Reactivity of the Unsaturated Dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ towards Boron, Silicon, and Tin Hydrides $[L_2 = Ph_2PCH_2PPh_2, (EtO)_2POP(OEt)_2]$. *X*-Ray Crystal Structures of $[Mn_2(\mu\text{-}H)(\mu\text{-}BH_4)(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)]$ and $[Mn_2(\mu\text{-}SnPh_2)_2(CO)_6\{\mu\text{-}(EtO)_2POP(OEt)_2\}]$

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The unsaturated dihydrocomplexes $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ $[L_2 = Ph_2PCH_2PPH_2$, dppm; $L_2{=}(EtO)_2POP(OEt)_2$, tedip] react under mild conditions with boron, silicon, or tin hydrides *via* insertion or elimination (H_2, C_6H_6) processes to afford the novel dimangano–main group element species $[Mn_2(\mu\text{-}H)(\mu\text{-}BH_4)(CO)_6(\mu\text{-}dppm)]$, $[Mn_2(\mu\text{-}H_2SiPh_2)(CO)_6(\mu\text{-}dppm)]$, $[Mn_2(\mu\text{-}H)(\mu\text{-}HSnPh_2)(CO)_6(\mu\text{-}L_2)]$, or $[Mn_2(\mu\text{-}SnPh_2)_2(CO)_6(\mu\text{-}L_2)]$; the crystal structures of the latter (L_2 = tedip) and the tetrahydroborate complex have been determined.

Unsaturated dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ (**1a,b**) $[L_2 = Ph_2PCH_2PPh_2$, dppm;[1] $L_2 = (EtO)_2POP(OEt)_2$, tedip[2]] have been found to be very valuable synthetic species because they react under mild conditions with transition metal compounds[2] and a range of small organic molecules,[1] thus allowing a highly selective preparation of species which are otherwise unaccessible or difficult to obtain. We have now found that these dihydrides also react readily with molecules containing X–H bonds (X = B, Si, Sn, P) leading to new dimangano–main group element species.

In marked contrast with the Lewis-acid type behaviour generally shown by the dihydrides (**1a,b**),[1] compound (**1a**) is able to react at room temp. with a typical Lewis acid such as BH_3 to yield the hydrido tetrahydroborato complex $[Mn_2(\mu\text{-}H)(\mu\text{-}BH_4)(CO_6)(\mu\text{-}dppm)]$ (**2**), (Scheme 1). Other boron hydrides also react with compound (**1a**) and we are currently investigating the relevance of these reactions in manganoborane synthesis. The structure of compound (**2**) (Figure 1) has been confirmed by an *X*-ray diffraction study.[†] The interesting feature in the structure of compound (**2**) is the geometry of the bridging tetrahydroborate group, which has two B–H bonds co-ordinated to the manganese atoms. This binding mode of a BH_4^- group to a dimetallic unit has been crystallographically characterized previously only in the iridium complex, $Ir_2Cp_2H_2(\mu\text{-}H)(\mu\text{-}BH_4)$.[3] There is a significant difference, however, in the way the B–H bonds interact with the metal atoms in these two compounds. In the iridium case, a distorted 'side-on' B–H to Ir interaction is present [B–H(Ir) = 1.77(8), B–Ir=2.214(6), (B)H–Ir = 1.61(8) Å and B–H–Ir = 81.8(4)°] whereas in (**3**) this interaction is better described in terms of a rather 'end-on' type [averaged values: B–H(Mn) = 1.21(4), Mn–B = 2.852(3), (B)H–Mn = 1.67(4) Å and B–H–Mn = 127.1(3)°]. 'End-on' *vs.* 'side-on' co-ordination of X–H bonds (X = H, C, Si, B) to metal fragments is a subject of current theoretical interest.[4]

Diphenylsilane reacts with compound (**1a**) in tetrahydrofuran (THF) at 65 °C yielding $[Mn_2(\mu\text{-}H_2SiPh_2)(CO)_6(\mu\text{-}dppm)]$ (**3**). On the basis of the spectroscopic data,[‡] a symmetrical arrangement of the silicon bridge, with two equivalent Si–H–Mn interactions *trans* to the phosphorus atoms is proposed (Scheme 1). This bonding mode of a H_2SiPh_2 ligand has been previously proposed only for $Re_2(H_2SiR_2)(CO)_8$ (R = Ph, Me) on the basis of NMR data, although *X*-ray studies on this compound (R = Ph) could not confirm this hypothesis.[5] In the case of compound (**3**), the situation of H bridging Si and Mn atoms is strongly suggested by its chemical shift and the low value of *J*(P–H),[‡] which is about one half the value found in most of our dppm-bridged dimanganese hydrides.

[†] *Crystal data* for compound (**2**): $C_{31}H_{27}BMn_2O_6P_2$, M = 678.2, monoclinic, space group $C2/c$, a = 23.085(3), b = 12.223(3), c = 24.768(9) Å, β = 115.68(4)°, Z = 8, U = 6298(2) Å^3, D_c = 1.43 g cm^{-3}, $F(000)$ = 2768, μ = 9.1 cm^{-1}. Final R = 0.0343 (R_w = 0.0391) for 3925 independent reflections with $I \geqslant 3\,\sigma(I)$, measured in the θ range 1—25° at room temp. with Mo-K_α radiation and graphite monochromator on a Philips PW1100 (ω-2θ mode). The structure was solved by direct methods and subsequent Fourier maps. Least squares refinements carried out in three blocks (463 parameters). All hydrogen atoms, including those in the dimetal environment, were found on a difference map and refined satisfactory with an overall isotropic thermal parameter. Compound (**5b**): $Mn_2Sn_2P_2O_{11}C_{38}H_{40}$, M = 1081.9, monoclinic, space group $C2/c$, a = 23.095(4), b = 10.385(1), c = 18.439(6) Å, β = 109.68(1)°, Z = 4, U = 4164(2) Å^3, D_c 1.726 g cm^{-1}, $F(000)$ = 2144. Final R = 0.0256 (R_w = 0.0275) for 2524 independent absorption corrected reflections with $I \geqslant 3\,\sigma(I)$ measured in the θ range 1—25° at room temp on a Philips PW1100 (ω-2θ mode) using Mo-K_α radiation and graphite monochromator. The structure was solved by direct methods and subsequent Fourier maps. Least squares refinements in three blocks (206 parameters). Hydrogen atoms were found on difference maps but not refined. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] *Selected spectroscopic data* for new compounds: $\nu(CO)$ in cm^{-1}, NMR chemical shifts in p.p.m. relative to internal tetramethylsilane (TMS) (^1H, ^{13}C) or external 85% $H_3PO_4(aq)$ (^{31}P), coupling constants in Hz. Compound (**2**): $\nu(CO)$ (toluene): 2055vs, 2022s, 1969s, 1947s, and 1932s; ^1H ([$^2H_8$]toluene, 253 K): δ 2.74 (m, CH_2, 2H), 2.58 (m, BH_2, 2H), −14.02 (br., Mn–H–B, 2H), and −17.09 [t, *J*(PH) 22, Mn_2 (μ-H), 1H]; $^{31}P\{^1H\}$([$^2H_8$]toluene, 253 K): δ 55.2 (s, Mn–P). Compound (**3**): $\nu(CO)$ (THF): 2037vw, 1995s, 1955vs, and 1925s; ^1H (C_6D_6): δ 3.99 [t, *J*(PH) 10, CH_2, 2H] and −13,09 [pseudotriplet, $|J(PH) + J(P'H)|$ 12, Mn–H–Si, 2H]; $^{31}P\{^1H\}$ (C_6D_6): δ 63.3 (s, Mn–P). Compound (**4a**): $\nu(CO)$ (hexane): 2037m, 1997m, 1954m, 1932m, and 1922s; ^1H ($CDCl_3$): δ 3.42, 3.24[AB syst. of triplets, *J*(AB) 13, *J*(PH) 12, CH_2, 2H] and −2.08 [s, $J(^{117}SnH) \approx J(^{119}SnH)$ 32, Mn–H–Sn, 1H], and −20.38 [dd, *J*(PH) 22 and 37, $Mn_2(\mu\text{-}H)$, 1H]; $^{31}P\{^1H\}$ ($CDCl_3$): δ 59.9[d, *J*(PP) 54, Mn–P] and 43.4 (d, Mn–P). Compound (**4b**): $\nu(CO)$: similar to (**4a**); ^1H ($CDCl_3$): δ 1.36, 1.34, 1.06, 0.97 [4 × t, *J*(HH)7, CH_3, 12H], −9.49 [d, *J*(PH) 29, $J(^{117}SnH) \approx J(^{119}SnH)$ 97, Mn–H–Sn, 1H], and −18.4 [t, *J*(PH) 28, $J(^{117}SnH) \approx J(^{119}Sn\ H)$ 124, $Mn_2(\mu\text{-}H)$, 1H]; $^{31}P\{^1H\}$ ($CDCl_3$, 243 K): δ 175.7 [d, *J*(PP) 87, Mn–P] and 165.3 (d, Mn–P). Compound (**5a**): $\nu(CO)$ (CH_2Cl_2): 2010s, 1972s, 1925sh, and 1915vs; $^{31}P\{^1H\}$ ($CDCl_3$): δ 45.9 (s, Mn–P). Compound (**5b**): $\nu(CO)$ (CH_2Cl_2): similar to (**5a**); $^{31}P\{^1H\}$: δ 168.4 (s, Mn–P).

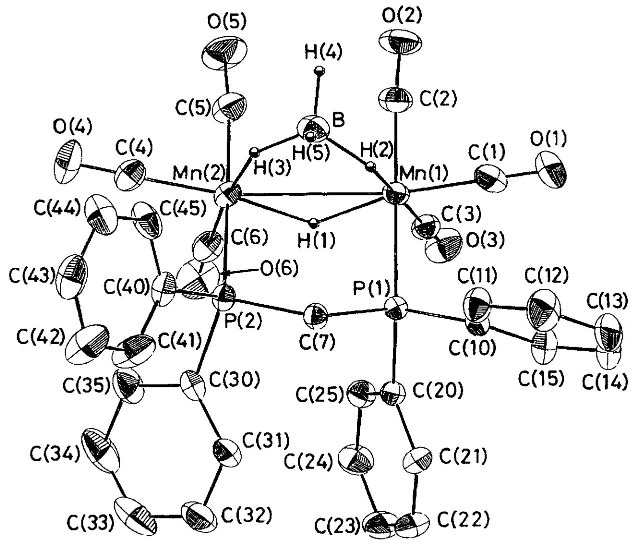


Figure 1. Molecular structure of [$Mn_2(\mu\text{-}H)(\mu\text{-}BH_4)(CO)_6(\mu\text{-}dppm)$] (**2**). Selected bond distances (Å): Mn(1)–Mn(2) 2.9889(6), Mn(1)–H(1) 1.64(3), Mn(2)–H(1) 1.70(3), Mn(1)–H(2) 1.65(4), Mn(2)–H(3) 1.68(4), B(1)–H(2) 1.24(4), B(1)–H(3) 1.18(4), B(1)–H(4) 1.08(4), B(1)–H(5) 1.09(4), B(1)–Mn(1) 2.557(3), B(1)–Mn(2) 2.607(4). Bond angles(°): Mn(1)–H(1)–Mn(2) 127.0(23), H(1)–Mn(2)–H(3) 98.3(17), Mn(2)–H(3)–B(1) 130.3(26), H(3)–B(1)–H(2) 118.4(24), B(1)–H(2)–Mn(1) 123.8(27), H(4)–B(1)–H(5) 110.2(27).

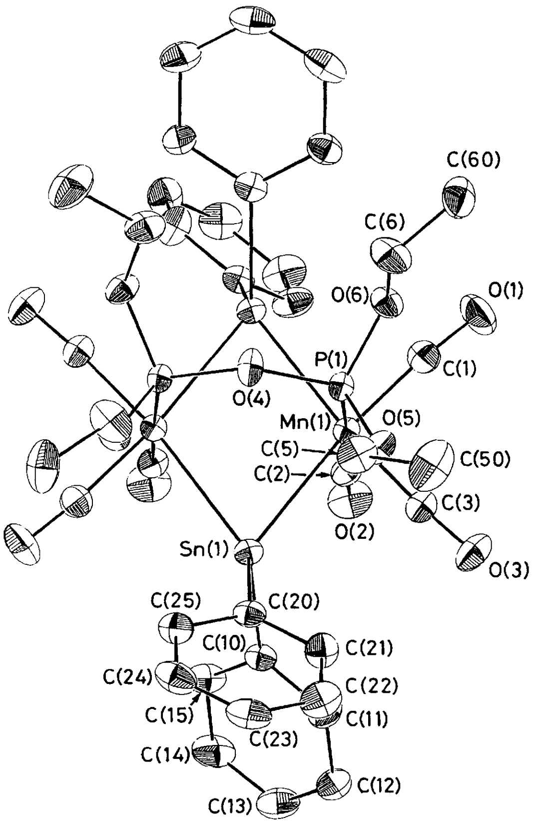
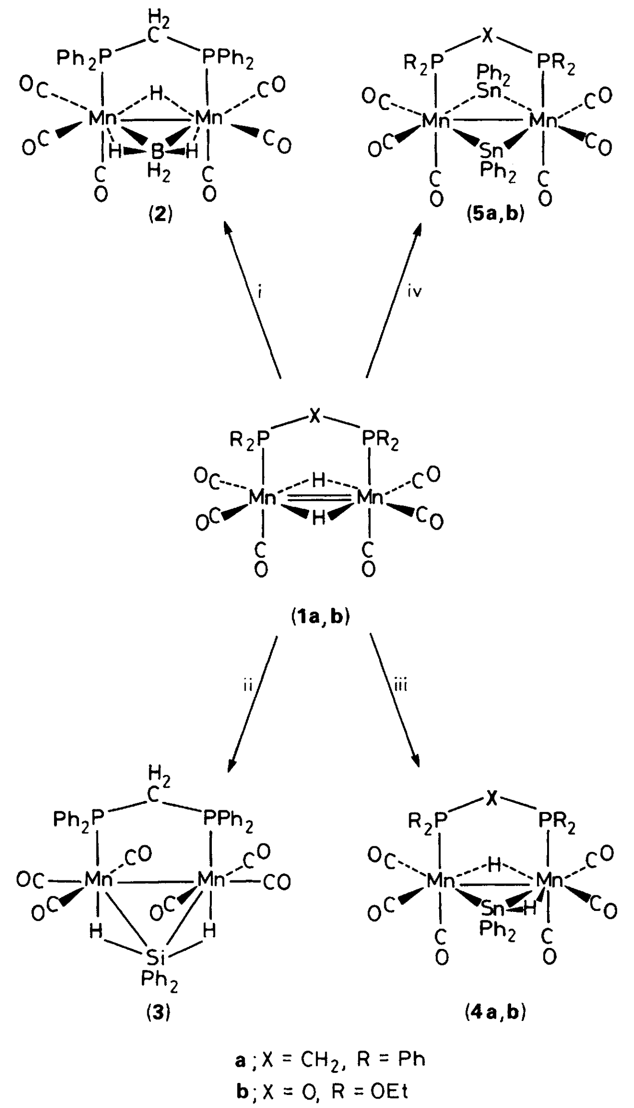


Figure 2. Molecular structure of [$Mn_2(\mu\text{-}SnPh_2)_2(CO)_6(\mu\text{-}tedip)$] (**5b**). Bond distances (Å): Mn(1)–Mn′(1) 3.1045(5), Mn(1)–Sn(1) 2.6053(5), Mn′(1)–Sn(1) 2.6178(6), Mn(1)–P(1) 2.2472(4). Bond angles(°): Mn(1)–Sn(1)–Mn′(1) 72.94(2), Sn(1)–Mn(1)–Sn′(1) 106.93(2), C(10)–Sn(1)–C(20) 98.6(1), P(1)–Mn(1)–Sn(1) 91.49(3).



Scheme 1. *Reagents and conditions*: i, 1.3 equiv. $BH_3\cdot THF$, toluene, room temp., 1 h; ii, 3 equiv. H_2SiPh_2, THF, 65 °C, 30 min; iii, 1 equiv. $HSnPh_3$, toluene, 0 °C, 30 min; iv, 2 equiv. $HSnPh_3$, toluene, room temp., 1.5 h.

Reactions of compounds (**1a,b**) with $HSnPh_3$ proceed under milder conditions than the previous silicon reaction but are, by contrast, less selective, and yield species which are structurally different from (**3**). Thus, the dark reaction of 1 equiv. of $HSnPh_3$ with (**1a**) or (**1b**) at 0 °C yields the compounds [$Mn_2(\mu\text{-}H)(\mu\text{-}HSnPh_2)(CO)_6(\mu\text{-}L_2)$] ($L_2$ = dppm) (**4a**) or (L_2 = tedip) (**4b**) as major products. However, when the reaction is carried out at room temp. and using 2 equiv. of $HSnPh_3$, the non hydridic species [$Mn_2(\mu\text{-}SnPh_2)_2(CO)_6(\mu\text{-}L_2)$] (**5a,b**) are the major products, along with some (**4a,b**) and other complexes yet uncharacterized. The structure of compounds (**5a,b**) was confirmed by an *X*-ray diffraction study† on (**5b**) (Figure 2). The molecule can be viewed as derived from the parent dihydride by replacement of the hydride ligands by two 'pseudo carbene' $SnPh_2$ moities; the usual electron counting formalism requires the presence of a single Mn–Mn bond, which is consistent with the experimental Mn–Mn distance [3.1045(5) Å: for example, 3.090(3) Å for $Mn_2(\mu\text{-}Br)(\mu\text{-}$

$AuPPh_3)(CO)_6(\mu\text{-tedip})^6]$. In the reactions just described, a C_6H_5 group from each original tin molecule is lost throughout the reaction (as C_6H_6, as determined by GC-MS).

The ability of the dihydrides (**1a,b**) to promote the elimination (intra- or inter-molecular) of small 'stable molecules' (H_2,CH_4,C_6H_6) under mild conditions seems to be a characteristic not exhibited so pronouncedly by related heavier transition metal unsaturated dihydrides [as $Os_3(\mu\text{-}H)_2(CO)_{10}$[7] or $Re(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)$[8]] probably because of the higher strength of the M–H bonds in the latter ones.[9]

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References

1 F. J. Garcia-Alonso, M. Garcia-Sanz, V. Riera, M. A. Ruiz, A. Tiripicchio, and M. Tiripicchio-Camellini, *Angew. Chem., Int. Ed. Eng.*, 1988, **27**, 1167.
2 V. Riera, M. A. Ruiz, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc., Chem. Commun.*, 1985, 1505.
3 T. M. Gilbert, F. J. Hollander, and R. G. Bergman, *J. Am. Chem. Soc.*, 1985, **107**, 3508.
4 J. Y. Saillard, in 'Topics in physical organometallic chemistry,' ed. M. Gielen, Freund Publishing House Ltd, London 1987, vol 2, ch 1.
5 W. A. Graham, *J. Organomet. Chem.* 1986, **300**, 81, and references cited therein.
6 V. Riera, M. A. Ruiz, A. Tiripicchio, and M. Tiripicchio-Camellini, *J. Chem. Soc., Dalton Trans.*, 1987, 1551.
7 F. W. B. Einstein, R. K. Pomeroy, and A. C. Willis, *J. Organomet. Chem.*, 1986, **311**, 257.
8 M. J. Mays, D. W. Prest, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1980, **171**; *J. Chem. Soc., Dalton Trans.*, 1982, 2021.
9 D. S. Moore and S. D. Robinson, *Chem. Soc. Rev.*, 1983, **12**, 415.