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Journal of Organometallic Chemistry 614–615 (2000) 262–268

Journal of Organo metallic Chemistry

Gas-phase reactions of *nido*-1-methylpentaborane with propyne and 2-pentyne. Formation of B-alkyl *nido* and *closo* carbaboranes

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Received 21 May 2000

Dedicated to Professor Sheldon G. Shore on the occasion of his 70th birthday in appreciation of his outstanding contributions to the areas of boron and transition metal cluster chemistry.

Abstract

The gas-phase reaction between 1-MeB_5H_8 and propyne at 230°C yields methyl derivatives of *nido*-2,3-dicarbahexaboranes and *closo*-2,4-dicarbaheptaboranes. The reaction between 1-MeB_5H_8 and 2-pentyne at 190°C gives analogous alkyl *nido*-carbaboranes (but not *closo*-carbaboranes). Detailed boron and proton NMR data on these products in conjunction with ab initio/GIAO/NMR computations show that the dicarbaboranes 2,4-Me_2-2,3-$C_2B_4H_6$ (**3**) and 2-Et-3,4-Me_2-2,3-$C_2B_4H_5$ (**12**) are produced in the gas-phase reactions of B_4H_{10} with ethyne and propyne, respectively. Early work on these two compounds identified them incorrectly as the first tricarbaboranes 2,3-Me_2-2,3,4-$C_3B_3H_5$ and 2-Et-3,4-Me_2-2,3,4-$C_3B_3H_4$, respectively. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: 1-Methylpentaborane; *nido*-Dicarbahexaborane clusters; *closo*-Dicarbaheptaboranes; GIAO structural/NMR calculations

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1. Introduction

Over three decades ago, the reaction between 1-MeB_5H_8 and excess HC≡CH at 250°C was reported to give four major carbaborane products: 2,3-$C_2B_4H_8$ and the three B-methyl derivatives, 1-Me-, 4-Me- and 5-Me-2,3-$C_2B_4H_7$ [1] (Fig. 1). Analogous products were obtained in the reaction involving MeC≡CMe in place of HC≡CH. On this basis the reaction between 1-MeB_5H_8 and MeC≡CH would be expected to give 2-Me-2,3-$C_2B_4H_7$ (**1**) and all four possible dimethyl derivatives: 1,2-Me_2- (**2**), 2,4-Me_2- (**3**), 2,5-Me_2- (**4**) and 2,6-Me_2-2,3-$C_2B_4H_6$ (**5**) (Fig. 2). Our interest in exploring this reaction was stimulated by our recent discovery that one of the main volatile products of the gas-phase reaction between B_4H_{10} and HC ≡ CH at 50°C was a dimethyl-2,3-dicarbahexaborane derivative [2,3], and not one of the first tricarbahexaboranes as had earlier been claimed [4–7].

On the basis of the ^{11}B- and ^{1}H-NMR data alone it was not possible to establish conclusively which of the two isomers was produced in the B_4H_{10}/ethyne reaction, 2,4-Me_2-2,3-$C_2B_4H_6$ (**3**) or 2,6-Me_2-2,3-$C_2B_4H_6$ (**5**), but $^{1}H\{^{11}B$ selective$\}-{}^{1}H$ subtraction spectra suggested that it was the former isomer [2,3]. Consistent with this assignment, the spectra also showed unusual long-range B–H couplings between the basal boron and the neighbouring methyl protons (i.e. *B*6-C2-CH_3 in (**3**)), similar to the long-range couplings observed in 1-MeB_5H_8 [8]. However, definitive confirmation was provided by use of the combined ab initio/GIAO/NMR method. The details of this study are now described in full.

The combined ab initio/IGLO or GIAO/NMR method has developed into a reliable technique for structure determination [9]. IGLO and GIAO NMR chemical shift calculations have been carried out on many known boranes and carbaboranes and have been

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PII: S0022-328X(00)00614-8

shown to give very good agreement with experimental ^{11}B chemical shifts [10]. However, it seemed unlikely that the method would be sufficiently precise to allow a definitive choice to be made between structures so closely related as the isomers **3** and **5**, solely on the basis of an isolated set of experimental chemical shifts for the compound in question. It was also anticipated that the margins for error would probably be increased by the presence of freely rotating alkyl groups in the compound.

To resolve this particular problem it was necessary to obtain spectra of both isomers so that their relative experimental shifts could be compared with the calculated values. This paper reports the synthesis of these closely related products, **3** and **5**, by the reaction between 1-MeB_5H_8 and MeC≡CH referred to earlier. We describe how the powerful ab initio/GIAO/NMR method has enabled their NMR spectra to be assigned and the compounds themselves to be identified, despite the fact that three of them are too similar in volatility to be separated from one another by low-temperature fractionation. We also report the unexpected formation of the *closo*-carbaheptaboranes, B,2-Me_2-2,4-$C_2B_5H_5$ (**6**–**9**) (Fig. 2), from the same reaction and, in the light of our findings, discuss the products from the reported [6] thermolysis of 2,4-Me_2-2,3-$C_2B_4H_6$ (**3**) (thought at the time to be 2,3-Me_2-2,3,4-$C_3B_3H_5$).

Boron and proton spectra on a product from the gas-phase reaction of B_4H_{10} and MeC≡CH, originally thought to be 2-Et-3,4-Me_2-2,3,4-$C_3B_3H_4$ [4–7], suggested that it might be either 2-Et-3,4-Me_2-2,3-$C_2B_4H_5$ (**12**) or the closely related isomer 2-Et-3,6-Me_2-2,3-$C_2B_4H_5$ (**14**) [2]. The $^1H\{^{11}B\ \text{selective}\}-^1H$ subtraction spectra showed long-range B–H couplings between the basal boron and the neighbouring methyl protons (i.e. *B*4-C3-C*H*$_3$ couplings), which tentatively identified the product as 2-Et-3,4-Me_2-2,3-$C_2B_4H_5$ (**12**) [2]. The synthesis and characterisation of the *nido*-carbahexaboranes 2-Et-3-Me-2,3-$C_2B_4H_6$ (**10**), 2-Et-1,3-Me_2- (**11**), 2-Et-3,4-Me_2- (**12**), 2-Et-3,5-Me_2- (**13**) and 2-Et-3,6-Me_2-2,3-$C_2B_4H_5$ (**14**) from the reaction of EtC≡CMe and 1-MeB_5H_8 are also described here (Fig. 3).

2. Experimental

Standard high-vacuum systems fitted with greaseless O-ring taps and spherical joints [J. Young (Scientific glassware) Ltd.] were used throughout. Propyne (Cambrian Gases) and 2-pentyne (Aldrich) were obtained commercially and 1-methylpentaborane, 1-$CH_3B_5H_8$, was prepared from B_5H_9, MeCl and $AlCl_3$ using a known procedure [11]. The high-field ^{11}B- and ^{1}H-NMR spectra were obtained on a Bruker AM-400 NMR instrument. The $^1H\{^{11}B\ \text{selective}\}$ experiments were performed by established methods [12].

2.1. Gas-phase reaction of MeB_5H_8 and MeC≡CH; carbaboranes 1–9

A mixture of 1-MeB_5H_8 (3 mmol) and MeC≡CH (30 mmol) was sealed in a 500 ml flask and heated to 190°C for 8 h and then to 230°C for 2 h. After the mixture was cooled, the volatiles were collected at −196°C and fractionated on a high-vacuum-low-temperature column [13]. The progress of the reaction was followed by bleeding the species leaving the column into an MS30 mass spectrometer via a 'Veridia' capillary of length 250 mm and internal diameter 0.1 mm [Jencons (Scientific) Ltd.]. In addition to the starting material, MeC≡CH, which left the column at −110°C, the following products were identified by their cut-offs in the mass spectra and by their ^{11}B- and ^{1}H-NMR spectra (column temperature and estimated yield based on 1-MeB_5H_8 in parentheses): 2-MeB_5H_8 (formed from the known rearrangement of 1-MeB_5H_8 at 200°C,

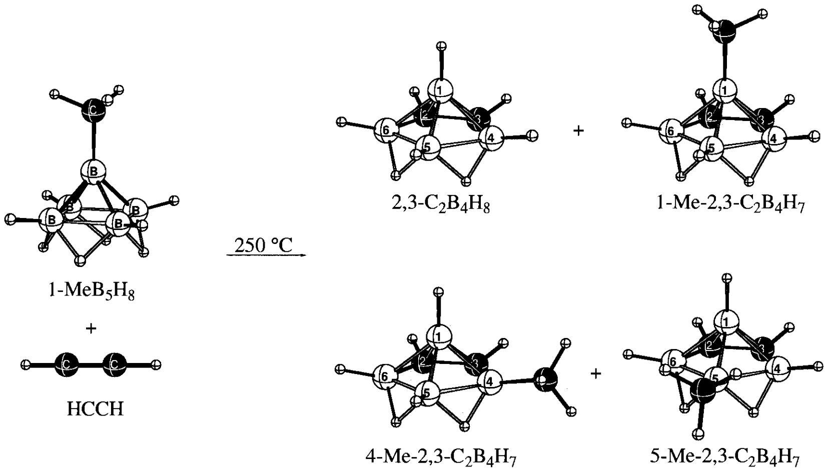

Fig. 1. The four major *nido* carbaborane products known to be produced in the reaction between 1-MeB_5H_8 and excess HC≡CH at 250°C.

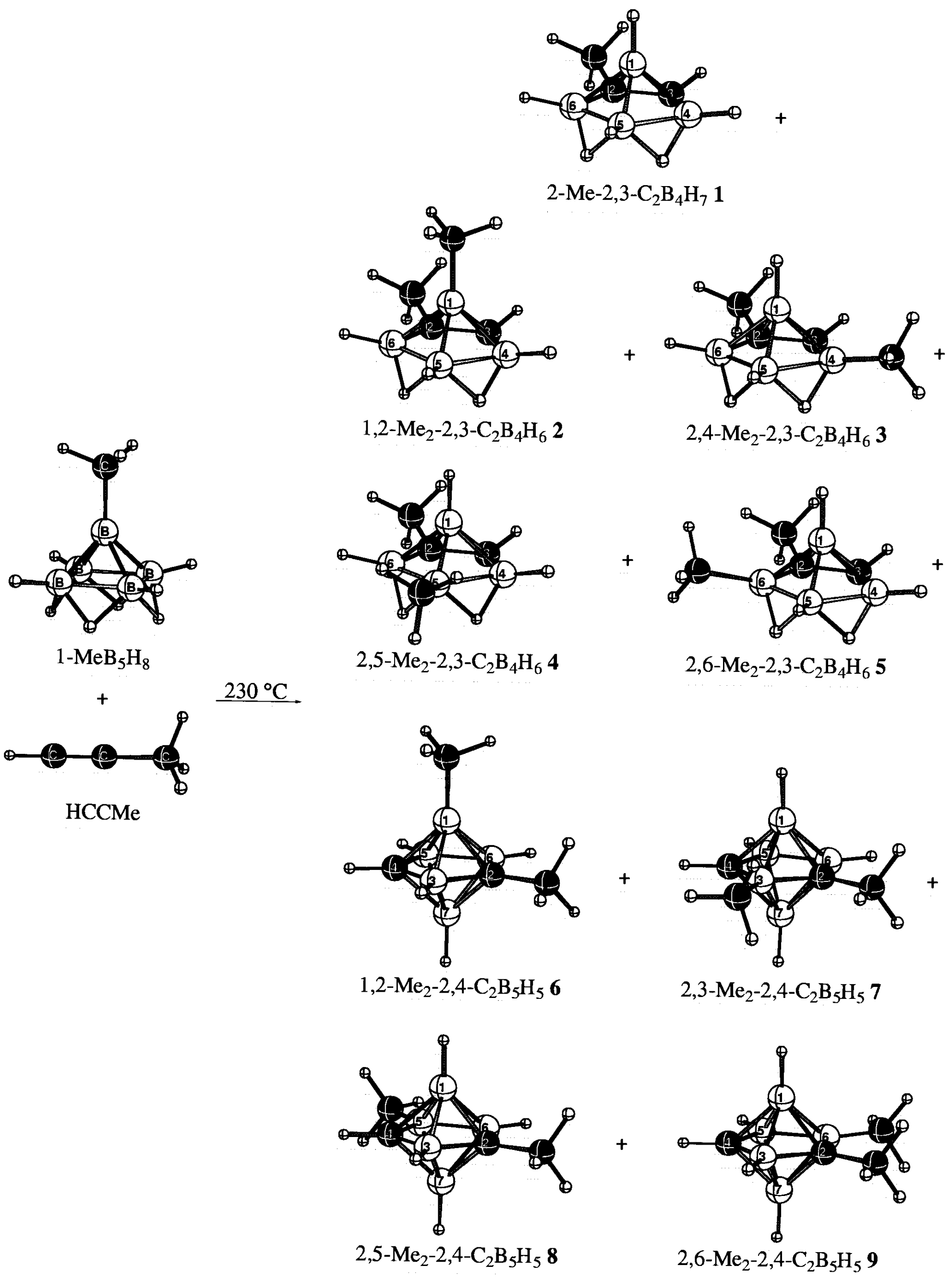

Fig. 2. The five *nido* products **1**–**5** expected to be formed in the reaction between 1-MeB_5H_8 and MeC≡CH, plus the four *closo* dimethyl derivatives **6**–**9** observed unexpectedly.

-64°C, 4%), the *nido* carbaboranes, **1** (-87°C, 7%), **2** (-58°C, 6%), a 0.9:1:0.8 mixture of **3**, **4** and **5** (-49°C, 12%), and the *closo* carbaboranes, 2,3-Me_2-2,4-$C_2B_5H_5$ (**7**) (-52°C, 1%) and a mixture of *closo*-1,2-, 2,5- and 2,6-Me_2-2,4-$C_2B_5H_5$ (compounds **6**, **8** and **9**, respectively) (-47°C, 0.1%). In addition, minor amounts of volatile species having cut-offs in their mass spectra at m/z 118, and mass spectral patterns characteristic of *nido*-CB_5H_9 derivatives were observed to leave the low-temperature column at -40°C.

*2.2. Gas-phase reaction of MeB_5H_8 and EtC≡CMe; carbaboranes **10**–**14***

A mixture of 1-MeB_5H_8 (3 mmol) and EtC≡CMe (30 mmol) was sealed in a 500 ml flask and heated to 190°C for 18 h. After the mixture was cooled, the volatiles were collected and fractionated as described above to give EtC≡CMe (-80°C), 1-MeB_5H_8 (-64°C), the *nido* carbaborane **10** (-45°C, 10%), and a mixture comprising **11**, **12**, **13** and **14** in the approximate ratio

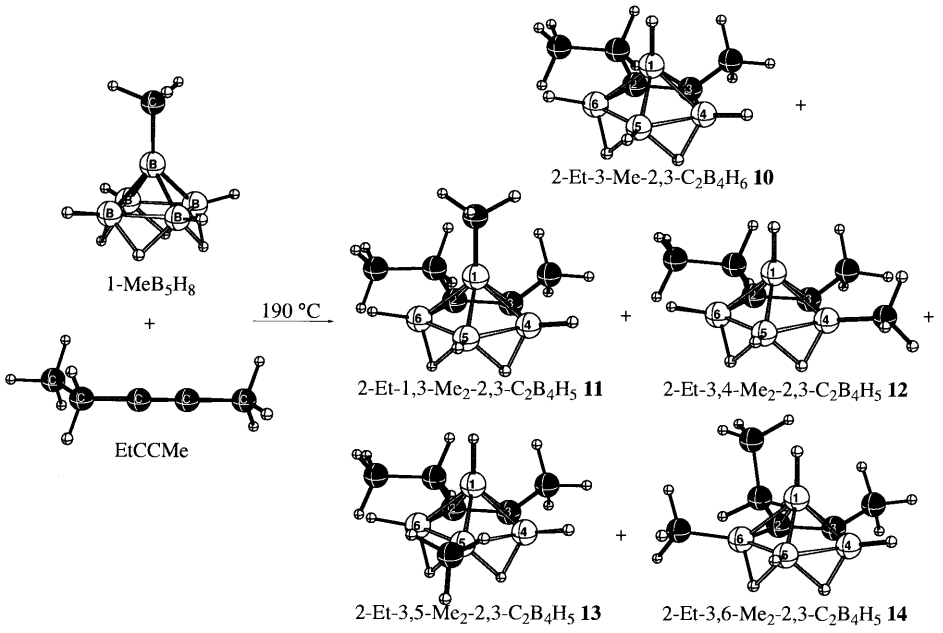

Fig. 3. The range of *nido*-carbahexaboranes from the reaction of EtC≡CMe and 1-MeB_5H_8 at 190°C.

1.8:1:1.5:1 (−37°C, 9%). A mixture of derivatives of 2-CB_5H_9 (−10°C, 0.5%) with mass cut-offs of *m*/*z* 146, and various alkyldiboranes was also obtained. No 2-MeB_5H_8 or volatile *closo*-$C_2B_5H_7$ derivatives were observed.

3. Computational details

The geometries of the structures shown in Figs. 1–4 were optimised at the MP2(fc)/6-31G* level (no imaginary frequencies were found at the HF/6-31G* level for all geometries) and for the geometries of carbaboranes **1**–**5** ^{11}B-NMR chemical shifts were computed at the GIAO-B3LYP/6-311G* level with the Gaussian 94 package [14]. The ^{11}B chemical shifts were referenced to B_2H_6, and $\delta(B_2H_6) = 16.6$ [15] was used for conversion to the experimental scale (i.e. relative to $BF_3 \cdot OEt_2$). Cartesian coordinates and absolute energies from the geometry optimisations at the //RMP2(fc)/6-31G* level of theory for structures shown in Figs. 1–4 are available as supplementary data.

4. Results and discussion

4.1. Carbaboranes from the reaction between MeC≡CH and 1-MeB_5H_8

All five expected *nido*-carbaboranes, comprising 2-Me–2,3-$C_2B_4H_7$ (**1**) [16] with a cut-off in the mass spectrum at *m*/*z* 90, and the four dimethyl derivatives of 2,3-$C_2B_4H_8$ (1,2-, 2,4-, 2,5- and 2,6-Me_2-2,3-$C_2B_4H_6$ (**2**–**5**), respectively), each with cut-offs in the mass spectra at *m*/*z* 104, were formed from the reaction between 1-MeB_5H_8 and MeC≡CH at 230°C. Compounds **3**, **4** and **5** were produced in a 0.9:1.0:0.8 ratio, but were not successfully separated by our low-temperature fractionation technique.

The ^{11}B signals in the high-field region were characteristic of apical boron atoms in *nido*-dicarbahexaboranes and were readily assigned to B1 [17]. The assignments of the resonances from boron atoms B5 in the ^{11}B{^{1}H} spectra of these compounds were also relatively straightforward because these signals were broadened compared with those of B4 and B6 [18,19]. To assign the resonances of boron atoms B4 and B6, and to confirm the other assignments, an ab initio/GIAO study was carried out on compounds **1**–**5**. ^{11}B-NMR chemical shifts for the carbaboranes **1**–**5**, calculated at the GIAO-B3LYP/6-311G*//MP2(fc)/6-31G* level, established the correct assignments of boron atoms B4 and B6, as indicated in Table 1. These results confirm that 2,4-Me_2-2,3-$C_2B_4H_6$ (**3**) is indeed

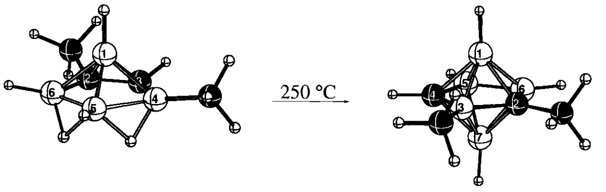

Fig. 4. Thermolysis at 250°C of the carbahexaborane derivative *nido*-2,4-Me_2–2,3-$C_2B_4H_6$ (**3**) is shown to give the *closo* heptaborane derivative 2,3-Me_2–2,4-$C_2B_5H_5$ (**7**).

Table 1
Experimental and calculated (GIAO-B3LYP/6-311G*//MP2(fc)/6-31G* in italics) ^{11}B-NMR chemical shifts for *nido*-carboranes **1**–**5**

	B1	B4	B5	B6
2-Me-2,3-$C_2B_4H_7$ (**1**)	−49.8 (*−54.6*)	−2.6 (*−4.6*)	0.1 (*−2.9*)	−3.1 (*−5.6*)
1,2-Me_2-2,3-$C_2B_4H_6$ (**2**)	−41.2 (*−45.9*)	−1.9 (*−3.4*)	0.5 (*−1.9*)	−2.4 (*−5.6*)
2,4-Me_2-2,3-$C_2B_4H_6$ (**3**)	−48.8 (*−53.4*)	7.7 (*6.4*)	−1.7 (*−4.1*)	−4.6 (*−6.7*)
2,5-Me_2-2,3-$C_2B_4H_6$ (**4**)	−48.8 (*−53.7*)	−3.3 (*−4.6*)	13.0 (*10.6*)	−3.3 (*−5.4*)
2,6-Me_2-2,3-$C_2B_4H_6$ (**5**)	−48.8 (*−53.6*)	−4.6 (*−6.5*)	−1.7 (*−4.0*)	6.3 (*4.4*)

produced in the gas-phase reaction of B_4H_{10} with ethyne.

The new *closo*-carbaheptaborane, 2,3-Me_2-2,4-$C_2B_5H_5$ (**7**), identified by NMR spectroscopy, is by far the most abundant of the four isomeric *closo*-carbaheptaboranes B,2-Me_2-2,4-$C_2B_5H_5$ (**6**–**9**) (all having cut-offs at *m*/*z* 114) produced from the reaction in minor amounts. They are presumed to arise from the thermolysis of *nido*-B,2-Me_2-2,3-$C_2B_4H_6$ derivatives. Interestingly *closo*-2-Me-2,4-$C_2B_5H_6$ (which would perhaps be expected to be formed from **1**) is not observed. In view of the fact that the attempted 'direct' preparations of *closo*-$C_2B_5H_7$ and 2,4-Me_2-2,4-$C_2B_5H_5$ from B_5H_9 with HC≡CH and MeC≡CMe at 300 and 285°C, respectively, were also unsuccessful [16], it would therefore appear that the methyl group at boron facilitates the formation of *closo*-$C_2B_5H_7$ derivatives.

4.2. Comments on earlier work

Thermolysis at 250°C of 2,4-Me_2-2,3-$C_2B_4H_6$ (**3**), thought at the time to be 2,3-Me_2-2,3,4-$C_3B_3H_5$, was reported to give a *closo*-B,2-Me_2-2,4-$C_2B_5H_5$ and a *nido*-C,B-Me_2-2,3,4-$C_3B_3H_5$ [6]. We now believe that the *closo* compound is 2,3-Me_2-2,4-$C_2B_5H_5$ (**7**) and that the *nido* product is, in fact, 2,5-Me_2-2,3-$C_2B_4H_6$ (**4**), present initially as an impurity. This conclusion is based on our earlier observation that **4** accompanies **3** as a minor isomer in the products from the reaction of B_4H_{10} and HC≡CH at 50°C [3].

Thus, it would appear that **7** is formed in the reaction of 1-MeB_5H_8 and MeC≡CH at 230°C from the decomposition of **3**, and that this reaction involves the direct preparation of *closo*-$C_2B_5H_7$ derivatives from alkynes and pentaboranes via a *nido*-$C_2B_4H_8$ derivative (Fig. 4). The first example of such a 'direct' preparation was achieved by a high-energy electric discharge of ethyne and pentaborane [20]. The preferred formation of **7** from **3** may also hold clues about the mechanism involved in the thermal conversion of 2,3-$C_2B_4H_8$ to 2,4-$C_2B_5H_7$ [21].

When 2,4-Me_2-2,3-$C_2B_4H_6$ (**3**) was thermolysed at the higher temperature of 300°C for 7 days it was reported to give two *closo*-Me_2-2,4-$C_2B_5H_5$ derivatives as volatile products [6]. At this same temperature, rearrangement of the *closo*-carbaheptaborane 3-Me-2,4-$C_2B_5H_6$ is known to produce an equilibrated mixture of 3-, 1- and 5-Me-2,4-$C_2B_5H_6$ in an approximate ratio of 5:5:3 [22]. On the reasonable assumption that the C(2)–Me linkage remains intact, we might therefore expect 2,3-Me_2-2,4-$C_2B_5H_5$ (**7**) to rearrange at 300°C to an equilibrated mixture of the four isomers, 2,3- **6**, 1,2- **7**, 2,5- **8** and 2,6- **9**, in a ratio of 5.0:5.0:1.5:1.5. It follows that the two *closo* derivatives reported from the thermolysis of 2,4-Me_2-2,3-$C_2B_4H_6$ (**3**) at 300°C are most probably **6** and **7**.

4.3. Carbaboranes from the reaction between EtC≡CMe and MeB_5H_8 at 190°C

The gas-phase reaction of EtC≡CMe and 1-MeB_5H_8 at 190°C gave 2-Et-3-Me-2,3-$C_2B_4H_6$ (**10**) as the major volatile product, together with minor amounts of the *nido*-dicarbahexaboranes **11**, **12**, **13** and **14**. These were identified by various boron and proton NMR experiments, including $^1H\{^{11}B\ \text{selective}\}-^1H$ subtraction and $^1H-^1H\{^{11}B\}$ COSY spectroscopy, and shown to be present in the mixture in a 1.8:1:1.5:1 ratio (Table 2). The spectroscopic data also confirm that the product from the gas-phase reaction of B_4H_{10} with propyne, originally thought to be 2-Et-3,4-Me_2-2,3,4-$C_3B_3H_4$, is in fact 2-Et-3,4-Me_2-2,3-$C_2B_4H_5$ (**12**); data for the latter have previously been reported [16].

The gas-phase reaction of B_5H_9 and MeC≡CMe was reported to give substantial yields of the *nido*-monocarbahexaboranes 3-Et-2-Me-2-CB_5H_7 and 4-Et-2-Me-2-CB_5H_7, as well as the major product, 2,3-Me_2-2,3-$C_2B_4H_6$ [23]. We therefore assume that the minor low-volatile product from the MeB_5H_8/EtC≡CMe reaction, with mass cut off of *m*/*z* 146 ($C_6B_5H_{19}$), is a mixture of trialkyl monocarbahexaboranes.

4.4. Proton NMR assignments in reported 4-alkyl-*nido*-dicarbahexaboranes

This study has enabled the proton NMR data reported for 4-($PhCH_2$)-2,3-Et_2-2,3-$C_2B_4H_5$ and 2,3,4-$(PhCH_2)_3$-2,3-$C_2B_4H_5$, generated from the reaction between $PhCH_2Br$ with the anions [2,3-Et_2-2,3-

Table 2
^{11}B- and ^{1}H-NMR data for new carbaboranes reported in this study[a]

	^{11}B[b]	^{1}H[c]
2	0.5 [d, 1 B, J_{BH_t} 165, B5], -1.9 [dd, 1 B, J_{BH_t} 152, J_{BH_μ} 50, B4], -2.4 [dd,1 B, J_{BH_t} 155, J_{BH_μ} 49, B6], -41.2 [s, 1 B, B1]	6.10 [s, 1 H, C3H], 3.64 [s, 1 H, B5H], 3.31 [s, 1H, B4H, 3.25 [s 1 H, B6H], 2.18 [s, 3 H, C2CH$_3$], -0.58 [s, 3 H, B1CH$_3$], -1.75 [s 1H, H_μ4/5]
5	6.3 [d, 1 B, J_{BH_t} 49, B6], -1.7 [d, 1 B, J_{BH_t} 150, B5], -4.6 [dd, 1 B, J_{BH_t} 154, J_{BH_μ} 48, B4], -48.8 [d, 1 B, J_{BH_t} 177, B1]	5.94 [s, 1 H, C3H], 3.44 [s, 1 H, B5H], 3.14 [s, 3H, C2CH$_3$, 0.59 [s 3 H, B6CH$_3$], -0.90 [s, 1 H, B1H], -1.56 [s 1H, H_μ5/6], -1.99 [s 1H, H_μ4/5]
6[d]	8.8 [d, 1 B, J_{BH_t} 182, B3], 7.2 [d, 1 B, J_{BH_t} 170[e], B6], 4.1 [d, 1 B, J_{BH_t} 170[e], B5], -10.0 [s, 1 B, B 1], -25.1 [d, 1 B, J_{BH_t} 176[e], B7]	
7	13.8 [s, 1 B, B3], 5.5 [d, 1 B, J_{BH_t} 150[e], B5], 2.0 [d, 1 B, J_{BH_t} 155[e], B6], -18.6 [d, 2 B, J_{BH_t} 175, B 1, B7]	5.18 [s, 1H, C4H], 4.00 [s, B5H, B6H], 2.08 [s, 3H, C2CH$_3$], 0.92 [s, 3H, B3CH$_3$], 0.23 [s, 2H, B1H, B7H]
10	-1.8 [d, 1 B, J_{BH_t} 157, B5], -3.9 [dd, 1 B, J_{BH_t} 155, J_{BH_μ} 55, B4], -4.4, [dd, 1B, J_{BH_t} 154, J_{BH_μ} 56, B6], -47.4 [d, 1 B, J_{BH_t}, 178, B 1]	3.52 [s, 1H, B5H], 3.28 [s, 1 H, B4H], 3.25 [s, 1 H, B6H], 2.47 (dq, 1 H, $^2J_{HH}$14,[e] $^3J_{HH}$7,[e] CH_aH_b), 2.33 (dq, 1 H, $^2J_{HH}$ 14,[e] $^3J_{HH}$7,[e] CH_aH_b), 2.09 [s, 3 H, C3CH$_3$], 1.21 (t, 3 H, $^3J_{HH}$7,[e] $CH_aH_bCH_3$), -0.88 [s, 1 H, B1H], -2.16 [s 1H, H_μ5/6], -2.17 [s 1H, H_μ4/5]
11	-0.8 [d, 1 B, J_{BH_t} 165, B5], -3.9 [dd, 1 B, J_{BH_t} 152, J_{BH_μ} 50, B4], -3.9 [dd, 1 B, J_{BH_t} 155[e], J_{BH_μ} 50[e], B6], -39.4 [s, 1 B, B 1]	3.57 [s, 1H, B5H], 3.18 [s, 2 H, B4H, B6H], 2.35 (q[f], 2, $^3J_{HH}$7,[e] CH_aH_b), 1.99 [s, 3H, C3CH$_3$], 1.18 (t, 3 H, $^3J_{HH}$7,[e] CH_2CH_3) -0.64 [s, 3 H, B1CH$_3$], -1.79 (s, 2 H, H_μ)
13	11.3 [s, 1 B, B5], -4.8 [dd, 2 B, J_{BH_t} 145[e], J_{BH_μ} 50[e], B4, B6], -46.2 [d, 1B, J_{BH_t} 179, B1]	3.11 [s, 2 H, B4H, B6H], 2.43 (q[f], 2, H, $^3J_{HH}$7,[e] CH_aH_b), 2.03 [s, 3H, C3CH$_3$], 1.24 (t, 3 H, $^3J_{HH}$7,[e] CH_2CH_3)-0.90 [s, 1 H, B1H], -1.54 (s, 2 H, H_μ)
14	5.2 [d, 1 B, J_{BH_t} 45[e], B5], -3.1 [d, 1 B, J_{BH_t} 150[e], B5], -6.3 [dd, 1 B, J_{BH_t} 155[e], J_{BH_μ} 50[e], B4], -42.2 [d, 1 B, J_{BH_t} 179, B 1]	3.29 [s, 1 H, B5H], 3.05 [s, 1 H, B4H], 2.40 (q[f], 2, H, $^3J_{HH}$7,[e] CH_aH_b), 2.03 [s, 3H, C3CH$_3$], 1.22 (t, 3 H, $^3J_{HH}$7,[e] CH_2CH_3), -0.90 [s, 1 H, B1H], -1.65 [s 1H, H_μ5/6], -2.08 [s 1H, H_μ4/5]

[a] NMR data for **1**, **3**, **4** and **12** have been reported [2,3,16]. Limited NMR data for **8** and **9**: -19.5 ppm (B 1,7) in the ^{11}B-NMR spectrum of **6**.

[b] 128 MHz; in CDC1$_3$ at -50°C (external reference $BF_3{\cdot}Et_2O = 0.00$ ppm).

[c] 400 MHz; in CDC1$_3$ at -50°C ($SiMe_4 = 0.00$ ppm)

[d] ^{1}H-NMR data for **6** not obtained

[e] Values uncertain due to peak overlap or poorly resolved peaks

[f] Apparent pattern.

$C_2B_4H_5]^-$ and $[2,3\text{-}(PhCH_2)_2\text{-}2,3\text{-}C_2B_4H_5]^-$, respectively [24], to be fully assigned. Details are given below [25,26].

5. Summary and conclusions

The gas-phase reactions of 1-methylpentaborane with propyne and 2-pentyne have been found to give alkyl derivatives of *nido*-$C_2B_4H_8$ as the major volatile products. Characterisation of these species by detailed NMR techniques has shown that 2,4-Me$_2$-2,3-$C_2B_4H_6$ (**3**) (not **5**) is produced in the gas-phase reaction between HC≡CH and B_4H_{10}, and that 2-Et-3,4-Me$_2$-2,3-$C_2B_4H_5$ (**12**) is produced in the MeC≡CH/B_4H_{10} reaction. In addition, the results presented here will aid identification of other 4-substituted *nido*-$C_2B_4H_8$ derivatives in the future. The study has also revealed that the reaction of 1-MeB$_5$H$_8$ with propyne at 230°C leads to the 'direct' preparation of *closo*-$C_2B_5H_7$ derivatives from alkyne and pentaborane, and that this occurs via a 2,3-$C_2B_4H_8$ intermediate. Thermolysis of the *nido*-carbahexaborane 2,4-Me$_2$-2,3-$C_2B_4H_6$ (**3**) is shown to produce predominantly *closo*-2,3-Me$_2$-2,4-$C_2B_5H_5$ (**7**) at 230–250°C.

Acknowledgements

We thank the Engineering and Physical Sciences Research Council for financial support (M.A.F.). The computational work was initiated and partly carried out at the University of Erlangen-Nürnberg.

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[26] Assigned ^{1}H-NMR data for 2,3,4-$(PhCH_2)_3$-2,3-$C_2B_4H_5$; 7.13 (m, 15, ArH), 3.89 (s*, 2; $C_3H_aH_b$), 3.80 (dq, 1, $^2J_{HH} \sim 14$ Hz; $C2CH_aH_b$), 3.65 (d, 1, $^2J_{HH} \sim 14$ Hz; $C2CH_aH_b$), 2.63 (s*, 2; CH_aH_bPh), -0.6 (q, 1; B1H), -1.35 (s, 1; $H_\mu(4,5)$), -2.05 (s, 1; $H_\mu(5,6)$). *Apparent patterns of the non-equivalent methylene protons, B5H and B6H are assumed as quartets at ca. 3 ppm.