Quenched gas-phase reactions of tetraborane(10), B_4H_{10}, with substituted alkynes: new *nido*-dicarbapentaboranes and *arachno*-monocarbapentaboranes‡

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New alkyl derivatives of the *nido*-dicarbapentaborane, 1,2-$C_2B_3H_7$, and *arachno*-carbapentaborane, 1-CB_4H_{10}, have been identified as the main volatile carbaborane products in quenched gas-phase reactions of tetraborane(10), B_4H_{10}, with alkyl-substituted ethynes RC≡CR′ (R = Me, Et, ^{n}Pr or ^{t}Bu, R′ = H; R = Me or Et, R′ = Me). The gaseous mixtures were heated at 70°C, and monitored by gas-phase mass spectrometry. Each reaction was quenched when the ethyne was used up. The quenched gas-phase reaction of B_4H_{10} and $Me_3SiC≡CH$ gave a single volatile carbaborane product, 1-Me_3Si-1,2-$C_2B_3H_6$.

Introduction

Polyhedral carbaboranes (carboranes) have long been synthesised from reactions of binary boranes with alkynes.[1] A widely-used synthesis involves the treatment of decaborane(14), $B_{10}H_{14}$, with a substituted alkyne RC≡CR′ in the presence of Lewis base to form the *closo*-carbaborane 1-R-2-R′-1,2(*ortho*)-$C_2B_{10}H_{10}$.[2] A less common route, in which pentaborane(9), B_5H_9, is used in place of $B_{10}H_{14}$ generally affords the carbaborane *nido* 2-R-3-R′-2,3-$C_2B_4H_6$.[3] However, the B_5H_9/alkyne system can also yield different carbaborane products such as small *closo*-carbaboranes if gas-phase conditions are used.[4,5]

Not long after these carbaboranes were first discovered, some 40 years ago, Grimes and co-workers reported a series of complex reactions of tetraborane(10), B_4H_{10}, with alkynes.[6-15] Many new carbaboranes were discovered from the gas-phase reactions of B_4H_{10} with ethyne HC≡CH. These reactions have also been explored more recently in Leeds. [16-19] The reactions were of three types, and the major carbaborane product in each case is shown below:

1) High-energy (‘Flash’) reaction[6,7,16,17]

$$B_4H_{10} + HC{\equiv}CH \xrightarrow{100^oC,\ \text{‘Flash’}} \textit{closo}\text{-}2,4\text{-}C_2B_5H_7\ (<1\%\ \text{yield})$$

2) Completed reaction[6,8-19]

$$B_4H_{10} + HC{\equiv}CH \xrightarrow{25\text{-}70^oC,\ 3\ \text{days}} \textit{nido}\text{-}2,4\text{-}Me_2\text{-}2,3\text{-}C_2B_4H_6\ \ (7\%)$$

3) Quenched reaction[10,13,19]

$$B_4H_{10} + HC{\equiv}CH \xrightarrow{25\text{-}70^oC,\ 20\text{-}60\ \text{min}} \textit{nido}\text{-}1,2\text{-}C_2B_3H_7\ (25\%)$$

Grimes, Bramlett and Vance[7,9] and the Leeds group[16,17,18] have also investigated the flash and completed gas-phase reactions of B_4H_{10} with propyne and 2-butyne under similar reaction conditions (see reactions 4 and 5 below), and Grimes and Ledoux have explored the completed gas-phase reaction of B_4H_{10} with trimethylsilylethyne - no volatile carbaborane product was obtained from this latter reaction.[14]

4) High-energy (‘Flash’) reactions[7,17]

$$B_4H_{10} + MeC{\equiv}CH \rightarrow \textit{closo}\text{-}2\text{-}Me\text{-}1,5\text{-}C_2B_3H_4\ (<1\%)$$
$$B_4H_{10} + MeC{\equiv}CMe \rightarrow \textit{closo}\text{-}2,3\text{-}Me_2\text{-}1,5\text{-}C_2B_3H_3\ (<1\%)$$

5) Completed reactions[9,18]

$$B_4H_{10} + MeC{\equiv}CH \rightarrow \textit{nido}\text{-}2\text{-}Me\text{-}2,3\text{-}C_2B_4H_7\ (8\%)$$
$$B_4H_{10} + MeC{\equiv}CMe \rightarrow \textit{nido}\text{-}2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_4H_6\ (10\%)$$

It is clear from these abridged equations that the gas-phase reactions of tetraborane(10) with ethynes are complex, with evidence of triple-bond cleavage having occurred in the formation of some of the products.† The methyl-substituted ethynes clearly yield carbaborane products that are quite different from those formed by the unsubstituted ethyne. Of the reactions listed, the highest yield of a volatile carbaborane product was obtained from the quenched gas-phase reactions of tetraborane(10) with ethyne, the *nido*-1,2-dicarbapentaborane, 1,2-$C_2B_3H_7$, being formed in *ca* 25% yield based on B_4H_{10} consumed. By contrast, 1,2-$C_2B_3H_7$, is not observed when the gas-phase reaction of B_4H_{10} and ethyne proceeds to completion.

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† The abridged equations above do not include other carborane products formed and may appear misleading. For example, a series of alkyl derivatives of $C_2B_3H_5$, $C_2B_4H_6$ and $C_2B_5H_7$ is also formed from the flash reaction of tetraborane(10) with ethyne with a total carborane yield of just above 3%.

The dicarbaborane decomposes or reacts rapidly in the presence of B_4H_{10} to give 2-$MeCB_5H_8$ and solids and reacts slowly with ethyne to give $C_4B_2H_6$ and solids;[15] it is stable in the gas-phase at 50ºC but decomposes in the liquid phase to form a white solid. From these observations it is concluded that 1,2-$C_2B_3H_7$ is not an intermediate in the formation of the major carbaborane products observed when the reaction of B_4H_{10} and ethyne is allowed to go to completion. This *nido*-carbaborane and the closely related phosphacarbaborane[20] 2-^{t}Bu-1,2-PCB_3H_5 are the only known heteroborane analogues of *nido*-pentaborane(9), B_5H_9. Remarkably, no derivatives of the *nido*-5-vertex carbaborane 1,2-$C_2B_3H_7$ have been reported.

Prior to our work at Leeds, quenched gas-phase reactions of B_4H_{10} with alkynes other than ethyne had not been reported. Here we discuss the most volatile carbaborane products identified in these quenched gas-phase reactions, which include the first derivatives of the *nido*-5-vertex carbaborane. Parts of this work have been reported in a communication and in conference proceedings elsewhere.[21,22]

Results and Discussion

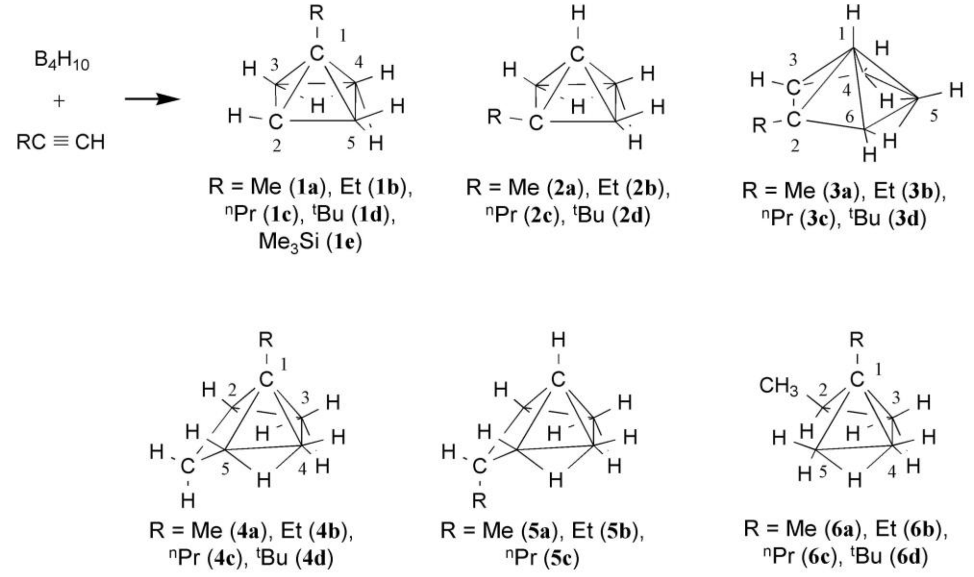
Our earlier study[19] of the quenched reaction of B_4H_{10} and ethyne established that the optimum conditions for convenience and maximum carbaborane yield involved an ethyne : tetraborane(10) ratio of 2 : 1 and a reaction temperature of 70ºC. An increase in the ratio led to an increase in the reaction time and to decomposition of the unstable carbaboranes, whereas a lower ratio resulted in a substantial amount of unreacted B_4H_{10}. Lowering the temperature also increased the reaction time, and raising it increased the likelihood of a flash reaction. The need to limit the pressure in the mass spectrometer imposed an upper limit of ca. 7.5 mmHg on the vapour pressure of the gaseous mixture in the 1-litre reaction vessel. In the work reported here, the quenched reactions and subsequent cold column fractionations of the collected volatiles were therefore each repeated many times to obtain adequate amounts of material for high field NMR spectroscopy.

Hydrogen and diborane were observed in all reactions but B_5H_{11}, the major decomposition product of B_4H_{10}, was absent. Peaks corresponding to the ethenes that might have been formed as a result of hydrogenation of the ethynes during the reaction were not observed. Carbaboranes of relatively low volatility, formed from tetraborane(10) and two ethyne molecules, were identified and will be discussed in detail elsewhere together with related carbaboranes formed from reactions of tetraborane(10) with ethyne and enynes.[19,23] White polymeric solids were produced in all reactions, but were not investigated further.

Quenched gas-phase reaction of B_4H_{10} with propyne

The most volatile carbaborane products in the quenched reaction of MeC≡CH and B_4H_{10} were separated by cold-column fractionation, and in order of decreasing volatility were found to have mass cut-offs of m/z 78, 90, 92 and 93. The fraction exhibiting a cut-off at m/z 78 was found, by high resolution accurate mass data and detailed NMR spectroscopy (Scheme 1), to be a 1:3 mixture of the isomers, 1-Me- and 2-Me-1,2-$C_2B_3H_6$ **1a** and **2a**. The accurate mass cut-off for this mixture was 78.0986 which is in very good agreement with the calculated value of 78.0983 for the formula $C_3B_3H_9$.

The boron-11 NMR data for the new *nido*-dicarbapentaboranes revealed four peaks, at -11.3, -13.4, -13.5 and -19.4 ppm (Figure 1). The 2D boron-11 COSY spectrum showed cross peaks between -11.3 and -13.4 and between -13.5 and -19.4 ppm. The intensities of these pairs of peaks are in a ratio of 2:1 corresponding to B(3,5) and the unique B(4) borons respectively. In the proton-coupled spectrum, the B(3,5) peaks



Scheme 1

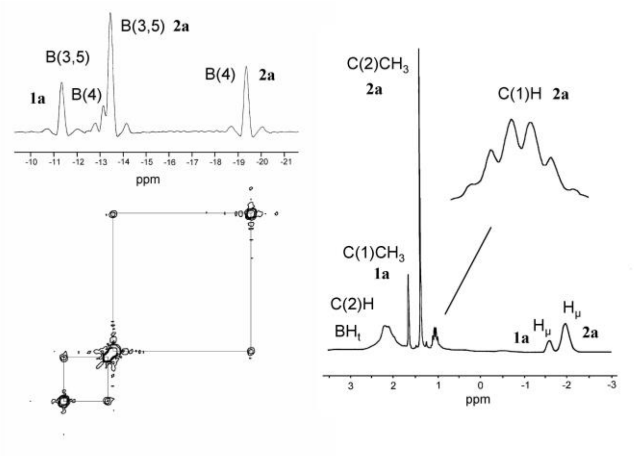
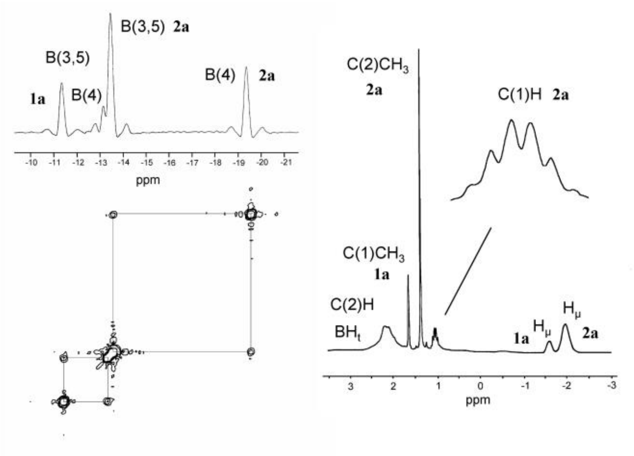


Figure 1. Boron-11 and proton NMR spectra of a 1:3 mixture of $MeC_2B_3H_6$ isomers **1a** and **2a**



substituted pentaboranes. A second fraction from the quenched reaction of MeC≡CH and B_4H_{10}, with a mass cut-off of 90, was identified, by comparison of the NMR data with literature values, as the known[28] 2-Me-2,3-$C_2B_4H_7$ **3a** . The Me-C-C-H link in propyne is retained in the formation of these *nido*-carbaboranes.

The third fraction (nominal mass cut-off m/z 92) was investigated by accurate mass measurements and detailed NMR spectroscopy. It was found to have an accurate mass cut-off of 92.1309 which agrees very well with the calculated value of 92.1311 for the formula $C_3B_4H_{12}$. This compound was originally isolated from the hot/cold reaction of B_4H_{10} with propyne and incorrectly identified at the time as a *hypho*-tricarbaheptaborane, $C_3B_4H_{12}$.[29] It is, in fact, an *arachno*-monocarbapentaborane of type CB_4H_{10} with a methyl group and a CH_2 bridge, and is best represented by the formula 1-Me-2,5-μ-CH_2-1-CB_4H_7 **4a**. Figure 2 shows the correct boron and proton NMR assignments for **4a**. This re-interpretation of the $C_3B_4H_{12}$ carbaborane was supported by our subsequent findings in quenched reactions of B_4H_{10} with propyne, and with 1- and 2-butyne, and by ab initio/NMR computations carried out by Hofmann and Schleyer.[21] Many *arachno*-monocarbapentaboranes of type 1-CB_4H_{10} with a bridge between B2 and B5 have since been reported.[30-,33] It is notable that the formation of **4a** involves cleavage of the triple bond present in the propyne, whereas this bond remains intact in the formation of **1a**, **2a** and **3a**.

A minor isomer often observed in the fraction of **4a** and was identified as 2,5-μ-*endo*-MeCH-1-CB_4H_8 **5a** on the basis of ab initio computations carried out elsewhere. The relative amounts of **4a** and **5a** varied between 5:1 and 40:1 for different samples collected from repeated reactions and fractionations. These carbaboranes were found to decompose or rearrange in minutes on warming to room temperature in chloroform or toluene, as monitored by boron and proton NMR spectroscopy. The fact that compound **4a** undergoes these transformations more rapidly than **5a** may explain why variations in the **4a**:**5a** ratio are observed from sample to sample. We have not yet succeeded in identifying the carbaborane products obtained by warming the unstable carbaboranes **4a** and **5a**, despite having a considerable NMR database on volatile boranes and carbaboranes. However, it has been shown elsewhere[33] that thermolysis of a similar equivalent (Scheme 2). The proton-decoupled boron-11 NMR data for this compound at room temperature reveal three peaks in the ratio 1:1:2, which on proton coupling give a sextet and two sets of doublets of sextets (Figure 3). The sextets arise from

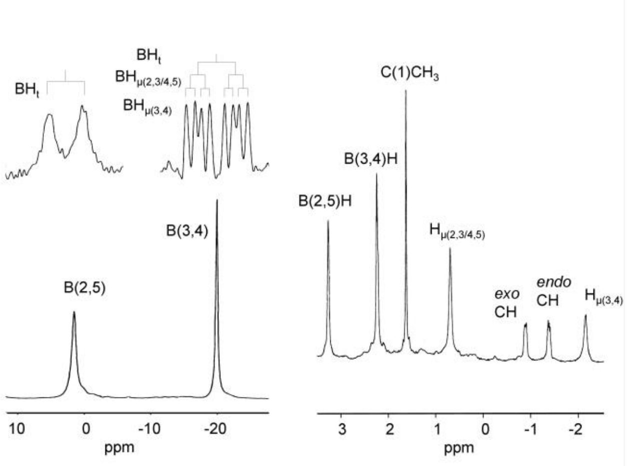
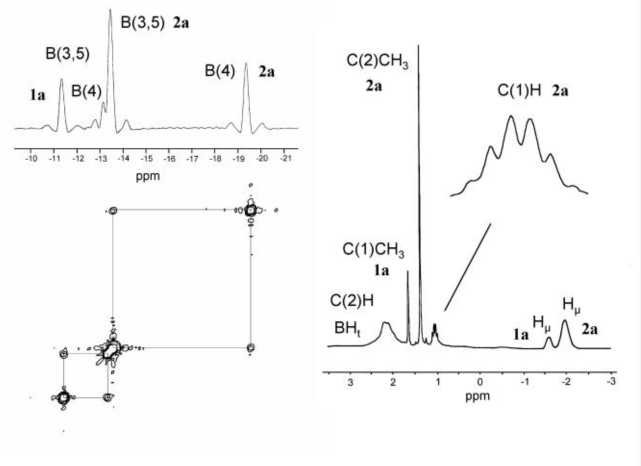
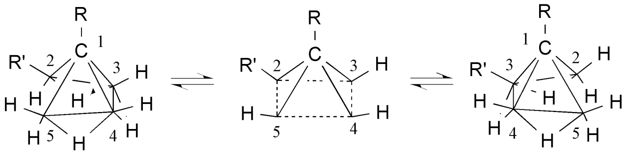


Figure 2. Boron and proton NMR spectra of 1-Me-2,5-μ-CH_2-1-CB_4H_7 **4a**



coupling with five fluxional hydrogens and the doublets are from coupling with the non-fluxional terminal hydrogens. Lowering the temperature from 297 K to 223 K leads to peak broadening in the ^{11}B NMR spectrum (recorded in toluene), with retention of the 1:1:2 pattern. Further lowering to 197 K gives a different peak pattern suggesting that a mixture of 2-Me- and 3-Me-1-Me-1-CB_4H_8 is present, which in theory would give 8 unique boron peaks – of equal intensities assuming a 1:1 mixture (Figure 3). Proton NMR data on **6a** show two singlets of equal intensity at 1.29 and 0.49 ppm. The latter peak sharpens on boron decoupling and is assigned to a methyl group attached to boron. Compound **6a** is also formed from the quenched gas-phase reaction of B_4H_{10} and allene, CH_2=C=CH_2, and supported by ab initio computations.[34] As in the cases of **4a** and **5a**, the formation of **6a** indicates that the triple bond from the propyne is cleaved.



All five *endo* and bridging hydrogens are scrambled rendering two equivalent BH groups observed by NMR spectroscopy in solution at RT

Scheme 2

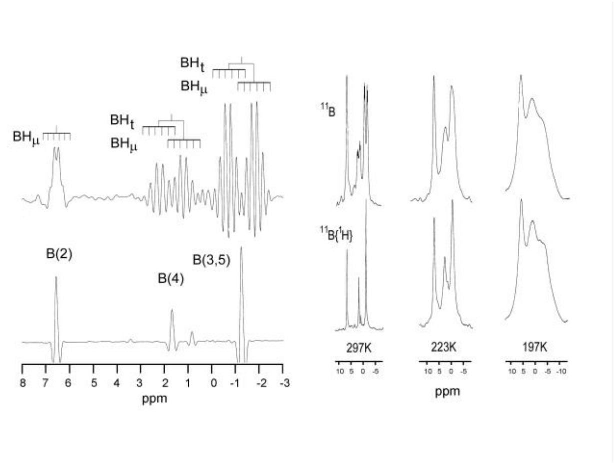


Figure 3. Boron NMR spectra of the fluxional 1-Me-B-CH_3-1-CB_4H_8 **6a**

Mass and proton NMR spectra of the products from the quenched reaction of B_4H_{10} with the partially deuterated propyne MeC≡CD showed that all these volatile carbaboranes retain a C-D bond. The proton spectrum of deuterated **3a** was consistent with a 1 : 1 mixture of 2,5-μ-*exo*-DCH- and 2,5-μ-*endo*-DCH-1-Me-1-CB_4H_7.

Quenched gas-phase reactions of B_4H_{10} with other alkynes

The most volatile products from the quenched reactions of B_4H_{10} with 1-butyne and 1-pentyne are analogous to those from the quenched reaction of B_4H_{10} with propyne (Scheme 1). The yields of the carbaborane products are listed in Table 1 together with the ratios of isomers for the $C_2B_3H_7$ derivatives obtained. These latter derivatives decompose rapidly in neat liquid states and slowly in solutions on warming to ambient temperature.

The quenched reaction of B_4H_{10} with 2,2-dimethyl-3-butyne, ^{t}BuC≡CH, gave the best yields of the dicarbapentaborane isomers, 1-^{t}Bu- and 2-^{t}Bu-1,2-$C_2B_3H_6$, and the bridging *arachno*-carbapentaborane, 1-^{t}Bu-2,5-μ-CH_2-1-CB_4H_7, but the other expected carbaboranes 2-^{t}Bu-2,3-$C_2B_4H_7$, 2,5-μ-^{t}BuCH-1-CB_4H_8 and B-Me-1-^{t}Bu-1-CB_4H_8 were either obtained in very small amounts or were completely absent. The differences in the yields of the products obtained from ^{t}BuC≡CH compared to other alkyl ethynes, RC≡CH, (Table 1) may be attributed to the effect of the bulky tertiary butyl group. Whereas *nido*-C_2B_4 derivatives have been synthesised from reactions of B_5H_9 with various alkynes, the unknown derivative *nido*-2,3-^{t}Bu$_2$-2,3-$C_2B_4H_6$ was not obtained from B_5H_9 and ^{t}BuC≡C^{t}Bu.[35] A minor volatile product, identified as the known[36] basket compound 2,4-(μ-^{t}BuCHCH$_2$)B_4H_8, is probably formed from 2,2-dimethyl-3-butene and B_4H_{10} present during the reaction. The bridged carbaborane 1-^{t}Bu-2,5-μ-CH_2-1-CB_4H_7 remained unchanged at room temperature in solution, as indicated by NMR spectroscopy, suggesting that this species is more stable than the other 1-R-2,5-μ-CH_2-1-CB_4H_7 compounds discussed here – an observation that is consistent with the higher

Table 1. Yields of volatile carbaboranes in percentage of total volatile carbaborane fraction and actual yields in brackets.

	1-R-1,2-$C_2B_3H_6$: 2-R-1,2-$C_2B_3H_6$ Isomer Ratio (**1**:**2**)	1,2-$C_2B_3H_7$ type (**1,2,7,8**)	2,3-$C_2B_4H_8$ type (**3,9**)	2,5-μ-CH_2-1-CB_4H_8 type (**4,5,10,11,12**)	1-CB_{10} type (**6,13**)
MeC≡CH	25 : 75	52 [7%]	11 [1.5%]	15 [2%]	7 [1%]
EtC≡CH	35 : 65	56 [8%]	11 [1.5%]	10 [1.5%]	12 [1.5%]
^{n}PrC≡CH	40 : 60	56 [8%]	14 [2%]	3 [0.5%]	14 [2%]
^{t}BuC≡CH	45 : 55	59 [12%]	0.5 [0.1%]	35 [7%]	0.5 [0.1%]
MeC≡CMe	-	39 [6%]	20 [3%]	26 [4%]	7 [1%]
EtC≡CMe	65 : 35[a]	45 [7%]	19 [3%]	26 [4%]	6 [1%]
Me_3SiC≡CH	100 : 0	100 [12%]	-	-	-
HC≡CH[b]	-	90[c] [25%]	0.5[d] [0.1%]	-	-
H_2C=C=CH_2[e]	-	-	-	89[f] [11%]	7[g] [1%]

[a]For 1-Et-2-Me-1,2-$C_2B_3H_5$ (**7b**): 1-Me-2-Et-1,2-$C_2B_3H_5$ (**8b**), [b]Reference 19 [c]1,2-$C_2B_3H_7$ [d]2,3-$C_2B_4H_8$ [e]Reference 34 [f]**4a**,**5a** [g]**6a**

yield obtained for the butyl derivative.

Products from the quenched reactions of B_4H_{10} with 2-butyne and 2-pentyne are depicted in Scheme 3, where two isomers of the bridged *arachno*-carbapentaboranes are identified. In the products from 2-butyne, the methyl group at the bridge exists in both *exo*- and *endo*- forms. The *exo*-isomer 1-Me-2,5-μ-*exo*-MeCH-1-CB_4H_7 **11a** is the minor isomer and is the only *exo*-isomer of the 1-R-2,5-μ-R′CH-1-CB_4H_7 type that is positively identified here and supported by computations reported elsewhere.[21] In the products from 2-pentyne, the methyl (**10b**) or ethyl (**12b**) group at the bridge exists in the *endo* position, with the former as the major isomer.

The quenched gas-phase reaction of tetraborane(10) with $Me_3SiC{\equiv}CH$ gave only one volatile carbaborane product, characterised by a mass cut-off at m/z 136 and a dominant peak at m/z 73 (Me_3Si^+). This product was identified by NMR spectroscopy as 1-Me_3Si-1,2-$C_2B_3H_6$ for which the B(4) peak value differs little from that of the parent carbaborane, 1,2-$C_2B_3H_7$; thus no 'trans' effect[27] is observed. The other possible isomer, 2-Me_3Si-1,2-$C_2B_3H_6$, was not present in the fractions collected.

Discussion of Results

Table 1 lists products obtained from the quenched gas-phase reactions carried out in this study, together with their yields. The quenched gas-phase reactions of B_4H_{10} with ethyne[19] and with allene[34] are included for comparison. Whereas ethyne gives the *nido*-carbapentaborane $C_2B_3H_7$ as the major product and *nido*-dicarbahexaborane $C_2B_4H_8$ as a minor product on reaction with B_4H_{10}, allene affords only bridged and fluxional *arachno*-carbapentaboranes as volatile carbaboranes. The reactions of B_4H_{10} with alkyl ethynes on the other hand result in all four carbaboranes as major volatile carbaborane products.

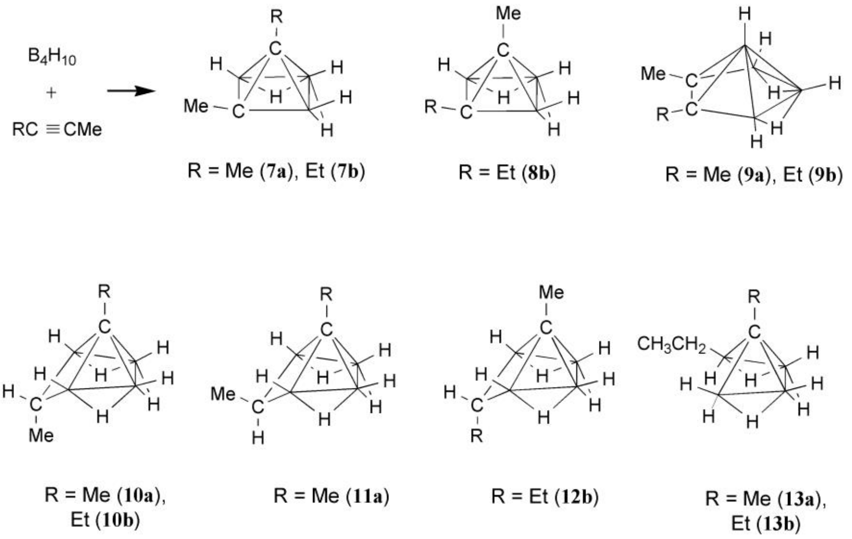
From gas-phase kinetic studies at 70°C, it is known that tetraborane(10) dissociates initially to the non-isolable intermediate $\{B_4H_8\}$ and H_2.[37,38] With ethenes, B_4H_{10} gives high yields of 'basket' compounds 2,4-μ-(RCHCHR′)B_4H_8, via the subsequent reaction of $\{B_4H_8\}$ with RCH=CHR′.[39,40,41] The mechanisms were corroborated by theoretical computations on the proposed reaction pathways.[42] Minor basket products were also present in which a second ethene molecule appears to have been hydroborated by B_4H_{10} to form an alkyl group –$RCHCH_2R$, since the basket compound formed initially does not give such products with ethenes.

The low yields of the volatile carbaborane products from reactions of B_4H_{10} and ethynes reported here, in contrast to high yields of the basket products from B_4H_{10} with ethenes, suggest that many pathways to different carbaborane products exist. From the results of Grimes's gas-phase kinetic study[10] on the thermolysis of B_4H_{10} with ethyne it seems likely that $\{B_4H_8\}$ formed initially from B_4H_{10} then reacts with an ethyne molecule to yield an intermediate $\{C_2B_4H_{10}\}$.

Depending on the path taken, $\{C_2B_4H_{10}\}$ may

a) lose a $\{BH_3\}$ intermediate to give $C_2B_3H_7$,
b) lose H_2 to form $C_2B_4H_8$ or
c) react with a second ethyne molecule to give an intermediate $\{C_4B_4H_{12}\}$

An alternative route to $C_2B_3H_7$ from the reaction of $\{B_3H_7\}$ and ethyne was proposed by McKee in the first of his theoretical investigations into the complex reaction pathways of tetraborane(10) with unsaturated hydrocarbons.[43] However, on the basis of experimental work, $\{B_3H_7\}$ is not considered to be present in the initial stages of the thermolysis of B_4H_{10}.[38] The triborane carbonyl B_3H_7CO, a precursor to $\{B_3H_7\}$, gives a high energy 'flash' reaction at -20°C with ethyne, resulting in several *closo*-carbaborane products from which $C_2B_3H_7$ may well be formed as an intermediate. McKee's second theoretical paper[44] supports the formation of $\{C_2B_4H_{10}\}$ from the reaction of $\{B_4H_8\}$ and ethyne and also the removal of $\{BH_3\}$ from $\{C_2B_4H_{10}\}$ to give $C_2B_3H_7$.



Scheme 3

The quenched reaction of B_4H_{10} with allene to give two distinct *arachno*-monocarbapentaboranes (bridged and fluxional) resembles the reaction of B_4H_{10} with ethene, in that reactions of $\{B_4H_8\}$ and of B_4H_{10} with the unsaturated hydrocarbon both occur. The major difference between the two routes is the necessary cleavage of the double bond in the allene to yield the carbaboranes. A very recent theoretical investigation into the pathways for the reaction of B_4H_{10} with allene to form the carbaboranes supports these comments, but the complexity of the mechanism is reflected in the fact that 44 transition states were located![45]

Both distinct mechanisms in the reactions of B_4H_{10} with ethyne and of B_4H_{10} with allene probably occur in the quenched reactions reported here of B_4H_{10} with alkyl ethynes. The initial intermediate $\{RR'C_2B_4H_8\}$ formed from $\{B_4H_8\}$ and $RC{\equiv}CR'$ may follow four distinct pathways.

a) lose a $\{BH_3\}$ intermediate to give $RR'C_2B_3H_5$,
b) lose H_2 to form $RR'C_2B_4H_6$
c) cleave the triple bond during rearrangement into the bridging *arachno* carbaborane 1-R-2,5-CHR′-1-CB_4H_7 or
d) react with a second ethyne molecule to give an intermediate $\{R_2R'_2C_4B_4H_8\}$

Two observations suggest that pathway (d) may well be dominant. Firstly, for all gas-phase reactions reported here at 70°C (for which the alkyne:B_4H_{10} ratio was 2:1) the alkyl ethyne is used up before the B_4H_{10}. Secondly, on the basis of the low yields of the volatiles, it would seem that most of the boron consumed is incorporated into the non-volatile solids. The stable fluxional *arachno*-carbaborane B-CH_2R'-1-R-1-CB_4H_8 is presumably formed by hydroboration of B_4H_{10} with $RC{\equiv}CR'$ to give an intermediate $\{RR'C_2B_4H_{10}\}$ which then rearranges with cleavage of the triple bond.

In contrast to the many volatile carbaborane products obtained from the tetraborane(10) - alkyl ethyne reactions described here, only a single volatile product, 1-Me_3Si-1,2-$C_2B_3H_6$, was obtained from the quenched gas-phase reaction of B_4H_{10} and $Me_3SiC{\equiv}CH$. Interestingly, the time needed for the $Me_3SiC{\equiv}CH$ to be used up in the reaction was about 35 minutes – somewhat longer than the reaction times for the quenched tetraborane(10) – alkyl ethyne reactions (22 – 30 minutes) under near identical reaction conditions. Ethyne took a little longer (*ca*. 40 minutes) to disappear. These observations suggest that $Me_3SiC{\equiv}CH$ behaves like an ethyne rather than an alkyl ethyne in reactions with tetraborane(10), as other volatile carbaboranes that might have been expected (such as 1-Me_3Si-2,5-μ-CH_2-1-CB_4H_7 and B-CH_3-1-Me_3Si-1-CB_4H_8 and the known carbaborane 2-Me_3Si-2,3-$C_2B_4H_7$) are not observed.

The observation of only one isomer of $Me_3SiC_2B_3H_6$ from the reaction of $Me_3SiC{\equiv}CH$ with B_4H_{10} contrasts with the observation of a mixture of $RC_2B_3H_6$ isomers from the alkyl ethynes $RC{\equiv}CH$ listed in Table 1. More intriguing is the fact that the 1-isomer is identified for $Me_3SiC_2B_3H_6$, whereas the major components in all $RC_2B_3H_6$ compounds are identified as the 2-isomers. The pentaboranes $Me_3SiB_5H_8$ and MeB_5H_8 (closely related to $Me_3SiC_2B_3H_6$ and $MeC_2B_3H_6$ respectively) have been reported to undergo thermal rearrangements. The 2-isomer of $Me_3SiB_5H_8$ rearranges at 145°C to a 4:1 mixture of 1- and 2-isomers.[46] The 1-isomer of MeB_5H_8 rearranges at 200°C to a 9:1 mixture of the 2- and 1-isomers.[47] It seems likely that the mechanism(s) involved in the thermal rearrangements of the substituted pentaboranes also apply to the substituted *nido*-dicarbapentaboranes. However, the rearrangements in the carbaboranes are probably more facile since the maximum temperature used here is 70°C. A theoretical investigation is desirable to examine this hypothesis.

Conclusions

In the present study, quenched gas-phase reactions of tetraborane(10), B_4H_{10}, with alkyl ethynes have been carried out for the first time and shown to give the first C-alkyl derivatives of the *nido*-dicarbapentaborane 1,2-$C_2B_3H_7$ as the major volatile products. Both isomers of 1-R-2-R′-1,2-$C_2B_3H_5$ were obtained as mixtures from unsymmetrical ethynes RC≡CR′. In addition, *arachno*-monocarbapentaboranes were formed from these reactions, which were not present in the reported quenched reaction of B_4H_{10} with ethyne. Two types of *arachno*-monocarbapentaboranes of formula 1-CB_4H_{10} were identified, one with a bridging -CHR- group and one without such a bridge and fluxional in solution. In both cases cleavage of the triple bond is necessary for their formation.

The quenched gas-phase reaction of B_4H_{10} with trimethylsilylethyne, $Me_3SiC{\equiv}CH$, afforded just one volatile product, 1-Me_3Si-1,2-$C_2B_3H_6$. It is believed that this reaction has a similar pathway to that of the reaction of tetraborane(10) with ethyne. Tetraborane(10) is currently the only known borane precursor to 5-vertex *nido*-dicarbapentaboranes and fluxional 5-vertex *arachno*-monocarbapentaboranes.

Experimental Section

All reactions were carried out in standard high-vacuum systems fitted with greaseless O-ring taps and spherical joints (J.Young [Scientific Glassware] Ltd.). A 1-litre Pyrex bulb used for all gas-phase reactions in this study was contained in an isothermal vessel and attached via a capillary to a Kratos MS30 mass spectrometer and a MSS data system (Mass Spectrometry Services Ltd.). The high-vacuum low-temperature fractionating column was as described in the literature[48] but with a capillary connected at the exit of the column to the mass spectrometer. B_4H_{10} was produced from $NMe_4B_3H_8$ (Alfa Products) and BF_3 (Cambrian Gases) using a literature procedure.[49] Ethyne (B.O.C.), propyne (Cambrian Gases), 2-butyne (Lancaster) and other alkynes were obtained commercially. The partially deuteriated propyne MeC≡CD was made from MeC≡CH with D_2O and NaOH.[50]

Samples for NMR spectroscopy were transferred in the gas phase to re-sealable 5mm Young's tubes. Low-field measurements were made at 2.35 Tesla (100 MHz ^1H) on a Jeol FX100 instrument with a broad-band ^{11}B decoupling facility and high-field spectra were obtained at 9.4 Tesla (400 MHz ^1H; 128 MHz ^{11}B; 100 MHz ^{13}C) on a Bruker AM-400 instrument. Subtracted $^1H\{^{11}B$ selective$\}$ and line-narrowed 2D ^{11}B-^{11}B COSY experiments were carried out as described in literature elsewhere,[51] at 233 K for derivatives of types **1**, **2**, **4**, **5**, **7**, **8**, **10**, **11** and **12** and at 298 K for derivatives of types **3**, **6**, **9** and **13**. The J_{BHt} and $J_{BH\mu}$ coupling constants were obtained by resolution enhancements.

General Procedure

The alkyne (1.0 mmol) was first measured manometrically and condensed into a phial and the procedure was repeated for tetraborane(10) (0.5 mmol). The mixture was warmed to room temperature and then bled into the reaction vessel at 70°C. After a few seconds the gas pressure was measured (7.5 mmHg, 0.35 mmol of the mixture) and the vessel was sealed. The reaction was followed by the mass spectrometric method with 10 scans per minute until the alkyne peak disappeared. The reacted mixture was then condensed into a U-trap. For MeC≡CH, the *m/z* 40 peak vanished at about 30 minutes, MeC≡CMe (*m/z* 54) at 25, EtC≡CMe (*m/z* 68) at 25, EtC≡CH (*m/z* 54) at 25, $^nPrC{\equiv}CH$ (*m/z* 68) at 22, $^tBuC{\equiv}CH$ (*m/z* 82) at 30 and $Me_3SiC{\equiv}CH$ at 35. For comparison, a period of 40 minutes was needed for HC≡CH (*m/z* 26) to disappear under identical conditions. After a series of reactions, the combined volatile fraction was then subjected to a cold-column fractionation. The various fractions, with different mass cut-offs, were then characterized by high field ^{11}B and ^1H NMR spectroscopy, at 233 K for derivatives of types **1**, **2**, **4**, **5**, **7**, **8**, **10**, **11** and **12** and at 298 K for derivatives of types **3**, **6**, **9** and **13**. The J_{BHt} and $J_{BH\mu}$ coupling constants were obtained by resolution enhancements.

Products from B_4H_{10} and MeC≡CH:

1-Me-1,2-$C_2B_3H_6$ **1a**; $\delta(^{11}B)$ -11.3 (2B; dd, 2, J_{BHt} = 169, $J_{BH\mu}$ = 42; B3, B5), -13.1 (1B; dt; B4); $\delta(^1H\{^{11}B\})$ 2.50 (1H; s; B4H), 2.26 (1H; s; C2H), 2.20 (2H; s; B3H, B5H), 1.70 (3H; s; $C1CH_3$), -1.60 (2H; s; H_μ); $\delta(^{13}C)$ 65.1, C2; 10.0, CH_3; -12.0, C2.

2-Me-1,2-$C_2B_3H_6$ **2a**; $\delta(^{11}B)$ -13.5 (2B; dd, J_{BHt} = 169, $J_{BH\mu}$ = 47; B3, B5), -19.4 (1B; dt, J_{BHt} = 169, $J_{BH\mu}$ = 43; B4); $\delta(^1H\{^{11}B\})$ 2.26 (1H; s; B4H), 2.18 (2H; s; B3H, B5H), 1.41 (3H; s; $C2CH_3$), 1.08 (1H; sextet, J_{HCBH} ~ 3.7; C1H), -1.99 (2H; s; H_μ); $\delta(^{13}C)$ 73.4, C2; 14.6, CH_3; -15.4, C1.

2-Me-2,3-$C_2B_4H_7$ **3a;** $\delta(^{11}B)$ 0.1 (1B, d, J_{BHt} ~160; B5), -2.6 (1B, dd, J_{BHt} = 160, $J_{BH\mu}$ = 55; B4), -3.1 (1B, dd, J_{BHt} = 156, $J_{BH\mu}$ = 53; B6), -49.8 (d, J_{BHt} = 182; B1); 6.08 (1H; s; C3H), 3.51 (1H; s; B5H), 3.33 (1H; s; B4H), 3.25 (1H; s; B6H), 2.19 (3H; s; CH_3), -0.98 (1H; s; B1H), -2.12 (1H; s; $H_{\mu5,6}$), -2.13 (1H; s; $H_{\mu4,5}$).

1-Me-2,5-CH_2-1-CB_4H_7 **4a;** $\delta(^{11}B)$ 1.6 (2B, d, J_{BHt} ~145; B2,5), -20.1 (2B, ddd, J_{BHt} = 165, $J_{BH\mu2,3/4,5}$ = 63, $J_{BH\mu3,4}$ = 37; B3,4); 3.25 (2H; s; B2,5H), 2.23 (2H; s; B3,4H), 1.61 (3H; s; CH_3), 0.68 (2H; s; $H_{\mu2,3/4,5}$), -0.95 (1H; m, $^2J_{HH}$= 16, J_{HH}= 4; CH_{exo}), -1.40 (1H; m, $^2J_{HH}$= 16, J_{HH}= 6; CH_{endo}), -2.26 (1H; s; $H_{\mu3,4}$);

2,5-*endo*-MeCH-1-CB_4H_8 **5a;** 1.6 (2B; B2,5), -21.8 (2B, ddd, J_{BHt} = 169, $J_{BH\mu2,3/4,5}$ = 64, $J_{BH\mu3,4}$ = 37; B3,4); 0.68 (3H; d $^3J_{HH}$ = 8; CH_3), -0.27 (2H; s; $H_{\mu2,3/4,5}$), -0.80 (1H; m; CH_{exo});

1,B-Me_2-1-CB_4H_8 **6a,** $\delta(^{11}B)$ 6.6 (1B; sextet, $J_{BH\mu,endo}$ ~ 31; B2), 1.6 (1B; d of sextets, J_{BHt} = 132, $J_{BH\mu,endo}$ ~ 33; B4), -1.3 (2B; d of sextets, J_{BHt} = 142, $J_{BH\mu,endo}$ ~30; B3,5); 2.90 (1H; s; B4H), 2.55 (2H; s; B3,5H), 1.35 (5H; s; $H_{\mu,endo}$), 1.29 (3H; s; $C1CH_3$), 0.49 (3H; BCH_3).

Products from B_4H_{10} and EtC≡CH:

1-Et-1,2-$C_2B_3H_6$ **1b**, $\delta(^{11}B)$ -12.1 (2B; dd, 2, J_{BHt} = 171, $J_{BH\mu}$ = 44; B3, B5), -13.8 (1B; dt; B4); $\delta(^1H\{^{11}B\})$ 2.47 (1H; s; B4H), 2.29 (1H; s; C2H), 2.19 (2H; s; B3H, B5H), 2.04 (2H; q, J_{HH} = 7; $C1CH_2$), 0.95 (3H; t, J_{HH} = 7; CH_3), -1.67 (2H; s; H_μ).

2-Et-1,2-$C_2B_3H_6$ **2b**, $\delta(^{11}B)$ -13.8 (2B; dd, J_{BHt} = 168, $J_{BH\mu}$ = 41; B3, B5), -19.4 (1B; dt, J_{BHt} = 168, $J_{BH\mu}$ = 49; B4); $\delta(^1H\{^{11}B\})$

2.29 (1H; s; B4H), 2.16 (2H; s; B3H, B5H), 1.77 (3H; q, J_{HH} = 7; $C2CH_2$), 0.86 (4H; t, J_{HH} = 7 and m; CH_3 and C1H), -2.03 (2H; s; H_μ).

2-Et-2,3-$C_2B_4H_7$ **3b** $\delta(^{11}B)$ -0.5 (1B, d, J_{BHt} ~160; B5), -2.7 (1B, dd, J_{BHt} = 157, $J_{BH\mu}$ = 46; B4), -3.5 (1B, dd, J_{BHt} = 155, $J_{BH\mu}$ = 49; B6), -50.4 (d, J_{BHt} = 182; B1); $\delta(^1H\{^{11}B\})$ 6.12 (1H; s; C3H), 3.51 (1H; s; B5H), 3.33 (1H; s; B4H), 3.27 (1H; s; B6H), 2.47 (2H; q, J_{HH} = 7; $C2CH_2$), 1.16 (3H; t, J_{HH} = 7; CH_3), -0.99 (1H; s; B1H), -2.15 (1H; s; $H_{\mu5,6}$), -2.18 (1H; s; $H_{\mu4,5}$).

1-Et-2,5-CH_2-1-CB_4H_7 **4b** $\delta(^{11}B)$ 0.3 (2B, d, J_{BHt} ~149; B2,5), -20.6 (2B, ddd, J_{BHt} = 165, $J_{BH\mu2,3/4,5}$ = 64, $J_{BH\mu3,4}$ = 37; B3,4); $\delta(^1H\{^{11}B\})$ 3.27 (2H; s; B2,5H), 2.24 (2H; s; B3,4H), 1.95 (2H; q, J_{HH}= 7; $C\underline{H_2}CH_3$), 0.97 (3H; t, J_{HH}= 7; CH_3), 0.54 (2H; s; $H_{\mu2,3/4,5}$), -0.95 (1H; m, $^2J_{HH}$= 16, J_{HH}= 4; CH_{exo}), -1.41 (1H; m, $^2J_{HH}$= 16, J_{HH}= 6; CH_{endo}), -2.27 (1H; s; $H_{\mu3,4}$).

2,5-*endo*-EtCH-1-CB_4H_8 **5b** $\delta(^{11}B)$ 0.3 (2B; B2,5), -22.7 (2B, ddd, J_{BHt} = 169, $J_{BH\mu2,3/4,5}$ = 64, *J*$BH_{\mu3,4}$ = 37; B3,4).

1-Et,B-Me-1-CB_4H_8 **6b** $\delta(^{11}B)$ 6.7 (1B; sextet, $J_{BH\mu,endo}$ ~ 30; B2), -0.3 (1B; d of sextets, J_{BHt} = 132, $J_{BH\mu,endo}$ ~ 35; B4), -2.8 (2B; d of sextets, *J*BHt = 140, $J_{BH\mu,endo}$ ~32; B3,5); $\delta(^1H\{^{11}B\})$ 2.81 (1H; s; B4H), 2.50 (2H; s; B3,5H), 1.52 (2H; q; $C1CH_2$), 0.91 (3H; t; $CH_2C\underline{H_3}$), 1.18 (5H; s; $H_{\mu,endo}$), 0.46 (3H; BCH_3).

Products from B_4H_{10} and $^nPrC\equiv CH$:

1-^{n}Pr-1,2-$C_2B_3H_6$ **1c**, $\delta(^{11}B)$ -11.8 (2B; dd, J_{BHt} = 170, $J_{BH\mu}$ = 44; B3, B5), -13.5 (1B; dt; B4); $\delta(^1H\{^{11}B\})$ 2.51 (1H; s; B4H), 2.31 (1H; s; C2H), 2.22 (2H; s; B3H, B5H), 2.02 (2H; t, J_{HH} = 7; $C1CH_2$), 1.38 (3H; m; $C\underline{H_2}CH_3$), 0.95 (3H; t, J_{HH} = 7; CH_3), -1.61 (2H; s; H_μ).

2-^{n}Pr-1,2-$C_2B_3H_6$ **2c**, $\delta(^{11}B)$ -13.5 (2B; dd; B3, B5), -19.0 (1B; dt, J_{BHt} = 166, $J_{BH\mu}$ = 46; B4); $\delta(^1H\{^{11}B\})$ 2.22 (1H; s; B4H), 2.19 (2H; s; B3H, B5H), 1.71 (2H; t, J_{HH} = 7; $C1CH_2$), 1.34 (3H; m; $C\underline{H_2}CH_3$), 0.92 (4H; t, J_{HH} = 7 and m; CH_3 and C1H), -1.97(2H; s; H_μ).

2-Pr-2,3-$C_2B_4H_7$ **3c**; $\delta(^{11}B)$ 0.1 (1B, d, J_{BHt} ~161; B5), -2.7 (1B, dd, J_{BHt} = 154, $J_{BH\mu}$ = 45; B4), -3.0 (1B, dd, J_{BHt} = 157, $J_{BH\mu}$ = 49; B6), -50.0 (d, J_{BHt} = 181; B1); $\delta(^1H\{^{11}B\})$ 6.09 (1H; s; C3H), 3.53 (1H; s; B5H), 3.35 (1H; s; B4H), 3.27 (1H; s; B6H), 2.49 (2H; m; $C2CH_2$), 1.34 (2H; m; $C\underline{H_2}CH_3$), 0.97 (3H; t, J_{HH} = 7; CH_3), -0.97 (1H; s; B1H), -2.12 (1H; s; $H_{\mu5,6}$), -2.14 (1H; s; $H_{\mu4,5}$).

1-Pr-2,5-CH_2-1-CB_4H_7 **4c**; $\delta(^{11}B)$ 0.0 (2B, d, *J*BHt ~145; B2,5), -20.5 (2B, ddd, J_{BHt} = 165, $J_{BH\mu2,3/4,5}$ = 61, $J_{BH\mu3,4}$ = 36; B3,4); $\delta(^1H\{^{11}B\})$ 3.26 (2H; s; B2,5H), 2.20 (2H; s; B3,4H), 1.92 (2H; q, J_{HH}= 7; $C1C\underline{H_2}$), 1.32 (2H; q, J_{HH}= 7; $C\underline{H_2}CH_3$), 0.91 (3H; t, J_{HH}= 7; CH_3), 0.50 (2H; s; $H_{\mu2,3/4,5}$), -0.97 (1H; m, $^2J_{HH}$= 16, J_{HH}= 4; CH*exo*), -1.40 (1H; m, $^2J_{HH}$= 16, J_{HH}= 6; CH*endo*), -2.28 (1H; s; Hμ3,4).

2,5-*endo*-PrCH-1-CB_4H_8 **5c** $\delta(^{11}B)$ 0.0 (2B; B2,5), -23.5 (2B, ddd, J_{BHt} = 169, $J_{BH\mu2,3/4,5}$ = 64, $J_{BH\mu3,4}$ = 37; B3,4).

1-Pr,B-Me-1-CB_4H_8 **6c** $\delta(^{11}B)$ 7.0 (1B; sextet, $J_{BH\mu,endo}$ ~ 32; B2), 0.1 (1B; d of sextets, J_{BHt} = 135, $J_{BH\mu,endo}$ ~ 34; B4), -3.0 (2B; d of sextets, J_{BHt} = 140, $J_{BH\mu,endo}$ ~33; B3,5); $\delta(^1H\{^{11}B\})$ 2.83 (1H; s; B4H), 2.51 (2H; s; B3,5H), 1.61 (2H; q; $C1CH_2$), 1.33 (2H; m; $C\underline{H_2}CH_3$), 0.85 (3H; t; $CH_2C\underline{H_3}$), 1.12 (5H; s; $H_{\mu,endo}$), 0.50 (3H; BCH_3).

Products from B_4H_{10} and $^tBuC\equiv CH$:

1-^{t}Bu-1,2-$C_2B_3H_6$ **1d**, $\delta(^{11}B)$ -12.3 (2B; dd, J_{BHt} = 170, $J_{BH\mu}$ = 44; B3, B5), -14.2 (1B; dt; B4); $\delta(^1H\{^{11}B\})$ 2.44 (1H; s; B4H), 2.40 (1H; s; C2H), 2.22 (2H; s; B3H, B5H), 1.03 (9H; s; CH_3), -1.66 (2H; s; H_μ).

2-^{t}Bu-1,2-$C_2B_3H_6$ **2d**, $\delta(^{11}B)$ -14.5 (2B; dd, J_{BHt} = 170, $J_{BH\mu}$ = 46; B3, B5), -20.0 (1B; dt, J_{BHt} = 169, $J_{BH\mu}$ = 46; B4); $\delta(^1H\{^{11}B\})$ 2.24 (1H; s; B4H), 2.17 (2H; s; B3H, B5H), 0.93 (10H; s and m; CH_3 and C1H), -2.04 (2H; s; H_μ).

2-^{t}Bu-2,3-$C_2B_4H_7$ **3d**; $\delta(^{11}B)$ -0.3 (1B, d, J_{BHt} ~161; B5), -4.2 (1B, dd, J_{BHt} = 154, $J_{BH\mu}$ = 45; B4), -5.2 (1B, dd, J_{BHt} = 157, $J_{BH\mu}$ = 49; B6), -50.5 (d, J_{BHt} = 181; B1); $\delta(^1H\{^{11}B\})$ 6.08 (s; C3H), 3.50 (s; B5H), 3.34 (s; B4H), 3.31 (s; B6H), 1.16 (9H; s; CH3), -1.00 (s; B1H), -2.12 (s; $H_{\mu5,6}$), -2.14 (s; $H_{\mu4,5}$).

1-^{t}Bu-2,5-CH_2-1-CB_4H_7 **4d**; $\delta(^{11}B)$ -2.6 (2B; d, J_{BHt} ~146; B2,5), -20.4 (2B, ddd, J_{BHt} = 166, $J_{BH\mu2,3/4,5}$ = 61, $J_{BH\mu3,4}$ = 37; B3,4); $\delta(^1H\{^{11}B\})$ 3.24 (2H; s; B2,5H), 2.40 (2H; s; B3,4H), 1.02 (9H, s, CH_3), 0.31 (2H; s; $H_{\mu2,3/4,5}$), -1.10 (1H; m, $^2J_{HH}$= 16, J_{HH}= 4; CH_{exo}), -1.42 (1H; m, $^2J_{HH}$= 16, J_{HH}= 6; CH*endo*), -2.25 (1H; s; $H_{\mu3,4}$).

1-^{t}Bu,B-Me-1-CB_4H_8 **6d** $\delta(^{11}B)$ 6.3 (1B; m; B2), 0.1 (1B; m; B4), -3.0 (2B; m; B3,5); $\delta(^1H\{^{11}B\})$ 0.84 (9H; s; $C\underline{H_3}$), 0.50 (3H; BCH_3).

Products from B_4H_{10} and $MeC\equiv CMe$:

1,2-Me_2-1,2-$C_2B_3H_5$ **7a**, $\delta(^{11}B)$ -11.8 (2B; dd, J_{BHt} = 169, $J_{BH\mu}$ = 47; B3, B5), -17.2 (1B; dt, J_{BHt} = 168, $J_{BH\mu}$ = 47; B4); $\delta(^1H\{^{11}B\})$ 2.42 (1H; s; B4H), 2.02 (2H; s; B3H, B5H), 1.60 (3H; s; $C1CH_3$), 1.39 (3H; s; $C2CH_3$), -1.59 (2H; s; H_μ).

2,3-Me_2-2,3-$C_2B_4H_6$ **9a**, $\delta(^{11}B)$ -1.8 (1B, d, J_{BHt} ~160; B5), -3.8 (2B, dd, J_{BHt} = 155, $J_{BH\mu}$ = 51; B4,6), -46.9 (d, J_{BHt} = 181; B1); $\delta(^1H\{^{11}B\})$ 3.44 (s; B5H), 3.19 (s; B4H, B6H), 2.05 (s; CH_3), -0.95 (s; B1H), -2.14 (s; H_μ);

1-Me-2,5-*endo*-MeCH-1-CB_4H_7 **10a**; $\delta(^{11}B)$ 4.3 (2B; d, J_{BHt} ~146; B2,5), -20.4 (2B, ddd, J_{BHt} = 169, $J_{BH\mu2,3/4,5}$ = 61, $J_{BH\mu3,4}$ = 37; B3,4); $\delta(^1H\{^{11}B\})$ 3.26 (2H; s; B2,5H), 2.24 (2H; s; B3,4H), 1.60 (3H; s; $C1CH_3$), 0.63 (3H; d, $^3J_{HH}$ = 6; *endo* CH_3), 0.05 (2H; s; $H_{\mu2,3/4,5}$),-0.58 (1H; m; CH_{exo}), -2.21 (1H; s; $H_{\mu3,4}$);

1-Me-2,5-*exo*-MeCH-1-CB_4H_7 **11a** $\delta(^{11}B)$ 2.8 (2B; B2,5), -19.7 (2B, ddd, J_{BHt} ~ 173, $J_{BH\mu2,3/4,5}$ ~ 64, $J_{BH\mu3,4}$ = 37; B3,4); $\delta(^1H\{^{11}B\})$ 3.03 (2H; s; B2,5H), 2.17 (2H; s; B3,4H), 1.66 (3H; s; $C1CH_3$), 0.95 (3H; d, $^3J_{HH}$ = 6; *exo* CH_3), 0.78 (2H; s; $H_{\mu2,3/4,5}$), -1.10 (1H; m; CH_{endo}), -2.13 (1H; s; $H_{\mu3,4}$);

1-Me,B-Et-1-CB_4H_8 **13a** $\delta(^{11}B)$ 8.2 (1B; sextet, $J_{BH\mu,endo}$ ~ 30; B2), 1.0 (1B; d of sextets, J_{BHt} = 132, $J_{BH\mu,endo}$ ~ 35; B4), -1.8 (2B; d of sextets, J_{BHt} = 140, $J_{BH\mu,endo}$ ~32; B3,5); $\delta(^1H\{^{11}B\})$ 2.90 (1H; s; B4H), 2.58 (2H; s; B3,5H), 1.32 (5H; s; $H_{\mu,endo}$), 1.22 (3H; m; $C1CH_3$), 1.11 (2H; q; BCH_2), 1.00 (3H; t; $CH_2C\underline{H_3}$).

Products from B_4H_{10} and $EtC\equiv CMe$:

1-Et-2-Me-1,2-$C_2B_3H_5$ **7a**, $\delta(^{11}B)$ -12.5 (2B; dd; B3, B5), -17.9 (1B; dt; B4); $\delta(^1H\{^{11}B\})$ 2.39 (1H; s; B4H), 2.06 (2H; s; B3H, B5H), 1.89 (2H; q, J_{HH} = 7; $C1CH_2$), 1.36 (3H; s; $C2CH_3$), 1.04 (3H; t, J_{HH} = 7; CH_3), -1.74 (2H; s; H_μ).

2-Et-1-Me-1,2-$C_2B_3H_5$ **8b**, $\delta(^{11}B)$ -12.2 (2B; dd; B3, B5), -17.3 (1B; dt; B4); $\delta(^1H\{^{11}B\})$ 2.42 (1H; s; B4H), 2.02 (2H; s; B3H, B5H), 1.80 (2H; q, $J_{\mathrm{HH}} = 7$; C1CH$_2$), 1.54 (3H; s; C1CH$_3$), 0.95 (3H; t, $J_{\mathrm{HH}} = 7$; CH$_3$), -1.67 (2H; s; H$_\mu$).

2-Et-3-Me-2,3-C$_2$B$_4$H$_6$ **9b**,[52] $\delta(^{11}\mathrm{B})$ -1.8 (1B, d, J_{BHt} ~160; B5), -3.9 (1B, dd, $J_{\mathrm{BHt}} = 157$, $J_{\mathrm{BH\mu}} = 55$; B4), -4.4 (1B, dd, $J_{\mathrm{BHt}} = 154$, $J_{\mathrm{BH\mu}} = 56$; B6), -47.4 (d, $J_{\mathrm{BHt}} = 178$; B1); $\delta(^{1}\mathrm{H}\{^{11}\mathrm{B}\})$ 3.52 (s; B5H), 3.28 (s; B4H), 3.25 (s; B6H), 2.47 (dq, J_{HH}=14, J_{HH}=7; C$\underline{\mathrm{H}}_a$H$_b$CH$_3$), 2.33 (dq, J_{HH}=14, J_{HH}=7; CH$_a\underline{\mathrm{H}}_bCH_3$); 2.09 (3H; s; CH$_3$), 1.21 (t, J_{HH}=7; CH$_2C\underline{\mathrm{H}}_3$), -0.88 (s; B1H), -2.16 (s; H$_{\mu5,6}$), -2.17 (s; H$_{\mu4,5}$).

1-Et-2,5-*endo*-MeCH-1-CB$_4$H$_7$ **10b**; $\delta(^{11}\mathrm{B})$ 3.0 (2B; d, J_{BHt} ~146; B2,5), -21.1 (2B, ddd, $J_{\mathrm{BHt}} = 166$, $J_{\mathrm{BH\mu2,3/4,5}} = 65$, $J_{\mathrm{BH\mu3,4}} = 39$; B3,4); $\delta(^{1}\mathrm{H}\{^{11}\mathrm{B}\})$ 3.24 (2H; s; B2,5H), 2.24 (2H; s; B3,4H), 1.90 (2H; q, J_{HH}= 7; C$\underline{\mathrm{H}}_2$CH$_3$), 0.94 (3H; t, J_{HH}= 7; CH$_2$C$\underline{\mathrm{H}}_3$), 0.63 (3H; d, $^3J_{\mathrm{HH}} = 7$; *endo* CH$_3$), -0.09 (2H; s; H$_{\mu2,3/4,5}$), -0.61 (1H; m; CH$_{exo}$), -2.27 (1H; s; H$_{\mu3,4}$).

1-Me-2,5-*endo*-EtCH-1-CB$_4$H$_7$ **12b** $\delta(^{11}\mathrm{B})$ 3.5 (2B; B2,5), -20.3 (2B, ddd, $J_{\mathrm{BHt}} = 167$, $J_{\mathrm{BH\mu2,3/4,5}} = 61$, $J_{\mathrm{BH\mu3,4}} = 37$; B3,4); $\delta(^{1}\mathrm{H}\{^{11}\mathrm{B}\})$ 3.25 (2H; s; B2,5H), 2.26 (2H; s; B3,4H), 1.59 (3H; s; C1CH$_3$), 0.83 (2H; m; *endo* C$\underline{\mathrm{H}}_2$CH$_3$), 0.97 (3H; t, J_{HH}= 7; CH$_2$C$\underline{\mathrm{H}}_3$), -0.02 (2H; s; H$_{\mu2,3/4,5}$), -0.61 (1H; m; CH$_{exo}$), -2.21 (1H; s; H$_{\mu3,4}$).

1,B-Et$_2$-1-CB$_4$H$_8$ **13b** $\delta(^{11}\mathrm{B})$ 8.8 (1B; sextet, $J_{\mathrm{BH\mu,endo}}$ ~ 30; B2), 1.7 (1B; d of sextets, $J_{\mathrm{BHt}} = 132$, $J_{\mathrm{BH}\mu,endo}$ ~ 35; B4), -1.5 (2B; d of sextets, $J_{\mathrm{BHt}} = 140$, $J_{\mathrm{BH}\mu,endo}$ ~32; B3,5); $\delta(^{1}\mathrm{H}\{^{11}\mathrm{B}\})$ 2.90 (1H; s; B4H), 2.58 (2H; s; B3,5H), 1.22 (5H; s; H$_{\mu,endo}$), 1.50 (2H; q; C1CH$_2$), 1.11 (2H; q; BCH$_2$), 0.93 (3H; t; CH$_2$C$\underline{\mathrm{H}}_3$), 0.99 (3H; t; CH$_2$C$\underline{\mathrm{H}}_3$).

Products from B$_4$H$_{10}$ and Me$_3$SiC≡CH:

1-Me$_3$Si-1,2-C$_2$B$_3$H$_6$ **1e**, $\delta(^{11}\mathrm{B})$ -11.7 (2B; dd, $J_{\mathrm{BHt}} = 171$, $J_{\mathrm{BH\mu}} = 44$; B3, B5), -13.9 (1B; dt, $J_{\mathrm{BHt}} = 169$, $J_{\mathrm{BH\mu}} = 47$; B4); $\delta(^{1}\mathrm{H}\{^{11}\mathrm{B}\})$ 2.21 (1H; s; B4H), 2.11 (1H; s; C2H), 2.09 (2H; s; B3H, B5H), 0.11 (9H; s; CH$_3$), -2.09 (2H; s; H$_\mu$).

Products from B$_4$H$_{10}$ and EtC≡CEt:

The quenched gas-phase reactions of B$_4$H$_{10}$ with EtC≡CEt gave carbaborane products with cut-offs at *m/z* 120, 132, 134 and 135 which were not investigated further, but based on this study these products are likely to be 1,2-Et$_2$-1,2-C$_2$B$_3$H$_5$ (120), 2,3-Et$_2$-2,3-C$_2$B$_4$H$_6$[53] (132), 1-Et-2,5-μ-EtCH-1-CB$_4$H$_7$ (134) and 1-Et-B-EtCH$_2$-1-CB$_4$H$_8$ (136).

Notes and references

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