Synthesis of Small *nido*-Ferrapentaboranes; a Novel Borane-capped *nido*-Diferrapentaborane

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Pentaborane(9) reacts with $[Fe(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$ to give $[2,3\text{-}\{Fe(PMe_3)_2\}_2(\mu\text{-}H)B_4H_9]$ (**1**) and $[2\text{-}\{Fe(PMe_3)_3\}B_4H_8]$ (**2**) in yields of up to 1 and 22% respectively; the *X*-ray crystal structure of (**1**) shows a *nido*-pentaborane(9) structure in which a BH_3 fragment caps the Fe_2B face.

The chemistry of metallaboranes has revealed a rich diversity of polyhedral structural classes.[1] Here we report the synthesis of a new and unexpected tetraboron di-iron cluster. Treatment of a solution of pentaborane(9) with one equivalent of $[Fe(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$[2] for 24 h at ambient temperature followed by column chromatography on silica gave black, crystalline $[2,3\text{-}\{Fe(PMe_3)_2\}_2(\mu\text{-}H)B_4H_9]$ (**1**) (dark red-brown in solution) and orange, crystalline $[2\text{-}\{Fe(PMe_3)_3\}B_4H_8]$ (**2**) in 1 and 12% yields respectively [compound (**2**) is available in up to 22% yields using 1.5 equivalents of pentaborane(9)]. As part of our project on metal–boron clusters we have been trying to find routes to small metallaboranes that can be made on the gram scale.[3] Few easy, high-yield syntheses are known and consequently little reaction chemistry has been explored.[1] Compound (**2**) can be made in gram quantities, for example 5 g of $[Fe(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$ (one step from $FeCl_2$)[2] gives 1 g (22%) of (**2**). Thus, (**2**) is available for further reactivity studies. Solutions of (**1**) decompose in a few minutes in air, but the solid is more stable, decomposing slowly over 2—3 days, whereas (**2**) appears to be air-stable in the solid state but decomposes slowly in solution.

A single crystal *X*-ray diffraction study of (**1**) was carried

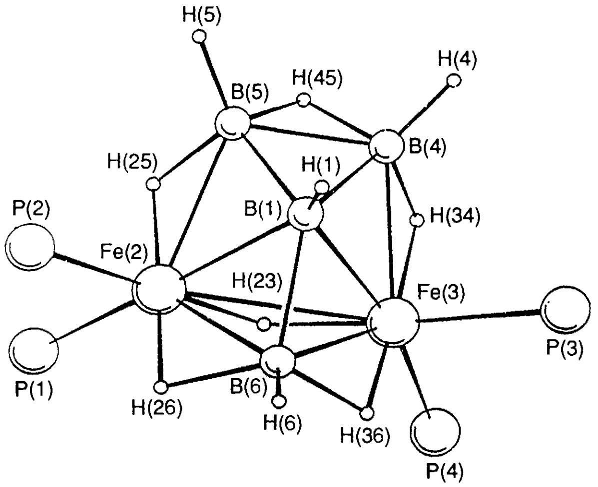

Figure 1. Molecular structure of compound (**1**). Selected bond distances (Å): Fe(2)–Fe(3) 2.7055(5), Fe–P(average) 2.186, Fe(2)–B(1) 2.109(3), Fe(2)–B(5) 2.132(3), Fe(2)–B(6) 2.020(3), Fe(3)–B(1) 2.107(3), Fe(3)–B(4) 2.109(3), Fe(3)–B(6) 2.024(3), Fe(2)–H(23) 1.66(3), Fe(3)–H(23) 1.64(3), B(1)–B(4) 1.743(5), B(1)–B(5) 1.736(5), B(1)–B(6) 1.821(5), B(4)–B(5) 1.782(5). Selected bond angles (°): Fe(2)–B(6)–Fe(3) 84.0(1), Fe(2)–H(23)–Fe(3) 110.1(19), Fe(2)–Fe(3)–B(4) 77.5(1), Fe(3)–Fe(2)–B(5) 77.4(1), B(1)–Fe(2)–B(6) 52.3(1).

out.† The structure is shown in Figure 1, and is best considered as a capped *nido*-square-pyramidal structural analogue of pentaborane(9) with two adjacent basal iron atoms and a non-crystallographic mirror plane. The Fe_2B face is capped by a boron atom with two equivalent Fe–H–B bridging hydrogen atoms. There are four bridging hydrogen atoms around the square base. Additionally, each boron atom is bonded to a terminal hydrogen atom, and each iron atom is bonded to two PMe_3 ligands. Capping by a BH fragment is known in cluster chemistry {for example the capped *closo*-molecules $[Co(\eta\text{-}C_5R_5)]_3B_4H_4$ (R = H, Me)},[4] but this is the first example of a *nido*-metallaborane capped by a BH_3 fragment.

A skeletal electron count[5] shows that (**1**) has seven skeletal electron pairs and is effectively isoelectronic with $B_6H_6{}^{2-}$ and the parent neutral borane B_6H_8, which, although not isolated, has been the subject of considerable theoretical interest. In particular, Wade and Fehlner have demonstrated that the face-capped square-pyramidal structure becomes favoured relative to the octahedron on protonation, although the total number of skeletal electrons remains the same.[6] The importance of protonation has also been shown by the observation that $[Os_6(CO)_{18}]^{2-}$ adopts a *closo*-structure whereas the neutral diprotonated compound, $[Os_6H_2(CO)_{18}]$, is a capped square pyramid.[7] The large number of bridging hydrogen atoms in (**1**) similarly leads to a preference for the capped square pyramid in (**1**). Compound (**1**) is the first metallaborane analogue of the parent species B_6H_8 which adopts a capped square-pyramidal structure. $[\{Co(\eta\text{-}C_5H_5)\}_2B_4H_6]$ has the same skeletal electron count as (**1**) but adopts a *closo*-octahedral structure.[8]

Compound (**1**) can also be considered notionally as a complex between the di-iron fragment $[\{Fe(PMe_3)_2\}(\mu\text{-}H)]^+$ and the $B_4H_9{}^-$ anion which is isoelectronic with the cyclopropylmethyl cation $C_4H_7{}^+$. This cation has been the centre of the classical–non-classical carbonium ion controversy and the weight of evidence now is more consistent with a non-classical structure.[9] Interestingly, the $B_4H_9{}^-$ fragment in this structure corresponds to a classical $C_4H_7{}^+$ structure.

Compound (**1**) has also been further characterised by multinuclear NMR spectroscopy‡ and elemental analysis. From an ^{11}B–^{11}B COSY NMR experiment, strong coupling is observed between the two boron atoms, B-1 and B-6, as well as coupling from B-1 to B-4 and B-5 consistent with the observed structure.

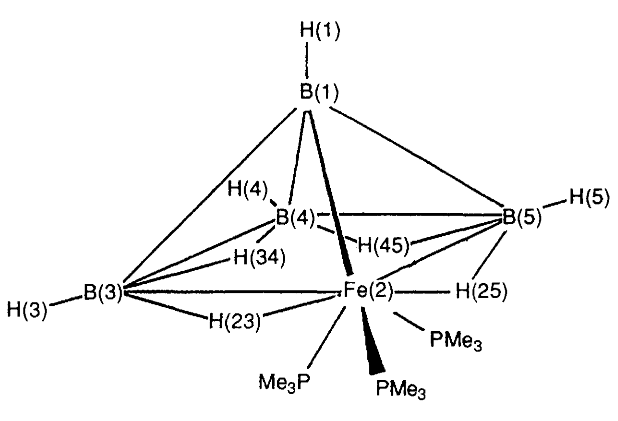

Figure 2. Proposed structure for (**2**), *nido*-$[2\text{-}\{Fe(PMe_3)_3\}B_4H_8]$.

Compound (**2**) has been characterised by multinuclear NMR spectroscopy‡ and elemental analysis as the basally substituted pentaborane(9) analogue $[2\text{-}\{Fe(PMe_3)_3\{B_4H_8]$ (see Figure 2). This contrasts with $[1\text{-}\{Fe(CO)_3\}B_4H_8]$ in which the $Fe(CO)_3$ fragment prefers the apical position.[10] The

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† Data were collected on an Enraf-Nonius CAD4 diffractometer (3° $< 2\theta < 50°$). The structure was solved from direct methods and Fourier syntheses and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms bonded to carbon atoms were included in calculated positions (C–H 0.96 Å) and refined riding on their attached atom. Hydrogen atoms bonded to boron atoms were located from a difference synthesis and their co-ordinates and isotropic thermal parameters refined. Crystallographic calculations were carried out using the Oxford 'CRYSTALS' package.[13]

Crystal data for (1): $C_{12}H_{46}B_4Fe_2P_4$, $M = 469.32$, monoclinic, space group $P2_1/n$, $a = 15.847(9)$, $b = 16.277(2)$, $c = 9.829(9)$ Å, $\beta = 91.11(8°)$, $U = 2534.8$ Å^3, $Z = 4$, $D_c = 1.229$ g cm^{-3}, $\mu = 13.89$ cm^{-1}, $F(000) = 1000$, $R = 0.031$ and $R_w = 0.034$ for 3072 observed reflections with $I > 3\sigma(I)$ and 240 refined least-squares parameters, $\lambda(\text{Mo-}K_\alpha) = 0.710\ 69$ Å, crystal size *ca.* 0.35 × 0.40 × 0.70 mm.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *Selected spectroscopic data* {solvent $[^2H_6]$benzene for (**1**) and (**2**)}, ^1H NMR at 200 MHz, ^{31}P NMR at 101 MHz and ^{11}B NMR at 64 MHz, chemical shifts (δ) in ppm and coupling constants in Hz. External references: ^{31}P NMR $P(O)(OMe)_3$; ^{11}B NMR $BF_3{\cdot}OEt_2$.

Compound (**1**): $^1H\{^{11}B\}$ NMR, 7.32 (1H, 6-H), 5.12 (2H, 4-H, 5-H), 1.29 (m, 36H, PMe_3), −0.44 (1H, 45-H), −0.64 (quart., 1H, 1-H), −20.26 (2H, 25-H, 34-H), −22.35 (t, *J* 22, 2H, 26-H, 36-H), −25.15 (t, *J* 33, 1H, 23-H); ^{11}B NMR, 78.0 (m, 1B, B-6), 26.9 (m, 2B, B-4, B-5), −21.3 (d, *J* 129, 1B, B-1); $^{31}P\{^1H\}$ NMR, 27.64 (d, *J* 35, 1P, PMe_3), 16.97 (d, *J* 35, 1P, PMe_3).

Compound (**2**): $^1H\{^{11}B\}$ NMR, 4.08 (1H, 4-H), 2.44 (2H, 3-H, 5-H), 1.33 (1H, 1-H), 1.11 (d, *J* 8, 9H, PMe_3), 1.08 (d, *J* 7, 18H, PMe_3), −2.64 (2H, 34-H, 45-H), −17.39 (2H, 23-H, 25-H); ^{11}B NMR, 0.3 (d, *J* 146, 1B, B-4), −11.4 (d, *J* 141, 2B, 3-B, 5-B), −32.6 (d, *J* 150, 1B, B-1): $^{31}P\{^1H\}$ NMR, 25.42 (d, *J* 37, 2P, PMe_3), 3.07 (t, *J* 37, 1P, PMe_3).

only group 8 metallaboranes that are isoelectronic with **(2)** are 2-[$Os(CO)(PPh_3)_2B_4H_8$][11] and 2-[$Ru(\eta\text{-}C_6Me_6)B_4H_8$].[12]

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