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Formation of ferraboranes from pentaborane(9) or $BH_3 \cdot$ thf and an electron-rich cyclopentadienyl iron phosphine hydride

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Abstract

$[(\eta^5\text{-}C_5R_5)Fe(PMe_3)_2H]$ (R = H, Me) can be made in good yields in a simple one-pot reaction between $FeCl_2$, PMe_3, C_5R_5H (R = H, Me) and Na/Hg in thf. Reaction of $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2H]$ with pentaborane(9) gives the known metallaborane $[(\eta^5\text{-}C_5H_5)\text{-}\textit{nido}\text{-}2\text{-}FeB_5H_{10}]$ (**1**) in improved yield as well as the new metallaboranes $[(\eta\text{-}C_5H_5)\text{-}\textit{nido}\text{-}2\text{-}FeB_5H_8\{\mu\text{-}5,6\text{-}Fe(\eta^5\text{-}C_5H_5)(PMe_3)(\mu\text{-}6,7\text{-}\mathbf{H})\}]$ (**2**), $[(\eta\text{-}C_5H_5)(PMe_3)\text{-}\textit{arachno}\text{-}2\text{-}FeB_3H_8]$ (**3**), $[(\eta^5\text{-}C_5H_5)_2\text{-capped-}\textit{nido}\text{-}2,3\text{-}Fe_2B_4H_8]$ (**4**), $[(\eta^5\text{-}C_5H_5)\text{-}\textit{nido}\text{-}2\text{-}FeB_4H_7(PMe_3)]$ (**5**) and $[(\eta^5\text{-}C_5H_5)\text{-}\textit{nido}\text{-}2\text{-}FeB_5H_8(PMe_3)]$ (**6**). Reaction of $[(\eta^5\text{-}C_5Me_5)Fe(PMe_3)_2H]$ with pentaborane(9) gives predominantly $[(\eta^5\text{-}C_5Me_5)\text{-}\textit{nido}\text{-}2\text{-}FeB_5H_{10}]$ (**7**) and $[(\eta^5\text{-}C_5Me_5)(PMe_3)\text{-}\textit{arachno}\text{-}2\text{-}FeB_3H_8]$ (**8**). Reaction of $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2H]$ with 2 equiv. of $BH_3 \cdot$ thf gives low yields of ferrocene and compound **3**. Compound **7** thermally isomerises to the apical isomer $[(\eta^5\text{-}C_5H_5)\text{-}\textit{nido}\text{-}2\text{-}FeB_5H_{10}]$ (**9**) in low yield. Compounds **1** and **7** deprotonate cleanly in the presence of KH at the unique B–H–B bridge to give $[(\eta^5\text{-}C_5H_5)\text{-}\textit{nido}\text{-}2\text{-}FeB_5H_9{}^-][K^+]$ (**10**) and $[(\eta^5\text{-}C_5Me_5)\text{-}\textit{nido}\text{-}2\text{-}FeB_5H_9{}^-][K^+]$ (**11**) respectively, whilst **6** deprotonates more slowly at one of two equivalent B–H–B bridges to give the fluxional anion $[(\eta^5\text{-}C_5H_5)\text{-}\textit{nido}\text{-}2\text{-}FeB_5H_7(PMe_3)^-]$ (**12**).

Keywords: Boron hydrides; Metallaboranes; Borane clusters; Iron; Phosphine hydrides; NMR spectroscopy

1. Introduction

The reaction of pentaborane(9) with transition-metal compounds or the $[\textit{nido}\text{-}B_5H_8{}^-]$ anion with transition-metal halide complexes gives a wide variety of metallaborane structures [1–3]. We have been exploring the reaction of transition-metal compounds with small boron hydrides, in particular $BH_3 \cdot$ thf [4–6] and pentaborane(9) [7–11,51]. We have shown that the reaction of $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)H_3]$ with pentaborane(9) gives several metallaboranes with 3–5 boron atoms including $[(\eta^5\text{-}C_5Me_5)\text{-}\textit{nido}\text{-}2\text{-}RuB_5H_{10}]$, $[(\eta^5\text{-}C_5Me_5)\text{-}\textit{arachno}\text{-}2\text{-}Ru(PMe_3)B_3H_8]$, $[(\eta^5\text{-}C_5Me_5)\text{-}\textit{arachno}\text{-}3\text{-}Ru(PMe_3)B_4H_9]$ and $[(\eta^5\text{-}C_5Me_5)(PMe_3)\text{-}\textit{nido}\text{-}2\text{-}RuB_5H_8]$ [7]. We decided to extend the study to the related reaction of pentaborane(9) with an electron-rich cyclopentadienyl iron phosphine hydride.

2. Results and discussion

As $[(\eta^5\text{-}C_5R_5)Fe(PMe_3)H_3]$ compounds are not known we concentrated on the diphosphine monohydride $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2H]$. $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2H]$ is available from the reaction of $[(\eta^6\text{-}C_6H_6)Fe(PMe_3)_2]$ with cyclopentadiene and we used this route for early preparations of the compound [12]. $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2H]$ can also be made by the sodium mirror reduction of $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_3{}^+]PF_6{}^-$ [13]. We decided to attempt a simpler route to $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2H]$ in a one-pot synthesis. Treatment of a slurry of anhydrous $FeCl_2$ with PMe_3 in thf with cyclopentadiene and excess sodium amalgam gave a 60% yield of NMR spectroscopically pure $[(\eta^5\text{-}C_5H_5)$

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$Fe(PMe_3)_2H]$ after recrystallisation from pentane at −78 °C. Similarly $[(\eta^5\text{-}C_5Me_5)Fe(PMe_3)_2H]$ was formed in 49% yield using pentamethylcyclopentadiene. These reactions represent an easy route to electron-rich half-sandwich iron compounds.

Treatment of $[(\eta^5\text{-}C_5H_5)Fe(PMe_3)_2H]$ with pentaborane(9) in toluene over 12 h gave a dark reaction mixture which was chromatographed on silica gel. Five bands were initially observed and six different compounds ultimately isolated (Fig. 1). The first purple band was recrystallised from pentane to give purple $[(\eta^5\text{-}C_5H_5)\text{-}\mathit{nido}\text{-}2\text{-}FeB_5H_{10}]$ (**1**) in 15% yield as shown by ^1H and ^{11}B NMR spectroscopy. Compound **1** was previously prepared together with traces of other ferraboranes by the low temperature reaction of $FeCl_2$, NaC_5H_5 and pentaborane(9) [14,15]. The thermolysis of pentaborane(9) with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$

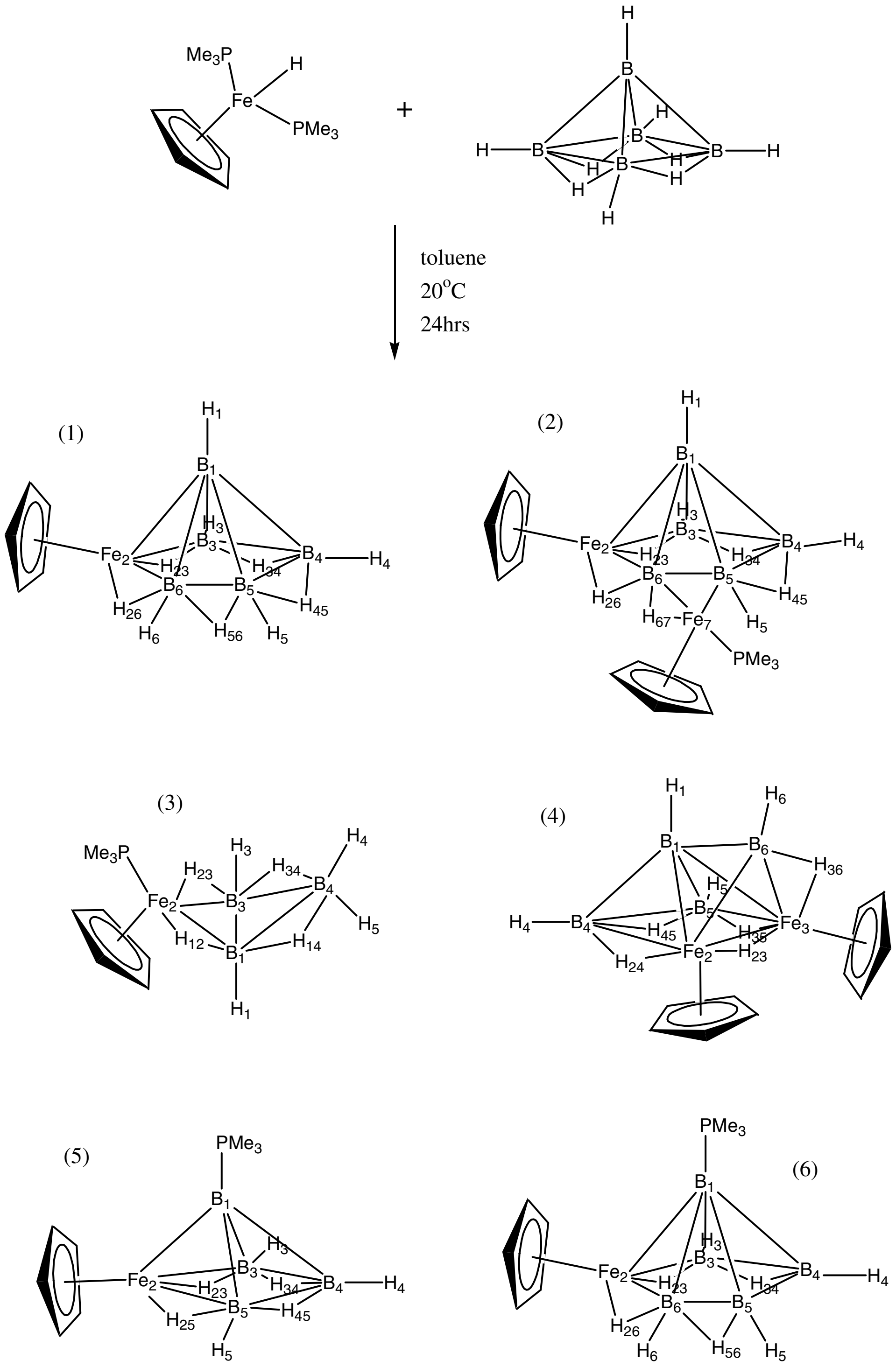

Fig. 1. Products formed from the reaction of $[(\eta\text{-}C_5H_5)Fe(PMe_3)_2H]$ with pentaborane(9).

is also reported to give a low yield of **1** [16]. The two-step synthesis of **1** from $FeCl_2$ in 15% is now possible on a large scale. This allows for a systematic study of its chemistry to be undertaken [17].

Further elution of the column gave a second brown band, which decomposed slowly on the column forming **1** and an immovable yellow band. However, rapid elution allowed the removal of this brown band which gave after repeated recrystallisation from pentane a 4% yield of brown crystals of the new metallaborane [(η-C_5H_5)-*nido*-2-FeB_5H_8{μ-5,6-Fe(η^5-C_5H_5)(PMe_3)(μ-6,7-H)}] (**2**). Up to 8% yields of **2** could be obtained from a reaction mixture containing ca. 2 equiv. of [(η^5-C_5H_5)Fe(PMe_3)$_2$H] and 1 equiv. of pentaborane(9).

Compound **2** has been characterised by ^1H, ^{11}B and ^{31}P NMR spectroscopy and elemental analysis. Elemental analysis was a little high for carbon (1.2%), which may be due to residual solvent. Several recrystallisations were necessary to obtain a solid product which was not suitable for X-ray diffraction. NMR spectroscopy was used to assign **2** as a *nido*-metallahexaborane with a base-substituted {Fe(η^5-C_5H_5)} fragment and a {Fe(η^5-C_5H_5)(PMe_3)(μ-5,6-H)} fragment bridging between the B(5)–B(6) edge (Fig. 1). The ^{11}B NMR spectrum shows 5 resonances in a 1:1:1:1:1 ratio, four of them doublets and one singlet, all the doublets collapsing to singlets with broad band ^1H decoupling. The $^1H\{^{11}B\}$ NMR spectrum of **2** shows two C_5H_5 resonances, a single PMe_3 resonance and nine resonances attributable to nine protons on the borane fragment. These nine resonances are assigned to four B–H terminal, two B–H–B bridging and three Fe–H–B bridging protons.

Selective $^1H\{^{11}B\}$ NMR decoupling experiments and a ^{11}B–^{11}B COSY study assisted in the assignment of the NMR spectra. Thus, in the ^1H spectrum, selective decoupling of B(6) caused the broad signal assigned to H(26) to sharpen to a singlet, whilst H(67) became a doublet due to ^{31}P coupling to the PMe_3 ligand. No protons in the ^1H NMR spectral region associated with terminal B–H protons were observed to sharpen. This suggests that the {Fe(η^5-C_5H_5)(PMe_3)(μ-5,6-H)} fragment is coordinated to B(6) via the bridging (B67) proton. Decoupling the apical boron atom B(1) sharpened H(1). Decoupling B(3) sharpened the terminal H(3) resonance and the bridging H(23) proton. Irradiation of B(4) caused H(3), H(34) and to lesser extent H(45) to sharpen. More importantly, decoupling of B(5) sharpens H(45), and H(5) the latter being a doublet due to ^{31}P coupling to the PMe_3 ligand. This strongly suggests that the basally-bridged {Fe(η^5-C_5H_5)(PMe_3)(μ-5,6-H)} fragment is bonded to B(5).

The proposed structure for **2** is unusual in that a metal fragment bridges two basal boron atoms. Basally bridging metal atoms in bimetallaboranes are rare. For example, the crystal structure of $Fe(CO)_3B_5H_8[Cu(PPh_3)_2]$ has shown the copper atom bridges the two basal boron atoms furthest from the iron atom [18]. Further, a metal is also known to bridge two basal boron atoms in small metallaboranes such as [$Fe(CO)_4B_6H_{10}$] [19], [$Fe(CO)_3B_7H_{12}$] [20], [$\{Cu(PPh_3)_3\}_2B_6H_9Fe(CO)_4$] [21] and [$W(PMe_3)_3$-$HB_5H_{10}$] [22].

The red-brown third band was rechromatographed eluting with light petroleum:diethyl ether 9:1 to give two bands, a red-brown band and a small green band. The red-brown band was recrystallised from pentane at −78 °C to give dark brown compound **3**. Compound **3** has been characterised by ^1H, ^{11}B and ^{31}P NMR spectroscopy, IR spectrometry and EI mass spectrometry as [(η^5-C_5H_5)(PMe_3)-*arachno*-2-FeB_3H_8]. We did not obtain suitable crystals for an X-ray diffraction study. The ^{11}B NMR spectrum is typical of a wing-substituted *arachno*-metallatetraborane giving a triplet of intensity 2 ($\delta = -39.38$ ppm) and a singlet of intensity 1 ($\delta = 5.62$ ppm). The proposed structure also agrees with the $^1H\{^{11}B\}$ NMR spectrum although the evidence cannot distinguish between the *endo* and *exo* cyclopentadienyl forms. The molecule [(η^5-C_5Me_5)-*arachno*-2-$ReH_3B_3H_8$] [23] has been crystallographically characterised and the pentamethylcyclopentadienyl ligand shown to be in the *exo* position. In addition, the crystal structure of [(η^5-C_5Me_5)-*arachno*-2-Ru(PMe_3)B_3H_8] shows the pentamethylcyclopentadienyl ligand in the *exo* position. Based on this information the structure for **3** shown in Fig. 1 shows the cyclopentadienyl ligand in the *exo* form for compound **3**. The terminal B–H protons were assigned by selectively decoupling the boron atoms. It was found that either the *exo* or *endo* proton resonance (it is impossible to tell which from the NMR data) of the terminal BH_2 unit coincided with the resonance of the two equivalent B–H terminal units. The difference in chemical shifts of the *exo* and *endo* terminal protons of the BH_2 unit was found to be 2.35 ppm (benzene-d_6). We note that most previously reported *arachno* 4-vertex metallaboranes give this difference as approximately 0.5 ppm [2,6,24–26].

To prove that the assignment was correct the two resonances assigned to the *exo* and *endo* hydrogens were selectively decoupled while observing the ^{11}B NMR. Decoupling the proton at $\delta = 4.40$ ppm collapsed the triplet to a doublet leaving the other doublet unaffected. Decoupling at $\delta = 2.05$ ppm collapsed the triplet to a doublet and the doublet to a singlet. This is consistent with the original assignment. A large shielding difference between the *exo* and *endo* hydrogens is rare but has been observed in *arachno*-2-[W(PMe_3)$H_3B_3H_8$], another metallaborane with the PMe_3 phosphine ligand attached to the metal centre [6]. In addition, [(η^5-C_5Me_5)-*arachno*-2-$ReH_3B_3H_8$] has *endo* and *exo* proton chemical shifts at $\delta = 6.35$ and 3.45 ppm [23].

The small green band was recrystallised from pentane to give green compound **4**. It was formed in very low yield and has only been characterised by ^1H and ^{11}B NMR spectroscopy. No signal was seen in the ^{31}P NMR spectrum. The ^1H NMR spectrum shows two resonances of equal intensity at $\delta = 4.33$ and 4.47 ppm assigned to η-C_5H_5 ligands and ^1H {^{11}B broad band} indicated eight inequivalent protons associated with the borane fragment. Four of the eight resonances can be assigned terminal B–H protons ($\delta = 13.05$, 8.05, 6.08 and 2.10 ppm), one as a B–H–B bridging proton ($\delta = -1.66$ ppm) and the remaining three resonances as Fe–H–B bridging protons ($\delta = -14.67$, -17.92 and -22.20 ppm). No Fe–H–Fe bridging protons were observed. If compound **4** is assumed to obey the electron-counting rules for clusters [27–30], then the above NMR data are consistent with a structure being either *pileo* (capped square pyramid) or *closo*. Three possible structures can be drawn, one with a *closo* structure and two with a *pileo* structure. For each structure there are four bridging hydrogen atoms.

The ^{11}B NMR resonance at $\delta = 109.0$ ppm in compound **4** is typical of small cage boron atoms adjacent to two metal centres [31,32]. For example, one of the boron atoms in $[(\eta^5\text{-}C_5Me_5)_2$-*pileo*-$2,3\text{-}Ru_2(\mu\text{-}H)B_4H_7]$ resonates at $\delta = 122.5$ ppm, the next highest resonance being at $\delta = 21.3$ ppm. The next lowest resonance in **4** is at a much higher chemical shift ($\delta = 49.3$ ppm). Therefore it is unlikely that **4** will be *closo* as this structure contains two boron atoms adjacent to two iron atoms and both these boron atoms would be expected to have somewhat similar chemical shifts. Another factor to support this hypothesis comes from experimental and theoretical studies on the protonation of some 6-vertex clusters. In particular Wade and Fehlner demonstrated that for the anion *closo*-$B_6H_6^{2-}$ the face capped square pyramidal structure becomes favoured relative to the octahedron on protonation, although the total number of skeletal electrons remains the same [33]. The importance of protonation has also been shown by the observation that $[Os_6(CO)_{18}]^{2-}$ adopts a *closo* structure whereas the neutral deprotonated compound $[Os_6H_2(CO)_{18}]$ is a capped square pyramid [34]. As compound **4** has four bridging hydrogen atoms, it seems unlikely that a *closo* cluster is the more stable structure. We note that the molecule $[Co_2(\eta^5\text{-}C_5H_5)_2\text{-}B_4H_6]$ has the same skeletal electron count as compound **4** and contains only two bridging hydrogen atoms. The crystal structure shows that it adopts a *closo* octahedral structure in agreement with solution NMR data [48]. A *closo* structure has been proposed for the biferrapentaborane cluster $[Fe(CO)_3B_5H_3(CO)_2]$ which has no bridging hydrogen atoms and two carbonyl groups bonded to cage boron atoms [35].

The two possible *pileo* structures for compound **4** differ essentially in the positions of the bridging hydrogen atoms. One possible *pileo* structure for **4** has a capping $\{BH_3\}$ group with two hydrogen atoms bridging the square Fe_2B_2 base. Two examples of a capped dimetallapentaborane are known, $[(\eta^5\text{-}C_5Me_5)_2$-*pileo*-$2,3\text{-}Ru_2(\mu\text{-}H)B_4H_7]$ [32] and $[(PMe_3)_2$-*pileo*-$2,3\text{-}Fe_2(H)B_4H_8]$ [8]. The former molecule has a capping {BH} group, as is also found in the capped-*closo* structures $[\{Co(\eta^5\text{-}C_5R_5)\}_3B_4H_4]$ (R = H, Me) [36]. The second molecule $[(PMe_3)_2$-*pileo*-$2,3\text{-}Fe_2(H)B_4H_8]$ has a capping $\{BH_3\}$ group. Although a $\{BH_3\}$-capped square pyramidal structure for compound **4** as in $[(PMe_3)_2$-*pileo*-$2,3\text{-}Fe_2(H)B_4H_8]$ seems plausible, it is inconsistent with the selective $^1H\{^{11}B\}$ NMR data. Decoupling any of the boron atoms does not sharpen more than one Fe–H–B bridging proton. Two such protons would be expected to sharpen if there was a capping $\{BH_3\}$ group. Thus, on the basis of the above discussion it is concluded that the most likely structure for **4**, although only characterised by but consistent with the NMR data, is the capped square pyramid structure $[(\eta^5\text{-}C_5H_5)_2$-*pileo*-$2,3\text{-}Fe_2B_4H_8]$ shown in Fig. 1. Interestingly, in the ^{11}B NMR the chemical shifts assigned for the capping boron atom in the B–H capped *closo* molecules $[(\eta^5\text{-}C_5Me_5)_2Ir_2B_5H_5]$ and $[(\eta^5\text{-}C_5Me_5)_2Co_2B_5H_5]$ are $\delta = 103.0$ ppm and 135.6 ppm, respectively [37,38]. This compares with the lowest field resonance at $\delta = 109.0$ ppm in compound **4** which is tentatively assigned a B–H capping boron atom.

The fourth pink-red band from the chromatography column was recrystallised from pentane to give an approximately 3% yield of pink-red $[(\eta^5\text{-}C_5H_5)Fe$-*nido*-$2\text{-}B_4H_7(PMe_3)]$ (**5**). Compound **5** has been characterised by ^1H, ^{11}B and ^{31}P NMR spectroscopy, IR spectrometry and EI mass spectrometry. We did not obtain suitable crystals for an X-ray diffraction study. The mass spectrum gave a parent envelope consistent with the given formula. The $^{31}P\{^1H\}$ NMR spectrum shows an equal intensity quartet and is assigned to a PMe_3 group coupled to a boron nucleus ($I = 3/2$). The ^{11}B NMR gave overlapping multiplets that collapsed and sharpened by broad band ^1H decoupling and could then be integrated. The peak at $\delta = -42.18$ ppm is a doublet in the $^{11}B\{^1H\}$ NMR spectrum and is assigned to an apical boron atom bonded to a PMe_3 group. The other two resonances are assigned to three basal B–H terminal units, two of which are magnetically equivalent. The ^1H NMR spectrum shows a broad resonance at $\delta = -15.16$ ppm (relative intensity 2) assigned to two Fe–H–B bridging protons, a broad resonance at $\delta = -4.48$ ppm (relative intensity 2) assigned to two B–H–B bridging protons, a sharp singlet at $\delta = 4.12$ ppm (relative intensity 5) assigned to a $(\eta\text{-}C_5H_5)$ group and a doublet at $\delta = 0.85$ ppm (relative intensity 9) assigned to a PMe_3 group. Broad band ^{11}B decoupling of the ^1H NMR spectrum gave resonances consistent with there being three B–H terminal protons at $\delta = 2.52$ ppm (relative intensity 2) and $\delta = 2.79$ ppm (relative intensity 1). No resonances were observed in the typical region for apical B–H protons ($\delta = -1$ to $+1$ ppm) consistent with there being a PMe_3 group attached to the apical boron atom. ^{11}B selective decoupling gave complete assignment of compound **5**, the experiments and electron-counting rules being consistent with a *nido*-metallapentaborane with an apical PMe_3 group (Fig. 1). Substitutions of phosphine ligands from the metal onto the borane cage are rare in metallaborane chemistry. For example, the reaction of $Fe_2(CO)_9$ with $(PPh_3)_2(CO)IrB_5H_8$ in C_6H_6 solution affords $[1,1,1\text{-}(CO)_3\text{-}2,2\text{-}(CO)_2\text{-}2,4\text{-}(PPh_3)_2$-*closo*-$1,2\text{-}FeIrB_5H_4]$ (**1**) in which one PPh_3 ligand, originally bonded to the iridium atom, is now terminally bonded to a boron atom in the metallaborane cage [39]. Other examples, in larger clusters, where a metal-bound phosphine ligand becomes attached to a boron atom in a metallaborane cage include [7-(PMe_2Ph)-7-$PtB_{16}H_{18}$-9′-(PMe_2Ph)] and [5-(η^5-C_5Me_5)-7-(PMe_2Ph)-*nido*-5-RhB_9H_{11}] [49,50].

The last pink-red band to be eluted from the chromatography column was recrystallised from toluene to give a ca. 4% yield of pink-red [(η^5-C_5H_5)-*nido*-2-$FeB_5H_8(PMe_3)$] (**6**). Compound **6** has been characterised by ^1H, ^{11}B and ^{31}P NMR spectroscopy, IR spectrometry and FAB mass spectrometry. We did not obtain suitable crystals for an X-ray diffraction study. The FAB mass spectrum gave a large parent envelope consistent with the given formula. The $^{31}P\{^1H\}$ NMR spectrum shows an equal intensity quartet and is assigned to a PMe_3 group coupled to a boron nucleus. The three ^{11}B NMR resonances are assigned to two sets of equivalent basal B–H units and an apical B–PMe_3 unit as proton decoupling did not collapse the doublet to a singlet. We note that the B–H terminal coupling is not resolved in the ^{11}B NMR spectrum. This coupling is however seen in [(η^5-C_5H_5)-*nido*-2-FeB_5H_{10}] (**1**), the apical H-substituted analogue of **6**. Further indication that the apical boron atom is bonded to a PMe_3 group was provided by ^{11}B decoupled ^1H NMR experiments. No resonances sharpened in the ^1H NMR spectrum in the typical region for apical B–H protons when broad band ^{11}B decoupled or when the apical boron was selectively decoupled. The assignments from the NMR data and the electron-counting rules are consistent with **6** being a *nido*-metallahexaborane with an apical PMe_3 group (Fig. 1).

The total yield of metallaborane products from the reaction of [(η^5-C_5H_5)$Fe(PMe_3)_2H$] with pentaborane(9) is about 40–42% after chromatography and recrystallisation. No other iron compounds including ferrocene were identified. In contrast, the reaction of [(η^5-C_5Me_5)$Ru(PMe_3)H_3$] with pentaborane(9) gave a 67% yield of four different metallaborane products, none of which has a phosphine group attached to the borane fragment [7]. This suggests that the phosphine-capped products **5** and **6** may be formed from a 16 electron {(η^5-C_5H_5)$Fe(PMe_3)H$} intermediate and pentaborane-PMe_3 or tetraborane-PMe_3 species formed from attack of the leaving phosphine PMe_3 ligand on pentaborane(9).

We also investigated the analogous reaction of [(η^5-C_5Me_5)$Fe(PMe_3)_2H$] with pentaborane(9). Several coloured products were observed by column chromatography, only two of which were isolated. These were [(η^5-C_5Me_5)-*nido*-2-FeB_5H_{10}] (**7**) and [(η^5-C_5Me_5)(PMe_3)-*arachno*-2-FeB_3H_8] (**8**). Both were characterised by comparison of their NMR data with the cyclopentadienyl iron compounds.

Grimes has shown that **1** readily isomerises on heating to give the apically subrogated metallaborane [(η^5-C_5H_5)-*nido*-1-FeB_5H_{10}] in low yield [14,15]. We carried out a similar experiment with the pentamethylcyclopentadienyl derivative **7**. Heating samples of **7** in sealed tubes at 180 °C gave 10–20% yields of a purple solid after recrystallisation from pentane. The product **9** gave very similar ^{11}B and ^1H NMR spectra to [(η^5-C_5H_5)-*nido*-1-FeB_5H_{10}]. No peaks due to the basal isomer were present in the spectra. Thus, in direct analogy to Grimes' results, product **9** is assigned as the apical isomer [(η^5-C_5Me_5)-*nido*-1-FeB_5H_{10}] (Fig. 2). This base-to-apex isomerisation is also known for *nido*-metallapentaboranes such as the conversion of [(η^5-C_5R_5)-*nido*-2-CoB_4H_8] to [(η^5-C_5R_5)-*nido*-1-CoB_4H_8] (R = H, Me) [40].

Compound **6** is structurally very similar to **1**, differing only in the number of bridging hydrogen atoms and an apically coordinated PMe_3 group. However, thermolysis of **6** in toluene or solid state pyrolysis at 200 °C did not show any products characteristic of an apically-substituted iron fragment. Only decomposition to $BH_3 \cdot PMe_3$ and iron metal was observed. The reason for this may be due to the stabilisation of the basal isomer by the apical PMe_3 group.

A red-purple solution of compound **1** deprotonated readily at 20 °C using KH either in benzene-d_6 (with added 18-crown-6) or in thf-d_8. Loss of the unique B–H–B bridging proton occurs to give pink-red [(η^5-C_5H_5)-*nido*-2-$FeB_5H_9^-$][K^+] (**10**) (Fig. 3). The anion in **10** has been reported previously in the compound [$Re(PMe_3)_5H_2$]$^+$[(η^5-C_5H_5)-*nido*-2-FeB_5H_9]$^-$ [17]. Likewise **7** deprotonates to give pink-red [(η^5-C_5Me_5)-*nido*-2-$FeB_5H_9^-$][K^+]

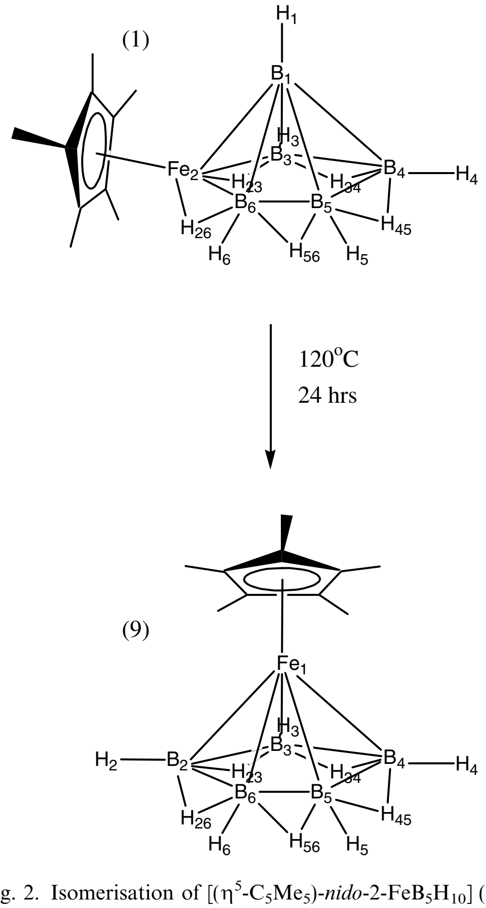

Fig. 2. Isomerisation of [(η^5-C_5Me_5)-*nido*-2-FeB_5H_{10}] (**7**).

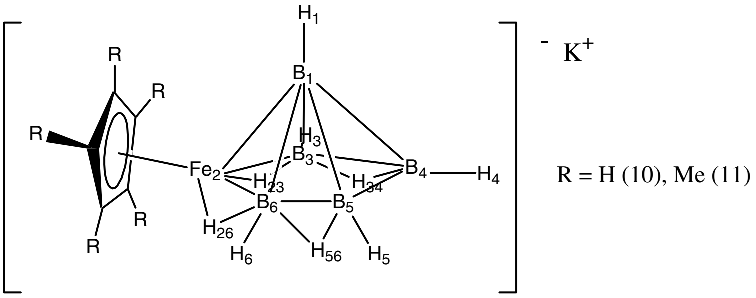

Fig. 3. Proposed structures for (**10**) and (**11**).

(**11**). A similar deprotonation of the unique B–H–B bridging proton has been shown to occur for the isostructural cluster [(CO)$_3$-*nido*-2-MnB$_5$H$_{10}$] giving the anion [(CO)$_3$-*nido*-2-MnB$_5$H$_9$$^-$] [39].

It was interesting to compare the deprotonation of compound **1** with compound **6** as the latter only has two equivalent B–H–B bridging hydrogen atoms. A red-brown solution of compound **6** deprotonated slowly over 48 h to give a deep green solution of compound **12** using KH and either benzene-d_6 (with added 18-crown-6) or thf-d_8. The ^{11}B, ^{31}P and ^{1}H[{^{11}B} NMR spectra are consistent with the formation of [(η^5-C$_5$H$_5$)-*nido*-2-FeB$_5$H$_7$-(PMe$_3$)$^-$][K$^+$] (**12**). The ^{11}B{^{1}H} NMR spectrum now showed three resonances with integral ratio 2:2:1. Cooling of a toluene-d_8 solution of **12** to −80 °C gave the same peaks and integral ratio. Further, in the ^{1}H NMR spectrum the Fe–H–B bridging hydrogen atoms are still observed to be equivalent although at a different chemical shift. This indicates that either the one remaining B–H–B bridging hydrogen atom has moved to the symmetrical bridging position or that there is rapid exchange of this hydrogen atom between the two equivalent B–H–B positions even at −80 °C on the NMR time scale.

Selective ^{1}H{^{11}B} NMR was used to distinguish between these two possibilities. If the proton is sitting in the B(4)–H–B(5) bridging position, decoupling of B(4,5) would be expected to considerably sharpen this proton resonance in the ^{1}H NMR, and for decoupling of B(3,6) to have little effect. Decoupling B(4,5) whilst observing ^{1}H did not show any appreciable sharpening of the B–H–B resonance at 20 °C while decoupling at B(3,6) only sharpened the broad resonance a small amount. It is assumed from these observations that the B–H–B proton in the anion **12** is not sitting in the unique B(4)–H–B(5) position but is exchanging rapidly between the two equivalent positions B(5)–H–B(6) and B(3)–H–B(4), possibly in a 1,3 shift (Fig. 4).

Compound **3** showed no sign of deprotonation using KH in either benzene-d_6 (with added 18-crown-6) or thf-d_8 at 20 °C. On warming a solution of **3** in thf-d_8 with added KH only degradation was observed. The ^{11}B NMR showed only starting material and a sharp nonet at $\delta = -34.3$ ppm characteristic of the [B$_3$H$_8$$^-$] ion. Compound **5** also showed no reaction with KH in thf-d_8.

Fehlner and co-workers have shown that the reaction of [(η^5-C$_5$H$_5$)Co(PMe$_3$)$_2$] (as well as other (η^5-C$_5$H$_5$)CoL$_2$ compounds) with BH$_3$ · thf gives, depending on the experimental conditions, a variety of unusual clusters, such as found in the metal-rich compound [{(η^5-C$_5$H$_5$)Co}$_4$B$_3$H$_2$] [41]. It seemed reasonable to compare the reactivity of [(η^5-C$_5$H$_5$)Fe(PMe$_3$)$_2$H] with BH$_3$ · thf also. Transition-metal hydrides have also been shown to react with BH$_3$ · thf. For example reaction of [W(PMe$_3$)$_3$H$_6$] with BH$_3$ · thf gives a 90% yield of [(PMe$_3$)$_3$-*arachno*-2-WH$_3$B$_3$H$_8$] [6]. Fehlner and co-workers have also reported the reaction of BH$_3$ · thf with transition-metal hydrides. [Fe(η^5-C$_5$Me$_5$)H$_2$]$_2$ gives the monometal cluster [(η^5-C$_5$Me$_5$)-*arachno*-1-FeB$_4$H$_{11}$] whilst [Ru(η^5-C$_5$Me$_5$)H$_2$]$_2$ gives the bimetallaborane cluster [Ru(η^5-C$_5$Me$_5$)$_2$-*nido*-1,2-Ru$_2$HB$_3$H$_7$] which reacts further with BH$_3$ · thf to give [(η^5-C$_5$Me$_5$)$_2$-*nido*-1,2-Ru$_2$(μ-H)B$_4$H$_9$] [42,43].

Reaction of [(η^5-C$_5$H$_5$)Fe(PMe$_3$)$_2$H] with 2 equiv. of BH$_3$ · thf at 0 °C over 3 h gives a dark red-brown solution from which two compounds were isolated in low yield by column chromatography. The first orange fraction was shown to be ferrocene by NMR whilst the second red-

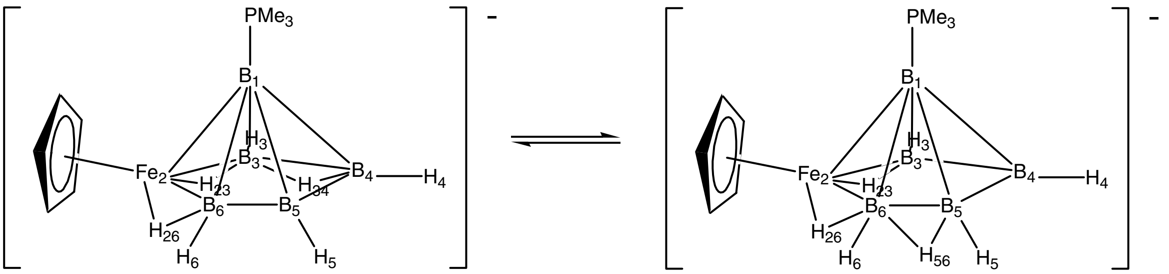

Fig. 4. Deprotonation of (**6**).

brown fraction was shown to be compound **3** [(η^5-C_5H_5)(PMe_3)-*arachno*-2-FeB_3H_8] by comparison of NMR data. The yield of the metallaborane is low (ca. 3%) making it a less favourable route than the reaction of [(η^5-C_5H_5)Fe(PMe_3)$_2$H] with pentaborane(9). The yield of **3** falls to zero if a large excess of $BH_3 \cdot$ thf is used.

The decomposition of monocyclopentadienyl iron compounds to the thermodynamically very stable ferrocene has been reported for the reaction of the anion [Fe(η^5-C_5H_5)(C_2H_4)$_2$$^-$] with trimethylphosphonium chloride [44]. This "thermodynamic sink" is not available in the reaction of monocyclopentadienyl cobalt compounds with $BH_3 \cdot$ thf since the formation of the 19-electron [Co(η-C_5H_5)$_2$] is far less favourable. Fehlner reports that reaction of monocyclopentadienyl metal chlorides with $BH_3 \cdot$ thf gives metallocene formation for manganese and iron and metal formation for nickel, whereas for cobalt and second or third row monocyclopentadienyl metal chlorides from Groups 5 to 9 a range of metallaboranes are formed [43,45–47]. They postulate that hydride formation occurs from loss of borane from a metal borohydride which can lead to metal reduction or metallocene formation. In the case of the reaction of [(η^5-C_5H_5)Fe(PMe_3)$_2$H] with $BH_3 \cdot$ thf {(η^5-C_5H_5)FeH} formation from loss of two PMe_3 ligands probably occurs leading to formation of metallic iron and ferrocene. This seems to be the dominant pathway competing with borane homologation and metallaborane formation.

3. Conclusion

The reaction of [(η^5-C_5R_5)Fe(PMe_3)$_2$H] (R = H, Me) with pentaborane(9) has led to the isolation of a number of new ferraborane clusters presumably via several competing pathways. In particular, compounds **5** and **6** are rare examples of apical terminal phosphine substituted metallaboranes. Homologation of $BH_3 \cdot$ thf takes place on reaction with [(η^5-C_5H_5)Fe(PMe_3)$_2$H] to give a low yield of the wing-tip butterfly metallatetraborane **3**.

4. Experimental

4.1. General methods and instrumentation

All preparations, manipulations and reactions were carried out under an inert atmosphere of dinitrogen using standard techniques for handling air-sensitive materials (Schlenk line and glove-box). Dinitrogen was purified by passage through a column containing basf catalyst and 4A molecular sieves. solvents were pre-dried over molecular sieves (4 or 5A), distilled from appropriate drying agents and stored under dinitrogen in Teflon valve ampoules. Deuterated solvents were stored over activated molecular sieves or sodium–potassium alloy. $BH_3 \cdot$ thf was used a 1 M solution in thf as supplied by Aldrich Chemical Co. Ltd. Chromatography was carried out on silica gel G (Fluka, type GF 254) under dinitrogen. Reaction mixtures were generally deposited as a "sand" on silica gel and admitted to the top of the column via a tipper tube under a gentle stream of dinitrogen. Solvents used fro chromatography (petroleum ether and diethyl ether) were not pre-dried but only flushed with dinitrogen before use. Pentaborane(9) was used from stock as a 0.25–0.4 M solution in toluene. [(η^5-C_5H_5)Fe(PMe_3)$_2$H] was prepared according to the literature method or as described below. The NMR spectra were obtained using Bruker AM-250 or AM-300 instruments. ^{1}H spectra were referenced internally with respect to the residual protiosolvent (C_6D_6, δ 7.10); ^{11}B and ^{31}P spectra were referenced internally relative to the deuterium lock signal using the SR command of standard Bruker software, with respect to the standards 85% H_3PO_4–D_2O (^{31}P) and BF_3–Et_2O (^{11}B). All chemical shifts are quoted in δ (ppm) and coupling constants in Hertz (HZ). Mass Spectra were obtained on an AEI MS 302 mass spectrometer, "updated" by a data handling system supplied by Mass Spectrometry Services Ltd., (EI OR FAB) by the SERC Mass Spectrometry Centre at the University College of Swansea. Elemental analysis was carried out by the analysis department of the Inorganic Chemistry Laboratory, Oxford University.

4.2. Preparation of [(η^5-C_5H_5)Fe(PMe_3)$_2$H]

PMe_3 (7.2 g, 94.7 mmol) was added to a stirred slurry of anhydrous $FeCl_2$ (4 g, 31.5 mmol) in thf (50 ml) at 20 °C. Sodium amalgam (2.5 g as a 1% solution) was added and as soon as the solution began to darken freshly cracked cyclopentadiene (2.5 ml, 37.8 mmol) was added. After 16 hours stirring volatiles were removed *in vacuo* and the residue extracted with pentane (3 × 40 ml) and filtered. The dark orange-brown solution was reduced in volume to 20 ml and left for 3 days at −78 °C. The brown solid was filtered off from the dark solution, washed quickly with cold pentane and pumped dry to leave an orange-brown semi-solid. The ^{1}H and ^{31}P NMR spectra showed the product to be pure [(η^5-C_5H_5)Fe(PMe_3)$_2$H]. Yield 5.2 g, 60%. Further recrystallisations from pentane at −78 °C gave a more solid product, although the semi-solid was considered pure enough for reaction with boranes.

4.3. Preparation of [(η^5-C_5Me_5)Fe(PMe_3)$_2$H]

A procedure identical to that in 4.2 was followed using pentamethylcyclopentadiene (5.1 g, 37.8 mmol). Crystallisation from pentane (20 ml) at −78 °C gave spectroscopically pure brown [(η^5-C_5Me_5)Fe(PMe_3)$_2$H]. Yield 5.3 g, 49%.

4.4. Reaction of [(η^5-C_5H_5)Fe(PMe_3)$_2$H] with pentaborane(9)

[(η^5-C_5H_5)Fe(PMe_3)$_2$H] (4.0 g, 14.6 mmol) was treated with a solution of pentaborane(9) in toluene (64 ml, 0.25 M) and stirred at 20 °C for 12 h. Silica gel was added and volatiles removed *in vacuo*. The resulting sand was transferred to the top of a chromatography column and eluted with light petroleum:diethyl ether 20:1 giving four bands, red purple **1**, brown **2**, red-brown **3**, pink **5**. Further elution with light petroleum:diethyl ether 1:1 gave a fifth pink-red band **6**, which was collected. The red-brown third band was rechromatographed eluting with light petroleum:diethyl ether 9:1 to give two bands, a red-brown band **3** and a small green band **4**. Solvent was removed *in vacuo* from all the bands collected. All bands were recrystallised from pentane at −78 °C except the last pink-red band **6**, which was recrystallised from toluene. Band **2** was recrystallised three times from pentane to get a crystalline solid. The six bands gave dark purple, brown, red-brown, green, pink-red and pink-red crystals of compounds [(η^5-C_5H_5)-*nido*-2-FeB_5H_{10}] (**1**), [(η^5-C_5H_5)-*nido*-2-FeB_5H_8{Fe(η^5- C_5H_5)(PMe_3)(μ-H)}] (**2**), [(η^5-C_5H_5)(PMe_3)-*arachno*-2-FeB_3H_8] (**3**), [(η^5-C_5H_5)$_2$-capped-*nido*-2,3-$Fe_2B_4H_8$] (**4**), [(η^5-C_5H_5)-*nido*-2-FeB_4H_7-(PMe_3)] (**5**) and [(η^5-C_5H_5)-*nido*-2-FeB_5H_8(PMe_3)] (**6**). Yields **1** 400 mg, 15%; **2** 260 mg, 8%; **3** 410 mg, 12%; **4** 2 mg, 0.05%; **5** 75 mg, 3%; **6** 130 mg, 4%.

NMR data: Compounds **2**–**6**, solvent benzene-d_6. ^1H NMR at 300 MHz, ^{31}P NMR at 121.49 MHz and ^{11}B NMR at 96.25 MHz.

Compound **2**: ^{11}B [$J(^{11}B–^1H)$ Hz] δ 97.1 (s, 1B, B6), 29.1 (d, 1B (145) B3), 15.6 (d, 1B (142) B4), −6.8 (d, 1B (140) B5), −38.8 (d, 1B (135) B1); $^1H\{^{11}B\}$ [$J(^{31}P–^1H)$ Hz] δ 6.14 (s, 1H, H3), 5.11 (s, 1H, H4), 4.29 (s, 5H, C_5H_5), 3.70 (s, 5H, C_5H_5), 3.26 (s, 1H, H5), 1.09 (d, 9H (12), PMe_3), 0.17 (s, 1H, H1), −1.75 (s, 1H, H34), −3.76 (s, 1H, H45), −13.60 (s, 1H, H26), −15.89 (s, 1H, H23), −18.59 (d, 1H (26), H67). Anal. Calc. for $C_{13}H_{28}B_5PFe_2$: C, 44.5; H, 8.3. Found: C, 45.5; H, 8.45%.

Compound **3**: ^{11}B [$J(^{11}B–^1H)$ Hz] δ 5.62 (t, 1B (137), B4), −39.38 (d, 2B (126), B1,3); $^1H\{^{11}B\}$ [$J(^{31}P–^1H)$ Hz] δ 4.40 (s, 1H, H4 *exo* or *endo*), 3.79 (s, 5H, C_5H_5), 2.05 (s, 2H, H1,3), 2.05 (s, 1H, H4 *exo* or *endo*), 0.85 (d, 9H (23), PMe_3), −1.41 (s, 2H, H14,34), −16.68 (d, 2H (79) H21,23); ^{31}P δ 17.72. MS(EI) Parent envelope observed with highest $P^+ = 239$ (calcd. 239). FT IR (Nujol mull, NaCl plates) cm^{-1}: 2516 (m), 2398 (m), 2374 (m) and 2333 (m) assigned to B-HT stretches; 1650 assigned to B–H–B stretches.

Compound **4**: ^{11}B [$J(^{11}B–^1H)$ Hz] δ 109 (d, 1B, (129) B6), 49.3 (d, 1B, (137) B5), 30.1 (d, 1B (122) B4), −18.9 (d, 1B (123), B1). $^1H\{^{11}B\}$ δ 13.05 (s, 1H, H6), 8.05 (s, 1H, H5), 6.08 (s, 1H, H4), 4.46 (s, 5H, C_5H_5), 4.35 (s, 5H, C_5H_5), 2.10 (s, 1H, H1), −1.66 (s, 1H, H45), −14.67 (s, 1H, H34), −17.92 (s, 1H, H25), −22.20 (s, 1H, H26).

Compound **5**: ^{11}B [$J(^{11}B–^{31}P)$ Hz] δ −8.64 (d, 1B, B4), −12.11 (d, 2B, B3,5), −42.18 (d, 1B (180), B1); $^1H\{^{11}B\}$ [$J(^1H–^{31}P)$ Hz] δ 4.12 (s, 5H, C_5H_5), 2.79 (s, 1H, H4), 2.52 (s, 2H, H3,5), 0.85 (d, 9H (12), PMe_3), −4.48 (s, 2H, H34,54) −15.16 (s, 2H, H23,25); ^{31}P [$J(^{11}B–^{31}P)$ Hz] δ 2.94 (q, 176). MS(EI) Parent envelope observed with highest $P^+ = 249$ (calcd. 249). FT IR (Nujol mull, NaCl plates) cm^{-1}: 2479 (m), 2427 (m) assigned to B-HT stretches; 1631 assigned to B–H–B stretches.

Compound **6**: ^{11}B [$J(^{11}B–^{31}P)$ Hz] δ 38.03 (d, 2B, B4,5), 14.45 (d, 2B, B3,6), −43.44 (d, 1B, (130) B1); $^1H\{^{11}B\}$ [$J(^1H–^{31}P)$ Hz] δ 7.04 (s, 2H, H4,5), 4.52 (s, 2H, H3,6), 4.08 (s, 5H, C_5H_5), 0.50 (d, 9H (12.5), PMe_3), −3.39 (s, 2H, H34,56), −16.58 (s, 2H, H23, 26); ^{31}P [$J(^{11}B–^{31}P)$ Hz] δ −3.47 (q, 150). MS(EI) Parent envelope observed with highest $P^+ = 261$ (calcd. 261). FT IR (Nujol mull, NaCl plates) cm^{-1}: 2476 (m), 2411 (m) assigned to B-HT stretches; 1730 (m) and 1772 (m) assigned to B–H–B symmetric and anti-symmetric stretches.

4.5. Reaction of [(η^5-C_5Me_5)Fe(PMe_3)$_2$H] with pentaborane(9)

[(η^5-C_5Me_5)Fe(PMe_3)$_2$H] (3.0 g, 8.7 mmol) was treated with a solution of pentaborane(9) in toluene (40 ml, 0.25 M) and stirred at 20 °C for 12 h. Silica gel (5 g) was added and volatiles removed *in vacuo*. The resulting sand was transferred to the top of a chromatography column and eluted with light petroleum:diethyl ether 20:1. Several bands were observed. Only two bands, red-purple and red-brown were collected, the others being of negligible amounts. The red-brown band was rechromatographed eluting with light petroleum:diethyl ether 9:1 to give two bands, a red-purple band and a orange-brown band. The combined fractions of the red-purple band were recrystallised from pentane at −78 °C to give dark purple crystals of [(η^5-C_5Me_5)-*nido*-2-FeB_5H_{10}] (**7**). Yield 340 mg, 15%. The orange-brown band was recrystallised from light petroleum at −78 °C to give orange-brown crystals of [(η^5-C_5Me_5)(PMe_3)-*arachno*-2-FeB_3H_8] (**8**). Yield 60 mg, 2%.

NMR data: Compounds **7** and **8**, solvent benzene-d_6. ^1H NMR at 300 MHz, ^{31}P NMR at 121.49 MHz and ^{11}B NMR at 96.25 MHz.

Compound **7**: ^{11}B [$J(^{11}B–^1H)$ Hz] δ 44.8 (d, 2B, (151), B3,6), 6.0 (d, 2B, (155), B4,5), −49.7 (d, 1B, (136), B1); $^1H\{^{11}B\}$ δ 6.59 (s, 2H, H3,6), 3.98 (s, 2H, H4,5), 1.59 (s, 15H, C_5Me_5), −0.84 (s, 1H, H1), −1.48 (s, 2H, H34,56), −2.25 (s, 1H, H45), −15.17 (s, 2H, H23,26).

Compound **8**: ^{11}B [$J(^{11}B–^1H)$ Hz] δ 4.6 (t, 1B (130), B4), −36.8 (d, 2B (124), B1,3); $^1H\{^{11}B\}$ [$J(^{31}P–^1H)$ Hz] δ 4.37 (s, 1H, H4 or 5), 2.20 (s, 2H, H5 or 4), 1.49 (s, 15H, C_5Me_5), 1.38 (s, 2H, H1,3), 0.86 (d, 9H (9), PMe_3), −1.44 (s, 2H, H14,34), −16.23 (d, 2H (21) H12,23); ^{31}P δ 15.65.

4.6. Isomerisation of [(η^5-C_5H_5)-nido-2-FeB_5H_{10}]

A 50 mg sample of **7** was heated in a sealed tube *in vacuo* at 200 °C for 3 days. Extraction of the residue with pentane followed by filtration and recrystallisation at −78 °C gave purple crystals of **9**. Yield 10 mg, 20%.

NMR data: Compound **9**, solvent benzene-d_6. ^1H NMR at 300 MHz and ^{11}B NMR at 96.25 MHz.

Compound **9**: ^{11}B [J(^{11}B–^{1}H) Hz] δ 6.8 (d, (158), B2–6); ^{1}H{^{11}B} δ 3.02 (s, 5H, H2–6), 2.12 (s, 15H, C_5Me_5), −4.31 (s, 5H, H23–26).

4.7. Reaction of [(η^5-C_5H_5)Fe(PMe_3)$_2$H] with $BH_3 \cdot$ thf

[(η^5-C_5H_5)Fe(PMe_3)$_2$H] (2.0 g, 7.3 mmol) was dissolved in pentane (20 ml) and the mixture cooled to 0 °C. $BH_3 \cdot$ thf (1.0 M solution in thf, 20 ml, 14 mmol) was added dropwise with stirring. The dark orange-brown solution was stirred at 0 °C for 4 h. Volatiles were removed *in vacuo* to give a dark brown oil. This residue was extracted with diethyl ether and the solution filtered. Silica gel (3 g) was added and volatiles again removed *in vacuo*. The sand was chromatographed as previously described eluting with diethyl ether:light petroleum 1:10. Two bands were collected, both orange-brown. Volatiles were removed from Band 1 and recrystallised from pentane at −78 °C to give orange-brown crystals of [(η^5-C_5H_5)(PMe_3)-*arachno*-2-FeB_3H_8] (**3**). Yield 60 mg, 3%. Band 2 was recrystallised from pentane and shown to be [(η^5-C_5H_5)$_2$Fe]. Yield 20 mg, 1.5%. When the reaction was carried out at 20 °C for longer periods only [(η^5-C_5H_5)$_2$Fe] was eluted from the column.

4.8. Deprotonation studies

Deprotonations were carried out in benzene-d_6 using KH (with added 18-crown-6) or in thf-d_8 using KH. Twenty milligram samples of compounds **1**, **3**, **6** and **7** were dissolved in the deuterio solvent and excess KH added. The mixture was filtered and then transferred to a 5 mm NMR tube and sealed *in vacuo*. Compounds **1**, **6** and **7** deprotonated quantitatively at 20 °C to give pink-red [(η^5-C_5H_5)-*nido*-2-$FeB_5H_9^-$][K^+] (**10**), pink-red [(η^5-C_5Me_5)-*nido*-2-$FeB_5H_9^-$][K^+] (**11**) and green [(η^5-C_5H_5)-*nido*-2-$FeB_5H_7(PMe_3)^-$][K^+] (**12**) as determined by NMR spectroscopy. Compounds **1** and **7** deprotonated immediately, whereas compound **6** took 48 h for deprotonation to go to completion. Compound **3** did not deprotonate as judged by NMR.

NMR data: Compounds **10**–**12**, solvent thf-d_8. ^{1}H NMR at 300 MHz, ^{31}P NMR at 121.49 MHz and ^{11}B NMR at 96.25 MHz.

Compound **10**: ^{11}B [J(^{11}B–^{1}H) Hz] δ 42.3 (br m, 2B, B3,6), 14.5 (br m, 2B, B4,5), −42.6 (d, 1B, (132) B1); ^{1}H{^{11}B} δ 7.49 (s, 2H, H3,6), 4.45 (s, 2H, H4,5), 4.04 (s, 5H, C_5H_5), −0.47 (s, 1H, H1), −3.43 (s, 2H, H34,56), −16.69 (s, 2H, H23,26).

Compound **11**: ^{11}B [J(^{11}B–^{1}H) Hz] δ 44.7 (br m, 2B, B3,6), 11.9 (br m, 2B, B4,5), −40.9 (d, 1B, (136) B1); ^{1}H{^{11}B} δ 7.16 (s, 2H, H3,6), 4.04 (s, 2H, H4,5), 1.58 (s, 15H, C_5Me_5), −1.06 (s, 1H, H1), −3.38 (s, 2H, H34,56), −16.17 (s, 2H, H23,26).

Compound **12**: ^{11}B [J(^{11}B–^{31}P) Hz] δ 22.0 (m, 2B, B3,6), 16.5 (m, 2B, B4,5), −41.9 (d, 1B (119), B1); ^{1}H{^{11}B} [J(^{1}H–^{31}P) Hz] δ 6.29 (s, 2H, H3,6), 4.75 (s, 2H, H4,5), 4.08 (s, 5H, C_5H_5), 0.50 (d, 9H (12) PMe_3), −4.73 (s, 1H, H34 or H56), −15.20 (s, 2H, H23,26); ^{31}P [J(^{11}B–^{31}P) Hz] δ 2.94 (br q, 149).

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