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Chelating Phosphane–Boranes as Hemilabile Ligands – Synthesis of $[Mn(CO)_3(\eta^2\text{-}H_3B{\cdot}dppm)][BAr^F{}_4]$ and $[Mn(CO)_4(\eta^1\text{-}H_3B{\cdot}dppm)][BAr^F{}_4]$

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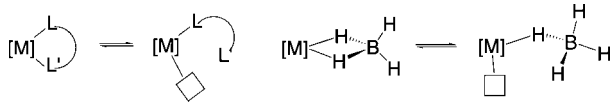
Manganese complexes bearing the chelating phosphane–borane ligand $H_3B{\cdot}$dppm [dppm = bis(diphenylphosphanyl)-methane] have been prepared. Addition of $H_3B{\cdot}$dppm to $Mn(CO)_5Br$ using $Na[BAr^F{}_4]$ as a halide-abstracting reagent affords $[Mn(CO)_3(\eta^2\text{-}H_3B{\cdot}dppm)][BAr^F{}_4]$ (**1**). This reacts with CO to open the bidentate borane to afford $[Mn(CO)_4(\eta^1\text{-}H_3B{\cdot}dppm)][BAr^F{}_4]$ (**2**) in which the borane is now bound in a monodentate manner. The CO addition is reversible, and placing **2** under vacuum (hours) regenerates **1** quantitatively, demonstrating that the chelating phosphane–boranes can act as hemilabile ligands. The complexes **1** and **2** have been fully characterised by NMR spectroscopy and X-ray crystallography.

Introduction

Reactions catalysed by Lewis acid transition metal fragments invariably rely on the generation of a vacant site on a cationic metal centre. Often this is generated by dissociation of a weakly bound ligand (e.g. solvent)[1] or anion.[2] An alternative mechanism – when a suitable ligand set is available – is one that involves a hemilabile ligand,[3–5] in which one donor atom in a chelate ligand has the ability to reversibly decoordinate in a catalytic cycle to reveal a coordinatively unsaturated metal centre. The design of hemilabile ligands is often based on ligands in which one end is a phosphane (which binds strongly) and the other a more weakly ligating group that can move away to generate a vacant site (Scheme 1). Examples of the weakly binding group include phosphane oxides,[6] sulfides,[7,8] and ether groups.[9] As pointed out nearly 30 years ago by Marks,[10] $[BH_4]^-$ can also potentially be a hemilabile ligand, by moving from η^2- to η^1-coordination modes (Scheme 1), thus generating the vacant site needed for substrate coordination. Examples of borohydride acting in this way are rare however, as on addition of ligand L loss of $H_3B{\cdot}$L often occurs with the concomitant generation of a metal hydride.[11,12] A recently reported observation of η^2- to η^1-borohydride hemilability comes from the addition of Lewis base (e.g. PMe_2Ph) to $Ru(PMe_2Ph)_2H(CO)(\eta^2\text{-}BH_4)$ to afford $Ru(PMe_2Ph)_3H(CO)(\eta^1\text{-}BH_4)$, although at temperatures above 300 K $H_3B{\cdot}PMe_2Ph$ is irreversibly lost to generate $Ru(PMe_2Ph)_3H_2(CO)$.[13]



Scheme 1.

One way of preventing borane loss would be to include the borohydride ligand in a chelate ring, allowing this potentially useful η^2- to η^1-transformation to occur without decomposition. Others[14,15] and we[16–18] have recently reported on the coordination chemistry of chelating phosphane–boranes $XH_2B{\cdot}$dppm (X = H, Cl, dppm = $PPh_2CH_2PPh_2$) in which one end of the ligand is valence-isoelectronic with borohydride while the other provides a firm phosphane anchor to the metal centre. These ligands show promise for hemilabile behaviour as the cationic complexes $[RuCp^*(\eta^2\text{-}XH_2B{\cdot}dppm)][Y]$ [X = H (**I**), Cl (**II**); Cp* = $\eta^5\text{-}C_5Me_5$; Y = $BAr^F{}_4$; PF_6] react with Lewis bases (CO, PMe_3) to open the borane from η^2 to η^1, thus forming $[RuCp^*(L)(\eta^1\text{-}XH_2B{\cdot}dppm)]^+$ (Scheme 2).[16,18] With these strong ligands the reaction is not reversible, and the ligand cannot be removed. The η^2-precursors **I** and **II** can thus be considered as being operationally unsaturated, effectively acting as a source of a reactive cationic 16-electron $\{RuCp^*(\eta^1\text{-}XH_2B{\cdot}dppm)\}^+$ fragment. The lack of borane loss on reaction with Lewis bases can be contrasted both with borohydride complexes, as discussed earlier, and also complexes of the monodentate phosphane–boranes developed by Shimoi, such as $MnCp^*(CO)_2(\eta^1\text{-}H_3B{\cdot}PMe_3)$, which react with weak Lewis bases to displace the borane.[19–21]

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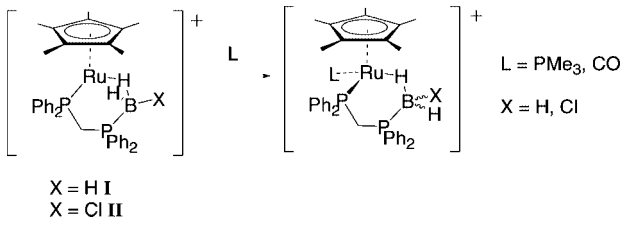
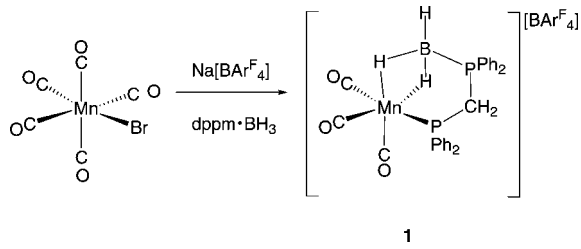


Scheme 2.



Scheme 3.

We report here the synthesis of some new cationic manganese complexes with the H_3B·dppm ligand. In these complexes the phosphane–borane opens and closes reversibly (i.e. shows true hemilabile behaviour) on the addition/removal of carbon monoxide.

Results

Treatment of $Mn(CO)_5Br$ with H_3B·dppm using $Na[BAr^F_4]$ as a halide-abstracting reagent results in the isolation of analytically pure (46% yield) $[Mn(CO)_3(\eta^2\text{-}H_3B{\cdot}dppm)][BAr^F_4]$ (**1**) (Scheme 3). The equivalent reactions with ClH_2B·dppm or BrH_2B·dppm[18] only resulted in mixtures of intractable products. Complex **1** has been fully characterised by NMR spectroscopy and X-ray crystallography, which all show that the chelating phosphane–borane adopts a bidentate (η^2) bridging mode of the BH_3 group. Figure 1 shows the solid-state structure of **1**.

The BH_3 fragment binds to the manganese atom through two B–H–Mn 3-centre-2-electron interactions. The hydrogen atoms associated with the BH_3 group were located in the final difference map and freely refined. Within the limits of confidence associated with the location of hydrides by X-ray crystallography the two hydrogen atoms that bridge to the metal atom have B–H bonds that can be considered longer than that to the terminal hydride [B1–H1a 1.07(3) Å, B1–H1b 1.30(4) Å, B1–H1c 1.24(3) Å], consistent with the 3c–2e bond description. The Mn–B distance is short [2.146(4) Å] mirroring that observed in the ruthenium complexes **I** and **II**,[16,18] being slightly longer than that found in three-coordinate boryl complexes of Mn such as $(CO)_5MnB(O_2C_6H_4)$ [2.108(6) Å][22] and comparable with the σ-borane complex $Mn(\eta^5\text{-}C_5H_4Me)(CO)_2(HB\{O_2C_4Me_4\})$ [2.149(2) Å].[23] It is significantly shorter than in the four-coordinate boryl complex $Mn(CO)_4(PMe_2Ph)(BH_2{\cdot}PMe_3)$ [2.314(2) Å] for which an $[Mn(CO)_4(PMe_2Ph)]^-$-$[BH_2(PMe_3)]^+$ bonding description is suggested.[19] A similar short distance is observed in $[Cr(CO)_4(\eta^2\text{-}BH_4)][PPN]$

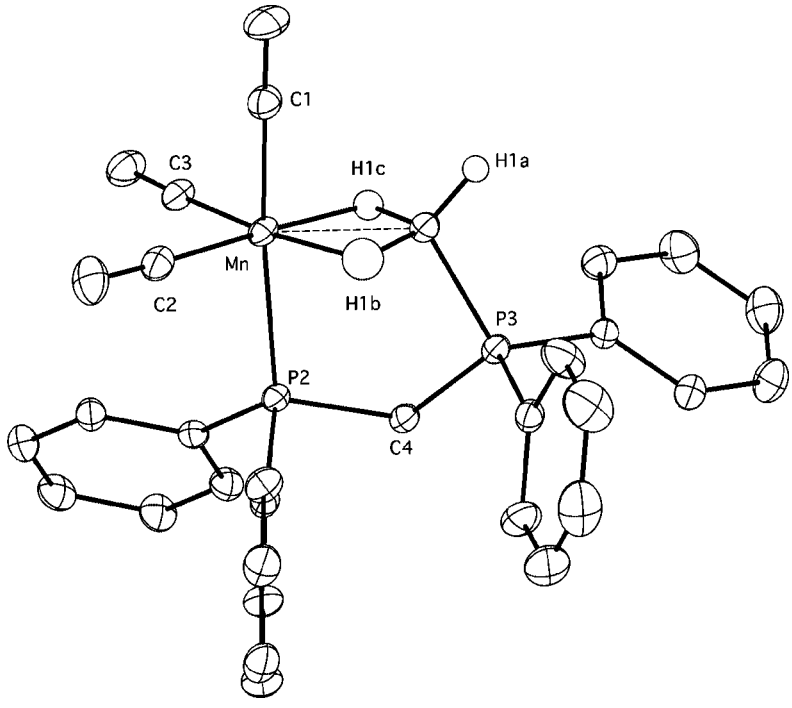


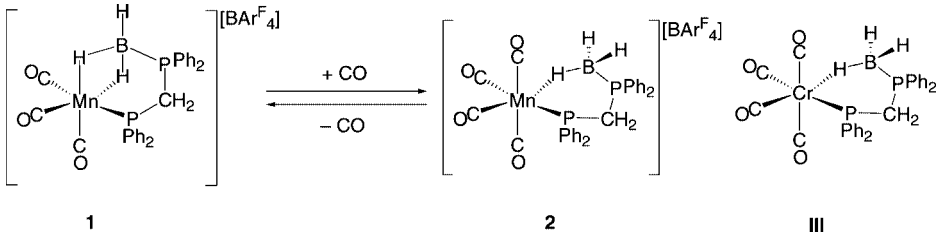
Figure 1. Solid-state structure of complex **1**. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted apart form those associated with the boron atom.

[2.29(1) Å] which is valence-isoelectronic with **1**.[24] As for **I** and **II**,[16,18] this interaction in **1** is best described as being like borohydride and not a dihydridoboryl complex, as the B–Mn–H and H–Mn–H angles are far more compressed than expected for a complex with two hydrides and a boryl ligand.[25] As expected for a relatively weakly bound BH_3 group, the M–C bond lengths associated with the carbonyl ligands *trans* to the bridging hydrides [Mn–C2 1.803(4) Å and Mn–C3 1.817(4) Å] are shorter than that *trans* to the phosphane group [Mn–C1 1.849(4) Å].

In solution, the ^{11}B NMR spectrum of **1** demonstrates the Mn···B interaction by a significant downfield shift of the signal of the H_3B·dppm ligand on coordination, from δ = –37.1 ppm in the free ligand to δ = 16.7 ppm ($\Delta\delta$ = +53.8 ppm) in **1**, consistent with η^2-coordination of the borane and a significant M···B interaction. In the $^1H\{^{11}B\}$ NMR spectrum two signals observed at δ = –9.08 (2 H) ppm and δ = 4.99 (1 H) ppm are assigned to the bridging and terminal BH groups, respectively, indicating that exchange between the terminal and bridging hydrides does not occur at room temperature. The methylene backbone in the dppm group is observed as an integral 2 H doublet of doublets, indicating time-averaged C_s symmetry in solution. The $^{31}P\{^1H\}$ NMR spectrum displays two peaks, a sharp doublet at δ = 73.7 ppm and a broad signal as δ = 15.6 ppm, the latter assigned to the boron-bound phosphorus atom. Other spectroscopic data are also in full accord with the solid-state structure.

Addition of CO (1 atm) to **1** results in the rapid formation of the tetracarbonyl complex $[Mn(CO)_4(\eta^1\text{-}H_3B\cdot dppm)][BAr^F{}_4]$ (**2**) and the opening of the phosphane–borane ligand form η^2 to η^1 (Scheme 4). The NMR spectroscopic data for **2** are very similar to those for the isoelectronic complex $Cr(CO)_4(\eta^1\text{-}H_3B\cdot dppm)$ (**III**).[16] A diagnostic high-field chemical shift change for the BH_3 signal in the $^{11}B\{^1H\}$ NMR spectrum to δ = –37.5 ppm (similar to the free ligand[16,26]) indicates the η^1-binding mode and loss of a significant M···B interaction. In the ^1H NMR spectrum, the BH_3 group is observed as a quadrupolar, broadened integral 3 H signal at δ = –3.74 ppm, which sharpens on decoupling of ^{11}B. The observation of one integral 3 H BH_3 signal at room temperature shows that the BH_3 group is rapidly spinning around the P–B bond at this temperature, exchanging terminal and bridging hydrides. Consistent with this fluxional process, the methylene group on the dppm ligand is observed as an integral 2 H doublet of doublets. In **III** this fluxional process also occurs but cannot be frozen out at low temperature. For **2**, cooling to 190 K (CD_2Cl_2) results in the observation of two broad signals in the ratio 2:1 at δ = 1.99 (fwhm = 160 Hz) ppm and δ = –15.52 (fwhm = 250 Hz) ppm in the $^1H\{^{11}B\}$ NMR spectrum, assigned to the terminal and bridging hydrides, respectively, showing that the exchange process has been halted. This difference between neutral **III** and cationic **2** can be attributed to the increased electrostatic attraction between the cationic manganese centre and the polarised $H^{\delta-}$–$B^{\delta+}$ group. At low temperature, the methylene protons for **2** are observed as a single integral 2 H broadened peak (fwhm = 50 Hz) centred at δ = 3.5 ppm in the $^1H\{^{11}B\}$ NMR spectrum, suggesting C_s symmetry for the molecule at low temperature. In the solid-state structure (see below) the molecule adopts C_1 symmetry, resulting in the methylene protons and the B–H protons being all inequivalent, contrary to the observation of just two signals for the B–H protons and one for the methylene group. However, due to the broadness of these signals at 190 K and the inherent difficulty associated with reliably integrating such broad signals, it is not possible to say whether inequivalent environments are present for each group, or instead if a low-energy libration of the bridging hydride around the Mn–B vector is occurring to make both the dppm methylene and BH_2 protons each equivalent.

The solid-state structure of **2** shows an η^1-binding mode for the phosphane–borane ligand, which forms a δ-agostic Mn–H–B interaction (Figure 2). The structural metrics are similar to those already discussed for **III**,[16] as expected for this isoelectronic pair and are consistent with a relatively weak δ-agostic Mn–H–B interaction [Mn···H 1.71(3) Å, Mn···B 2.748(3) Å]. Notably the Mn···B bond is long – being similar to that calculated for $[Mn(CO)_4(PH_3)(\eta^1\text{-}H_3B\cdot PMe_3)]^+$ [2.780 Å][19] and slightly shorter than observed for neutral $Cr(CO)_5(\eta^1\text{-}H_3B\cdot PMe_3)$ [2.79(1) Å].[21] The Mn–H–B angle of 134(2)° means that the molecule does not have C_s symmetry in the solid state, in contrast to the solution NMR spectroscopic data (vide supra). This angle is far more open than those observed in **1** [viz. 91(1), 93(1)°], consistent with move from didentate to monodentate coordination modes. The carbonyl ligand *trans* to the weakly bound H_3B group has the shortest Mn–C distance, as expected. The Mn···H distance in **2** is significantly shorter than that found in γ-agostic complex $[Mn(CO)_3(PCy_3)_2][BAr^F{}_4]$ [2.01(9) Å],[27] in part a consequence of the polarised Bδ⁺···Hδ⁻ group interacting with the cationic metal centre.



Scheme 4.

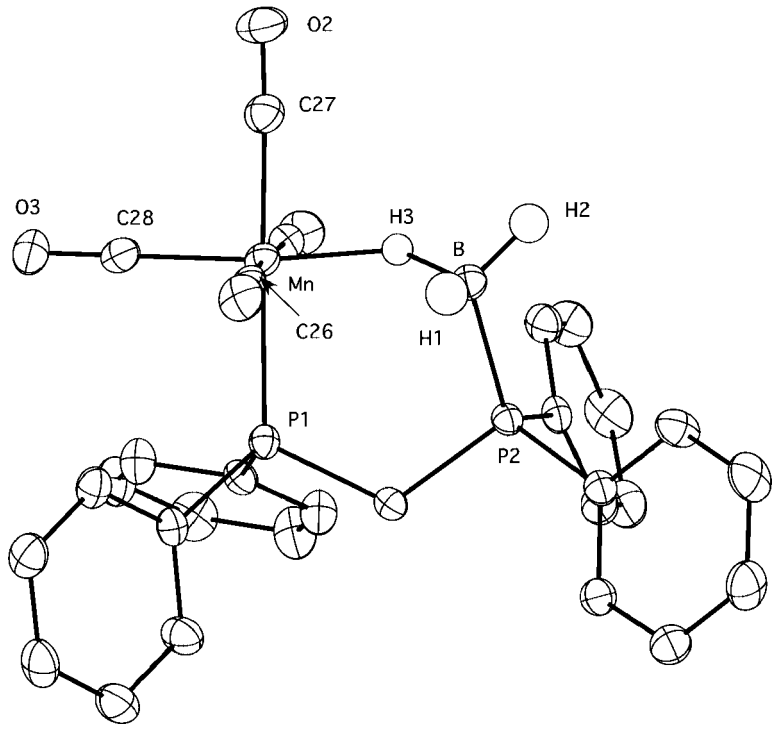


Figure 2. Solid-state structure of complex **2**. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted apart form those associated with the boron atom.

The addition of CO to **2** is reversible. Placing **2** under a dynamic vacuum (minutes) or under argon (days) regenerates **1** quantitatively in both the solid state and solution. For this reason, crystals of **2** are best obtained under CO and good microanalytical data could not be obtained. Addition of Lewis bases other than CO to **2** (MeCN, PR_3) resulted in decomposition. Addition of the weaker Lewis base H_2 did not displace the borane, and addition of D_2 did not result in H/D exchange. This is contrary to complexes **I** and **II** in which H/D exchange occurs, via a putative dihydride intermediate that results from the opening of the borane to η^1.[16,18] Presumably, the cationic $\{Mn(CO)_3\}^+$ fragment is reluctant to undergo oxidative addition of H_2 and thus no H/D exchange is observed in **1**.

Interestingly, the complex isoelectronic with **2**, $Mn(CO)_5(\eta^1\text{-}BH_4)$, has only been briefly reported as a possible intermediate in the formation of $Mn_3(CO)_{10}(BH_3)_3H$ from $Al[BH_4]$ and $Mn(CO)_5Br$,[28] while the borohydride complex equivalent to **1**, $Mn(CO)_4(\eta^2\text{-}BH_4)$, has not been reported apart from a calculated structure.[29] Related complexes with monodentate phosphanes such as $[Mn(CO)_4(PMe_2Ph)(\eta^1\text{-}H_3B{\cdot}PMe_3)][BAr^F{}_4]$[19] and $MnCp^*(CO)_2(\eta^2\text{-}H_3B{\cdot}PMe_3)$[20] are also unstable in solution. The stability of **2** is doubtlessly associated with the chelate ring, as we have commented on previously.[16]

Conclusions

As with our earlier studies,[16,18] the results we report here show that the chelating phosphane–borane ligand $H_3B{\cdot}$dppm can open from η^2 to η^1 on addition of Lewis bases. For $[Mn(CO)_3(\eta^1\text{-}H_3B{\cdot}dppm)][BAr^F{}_4]$ this opening is reversible, and this observation of hemilabile behaviour suggests that, with suitable systems and substrates, they have the potential for application in catalysis.

Experimental Section

General: All manipulations were carried out under argon, using standard Schlenk-line and glove-box techniques, unless otherwise stated. Glassware was pre-dried in an oven at 130 °C and flamed with a blowtorch under vacuum prior to use. Solvents were dried with activated alumina, copper or molecular sieves columns by using an MBraun solvent purification system and stored under slight vacuum in ampoules equipped with Young's taps. CD_2Cl_2 was distilled under vacuum from CaH_2. $Mn(CO)_5Br$,[30] $Na[BAr^F{}_4]$[31] and $H_3B{\cdot}$dppm[26] were prepared according to published routes. All other chemicals were used as received from Aldrich and Strem. Microanalyses were performed by Elemental Microanalysis Ltd, Devon, UK.

NMR Spectroscopy: ^1H, $^1H\{^{11}B\}$, $^{11}B\{^1H\}$, ^{11}B and $^{31}P\{^1H\}$ NMR spectra were recorded with Bruker Avance 300 MHz or 400 MHz spectrometers. Resonances were referenced to residual hydrogen from the solvent for ^1H and $^1H\{^{11}B\}$ NMR spectra (CD_2Cl_2: δ = 5.30 ppm). ^{11}B, $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ spectra were referenced against $BF_3{\cdot}OEt_2$ (external) and 85%% H_3PO_4 (external), respectively. Values are quoted in ppm. Coupling constants are quoted in Hz.

X-ray Crystallography: The crystal structure data for compounds **1** and **2** were collected with a Nonius KappaCCD diffractometer (Tables 1 and 2). Structure solution, followed by full-matrix least-squares refinement was performed using the SHELX suite of programs throughout.[32] Hydrogen atoms were included at calculated

Table 1. Details of crystallographic data collection and refinement for complexes **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{60}H_{37}B_2F_{24}MnO_3P_2$	$C_{61}H_{37}B_2F_{24}MnO_4P_2 \cdot 0.35CH_2Cl_2 \cdot 0.65\ C_5H_{12}$
M_r [g mol^{1}]	1400.40	1505.02
Crystal size [mm]	0.70 × 0.40 × 0.30	0.35 × 0.28 × 0.23
Crystal colour	orange	yellow
Crystal system	monoclinic	orthorhombic
Space group	*C*2/*c*	*Pbca*
a [Å]	25.4630(3)	13.3490(2)
b [Å]	12.37800(10)	26.4730(5)
c [Å]	38.1190(4)	38.1720(7)
β [°]	91.98	90
V [Å^3]	12007.2(2)	13489.5(4)
Z	8	8
$D_{calcd.}$ [g cm^{-3}]	1.549	1.482
μ [mm^{-1}]	0.393	0.383
F(000)	5616	6064
T [K]	150(2)	150(2)
λ [Å]	0.71073	0.71073
Θ range [°]	3.22 to 28.68	3.53 to 28.26
Reflections collected	34057	52244
Data/parameters	10178/913	14338/936
Goodness-of-fit on F^2	1.078	1.020
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0602, wR_2 = 0.1308	R_1 = 0.0515, wR_2 = 0.1154
Largest diff. peak/hole [e·Å^{-3}]	0.588/–0.670	0.532/–0.416

Table 2. Selected bond lengths [Å] and angles [°] for complexes **1** and **2**.

Compound **1**					
Mn–C(1)	1.849(4)	Mn–C(2)	1.803(4)	Mn–C(3)	1.817(4)
Mn–B(1)	2.146(4)	Mn–P(2)	2.3428(9)	B(1)–P(1)	1.944(4)
Mn–H(1B)	1.68(4)	Mn–H(1C)	1.69(3)	B(1)–H(1A)	1.07(3)
B(1)–H(1B)	1.30(4)	B(1)–H(1C)	1.24(3)		
C(2)–Mn–B(1)	129.67(15)	C(3)–Mn–B(1)	139.74(16)	C(1)–Mn–B(1)	87.24(15)
B(1)–Mn–H(1C)	35(1)	B(1)–Mn–H(1B)	37(1)	H(1B)–Mn–H(1C)	72(2)
Compound **2**					
Mn–C(26)	1.883(3)	Mn–C(27)	1.868(3)	Mn–C(28)	1.816(3)
Mn–C(29)	1.871(3)	Mn–P(1)	2.3321(8)	B(1)–P(2)	1.929(3)
Mn–H(1)	1.71(3)	B–H(1)	1.08(3)	B–H(2)	1.05(3)
B–H(3)	1.26(3)	Mn–B(1)	2.748(3)	B–H(3)–Mn	134(2)

positions throughout apart from those associated with the borane which were located in the final Fourier difference map and refined without constraints. For complex **2** two, partial occupancy, solvent molecules (CH_2Cl_2 and pentane) were included in the refinement. CCDC-284481 (**1**) and -284482 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[(CO)$_3$Mn(η^2-BH$_3$·dppm)][BAr$^F_4$] (1): $NaBAr^F_4$ (0.267 g, 0.301 mmol) was dissolved in 10 mL of diethyl ether and added to a mixture of $(CO)_5MnBr$ (0.083 g, 0.301 mmol) and dppm·BH_3 (0.120 g, 0.301 mmol) in 20 mL of CH_2Cl_2. The solution was stirred for 2 d with regular degassing of the solution to remove the released CO. The reaction mixture was filtered to remove the insoluble NaBr to give an orange solution. Solvent was removed in vacuo to leave an orange solid. Crystals suitable for an X-ray diffraction study were grown by dissolving the solid in a minimum of CH_2Cl_2 and layering with pentane to yield orange crystals (0.183 g, 46% yield). $^1H\{^{11}B\}$ NMR (CD_2Cl_2): *δ* = 7.79–7.24 (m, 32 H, Ph, BAr_4^F), 4.99 (s, 1 H, B*H*), 2.90 [dd, *J*(PH) = 10.5 Hz, *J*($P_{(BH3)}$H) = 12.5 Hz, 2 H, C*H*$_2$], –9.08 [br. d, *J*(PH) = 6 Hz, 2 H, B*H*$_2$] ppm. $^{31}P\{^1H\}$ (CD_2Cl_2): *δ* = 73.7 [d, *J*(PP) = 102.1 Hz, 1 P, *P*Ph$_2$], 15.6 (br., 1 P, *P*BH$_3$) ppm. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): *δ* = 16.7 (br. s, 1 B, *B*H$_3$), –5.9 (s, 1 B, BAr^F_4). $C_{60}H_{37}B_2F_{24}MnP_2$ (1400): calcd. C 51.46, H 2.66; found C 51.60, H 2.74. IR (KBr): $\tilde{\nu}_{max}$ = 2519 (m, BH), 2070 (s, CO), 2010 (s, CO), 1975 (s, CO) cm^{-1}.

[(CO)$_4$Mn(η^1-BH$_3$·dppm)][BAr$^F_4$] (2): A CH_2Cl_2 solution of [(CO)$_3$Mn(η^2-BH$_3$·dppm)][BAr^F_4] (0.100 g, 0.074 mmol) was stirred under CO for 15 min to give a yellow solution. The compound loses a carbonyl group in vacuo to give **2**. Crystals suitable for an X-ray diffraction study were grown by layering the CO-saturated CH_2Cl_2 solution with CO-saturated pentane to yield yellow crystals. ^1H NMR (CD_2Cl_2): *δ* = 7.78–7.30 (m, 32 H, Ph, BAr_4^F), 3.54 [dd, *J*(PH) = 11.5 Hz, *J*($P_{(BH3)}$H) = 11.9 Hz, 2 H, C*H*$_2$], –3.74 [br., *J*(BH) 61.4 Hz, 3 H, B*H*$_3$]. Selected $^1H\{^{11}B\}$ NMR (CD_2Cl_2) data: *δ* = –3.74 [br. d, *J*(PH) = 8 Hz, 3 H, B*H*$_3$] ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* = 55.2 [d, 1 P, *J*(PP) = 54.7 Hz, *P*Ph$_2$], 16.0 (br., 1 P, *P*BH$_3$) ppm. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): *δ* = –5.9 (s, 1 B, BAr_4^F), –37.5 (br. s, 1 B, *B*H$_3$) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2498 (m, BH), 2440 (m, BH) 2112 (s, CO), 2053 (s, CO), 2028 (s, CO), 2000 (s, CO) cm^{-1}. Selected low-temperature NMR spectroscopic data (190 K): $^1H\{^{11}B\}$ NMR (CD_2Cl_2): *δ* = 3.50 (br., 2 H, CH_2), 1.99 (v br., 2 H, B*H*), –15.52 (br., 1 H, B*H*) ppm.

Acknowledgments

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