)	19.3 (19.4)
(**2**) $Mn_2(C_6H_{11})_4(dmpe)$	Dark orange	117 (decomp.)	59.5 (60.8)	10.0 (10.2)	10.7 (10.4)
(**3**) $MnH(CH_2{=}CH_2)(dmpe)_2$	Yellow-orange	170 (decomp.)	43.7 (43.8)	9.8 (9.7)	32.4 (32.2)
(**4**) $Li_4[MnH(C_2H_4)(dmpe - H)_2]_2 \cdot 2Et_2O$	Yellow	180 (decomp.)	45.8 (45.8)	9.7 (10.0)	26.7 (26.2)
(**5**) $[Mn(AlH_4)(dmpe)_2]_2$	Yellow	200 (decomp.)	37.3 (37.3)	9.5 (9.4)	31.9 (32.1)
(**6**) $MnH_3(dmpe)_2$	Yellow	144 (decomp.)	40.2 (40.2)	9.9 (9.8)	35.0 (34.6)

[a] Required values are in parentheses.

Table 5. Crystallographic data

Complex	$Mn_2(C_6H_{11})_4(dmpe)$ (**2**)	$Li_4[MnH(C_2H_4)(dmpe - H)_2]_2 \cdot 2Et_2O$ (**4**)	$[Mn(AlH_4)(dmpe)_2]_2$ (**5**)
(*a*) Crystal data			
Formula	$C_{30}H_{60}Mn_2P_2$	$C_{36}H_{90}Li_4Mn_2O_2P_8$	$C_{24}H_{72}Al_2Mn_2P_8$
M	592.63	940.545	772.47
Crystal system	Orthorhombic	Monoclinic	Monoclinic
a/Å	12.653(4)	20.450(3)	9.313(2)
b/Å	14.832(6)	10.777(2)	13.515(3)
c/Å	18.114(3)	24.047(1)	16.982(3)
β/°		102.45(2)	97.01(2)
U/Å^3	3 399.87	5 175.27	2 121.50
T/K	295	295	273
Space group	*Pccn*	*I*2/*a**	$P2_1/n$
Z	4	4	2
D_c/ g cm^{-3}	1.16	1.21	1.21
μ(Mo-K_α)/cm^{-1}	7.96	7.05	7.83
(*b*) Data collection			
ω scan width	0.8 + 0.35tanθ	0.8 + 0.35tanθ	0.8 + 0.35tanθ
$\theta_{min.}, \theta_{max.}$	1.5, 25.0	1.5, 25.0	1.5, 25.0
Total data	3 255	4 946	4 176
Total unique	2 981	4 554	3 716
Total observed	1 541 $[F_o > 4\sigma(F_o)]$	3 355 $[F_o > 4\sigma(F_o)]$	3 131 $[F_o > 3\sigma(F_o)]$
(*c*) Refinement			
No. of parameters	175	375	307
Weights	$1/[\sigma^2(F_o) + 0.0003(F_o)^2]$	$1/[\sigma^2(F_o) + 0.0008(F_o)^2]$	$1/[\sigma^2(F_o) + 0.0008(F_o)^2]$
Final *R*	0.060	0.0400	0.0415
Final *R′*	0.080	0.0419	0.0415

* Alternative setting of *C*2/*c*.

ether, 1.26 mmol). On warming to room temperature, the solution turned yellow. After stirring for 12 h, the solvent was removed, and the residue extracted with light petroleum (50 cm^3). The filtered extract was concentrated to *ca.* 30 cm^3 and cooled to −20 °C to give yellow plates of *complex* (**1**). Yield: 0.20 g, 53%. The compound may also be crystallized from toluene.

E.s.r.(mT): 72(*y*), 151(*z*), 161(*x*), 490(*x*), 705(*x*), 985(*y*), 1 135(*z*). I.r.: 2 760vs, 2 730m, 2 705w, 2 672m, 2 620w, 2 508w, 2 340w, 1 937w, 1 425s, 1 368w, 1 345w, 1 305m, 1 287m, 1 183m, 1 140s, 1 102s, 995m, 946s, 920w, 895s, 863m, 825m, 798s, 730s, 718s, 707w, 492m, 418w, 390w, 362m, 270m, and 240m cm^{-1}.

(b) *From* $MnCl_2$. To $MnCl_2$ (0.62 g, 4.92 mmol) and dmpe (1.0 cm^3, 6.0 mmol) in diethyl ether (50 cm^3) was added $MgBu^t_2$ (9.0 cm^3 of a 0.56 mol dm^{-3} solution in diethyl ether, 5.04 mmol). The solution developed a yellow colour, and after stirring for 12 h was treated as above to yield *complex* (**1**).

2. [1,2-*Bis(dimethylphosphino)ethane*]*tetrakis(cyclohexyl)dimanganese*(II) (**2**).—To a suspension of $MnCl_2$ (0.87 g, 6.9 mmol) and dmpe (1 cm^3, 6.0 mmol) in diethyl ether (100 cm^3) at 78 °C was added $Mg(C_6H_{11})Cl$ (11.5 cm^3 of a 1.2 mol dm^{-3} solution in diethyl ether, 13.8 mmol). The solution was warmed to room temperature and stirred for 1 h; 1,4-dioxane (2 cm^3) was added and stirring continued for a further 1 h when the solution was filtered, the solvent removed, and the residue extracted with

light petroleum (100 cm^3) and then toluene (50 cm^3). The combined extracts were filtered, concentrated, and cooled to -20 °C to give yellow orange crystals of (**2**). Yield: 0.47 g, 23%. I.r.: 2 800m, 2 740w, 2 645w, 1 440s, 1 328w, 1 298m, 1 281m, 1 250w, 1 150m, 1 020m, 1 009m, 982w, 962w, 958m, 940s, 928s, 885m, 860s, 854s, 823m, 792m, 730m, 700m, 635br,w, 472m, and 400m cm^{-1}.

3. trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*](*ethylene*)*hydridomanganese*(I) (**3**).—(a) *From* $MnBr_2(dmpe)_2$. To $MnBr_2(dmpe)_2$ (0.50 g, 0.97 mmol) in diethyl ether (50 cm^3) at -78 °C was added $MgEt_2$ (1.25 cm^3 of a 0.8 mol dm^{-3} solution in diethyl ether, 1.0 mmol). Upon warming to room temperature, the solution turned orange, then yellow. After stirring for 3 h, the solvent was removed, and the residue extracted with light petroleum (2 × 50 cm^3). The filtered extracts were combined, concentrated to *ca.* 5 cm^3, and cooled to give yellow-orange prisms of *complex* (**3**). Yield: 0.16 g, 43%. N.m.r.: ^1H, δ -11.89 [quin, Mn–H, J(P–H) = 56.5], 0.87 [quin, $CH_2{=}CH_2$, J(P–H) = 4.4 Hz], 1.00 (s, PMe_2), 1.19 (s, PMe_2), 1.38 (m, PCH_2); ^{13}C-{^1H}, δ 31.5 (s, $CH_2{=}CH_2$), proton-coupled spectrum shows a triplet with J(C–H) = 150 Hz, 14.1 (s, PMe_2), 27.4 (s, PMe_2), 32.6 ['quin', PCH_2, J(P–C) = 11.4 Hz]; ^{31}P-{^1H}, δ 81.8 (s, $w_{\frac{1}{2}}$ = 150 Hz). I.r.: 3 020w, 3 005w, 2 818m, 1 725s,br, 1 465m, 1 420s, 1 290s, 1 275s, 1 223w, 1 175s, 1 116m, 1 067m, 992w, 935vs, 885m, 856w, 840w, 826m, 798w, 780m, 730w, 705s, 688w, 672s, 634s, 620s, 564s, 512m, 465m, 435m, 422s, 374s, and 305s cm^{-1}.

Table 6. Fractional atomic co-ordinates (× 10^4) for $Mn_2(C_6H_{11})_4(dmpe)$ (**2**).

Atom	*x*	*y*	*z*
Mn	2 721(1)	3 361(1)	3 023(1)
P(1)	2 713(2)	3 734(1)	1 633(1)
C(1)	2 220(7)	2 991(5)	918(4)
C(2)	1 910(8)	4 725(6)	1 462(5)
C(3)	3 985(8)	4 072(7)	1 284(5)
C(11)	3 928(5)	2 276(5)	3 250(4)
C(12)	4 144(5)	2 254(5)	4 087(4)
C(13)	5 207(8)	1 985(10)	4 294(5)
C(14)	6 057(8)	2 086(9)	3 865(6)
C(15)	5 890(6)	2 075(7)	3 041(5)
C(16)	4 845(7)	2 414(13)	2 816(5)
C(21)	2 921(7)	4 617(6)	3 561(6)
C(22)	3 851(9)	4 866(6)	3 895(8)
C(23)	4 004(8)	5 766(6)	4 277(6)
C(24)	3 082(10)	6 311(7)	4 326(8)
C(25)	2 181(8)	6 110(8)	4 005(9)
C(26)	2 031(7)	5 207(6)	3 623(6)

(b) *From* $MnCl_2$. To $MnCl_2$ (1.06 g, 8.41 mmol) and dmpe (2.5 cm^3, 16.67 mmol) in diethyl ether (80 cm^3) at -78 °C was added $MgEt_2$ (11.0 cm^3 of a 0.8 mol dm^{-3} solution in diethyl ether, 8.8 mmol). The solution was warmed to room temperature and treated as above to give *complex* (**3**). Yield: 1.50 g, 46%.

4. *Lithiation of* $MnH(C_2H_4)(dmpe)_2$ (**3**).—To $MnH(C_2H_4)(dmpe)_2$ (0.59 g, 1.5 mmol) in light petroleum (50 cm^3) at -78 °C was added $LiBu^t$ (1.9 cm^3 of a 1.6 mol dm^{-3} solution in pentane, 3 mmol). On warming to room temperature and stirring overnight a yellow precipitate resulted. The solvent was removed, the residue washed with light petroleum (40 cm^3) and extracted with diethyl ether (50 cm^3). On concentrating the solution to *ca.* 35 cm^3 and cooling to -20 °C yellow crystals of $Li_4[MnH(C_2H_4)(dmpe - H)_2]_2{\cdot}2Et_2O$ (**4**) were obtained. Yield: 0.23 g, 33%. I.r.: 3 020w, 2 792w, 1 645m, 1 420s, 1 285s, 1 280s, 1 270s, 1 170s, 1 148m, 1 105s, 1 050m, 930m, 910s, 875m, 852m, 840m, 835m, 798m, 780m, 715s, 700m, 670s, 622s, 520m, and 440m cm^{-1}.

Table 7. Fractional atomic co-ordinates (× 10^4) for $Li_4[MnH(C_2H_4)(dmpe - H)_2]_2{\cdot}2Et_2O$ (**4**)

Atom	*x*	*y*	*z*
Mn	6 326(0.5)	4 524(0.5)	3 542(0.5)
P(1)	7 449(0.5)	4 213(1)	3 672(0.5)
P(2)	6 554(1)	6 438(1)	3 298(0.5)
P(3)	6 137(0.5)	2 603(1)	3 858(0.5)
P(4)	5 367(0.5)	5 014(1)	3 771(0.5)
C(1)	7 799(2)	5 492(4)	3 303(2)
C(2)	7 468(2)	6 689(4)	3 419(2)
C(3)	5 424(2)	2 690(4)	4 224(2)
C(4)	4 912(2)	3 598(4)	3 909(2)
C(5)	5 673(2)	4 194(4)	2 739(1)
C(6)	6 327(2)	3 827(5)	2 719(2)
C(11)	7 779(2)	2 886(5)	3 341(2)
C(12)	7 947(2)	4 143(4)	4 394(1)
C(21)	6 284(3)	7 009(7)	2 558(3)
C(22)	6 344(4)	7 825(5)	3 669(4)
C(31)	6 765(2)	1 819(3)	4 390(2)
C(32)	5 818(3)	1 369(5)	3 330(2)
C(41)	5 384(3)	5 851(5)	4 438(2)
C(42)	4 684(1)	5 852(6)	3 297(2)
O(1)	6 533(1)	751(3)	5 655(1)
C(51)	6 437(6)	−1 342(7)	5 284(3)
C(52)	5 819(3)	1 053(6)	5 650(3)
C(53)	6 784(4)	−501(5)	5 740(3)
C(54)	5 606(4)	694(6)	6 148(3)
Li(1)	6 980(3)	3 822(5)	4 629(2)
Li(2)	7 935(3)	2 100(6)	4 657(3)
H(1)	6 578(20)	5 022(37)	4 104(17)
H(11)	7 736(25)	5 312(42)	2 893(23)
H(12)	8 236(23)	5 534(35)	3 428(17)
H(21)	7 588(23)	6 860(41)	3 815(20)
H(22)	7 501(27)	7 502(46)	3 150(22)
H(31)	5 609(18)	3 049(34)	4 608(16)
H(32)	5 286(20)	1 784(39)	4 275(16)
H(41)	4 676(18)	3 225(34)	3 535(16)
H(42)	4 601(19)	3 854(32)	4 132(15)
H(111)	7 634(22)	2 135(43)	3 446(16)
H(112)	8 230(23)	2 940(38)	3 443(17)
H(113)	7 647(21)	2 990(39)	2 960(20)
H(121)	7 907(18)	4 883(33)	4 606(15)
H(122)	8 292(20)	4 063(34)	4 372(15)
H(211)	6 512(30)	7 810(58)	2 524(26)
H(212)	5 793(32)	7 052(53)	2 481(24)
H(213)	6 477(34)	6 442(57)	2 331(26)
H(221)	5 869(29)	7 910(49)	3 554(22)
H(222)	6 575(24)	8 530(44)	3 571(18)
H(223)	6 505(29)	7 687(53)	4 037(24)
H(311)	6 548(20)	1 228(36)	4 469(16)
H(312)	7 046(20)	1 468(33)	4 105(17)
H(321)	5 771(24)	776(44)	3 469(20)
H(322)	6 170(25)	1 241(43)	3 059(20)
H(323)	5 470(30)	1 696(51)	3 031(24)
H(411)	4 981(32)	5 898(51)	4 534(24)
H(412)	5 535(25)	6 697(51)	4 430(21)
H(413)	5 677(26)	5 350(46)	4 755(21)
H(421)	4 497(29)	5 462(49)	2 922(26)
H(422)	4 836(23)	6 576(42)	3 157(19)
H(423)	4 358(28)	5 874(44)	3 460(21)
H(51)	5 336(23)	3 490(38)	2 738(18)
H(52)	5 491(21)	4 998(38)	2 549(17)
H(61)	6 431(19)	2 871(38)	2 711(16)
H(62)	6 580(20)	4 352(34)	2 550(17)

Table 8. Fractional atomic co-ordinates (× 10^4) for $[Mn(AlH_4)(dmpe)_2]_2$ (**5**)

Atom	*x*	*y*	*z*
Mn(1)	10 438(1)	1 906	1 361
Al(1)	10 154(1)	297(1)	773(1)
P(1)	8 979(1)	3 184(1)	1 114(1)
C(11)	9 530(5)	4 486(3)	1 218(3)
C(12)	7 882(6)	3 286(4)	147(3)
C(13)	7 490(5)	3 169(3)	1 744(3)
P(2)	8 866(1)	1 453(1)	2 174(1)
C(21)	9 400(5)	864(3)	3 133(2)
C(22)	7 322(4)	660(4)	1 819(3)
C(23)	7 861(4)	2 552(3)	2 471(3)
P(3)	12 064(1)	2 401(1)	593(1)
C(31)	11 606(5)	2 838(4)	−421(3)
C(32)	13 520(5)	1 578(4)	419(3)
C(33)	13 102(5)	3 468(4)	1 042(3)
P(4)	12 004(1)	2 534(1)	2 317(1)
C(41)	11 572(5)	3 297(4)	3 152(3)
C(42)	13 239(5)	1 665(4)	2 870(3)
C(43)	13 319(5)	3 401(4)	1 932(3)
H(1a)	11 342(13)	901(13)	1 549(12)
H(1b)	9 366(14)	1 512(13)	593(12)
H(2a)	8 858(14)	27(13)	−78(12)
H(2b)	9 905(14)	−617(13)	1 249(12)
H(111)	10 245(14)	4 624(13)	839(12)
H(112)	9 984(14)	4 531(13)	1 746(12)
H(113)	8 675(14)	4 980(13)	1 128(12)
H(121)	8 579(14)	3 314(13)	−331(12)
H(122)	7 473(14)	2 704(13)	59(12)
H(123)	7 187(14)	3 767(13)	158(12)
H(131)	7 175(13)	3 798(13)	1 850(12)
H(132)	6 445(14)	2 888(13)	1 350(12)
H(211)	10 178(14)	1 250(13)	3 483(12)
H(212)	8 613(14)	716(13)	3 350(12)
H(213)	9 847(14)	323(13)	2 975(12)
H(221)	7 000(14)	900(13)	1 340(12)
H(222)	7 715(14)	5(13)	1 753(12)
H(223)	6 541(14)	606(13)	2 152(12)
H(231)	8 574(14)	2 992(13)	2 873(12)
H(232)	6 891(14)	2 268(13)	2 711(12)
H(311)	12 496(14)	3 069(13)	−580(12)
H(312)	11 009(14)	3 352(13)	−453(12)
H(313)	11 199(14)	2 203(13)	−793(12)
H(321)	13 087(14)	1 019(13)	3(12)
H(322)	14 171(14)	1 793(13)	162(12)
H(232)	13 927(14)	1 189(13)	839(12)
H(331)	12 252(14)	4 194(13)	870(12)
H(332)	13 929(14)	3 553(13)	835(12)
H(411)	12 387(14)	3 581(13)	3 439(12)
H(412)	11 040(14)	3 918(13)	2 950(12)
H(413)	10 962(14)	2 916(13)	3 505(12)
H(421)	12 744(14)	1 235(13)	3 200(12)
H(422)	14 035(14)	2 103(13)	3 233(12)
H(423)	13 747(14)	1 411(13)	2 453(12)
H(431)	13 795(14)	2 796(13)	1 839(12)
H(432)	14 428(14)	3 292(13)	2 242(12)

5. *Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*](*tetrahydroaluminato*)*manganese*(I) (**5**).—To $MnBr_2(dmpe)_2$ (0.75 g, 1.46 mmol) in toluene (30 cm^3) at −78 °C was added a suspension of $LiAlH_4$ (0.4 g, 10.5 mmol) in toluene (30 cm^3) at −78 °C. Upon warming to room temperature, the solution turned yellow and slow gas evolution was observed. After stirring for 12 h, the solvent was removed, and the residue extracted with light petroleum (50 cm^3). The filtered extract was cooled to −20 °C to give yellow prisms of *complex* (**5**). Yield: 0.25 g, 44%. The complex may also be crystallized from toluene.

N.m.r.: ^1H (298 K), δ −15.02 (s, Mn–H–Al, $w_{\frac{1}{2}}$ = 100), 5.05 (s, Al–H, $w_{\frac{1}{2}}$ = 13 Hz), 1.73 [d, PMe_2, *J*(P–H) = 4.4], 1.59 [d, PMe_2, *J*(P–H) = 6.0], 1.27 [d, PMe_2, *J*(P–H) = 4.8 Hz], 0.88 (s, PMe_2), 1.12 (m, PCH_2); ^1H (183 K), −15.02 (s, Mn–H–Al, $w_{\frac{1}{2}}$ = 100 Hz), 5.34 (s, Al–H–Al, $w_{\frac{1}{2}}$ = 45.8 Hz), 4.76 (s, Al–H, $w_{\frac{1}{2}}$ = 37.5 Hz); ^{13}C-{^1H}, δ 31.6 ['t', PMe_2, '*J*(P–C)' = 12.1], 27.0 [d, PMe_2, *J*(P–C) = 17.0], 23.9 ['t', PMe_2, '*J*(P–C)' = 2.2], 22.9 [d, PMe_2, *J*(P–C) = 13.1], 34.9 ['quin', PCH_2, '*J*(P–C)' = 11.0], 33.1 ['quin', OCH_2, '*J*(P–C)' = 11.0 Hz]; ^{31}P-{^1H}, δ 76 (s, $w_{\frac{1}{2}}$ = 900 Hz); ^{27}Al-{^1H}, δ 65 ('t', $w_{\frac{1}{2}}$ = 4 900 Hz). I.r.: 2 805w, 1 740s, 1 610s, 1 450s, 1 430m, 1 420m, 1 287m, 1 272m, 1 222w, 1 062w, 970m,br, 925s, 895m, 882m, 842s, 828s, 797w, 770w, 705m, 680s, 635s, 622s, 564s, 458m, 410s, 384m, and 269m cm^{-1}.

6. *Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*trihydridomanganese*(III). (**6**)—To a solution of $[Mn(AlH_4)(dmpe)_2]_2$ (**5**) (0.72 g, 0.93 mmol) in diethyl ether was added distilled water dropwise until gas evolution ceased. The solution was filtered, evaporated, and the residue extracted with light petroleum. The filtered extract was concentrated and cooled to −20 °C to give yellow *prisms of complex* (**6**). Yield: 0.51 g, 75%.

N.m.r.: ^1H, δ −12.67 [quin, Mn–H, *J*(P–H) = 28.6 Hz], 1.39 (s, PMe_2, PCH_2); ^{31}P-{^1H}, δ 88 (s, $w_{\frac{1}{2}}$ = 150 Hz). I.r.: 2 805w, 1 680m,br, 1 420m, 1 280m, 1 265m, 1 222w, 1 062w, 920s,br, 880m, 830m, 790m, 708s, 680s, 630s, 590m, 470m, 422s, 392m, and 383w cm^{-1}.

E.S.R. Spectra.—Toluene solutions of $MnBu^t_2(dmpe)$ (**1**) and $Mn_2(C_6H_{11})_4(dmpe)$ (**2**) were prepared by dissolution of crystalline samples. A pure sample of $Mn(C_6H_{11})_2(dmpe)$ was obtained by adding excess dmpe to a toluene solution of the dimer. Samples were transferred under argon to quartz tubes and frozen at −196 °C before insertion into a liquid-nitrogen cooled probe. Analyses of the spectra were performed using the *D–B* plot method, for external fields parallel to the principal directions of the zero-field splitting tensor.[4] After the initial assignment of observed resonances to specific transitions, final refinements were performed using the program MNES, which finds the best-fit Hamiltonian parameters (*D* and λ) by an iterative least-squares procedure.[37]

Crystallographic Studies.—Crystals of all three compounds (**2**), (**4**), and (**5**) were sealed under argon in glass capillaries for *X*-ray work. Following preliminary photography, unit-cell and intensity data were obtained using an Enraf-Nonius CAD4 diffractometer and graphite-monochromatized Mo-K_α radiation (λ = 0.710 69 Å), by following standard procedures.[38] The structures were solved and refined *via* use of the heavy-atom method and full-matrix least squares.[39]

For complex (**2**), high thermal motion and/or conformational disorder made location of hydrogen atoms difficult and led to some artificially low C–C distances in the rings. Accordingly all CH_2 and CH_3 hydrogens were inserted in idealised positions with C–H distances of 1.080 Å, and assigned group isotropic thermal parameters which were refined. No hydrogen atom was included for the bridging cyclohexyl carbon C(11) although the single hydrogen on the terminal cyclohexyl carbon C(21) was included. Attempts were made to recollect data for this compound at reduced temperatures, but even on cooling only to

-20 °C, the crystals tended to crack, suggesting strongly that they are very strained. For complexes **(4)** and **(5)**, development and refinement of the structures proceeded very smoothly and all hydrogens were experimentally located and freely refined with individual isotropic thermal parameters. Crystallographic data for all structures are given in Table 5. Final atomic co-ordinates are given in Tables 6, 7, and 8.

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