Re-identification of the Major Volatile Carbaboranes from the Gas-phase Reactions of Tetraborane(10) and Alkynes at 50 °C

Mark A. Fox and Robert Greatrex*

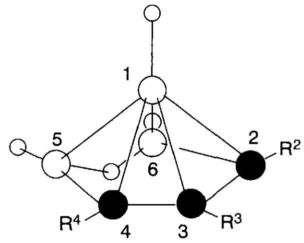
School of Chemistry, University of Leeds, Leeds, UK LS2 9JT

Three of the major volatile products from gas-phase reactions of B_4H_{10} with alkynes, previously reported to be the tricarbahexaborane(7) derivatives 2,3-Me_2-2,3,4-$C_3B_3H_5$ **2**, 2,4-Me_2-2,3,4-$C_3B_3H_5$ **3** and 2-Et-3,4-Me_2-2,3,4-$C_3B_3H_4$ **4**, are now shown to be the new dicarbahexaborane(8) derivatives, 2,4-Me_2-2,3-$C_2B_4H_6$ **6**, 5-Et-2,3-$C_2B_4H_7$ **7** and 2-Et-3,4-Me_2-2,3-$C_2B_4H_5$ **8**, respectively; this leaves 2-Me-2,3,4-$C_3B_3H_6$ **1** as the only authentic, well characterised *nido*-2,3,4-tricarbahexaborane species to have been reported.

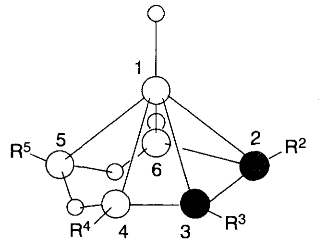
The reaction between B_4H_{10} and excess ethyne at 25–50 °C has been reported to give 2-Me-2,3,4-$C_3B_3H_6$ **1**, 2,3-Me_2-2,3,4-$C_3B_3H_5$ **2** and 2,4-Me_2-2,3,4-$C_3B_3H_5$ **3** as the major volatile carbaborane products.[1–4] When propyne was used instead of ethyne the carbaboranes were thought to be 2-Et-3,4-Me_2-2,3,4-$C_3B_3H_4$ **4** and 2-Me-2,3-$C_2B_4H_7$ **5**.[3] Little is known about the mechanisms of these complex, facile reactions, but the presence of odd numbers of carbon atoms in **2–4** was regarded as important evidence for unprecedented carbon–carbon bond cleavage under very mild conditions,[3] and it was suggested that this might proceed *via* elimination of fragments such as $\{CBH_3\}$ from larger reactive intermediates.[4] In a recent study of these and related reactions we have isolated novel alkyl derivatives of the type *arachno*-1-R-2,5-μ-CR^1R^2-1-CB_4H_7 (*e.g.* R = Me, $R^1 = R^2 = H$), which provide further insights into the C≡C triple bond cleavage under mild conditions and in the absence of metal catalysts.[5]

We now find, from experiments carried out under identical conditions to those employed in the pioneering work of Grimes and coworkers, that **2**, **3** and **4** were incorrectly characterised. In a typical reaction, B_4H_{10} (3 mmol) and the alkyne (30 mmol) were held in a sealed 1 l pyrex flask at 50 °C for 3 days. High-resolution accurate mass spectra of the volatile products showed cut-offs corresponding to the molecular formula $C_4B_4H_{12}$ for **2** and **3**, and $C_6B_4H_{16}$ for **4**, and NMR data suggested that these compounds, originally thought to be tricarbahexaboranes, are in fact the new dicarbahexaborane derivatives 2,4-Me_2-2,3-$C_2B_4H_6$ **6**,[6]† 5-Et-2,3-$C_2B_4H_7$ **7**‡ and 2-Et-3,4-Me_2-2,3-$C_2B_4H_5$ **8**,§ respectively. The same volatile products were also obtained from reactions in which the starting materials were present in a 1 : 1 rather than a 1 : 10 ratio. Although **6** and **8** contain even numbers of carbon atoms, an alkyne C–C bond cleavage is seen to be required for their formation.

Our ^1H NMR spectra of **1**, **6** and **7** compare well with those described by Grimes and coworkers[1,3] for **1**, **2** and **3**. The ^{11}B spectrum of **1** is also in good agreement with the reported data, but the boron spectra of **6** and **7** feature additional resonances at δ 7.7 and 15.1, respectively. In the early boron spectra, which were recorded in an external laboratory and covered a limited frequency range,[7] the additional peaks would have been off-scale to low-field. Fortuitously, the resulting spectra are remarkably similar to one another, and it is easy to see how the original mistake was made. On the basis of modern 2D ^{11}B–$^{11}B\{^1H\}$ COSY and $^1H\{^{11}B_{selective}\}$–$^1H$ subtraction spectra, these resonances are shown unequivocally to be related to the other main peaks in the spectra, and are assigned to the alkyl-substituted boron atoms, B(4) in **6** and B(5) in **7**. A further notable feature is the unusual chemical shift of δ −3.64 observed for the bridging proton in the tricarbahexaborane **1**;¶ this distinguishes **1** from the dicarbahexaboranes, which generally have bridge-proton chemical shifts in the range δ −1.5 to −2.4.[8–11]



	R^2	R^3	R^4
1	Me	H	H
2	Me	Me	H
3	Me	H	Me
4	Et	Me	Me



	R^2	R^3	R^4	R^5
5	Me	H	H	H
6	Me	H	Me	H
7	H	H	H	Et
8	Et	Me	Me	H

The genuine tricarbahexaborane, **1**, differs markedly from **2** and **3** in that it is the only one of the three compounds to react readily with $Mn_2(CO)_{10}$ in the gas phase to produce a metal π-complex in high yield, and its anion is the only one to form the π-complex when treated with $BrMn(CO)_5$ in diglyme solution.[12] The chemistry reported for **2** and **3** is typical of that of other $C_2B_4H_8$ derivatives.[12,13] Both compounds undergo bridge-deprotonation and re-deuteriation, and **2** yields a $C_2B_5H_7$ derivative on thermal decomposition, as expected.[14,15]

The mechanism of the gas-phase reaction, which now needs to account for the production of **1**, **6** and **7**, may be somewhat simpler than previously envisaged. For example, the proposed intermediate $\{C_4B_4H_{12}\}$,[4] itself formed by attack of first one and then a second molecule of C_2H_2 on the reactive intermediate $\{B_4H_8\}$, could be common to the production of all three species. Formation of **1** would require elimination of a $\{BH_3\}$ moiety as already suggested, but the dicarbaboranes **6** and **7** could be generated simply by rearrangement of $\{C_4B_4H_{12}\}$. There is no need to invoke elimination of the unusual species $\{CBH_3\}$, tentatively suggested by Franz and Grimes. The products from the reaction of B_4H_{10} and C_2D_2 are also consistent with this mechanism.[4,13]

In the light of the present study it would appear that 2-Me-2,3,4-$C_3B_3H_6$ **1**, first reported by Bramlett and Grimes in 1966,[1] remains the only well characterised *nido*-2,3,4-tricarbahexaborane species. There were early speculations that the parent compound 2,3,4-$C_3B_3H_7$ might have been synthesised but these were later discounted,[3,7] and the hexaalkyl species 1,5,6-Et_3-2,3,4-Me_3-2,3,4-C_3B_3H has been identified by mass spectrometry only.[16]

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Footnotes

† *Spectroscopic data* for **6**: ^{11}B NMR ($CDCl_3$, 128 MHz, *J*/Hz) δ 7.7 [d, 1 B, J_{BH_μ} 44, B(4)], −1.7 [d, 1 B, J_{BH_t} 150, B(5)], −4.6 [dd, 1 B, J_{BH_t} 154, J_{BH_μ} 48, B(6)], −48.8 [d, 1 B, J_{BH_t} 177, B(1)]; $^1H\{^{11}B\}$ NMR ($CDCl_3$, 400 MHz) δ 5.79 [s, 1 H, C(3)H], 3.44 [s, 1 H, B(5)H], 3.14 [s, 1 H, B(6)H], 2.16 [s, 3 H, C(2)Me], 0.59 [s, 3 H, B(4)Me], −0.90 [s, 1 H, B(1)H], −1.63 [s,

1 H, $H_\mu(4,5)$], −1.99 [s, 1 H, $H_\mu(5,6)$]. Accurate mass measurement of **6**: *m/z* 104.1316. Calc. for $C_4B_4H_{12}$, 104.1311. These data characterise **6** as a dicarbahexaborane, Me_2-2,3-$C_2B_4H_6$. The compound was shown to be the 2,4-Me_2 rather than the 2,6-Me_2 isomer by $^1H\{B_{selective}\}-^1H$ subtraction spectra and this was confirmed by the application of the *ab initio*/IGLO/NMR method. Full details of this study will be reported later.[6] Yields were very difficult to measure accurately. The volatile products are estimated to account for only *ca.* 5% of the boron; **6** constitutes *ca.* 33% of the total volatile carbaborane fraction.

‡ *Spectroscopic data* for **7**: ^{11}B NMR ($CDCl_3$, 128 MHz, *J*/Hz) δ 15.1 [s, 1 B, B(5)], −2.6 [dd, 2 B, J_{BH_t} 155, J_{BH_μ} 52, B(4), B(6)], −52.7 [d, 1 B, J_{BH_t} 180, B(1)]; $^1H\{^{11}B\}$ NMR ($CDCl_3$, 400 MHz) δ 6.32 [s, 2 H, C(2)H, C(3)H], 3.39 [s, 2 H, B(4)H, B(6)H], 1.21 (s, 3 H, Me), 1.14 (s, 2 H, CH_2), −0.96 [s, 1 H, B(1)H], −1.56 (s, 2 H, H_μ). Accurate mass measurement of **7**: *m/z* 104.1316. Calc. for $C_4B_4H_{12}$, 104.1311. **7** constitutes *ca.* 27% of the total volatile carbaborane fraction.

§ *Spectroscopic data* for **8**: ^{11}B NMR ($CDCl_3$, 128 MHz, *J*/Hz) δ 5.2 [d, 1 B, J_{BH_μ} *ca.* 43, B(4)], −3.1 [d, 1 B, J_{BH_t} *ca.* 150, B(5)], −6.8 [dd, 1 B, J_{BH_t} 155, J_{BH_μ} 47, B(6)], −46.2 [d, 1 B, J_{BH_t} 179, B(1)]; $^1H\{^{11}B\}$ NMR ($CDCl_3$, 400 MHz) δ 3.29 [s, 1 H, B(5)H], 3.05 [s, 1 H, B(6)H], 2.40 (m, 1 H, CH_2), 2.27 (m, 1 H, CH_2), 1.92 [s, 3 H, C(3)Me], 1.16 (t, 3 H, J_{HH} 7, CH_2*Me*), 0.52 [s, 3 H, B(4)Me], −1.02 [s, 1 H, B(1)H], −1.65 [s, 1 H, $H_\mu(4,5)$], −2.07 [s, 1 H, $H_\mu(5,6)$]. Accurate mass measurement of **8**: *m/z* 132.1627. Calc. for $C_6B_4H_{16}$, 132.1624. These data characterise **8** as a dicarbahexaborane, $EtMe_2$-2,3-$C_2B_4H_5$. It was shown by $^1H\{B_{selective}\}-^1H$ subtraction spectra to be 2-Et-3,4-Me_2-2,3-$C_2B_4H_5$ rather than 2-Et-3,6-Me_2-2,3-$C_2B_4H_5$. **8** constitutes *ca.* 10% of the total volatile carbaborane fraction.

¶ *Spectroscopic data* for **1**: ^{11}B NMR ($CDCl_3$, 128 MHz, *J*/Hz) δ −0.1 [dd, 2 B, J_{BH_t} 154, J_{BH_μ} 53, B(5), B(6)], −52.6 [d, 1 B, J_{BH_t} 192, B(1)]; $^1H\{^{11}B\}$ NMR ($CDCl_3$, 400 MHz) δ 6.74 [s, 1 H, C(3)H], 5.10 [s, 1 H, C(4)H], 3.37 [s, 2 H, B(5)H, B(6)H], 2.13 (s, 3 H, Me), −0.85 [s, 1 H, B(1)H], −3.66 (s, 1 H, H_μ). Accurate mass measurement of **1**: *m/z* 90.0987. Calc. for $C_4B_3H_9$, 90.0983. **1** constitutes *ca.* 21% of the total volatile carbaborane fraction.

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