Reactivity of the Unsaturated Dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ ($L_2 = Ph_2PCH_2PPh_2$, $(EtO)_2POP(OEt)_2$) toward Boron Hydrides. X-ray Crystal Structure of $[Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_5(\mu\text{-}Ph_2PCH_2PPh_2)]$, a Molecule Displaying a Novel Coordination Mode of the Tetrahydroborate Ligand

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The unsaturated dihydrides $Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)$ ($L_2 = Ph_2PCH_2PPh_2$, dppm; $(EtO)_2POP(OEt)_2$, tedip) react with $BH_3{\cdot}THF$ at room temperature to give the hexacarbonyl complexes $Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_6(\mu\text{-}L_2)$, containing a tetrahydroborate ligand symmetrically coordinated through two of its B–H bonds. The latter species lose easily a CO ligand to give the pentacarbonyl complexes $Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_5(\mu\text{-}L_2)$ containing an asymmetrically coordinated tetrahydroborate ligand. The latter (L_2 = dppm) crystallizes in the monoclinic space group $P2_1/a$ ($a = 12.908(2)$ Å, $b = 15.735(2)$ Å, $c = 15.960(1)$ Å, $\beta = 111.54(1)°$, $V = 3015.2(8)$ Å^3, $Z = 4$). The structure was refined to $R = 0.031$ ($R_w = 0.031$) for 4968 reflections with $I > 3\sigma(I)$. The tetrahydroborate ligand binds the dimetal center through three of its hydrogen atoms which thus complete distorted octahedral environments around the manganese atoms. Binding to Mn(2) is made in a rather end-on way through H(3) (B–Mn(2) = 2.480 Å, B–H(3)–Mn(2) 118.1(20)°) whereas binding to Mn(1) is made through H(2) and H(4) in a side-on way (B–Mn(1) = 2.048(4) Å, B–H–Mn(1) = 87.9(16) and 89.5(17)°, respectively). Reaction of the manganese dihydrides with "B_3H_7" at room temperature gave a mixture of the hexacarbonyl and pentacarbonyl tetrahydroborate complexes, the latter as major products. Finally, reaction with BEt_3 in the presence of water gave the ethoxy complexes $Mn_2(\mu\text{-}H)(\mu\text{-}OEt)(CO)_6(\mu\text{-}L_2)$ in good yields, although the reaction pathway remains obscure. The structure and bonding in the tetrahydroborate complexes is compared with that of boron hydrides or metal clusters by using isolobal relationships.

Introduction

The unsaturted dihydrides $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-}L_2)]$ (**1a,b**) [**a**, $L_2 = Ph_2PCH_2PPh_2$ or dppm;[1] $L_2 = (EtO)_2POP(OEt)_2$ or tedip[2]] are quite reactive species toward a variety of molecules under mild conditions. The chemical behavior of **1a,b** is dominated by the electron deficiency of the $Mn_2(\mu\text{-}H)_2$ (Mn=Mn) moiety, and thus easy reactions take place with electron donor molecules such as alkynes,[1] nitriles or isonitriles,[3] phosphines,[4] thiols,[1a] sulfur,[5] or carbon dioxide, and other heterocumulenes.[6] In a preliminary study[7] we found that molecules lacking nonbonding electron pairs but having H–E bonds (E = Si, Sn, B) also react with complexes **1a,b** under mild conditions. In this paper we report our results on the reactions of **1a,b** with several boron hydrides. Two main considerations prompted us to initiate this study. In first place, there was some intrinsic interest in the reactivity of **1a,b** toward boron hydrides. In fact, theoretical studies[8] on the bonding in unsaturated moieties $M_2(\mu\text{-}H)_2$ (M=M), such as those present in **1a,b** or related dihydrides[9] have established some similitude with the bonding in diborane. Thus, the interaction between **1a,b** and boranes could model condensation reactions between boron hydrides. Moreover, little information on this type of reaction is available. Only the reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with $BH_3{\cdot}THF$ appears to have been studied, leading to the formation of a μ_3-BCO ligand.[10] On the other hand, the reactions between **1a,b** and boranes could be themselves

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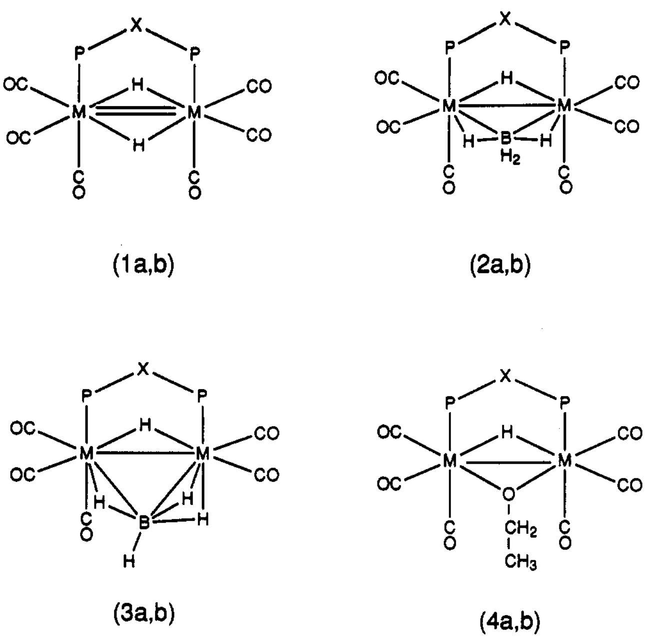
Chart I



(1a,b) (2a,b) (3a,b) (4a,b)

a: PXP = $Ph_2PCH_2PPh_2$; b: PXP = $(EtO)_2POP(OEt)_2$

useful synthetic routes to manganoborane compounds, of which only a limited number is known. Metalloborane chemistry continues being an active research field.[11] It provides not only species exhibiting novel reactivity, structural, and bonding features but also species able to act as catalysts or precursors for novel solid materials.

Results and Discussion

Reactions of Dihydrides 1a,b with BH_3·THF. Compound **1a** reacts readily with a slight excess of BH_3·THF in toluene at room temperature to give the tetrahydroborate complex [$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_6(\mu\text{-dppm})$] (**2a**) in high yield. The tedip-bridged dihydride **1b** undergoes a similar reaction to give [$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_6(\mu\text{-tedip})$] (**2b**) (Chart I). Compound **2b**, however is unstable and gives back the starting complex **1b** upon removal of the excess of borane adduct from the medium. The structure of **2a** was confirmed by an X-ray study[7] (Figure 1a), which showed the presence of a tetrahydroborate ligand bridging the dimetal center in a symmetrical way through two of its B–H bonds.

Spectroscopic data for **2a** and **2b** indicate, on one hand, that they are isostructural with each other and, on the other, that they keep in solution the main structural features found in the crystal for **2a**. The IR spectra of these species show five strong CO stretching bands with a pattern characteristic of many compounds of the type [$Mn_2(\mu\text{-}H)(\mu\text{-}X)(CO)_6(\mu\text{-}L_2)$] previously prepared in our laboratory (X = halide, phosphide, acetylide, carboxylate, etc.). Besides, two weak bands around 2400 cm^{-1} are also observed, corresponding to the terminal B–H bond stretching modes of the tetrahydroborate ligands.[12] The stretching modes of the bridging bonds were not observed, being probably hidden under the ν(CO) bands.

Both **2a** and **2b** exhibit a single resonance in the $^{31}P\{^1H\}$ spectra, indicative of identical chemical environments for the two metallic centers in these molecules, and thus of a symmetrical coordination of the tetrahydroborate group. The latter gives rise to two separated ^1H resonances (+2.9 and −14.0 ppm at 243 K for **2a**) which correspond respectively to terminal B–H and bridging B–H–Mn hydrogen atoms, each integrating as 2 H. The chemical shifts are as expected,[11d,12] but the ^{11}B shift of **2a** (−31.8 ppm) is well out of the usual region[11d] ($\delta > 0$ ppm) where B–H moieties bonded to transition metal centers appear. Some similarly shielded resonances, however, have been previously reported (for example, −30.6 ppm for [$V_2\{\mu\text{-}H_2ZnBH_4\}_2(PPh_2Me)_4$][13] or −30.0 ppm for [$W_2(\mu\text{-CMe})(\mu\text{-BHEt})(CO)_4(C_5H_5)_2$][14]). Finally, the bridging hydrido ligands in **2a** and **2b** give rise to highly shielded resonances as expected, exhibiting coupling with two equivalent phosphorus atoms.

Compound **2a** undergoes slow (on the NMR time scale) exchange between terminal and bridging B–H hydrogen atoms. This is not evident from the room temperature ^1H NMR spectra, still showing separated, although quite broad, resonances at +2.5 and −14.5 ppm. On a rise in temperature, however, these signals broaden further and eventually collapse into a single broad resonance at −6.0 ppm, the average chemical shift. The process does not involve the $Mn_2(\mu\text{-}H)$ hydrido ligand at any stage, in contrast with the behavior observed for the trimetal-bonded BH_4^- group in the clusters [$M_3(\mu\text{-}H)BH_4(CO)_9$] (M = Fe,[15] Ru[16]). The coalescence temperature is 310 ± 2 K, which allows an estimate[17] of the free energy of activation for the process of 12.2 ± 0.1 kcal·mol^{-1}, at that temperature. This value is within the range of energies found for bidentate tetrahydroborate ligands bonded to mononuclear centers, which are usually fluxional.[12] Accordingly, we propose for **2a** a mechanism for the hydrogen exchange similar to those proposed for some mononuclear species,[12] involving a transient decoordination of one of the B–H bonds (Figure 2). It should be noted that no exchange between terminal and bridging B–H hydrogen atoms was observed for [$Ir_2(\mu\text{-}BH_4)(\mu\text{-}H)H_2(C_5Me_5)_2$],[18] the closest structural analogue of **2a** as far as BH_4^- coordination is concerned. This can be an effect of a higher strength in the bonding of this ligand to the diiridium center ("side-on" type), when compared with **2a** ("end-on" type.[7] See also next section) and is consistent with the dissociative mechanism proposed for **2a**.

The reaction leading to complexes **2** can be viewed as an insertion of borane into a $Mn_2(\mu\text{-}H)$ bridge in the dihydrides **1**. This process is an unusual way of generating tetrahydroborate complexes, most commonly prepared by reaction of suitable transition metal complexes and alkali-metal tetrahydroborates.[11d,12] It has to be noted that the related reaction between [$Os_3(\mu\text{-}H)_2(CO)_{10}$] and BH_3·THF

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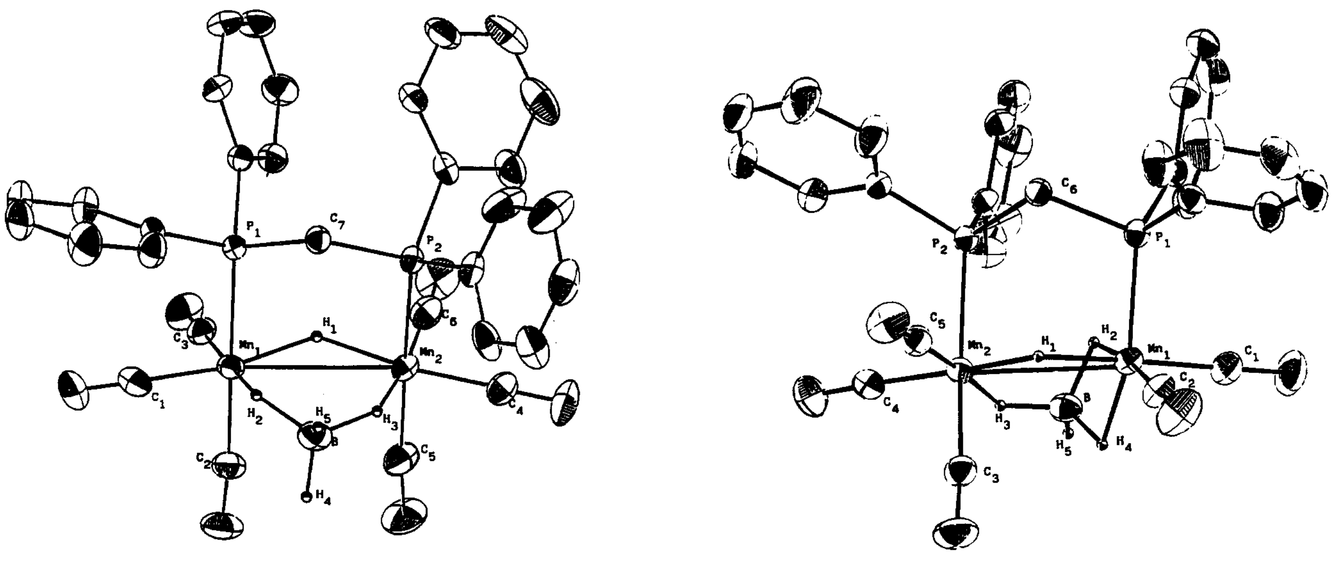


(a) (b)

Figure 1. Molecular structures of compounds **2a**[7] (left) and **3a** (right). C(phenyl) and O(carbonyl) labels are ommitted for clarity.

Table I. Spectroscopic Data for New Compounds

compd	ν(CO)/cm^{-1}	ν(B–H)^a/cm^{-1}	^{31}P{^{1}H} NMR/δ^b	^{11}B{^{1}H} NMR/δ^b
[$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_6(\mu\text{-dppm})$] (**2a**)	2046 (vs), 2017 (s), 1971 (s), 1950 (s), 1937 (s)^c	2472 (w), 2333 (w)	53.3 (s, br)	–31.8 (s, br)^d
[$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_6(\mu\text{-tedip})$] (**2b**)	2062 (vs), 2032 (s), 1992 (vs), 1973 (m), 1955 (vs)^e	2475 (w), 2360 (w)	168.4 (s, br)	18.1 (s, br)
[$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_5(\mu\text{-dppm})$] (**3a**)	2032 (vs), 1968 (s), 1957 (s), 1931 (s), 1906 (s)^c	2487 (w)	88.3, 60.4 (2 × d, J_{PP} = 74 Hz)	15.2 (s, br)^d
[$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_5(\mu\text{-tedip})$] (**3b**)	2049 (vs), 1993 (s), 1978 (s), 1952 (s), 1934 (s)^e	2466 (w)	198.7, 168.4 (2 × d, J_{PP} = 80 Hz)^f	13.4 (s, br)
[$Mn_2(\mu\text{-}H)(\mu\text{-}OCH_2CH_3)(CO)_6(\mu\text{-tedip})$] (**4b**)	2047 (s), 2016 (s), 1967 (m), 1950 (m), 1934 (vs)^e		160.5 (s, br)	

[a] KBr pellet. [b] Recorded in C_6D_6 solutions at room temperature unless otherwise stated. Chemical shifts (δ) in units of ppm relative to internal BF_3 (^{11}B, 128.38 MHz) or external 85% aqueous H_3PO_4 (^{31}P, 121.44 MHz). [c] Toluene solution. [d] 338 K. [e] Petroleum ether solution. [f] Toluene-d_8 solution, at 243 K.

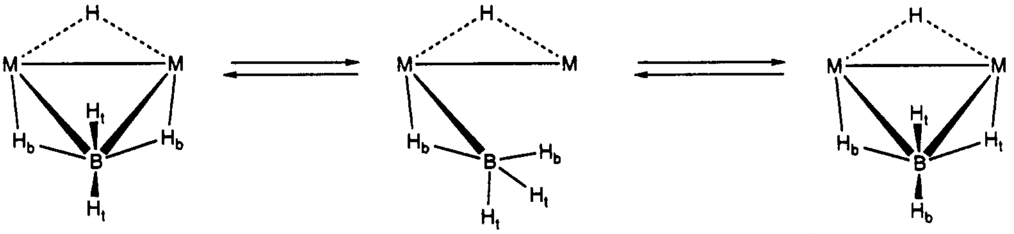


Figure 2. Schematic view of the proposed mechanism for the exchange between B–H positions in compound **2a**.

did not lead to tetrahydroborate complexes, although the latter were supposed to be formed as intermediate species.[10]

Compounds **2a** and **2b** are unstable in solution and give up a CO molecule. This occurs slowly at room temperature and more rapidly under thermal or photochemical activation. In both cases, the pentacarbonyl species [$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_5(\mu\text{-}L_2)$] (**3a,b**) (**a**; L_2 = dppm; **b**, L_2 = tedip) are obtained in good yield. The process is less selective for **2b**, which also loses some BH_3, even in the presence of excess BH_3·THF, to regenerate dihydride **1b**. The structure of **3a** has been determined by a single crystal X-ray study and is shown in Figure 1b. The most relevant feature in the molecule is the asymmetric tridentate coordination of the tetrahydroborate ligand, bonded to the $Mn(CO)_3$ center through one B–H bond and to the $Mn(CO)_2$ center through two other ones.

Spectroscopic data for **3a** and **3b** are both consistent with the main structural features found in the crystal for **3a**. The observation of a single carbonyl band above 2000 cm^{-1} and its very strong intensity relative in the IR spectra of these species is indicative of the presence of a single $Mn(CO)_3$ group in the molecule, with a local facial arrangement of the CO ligands. The IR spectra also exhibit a single band in the region of terminal B–H stretching modes, as expected for a tridentate BH_4^- ligand.[12] As was the case for **2a,b**, no B–H (bridging) stretching bands could be identified in the IR spectra of these pentacarbonyl species.

The ^{31}P NMR spectra of **3a,b** display two resonances, that at higher field having a chemical shift similar to those found for the hexacarbonyl species **2a,b**. Thus the low field resonance is assigned to the phosphorus atom bonded

Table II. Experimental Data for the Crystallographic Analysis of $[Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_5(\mu\text{-}Ph_2PCH_2PPh_2)]$ (3a)

formula	$C_{30}H_{27}BMn_2O_5P_2$
MW	650.2
cryst syst	monoclinic
space group	$P2_1/a$
a, Å	12.908(2)
b, Å	15.735(2)
c, Å	15.960(1)
β, deg	111.54(1)
V, Å^3	3015.2(8)
Z	4
ρ_{calc}, g·cm^{-3}	1.43
no. of reflns for lattice param determn	25
range, deg	14.8–15
$F(000)$	1328
μ, cm^{-1}	9.4
temp, °C	18
cryst size, mm	0.55 × 0.45 × 0.30
diffractometer	Enraf-Nonius CAD-4
radiation	Mo Kα
monochromator	graphite
scan type	ω–2θ
scan width	$1.0 + 0.34 \tan \theta$
θ range, deg	1–28
std reflns	two, measured every 2 h
no. of measd reflns	7240
no. of reflns used $I \geq 3\sigma(I)$	4968
min, max height in final $\Delta\rho$, e·Å^{-3}	–0.24, 0.28
no. of refined params	446
$R = [\sum\|\Delta F\|/\sum F_o]$	0.031
$R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$	0.031
$w = 1$	

to the dicarbonyl–metal center. In spite of this chemical nonequivalence, the hydrido ligand of the molecule still gives rise to a triplet in the ^1H NMR spectrum, which is interpreted as an accidental degeneracy of the two P–H coupling constants involved. The proton spectra of **3a,b** are also consistent with an asymmetric tridentate coordination of the BH_4^- ligand, as that gives rise in both cases to four distinct resonances. That one at ca. 4 ppm corresponds to the terminal B–H atom whereas the other three ones, in the range –8 to –14 ppm, are consistent with B–H–Mn moieties. Comparison between chemical shifts for the B–H–Mn resonances in complexes **3** and **2** suggest that the more shielded resonance is probably derived from the B–H bond coordinated to the tricarbonyl manganese center in **3a,b**. Interestingly, this proton resonance is also the one most sharpened upon ^{11}B broad-band irradiation.

The $^{11}B\{^1H\}$ NMR spectra of **3a,b** show relatively deshielded resonances, as expected. When compared with those for compounds **2a,b**, however, opposite trends are observed. Thus, on going from the hexacarbonyl to the pentacarbonyl complexes, deshielding in the ^{11}B tetrahydroborate resonance is observed for the dppm complex but shielding occurs for the tedip compound. Clearly then, the origin of these chemical shift variations cannot be attributed only to the change in the coordination mode (from bidentate to tridentate) of the tetrahydroborate ligand.

The spontaneous decarbonylation yielding complexes **3** from **2** at room temperature is rather unusual for species of the type $[Mn_2(\mu\text{-}H)(\mu\text{-}X)(CO)_6(\mu\text{-}L_2)]$ (L_2 = dppm or tedip; X = halide, phosphide, acetylide, carboxylate, etc.), which are usually quite robust in this respect. At the moment we cannot offer a satisfactory explanation to account for this behavior of complexes **2**.

Table III. Atomic Coordinates and Thermal Parameters for Non-Hydrogen Atoms in Compound 3a

atom	x/a	y/b	z/c	U(equiv)/Å^2
Mn(1)	0.36087(3)	0.04939(3)	0.29214(3)	0.0415
Mn(2)	0.14402(3)	0.12645(2)	0.24861(3)	0.0399
P(1)	0.30013(5)	–0.08002(4)	0.24184(4)	0.0387
P(2)	0.08333(5)	–0.01195(4)	0.25104(4)	0.0370
C(1)	0.4981(3)	0.0138(2)	0.3536(2)	0.0584
C(2)	0.4057(2)	0.0781(2)	0.2028(2)	0.0572
C(3)	0.1946(3)	0.2309(2)	0.2344(2)	0.0566
C(4)	0.0358(3)	0.1727(2)	0.2797(2)	0.0549
C(5)	0.0597(2)	0.1245(2)	0.1317(2)	0.0515
C(6)	0.1476(2)	–0.0809(2)	0.1910(2)	0.0402
C(10)	0.3257(2)	–0.1658(2)	0.3241(2)	0.0433
C(11)	0.3660(2)	–0.1488(2)	0.4160(2)	0.0491
C(12)	0.3724(3)	–0.2133(2)	0.4762(2)	0.0604
C(13)	0.3394(3)	–0.2930(3)	0.4468(3)	0.0676
C(14)	0.3017(3)	–0.3118(2)	0.3568(3)	0.0663
C(15)	0.2959(3)	–0.2485(2)	0.2951(2)	0.0557
C(20)	0.3448(2)	–0.1274(2)	0.1566(2)	0.0459
C(21)	0.4554(3)	–0.1466(2)	0.1798(2)	0.0652
C(22)	0.4947(3)	–0.1781(3)	0.1167(3)	0.0759
C(23)	0.4262(4)	–0.1905(3)	0.0309(3)	0.0788
C(24)	0.3175(4)	–0.1731(4)	0.0072(3)	0.0901
C(25)	0.2748(3)	–0.1420(3)	0.0694(2)	0.0723
C(30)	0.1021(2)	–0.0672(2)	0.3556(2)	0.0419
C(31)	0.1355(3)	–0.0244(2)	0.4361(2)	0.0589
C(32)	0.1467(4)	–0.0668(3)	0.5147(2)	0.0715
C(33)	0.1256(3)	–0.1514(3)	0.5133(3)	0.0654
C(34)	0.0924(3)	–0.1945(2)	0.4343(3)	0.0600
C(35)	0.0796(2)	–0.1535(2)	0.3554(2)	0.0495
C(40)	–0.0653(2)	–0.0270(2)	0.1887(2)	0.0455
C(41)	–0.1398(3)	0.0044(2)	0.2246(3)	0.0656
C(42)	–0.2531(3)	–0.0016(3)	0.1777(4)	0.0802
C(43)	–0.2935(3)	–0.0397(3)	0.0957(4)	0.0862
C(44)	–0.2212(4)	–0.0725(4)	0.0609(3)	0.0955
C(45)	–0.1073(3)	–0.0663(3)	0.1068(3)	0.0765
O(1)	0.5883(2)	–0.0093(2)	0.3892(2)	0.0854
O(2)	0.4370(2)	0.0983(2)	0.1474(2)	0.0869
O(3)	0.2199(2)	0.2980(2)	0.2229(2)	0.0836
O(4)	–0.0309(2)	0.2040(2)	0.2997(2)	0.0807
O(5)	0.0058(2)	0.1243(2)	0.0567(1)	0.0748
B(1)	0.3146(3)	0.1115(2)	0.3856(2)	0.0487

Table IV. Atomic Coordinates and Thermal Parameters for Hydrogen Atoms in Compound 3a

atom	x/a	y/b	z/c	U(iso)/Å^2
H(1)	0.236(2)	0.085(2)	0.220(2)	0.059(4)
H(2)	0.316(2)	0.035(2)	0.278(2)	0.059(4)
H(3)	0.226(2)	0.136(2)	0.362(2)	0.059(4)
H(4)	0.376(2)	0.139(2)	0.353(2)	0.059(4)
H(5)	0.338(2)	0.130(2)	0.455(2)	0.059(4)
H(11)	0.393(3)	–0.093(2)	0.440(2)	0.082(2)
H(12)	0.402(3)	–0.203(2)	0.536(2)	0.082(2)
H(13)	0.343(3)	–0.334(2)	0.485(2)	0.082(2)
H(14)	0.275(3)	–0.363(2)	0.333(2)	0.082(2)
H(15)	0.265(3)	–0.259(2)	0.235(2)	0.082(2)
H(21)	0.501(3)	–0.139(2)	0.237(2)	0.082(2)
H(22)	0.569(3)	–0.188(2)	0.134(2)	0.082(2)
H(23)	0.455(3)	–0.204(2)	–0.011(2)	0.082(2)
H(24)	0.267(3)	–0.187(2)	–0.044(2)	0.082(2)
H(25)	0.200(3)	–0.137(2)	0.053(2)	0.082(2)
H(31)	0.151(3)	0.029(2)	0.438(2)	0.082(2)
H(32)	0.167(3)	–0.038(2)	0.561(2)	0.082(2)
H(33)	0.126(3)	–0.177(2)	0.561(2)	0.082(2)
H(34)	0.076(3)	–0.254(2)	0.432(2)	0.082(2)
H(35)	0.054(3)	–0.183(2)	0.301(2)	0.082(2)
H(41)	–0.106(3)	0.029(2)	0.277(2)	0.082(2)
H(42)	–0.298(3)	0.017(2)	0.213(2)	0.082(2)
H(43)	–0.371(3)	–0.045(2)	0.065(2)	0.082(2)
H(44)	–0.240(3)	–0.098(2)	0.010(2)	0.082(2)
H(45)	–0.070(3)	–0.085(2)	0.082(2)	0.082(2)
H(61)	0.126(3)	–0.136(2)	0.191(2)	0.082(2)
H(62)	0.133(3)	–0.058(2)	0.136(2)	0.082(2)

Structure and Bonding in Compounds 2a and 3a. The crystal structures of compounds **2a**[7] and **3a** are displayed in Figure 1. Table V contains bond distances and angles in compound **3a**. In both cases, the environment around each manganese atom is approximately octahedral if we ignore the boron atom and the Mn–Mn

Table V. Selected Bond Distances (Å) and Angles (deg) in Compound 3a

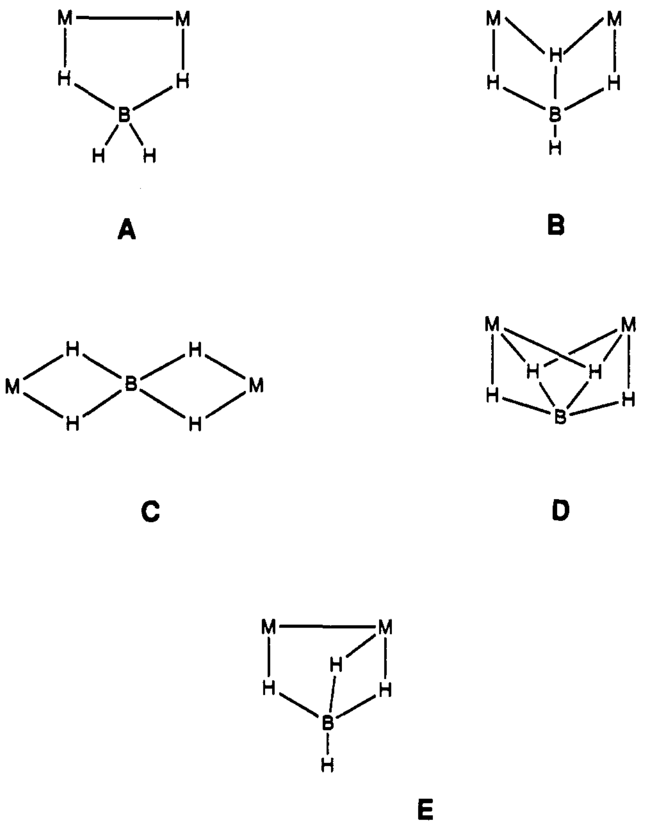
Mn(1)–Mn(2)	2.8913(6)	Mn(1)–P(1)	2.2234(8)
Mn(1)–C(1)	1.771(3)	Mn(1)–C(2)	1.782(3)
Mn(1)–B(1)	2.048(4)	Mn(1)–H(1)	1.70(3)
Mn(1)–H(2)	1.69(3)	Mn(1)–H(4)	1.68(3)
Mn(2)–P(2)	2.3197(8)	Mn(2)–C(3)	1.812(3)
Mn(2)–C(4)	1.799(3)	Mn(2)–C(5)	1.782(3)
Mn(2)–B(1)	2.480(3)	Mn(2)–H(1)	1.56(3)
Mn(2)–H(3)	1.74(3)	C(1)–O(1)	1.152(4)
C(2)–O(2)	1.144(3)	C(3)–O(3)	1.140(3)
C(4)–O(4)	1.136(3)	C(5)–O(5)	1.143(3)
B(1)–H(2)	1.21(3)	B(1)–H(3)	1.13(3)
B(1)–H(4)	1.19(3)	B(1)–H(5)	1.07(3)

C(1)–Mn(1)–P(1)	93.4(1)	C(2)–Mn(1)–P(1)	96.8(1)
C(2)–Mn(1)–C(1)	88.3(1)	H(1)–Mn(1)–P(1)	86.3(9)
H(1)–Mn(1)–C(1)	171.2(9)	H(1)–Mn(1)–C(2)	83.0(9)
H(2)–Mn(1)–P(1)	89.4(10)	H(2)–Mn(1)–C(1)	94.5(9)
H(2)–Mn(1)–C(2)	173.1(10)	H(2)–Mn(1)–H(1)	94.3(13)
H(4)–Mn(1)–P(1)	158.2(9)	H(4)–Mn(1)–C(1)	93.6(9)
H(4)–Mn(1)–C(2)	104.0(10)	H(4)–Mn(1)–H(1)	89.9(13)
H(4)–Mn(1)–H(2)	69.5(13)	C(3)–Mn(2)–P(2)	172.9(1)
C(4)–Mn(2)–P(2)	94.3(1)	C(4)–Mn(2)–C(3)	91.1(1)
C(5)–Mn(2)–P(2)	85.5(1)	C(5)–Mn(2)–C(3)	89.6(1)
C(5)–Mn(2)–C(4)	93.3(1)	H(1)–Mn(2)–P(2)	84.9(10)
H(1)–Mn(2)–C(3)	89.7(10)	H(1)–Mn(2)–C(4)	178.6(10)
H(1)–Mn(2)–C(5)	85.5(10)	H(3)–Mn(2)–P(2)	98.1(9)
H(3)–Mn(2)–C(3)	86.9(9)	H(3)–Mn(2)–C(4)	85.3(9)
H(3)–Mn(2)–C(5)	176.2(9)	H(3)–Mn(2)–H(1)	95.9(13)
O(1)–C(1)–Mn(1)	176.2(3)	O(2)–C(2)–Mn(1)	177.7(3)
O(5)–C(5)–Mn(2)	179.2(3)	P(2)–C(6)–P(1)	112.5(1)
H(3)–B(1)–H(2)	110.7(19)	H(4)–B(1)–H(2)	106.5(19)
H(4)–B(1)–H(3)	119.6(19)	H(5)–B(1)–H(2)	110.9(20)
H(5)–B(1)–H(3)	96.8(20)	H(5)–B(1)–H(4)	112.1(20)
Mn(2)–H(1)–Mn(1)	124.8(17)	B(1)–H(2)–Mn(1)	87.9(16)
B(1)–H(3)–Mn(2)	118.1(20)	B(1)–H(4)–Mn(1)	89.5(17)

bond. Thus, the B–H–Mn hydrogen atoms are placed forming angles of ca. 90 or 180° with the other ligands in the molecule. This is less perfectly achieved for the more constrained coordination of the tetrahydroborate ligand found in **3a** [for example H(3)–Mn(2)–C(5) = 176.2(9)° and H(2)–Mn(1)–C(2) = 173.1(10)°, but H(4)–Mn(1)–P(1) = 158.2(9)°]. The intermetallic separations, in the range 2.9–3.0 Å, are significantly longer than that in the unsaturated precursor **1a** (2.699(2) Å)[1a] and similar to other singly bonded bis octahedral hydrido dimanganese complexes.[1b,19] In fact, single bond orders are formally predicted for both **2a** and **3a** by consideration of the 18-electron rule, if we recognize each coordinated B–H bond as a 2-electron ligand. However, the significant shortening (ca. 0.1 Å) of the intermetallic distance on going from **2a** to **3a** (and thus from 2 to 3 coordinated B–H bonds) might be indicative of the presence of some degree of unsaturation in **3a**, a point which will be further discussed below.

The coordination geometries of the tetrahydroborate ligand in compounds **2a** and **3b** deserve some comments. Previous examples of tetrahydroborate groups bridging two metal atoms correspond to symmetrical arrangements (Chart II) involving two hydrogen atoms (A, as in **2a** or $[Ir_2(\mu\text{-}H)(\mu\text{-}BH_4)H_2(C_5Me_5)_2]$,[18] three (B, as in $[Co_2(\mu\text{-}BH_4)_2\{Ph_2P(CH_2)_5PPh_2\}_2]$[20] or $[Th(\mu\text{-}H_3BMe)(H_3BMe)_3]_2\cdot OR_2$[21]), or four (C, as in $[Ru_2(\mu\text{-}BH_4)H_2(tripod)_2]BF_4$[22] and $[Cu_2(\mu\text{-}BH_4)(PPh_3)_4]ClO_4$,[23] or D, as in $[Ce_2(\mu\text{-}BH_4)_2(\eta\text{-}C_5H_3{}^tBu_2)_4]$[24]). Thus, complex **3b** is the first example of an asymmetric, tridentate coordination of a tetrahydroborate group bridging two metal atoms (E).

Chart II



Examination of the structural parameters for the Mn···H···B interactions in **2a** and **3a** reveals important differences. In the first case, those interactions are characterized by relatively large Mn–H–B angles (average 127.1(3)°), and Mn–B distances (average 2.582(3) Å).[7] A similar situation is found in **3a** for the B–H(3)–Mn(2) interaction [B–H(3)–Mn(2) = 118.1(20)°, B–Mn(2) = 2.480(3) Å]. In contrast, the B–H–Mn(1) interactions in the latter compound display quite a short distance and small angles [B–Mn(1) = 2.048(4) Å, B–H–Mn(1) = 87.9(16) and 89.5(17)°]. Thus, we can speak of a side-on coordination[25] of the B–H bonds in the latter case and end-on coordination for **2a** or B–H(3) in **3a**. It should be pointed out that the B–Mn(1) distance in **3a** is not only shorter than those found in other manganoborane compounds containing B–H–Mn bonds, as $[Mn_3(\mu\text{-}H)(\mu\text{-}B_2H_6)(CO)_{10}]$ (average 2.30(2) Å)[26] or $[Mn(CO)_3B_8H_{13}]$ (average 2.256(4) Å),[27] but even shorter than the direct (unbridged) Mn–B distances in $[Mn(CO)_3(B_9H_{12}\cdot OC_4H_8)]$ (2.196(6) Å).[28] For mononuclear species, it is well-known that bidentate BH_4^- groups generally display M–B dis-

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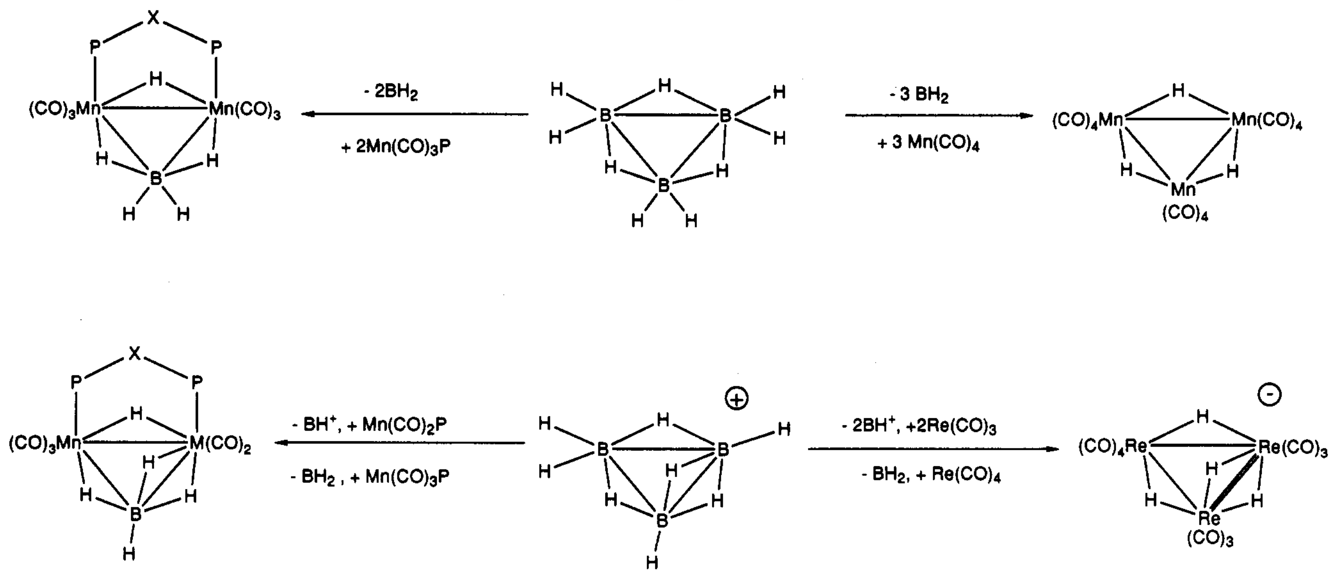
Scheme I. Formal Relationships between Complex 2a or 3a with Boranes and Metal Clusters

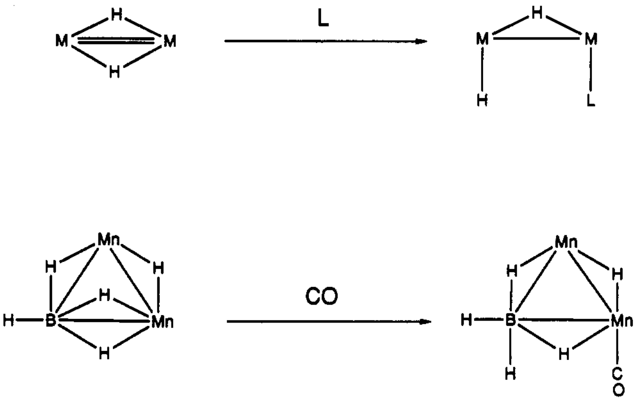


tances shorter than analogous monodentate ones, but differences are usually smaller than those found in complex **3a** (considering BH_4^- as monodentate toward Mn(2) and bidentate toward Mn(1)). For example, the difference between Cu–B distances in [$Cu(BH_4)(PPh_3)_2$][29] and [$Cu(BH_4)(PPh_2Me)_3$][30] is 0.33 Å, whereas B–Mn(1) and B–Mn(2) in **3a** differ by 0.432 Å. Thus, there might be some other causes behind the short B–Mn(1) distance in **3a**, as will be pointed out immediately. Other geometrical features in the BH_4^- groups in **2a** or **3b** are not unusual. Thus the hydrogen atoms define a distorted tetrahedral environment around the boron atoms, with B–H distances only slightly longer for the coordinated hydrogen atoms.

It is worthwhile to relate the structures of compounds **2a** and **3a** with those of the boron hydrides or even with metal clusters by using isolobal relationships.[31] Thus, considering the relationship $MnL_4 \leftrightarrow BH_2$ we can compare **2a** with [$Mn_3(\mu$-$H)_3(CO)_{12}$][32] or the hypothetical B_3H_9, for which Wade's[31b] or Lipscomb's[33] rules predict a similar geometry (arachno, or *styx* index 3003) (Scheme I). Noticeably, B_3H_9 is generally through to be an intermediate in the thermolysis of diborane.[11a] It would be formed by reaction of B_2H_6 with BH_3, a process analogous to the formation of **2a** from **1a** and BH_3·THF.

In a similar way and by adding now the relationship $MnL_3 \leftrightarrow BH^+$, we can compare **3a** with [$Re_3(\mu$-$H)_4(CO)_{10}$]$^-$ [34] or the hypothetical $B_3H_8^+$, for which a nido structure (*styx* index 4001) is predicted (Scheme I). Apart from the obvious topological analogy between **3a** and the trirhenium species, it is tempting to extend the comparison to the electronic structure of these molecules. Thus, **3a** could perhaps be considered as an electron deficient species, much in the same way as the trirhenium species or even **1a** are. Whatever the correctness of this statement, the idea seems useful, as it would provide a rationale for the shortening of the intermetallic distance in **3a** relative to **2a**, or even for the short B–Mn(1) distance in the former. Interestingly, **3a** takes up easily a CO molecule at room temperature to regenerate **2a**, a reaction reminiscent of the bridge-opening process occurring in unsaturated dihydrides such as [$Re_2(\mu$-$H)_2(CO)_6(\mu$-$L_2)$][35] (L_2 = dppm, tedip) or [$Os_3(\mu$-$H)_2(CO)_{10}$][36] upon reaction with 2-electron donor molecules (Scheme II). It is however to be confirmed by experiment whether this analogy can be extended to other sorts of reactions.

Scheme II. Reactivity Analogy between 3a and Transition Metal (M) Unsaturated Dihydrides



Reactions of Dihydrides 1a,b with Other Boron Species. Given the mild conditions under which BH_3·THF reacts with compounds **1a,b** it was throught that other simple boranes would also form new manganoborane species through reaction with these dihydrides. Our attempts in that direction have been, however, unsuccessful. No reaction was observed, for example, with "stable" borane adducts such as BH_3·PPh_3 or BH_3·NMe_3

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under either thermal or photochemical conditions. Thus, the absence of an accessible LUMO on the boron atom seems to prevent any reaction from occurring. No reaction was observed with the substituted diborane $B_2(\mu\text{-}H)_2(C_8H_{14})_2$, although in this case steric requirements might be on the unfavorable side.

The species "B_3H_7", prepared in situ as described in the literature,[37] does react with **1a** but gives no new complexes. In fact, no reaction was detected below −40 °C (the temperature above which decomposition of this species occurs to yield B_4H_{10} and B_5H_9[37]), and warming to room temperature was necessary. Surprisingly, a mixture of **2a** and **3a**, with the latter being the major species, was formed. However, **3a** cannot have been formed alone from **2a** in such relative high amounts, under the conditions of the experiment. Therefore, we believe that different pathways are responsible for the formation of **2a** and **3a** in this reaction. We cannot offer a reasonable proposal for these processes, but we note that the dimethyl sulfide adduct of B_3H_7 decomposes in the presence of excess Me_2S to give $BH_3{\cdot}SMe_2$.[38] Thus, it is possible that **2a** and **3a** derive from a transient adduct "**1a**$\cdot B_3H_7$" susceptible to thermal decomposition through different pathways.

Finally, it was of interest to examine whether boron species having no B–H bonds, but still Lewis acid character, would react with complexes **1a,b**. This would require the dihydrides to behave as neat electron donors, something that we have shown recently using gold and silver acidic fragments.[39] No reaction was observed when BPh_3 was used. In the case of BEt_3, however, a very slow reaction occurred both with **1a** and **1b** at room temperature, to give in moderate yields the corresponding alkoxo complexes $[Mn_2(\mu\text{-}H)(\mu\text{-}OEt)(CO)_6(\mu\text{-}L_2)]$ (**4a,b**). Compound **4a** had been previously prepared in our laboratory from **1a** and acetaldehyde.[40] On the other hand, spectroscopic data for **4b** indicate that this species is structurally related with its dppm analogue and will not be discussed in detail. Particularly informative data are the hydrido resonance at −12.04 ppm, exhibiting the usual *cis* coupling with two equivalent phosphorus atoms and the ^{13}C resonances due to the bridging ethoxy group, at 82.2 and 20.9 ppm, noticeably deshielded compared to those of the ethoxy groups in the tedip ligand. Obviously, there was some undesired oxygen source in the reaction mixtures leading to complexes **4a,b**. Addition of dioxygen to the reaction mixtures made no significant effect, but addition of water substantially increased the rate of formation of **4a,b**. At present, the precise role of water as well as that of BEt_3 itself in this reaction is obscure. We must note that the dihydrides **1a,b** do not react with water or ethanol (a likely final product in the very slow hydrolysis of BEt_3) or even $B(OEt)_3$ at significant rates. Thus, it is possible that water plays its part once some BEt_3 has reacted with the manganese dihydride to yield some sort of unstable acid–base adduct, although it is quite clear that we have no data so as to exclude other alternatives.

Experimental Section

General Procedures. All reactions were carried out under a dry oxygen-free nitrogen atmosphere using Schlenk-tube techniques. Filtrations were routinely carried out through diatomaceous earth. Solvents were purified by standard procedures[41] and distilled under nitrogen prior to use. Petroleum ether refers to the fraction distilling in the range 60–65 °C. Photochemical reactions were performed with an Applied Photophysics 400-W mercury lamp using Pyrex jacketed Schlenk tubes maintained at the desired temperature with a Haake F-3 machine. Alumina for column chromatography was deactivated by appropriate addition of water under nitrogen to the commercial material (Aldrich, neutral, activity I). $Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})$ (**1a**),[1b] $Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-tedip})$ (**1b**),[2] and "B_3H_7"[37] were prepared by literature methods. $BH_3{\cdot}THF$ (1 M THF solution), $[NMe_4]B_3H_8$, and BEt_3 (1 M hexane solution) were purchased from commercial suppliers and used without further purification. IR spectra were recorded on a Perkin-Elmer 577 and FT 1720 X spectrophotometers, using CaF_2 cells for solution measurements and Nujol mulls or KBr pellets for solid-state measurements. ^1H (300.13 MHz), ^{31}P (121.44 MHz), ^{13}C (75.469 MHz) NMR spectra were recorded on a Bruker AC-300 spectrometer. $^{11}B\{^1H\}$ (128.38 MHz) and $^1H\{^{11}B\}$ or $^1H\{^{31}P\}$ spectra were measured on a Bruker AMX-400 instrument. Chemical shifts (ppm) are referenced against internal TMS (^1H, ^{13}C), external 85% H_3PO_4 aqueous solution (^{31}P), or internal BF_3 (^{11}B). Elemental analyses (C, H) were performed with a Perkin-Elmer 240B microanalyzer.

$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_6(\mu\text{-dppm})$ (2a). A solution of compound **1a** (0.05 g, 0.075 mmol) in toluene (10 mL) was treated at room temperature with $BH_3{\cdot}THF$ (0.1 mL of a 1 M solution in THF, 0.1 mmol) for 30 min, giving a yellow solution. Filtration of the solution and removal of the solvent under vacuum gave a residue which was washed with petroleum ether (3 × 5 mL), yielding compound **2a** as a yellow microcrystalline powder (0.038 g, 74%). The crystals used for the X-ray study[7] were grown by slow diffusion of a toluene solution of **2a** into a layer of petroleum ether, at room temperature. Anal. Calcd for $C_{31}H_{27}BMn_2O_6P_2$: C, 54.9; H, 4.0. Found: C, 54.7; H, 3.9. ^1H NMR (300.13 MHz, toluene-d_8, 243 K): δ 8.0–6.5 (m, Ph, 20 H), 2.9 (br, B–H, 2 H), 2.6, 2.5 (br, CH_2, 2 × 1 H), −14.0 (br, B–H–Mn, 2 H), −17.1 (t, J_{PH} = 21, Mn–H–Mn, 1 H). ^1H NMR (400.13 MHz, C_6D_6, 295 K): δ 2.6, 2.5 (ABX_2 system, $J_{PH} \approx J_{HH} = 13$, CH_2, 2 × 1 H).

$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_5(\mu\text{-dppm})$ (3a). Method A. A solution of "B_3H_7"[37] was prepared *in situ* by stirring $[NMe_4][B_3H_8]$ (0.14 g, 1.2 mmol) and I_2 (0.15 g, 0.6 mmol) in toluene (5 mL) for 1 h at −60 °C. Compound **1a** (0.08 g, 0.12 mmol) was then added, and the mixture was allowed to reach room temperature and further stirred for 1 h. Removal of the solvent under vacuum and extraction of the residue with petroleum ether left a yellow solid. This solid was extracted with toluene, giving a yellow solution which was filtered. Workup as described above yielded compound **2a** as a yellow powder (0.020 g, 24%). The petroleum ether extracts were chromatographed on alumina (activity III, 30 × 3 cm) at −30 °C. Elution with dichloromethane–petroleum ether (1:9) gave an orange fraction which yielded, after removal of solvents under vacuum, compound **3a** as an orange microcrystalline powder (0.035 g, 45%). The crystals used in the X-ray study were grown by slow diffusion of a toluene solution of **3a** into a layer of petroleum ether at room temperature. Anal. Calcd for $C_{30}H_{27}BMn_2O_5P_2$: C, 55.4; H, 4.2. Found: C, 55.2; H, 4.1. $^1H\{^{11}B\}$ NMR (400.13 MHz, C_6D_6, 338 K): δ 7.8 (m, Ph, 20 H), 4.3 (s, br, $w_{1/2}$ 47, B–H, 1 H), 3.3, 2.7 (2 × q, $J_{PH} \approx J_{HH} = 11$, CH_2, 2 × 1 H), −8.6, −12.1 (2 × s, br, $w_{1/2}$ 60, B–H–Mn, 2 × 1 H), −11.5 (t, J_{PH} = 24, Mn–H–Mn, 1 H), −14.6 (s, br, $w_{1/2}$ 25, B–H–Mn, 1 H).

Method B. A toluene solution (10 mL) of compound **2a** (0.030 g, 0.04 mmol) was heated at 70 °C for 2 h, giving an orange solution. Workup as in method A yielded 0.020 g (70%) of compound **3a** as an orange microcrystalline solid.

$Mn_2(\mu\text{-}BH_4)(\mu\text{-}H)(CO)_6(\mu\text{-tedip})$ (2b). A 3-fold excess of a 1 M THF solution of $BH_3{\cdot}THF$ (0.2 mL, 0.22 mmol) was added to a petroleum ether (10 mL) solution of complex **1b** (0.040 g,

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0.07 mmol), and the mixture was stirred at room temperature for 45 min. Removal of solvent under vacuum gave a yellow oily residue containing complex **2b** as the major carbonyl species (>95% as determined by ^{31}P NMR spectroscopy). All attempts to further purify or crystallize this residue resulted in progressive decomposition of the complex. Thus, satisfactory microanalytical data for **2b** could not be obtained. ^1H NMR (300.13 MHz, toluene-d_8, 243 K): δ −15.1 (br, $w_{1/2}$ 130, B–H–Mn, 2 H), −18.3 (br, $w_{1/2}$ 130, Mn–H–Mn, 1 H). $^1H\{^{11}B\}$ NMR (400.13 MHz, C_6D_6, 295 K): δ −14.9 (vbr, B–H–Mn, 2 H), −18.26 (t, J_{PH} = 29, Mn–H–Mn, 1 H). The resonances for the terminal B–H atoms or the ethoxy groups of the tedip ligands in compound **2b** could not be assigned unambiguously in any of these spectra, due to the presence of substantial amounts of residual petroleum ether and BH_3·THF in the oily materials analyzed.

$Mn_2(\mu$-$BH_4)(\mu$-$H)(CO)_5(\mu$-tedip) (3b). A freshly prepared solution of **2b**, made as described previously from **1b** (0.05 g, 0.093 mmol) and BH_3·THF (0.028 mL, 0.28 mmol) was irradiated with visible–UV light for 10 min at −20 °C. The orange resulting mixture was then chromatographed on alumina (activity III, 30 × 3 cm) at −40 °C. Elution with petroleum ether gave a red-purple fraction which yielded, after removal of solvent under vacuum, 0.008 g of compound **1b** (16%). Further elution with dichloromethane–petroleum ether (1:19) gave an orange fraction which yielded, after similar workup, compound **3b** as an orange microcrystalline solid (0.036 g, 74%). Anal. Calcd for $C_{13}H_{25}BMn_2O_{10}P_2$: C, 29.8; H, 4.8. Found: C, 30.0; H, 4.7. $^1H\{^{11}B\}$ NMR (400.13 MHz, C_6D_6, 295 K): δ 4.15–3.95 (m, OCH_2, 2 H), 3.80 (br, B–H, 1 H), 3.75–3.35 (m, OCH_2, 6 H), 1.13, 0.96, 0.87, 0.77 (4 × t, J_{HH} = 7, CH_3, 4 × 3 H), −9.50, −12.40, −13.45 (3 × s, br, B–H–Mn, 3 × 1 H), −12.59 (t, J_{PH} = 32, Mn–H–Mn, 1 H).

$Mn_2(\mu$-$H)(\mu$-OEt$)(CO)_6(\mu$-dppm) (4a). Triethylboron (0.3 mL of a 1 M solution in hexane, 0.3 mmol) and distilled water (1 mL) were added to a solution of **1a** (0.050 g, 0.075 mmol) in toluene (10 mL), and the mixture was stirred at room temperature for 12 h, giving a yellow mixture. The organic phase was then transferred onto anhydrous $MgSO_4$, stirred for 2 h, and filtered. Removal of solvent from the filtrate gave an oily residue which yielded, after recrystallization from petroleum ether at −20 °C, compound **4a** as a yellow microcrystalline powder (0.037 g, 65%). Spectroscopic and microanalytical data for **4a** were identical with those for the product resulting from reaction of **1a** and acetaldehyde.[40]

$Mn_2(\mu$-$H)(\mu$-OEt$)(CO)_6(\mu$-tedip) (4b). A petroleum ether solution (10 mL) of compound **1b** (0.050 g, 0.093 mmol) was treated with triethylboron (0.3 mmol) and water (1 mL) as described for **4a** for 3 days. Workup as for the latter yielded compound **4b** as a yellow powder (0.025 g, 45%). Anal. Calcd for $C_{16}H_{26}Mn_2O_{12}P_2$: C, 33.0; H, 4.5. Found: C, 32.8; H, 4.5. ^1H NMR (300.13 MHz, C_6D_6, 295 K): δ 3.80–3.60 (m, OCH_2, 10 H), 1.21 (t, J_{HH} = 7, μ-OCH_2CH_3, 3 H), 0.97 (t, J_{HH} = 7, CH_3–tedip–, 12 H), −12.04 (t, J_{PH} = 31, Mn–H–Mn, 1 H). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 295 K): δ, 220.5, 217.6, 212.8 (3 × m, br, Mn–CO), 82.2 (s, μ-OCH_2), 61.8 (s, P–OCH_2), 20.9 (s, μ-OCH_2CH_3), 15.9, 15.8 (2 × s, P–OCH_2CH_3).

Crystal Structure Determination of Compound 3a. Details of the data collection and refinements for this crystal structure determination are given in Table II. The structure was solved by direct methods and subsequent Fourier maps. An empirical absorption correction using Ψ scans of two reflections was applied. Non-hydrogen atoms were anisotropically refined. Hydrogen atoms were found on difference maps and their positions refined. They were given two overall isotropic parameters, one for BH_4 or hydride H atoms and another for the remaining H atoms in the molecule. Refinements were carried out in two blocks with CRYSTALS.[42] Atomic scattering factors corrected from anomalous dispersions were taken from CRYSTALS.[42] No extinction correction was necessary. The final R was 0.031 (R_w = 0.031). The maximum shift/esd was 0.2. A perspective view of the molecule is shown in Figure 1b. Thermal vibration ellipsoids enclose 30% of electron density. Atomic coordinates and selected bond distances and angles are given in Tables III–V.

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Supplementary Material Available: Drawing of the molecular structure of compound **3a** showing the full atom numbering scheme and tables of bond distances and angles and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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