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

Mark A. Fox,*a Robert Greatrex*ab and Alirea Nikrahi*b

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New alkyl derivatives of the nido-dicarbapentaborane, 1,2-C$_2$B$_5H$_7, and arachno-carbapentaborane, 1-CB$_3$H$_{10}$, 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, Pr or 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$_5$SiC≡CH gave a single volatile carbaborane product, 1-Me$_3$Si-1,2-C$_2$B$_5$H$_6$.

Introduction

Polyhedral carbaboranes (carbaboranes) have long been synthesised from reactions of binary boranes with alkynes.† 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$_2$B$_5$H$_6$. 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$_2$B$_5$H$_6$. However, the B$_5$H$_9$/alkyne system can also yield different carbaborane products such as small closo-carbaboranes if gas-phase conditions are used.‡

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.§,10 Many new carbaboranes were discovered from the gas-phase reactions of $B_4H_{10}$ with ethynyl 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§,16,17

\[ B_4H_{10} + HC≡CH \rightarrow closo-2,4-C_2B_5H_7 \ (<1\% \ yield) \]

2) Completed reaction§,18

\[ 25-70°C, \ 3 \ days \]

\[ B_4H_{10} + HC≡CH \rightarrow nido-2,4-Me_2-2,3-C_2B_5H_6 \ (7\%) \]

3) Quenched reaction‡,13,19

\[ 25-70°C, \ 20-60 \ min \]

\[ B_4H_{10} + HC≡CH \rightarrow nido-1,2-C_2B_5H_7 \ (25\%) \]

Grimes, Bramlett and Vance7,8 and the Leeds group16,17,18 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 trimethylsilyl ethyne - no volatile carbaborane product was obtained from this latter reaction.14

4) High-energy (‘Flash’) reactions§,17

\[ B_4H_{10} + MeC≡CH \rightarrow closo-2-Me-1,5-C_2B_5H_7 \ (<1\%) \]

\[ B_4H_{10} + MeC≡CMe \rightarrow closo-2,3-Me_2-1,5-C_2B_5H_7 \ (<1\%) \]

5) Completed reactions,9,18

\[ B_4H_{10} + MeC≡CH \rightarrow nido-2-Me-2,3-C_2B_5H_7 \ (8\%) \]

\[ B_4H_{10} + MeC≡CMe \rightarrow nido-2,3-Me_2-2,3-C_2B_5H_6 \ (10\%) \]

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$_2$B$_5$H$_7$, being formed in ca 25% yield based on $B_4H_{10}$ consumed. By contrast, 1,2-C$_2$B$_5$H$_7$, is not observed when the gas-phase reaction of $B_4H_{10}$ and ethyne proceeds to completion.

† The abridged equations above do not include other carbaborane products formed and may appear misleading. For example, a series of alkyl derivatives of C$_2$B$_5$H$_7$, C$_2$B$_5$H$_8$, and C$_2$B$_5$H$_9$ is also formed from the flash reaction of tetraborane(10) with ethyne with a total carbaborane yield of just above 3%.
The dicarbaborane decomposes or reacts rapidly in the presence of B₄H₁₀ to give 2-MeC₆B₃H₄ and solids and reacts slowly with ethyne to give C₃B₂H₆ and solids; it is stable in the gas-phase at 50°C but decomposes in the liquid phase to form a white solid.

From these observations it is concluded that 1,2-C₂B₃H₇ is not an intermediate in the formation of the major carbaborane products observed when the reaction of B₄H₁₀ and ethyne is allowed to go to completion. This nido-carbaborane and the closely related phosphacarbaborane 2-2,1,2-PCB₃H₄ are the only known heteroborane analogues of nido-pentaborane(9), B₅H₉. Remarkably, no derivatives of the nido-5-vertex carbaborane 1,2-C₂B₃H₇ have been reported.

Prior to our work at Leeds, quenched gas-phase reactions of B₄H₁₀ 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 ²⁹ of the quenched reaction of B₄H₁₀ 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 70°C. 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 B₄H₁₀. 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 B₄H₁₀, the major decomposition product of B₄H₁₀, was absent. Peaks corresponding to the ethynes 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.²¹,²³ White polymeric solids were produced in all reactions, but were not investigated further.

Quenched gas-phase reaction of B₄H₁₀ with propyne

The most volatile carbaborane products in the quenched reaction of MeC≡CH and B₄H₁₀ 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-C₂B₃H₆, 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 C₃B₆H₆.

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...
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 5a was identified as 2,5-μ-endo-MeCH-1-CB$_7$H$_4$ 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

Figure 1. Boron-11 and proton NMR spectra of a 1:3 mixture of MeC$_2$B$_6$H$_6$ isomers 1a and 2a

Figure 2. Boron and proton NMR spectra of 1-Me-2,5-μ-CH$_2$-1-CB$_7$H$_4$ 4a

Figure 3. Mass spectrometric analysis of a 1:1.2 mixture of 1-Me-2,5-μ-CH$_2$-1-CB$_7$H$_4$ 4a and 2,5-μ-CB$_7$H$_4$ 5a.
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$_4$H$_8$ is present, which in theory would give 8 unique boron

![Scheme 2](image)

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 sharpen 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$_4$H$_{10}$ and allene, CH$_2$=C=CH$_2$, and supported by ab initio computations. As in the cases of 4a and 5a, the formation of 6a indicates that the triple bond from the propyne is cleaved.

Mass and proton NMR spectra of the products from the quenched reaction of B$_4$H$_{10}$ 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$_4$H$_8$.

Quenched gas-phase reactions of B$_4$H$_{10}$ with other alkynes

The most volatile products from the quenched reactions of B$_4$H$_{10}$ with 1-butene and 1-pentyne are analogous to those from the quenched reaction of B$_4$H$_{10}$ with propyne (Scheme 1). The yields of the carbaborane products are listed in Table 1 together with the ratios of isomers for the C$_2$B$_4$H$_8$ 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$_4$H$_{10}$ with 2,2-dimethyl-3-butyne, 3-Bu≡C=CH, gave the best yields of the dicarbaborane isomers, 1-3-Bu and 2-3-Bu-1,2-C$_2$B$_3$H$_{10}$ and the bridging arachnoidicarbaborane, 1-3-Bu-2,5-µ-CH$_2$-1-CB$_4$H$_8$, but the other expected carbaboranes 2-3-Bu-2,3-C$_2$B$_3$H$_{10}$, 2,5-µ-3-BuCH$_2$-1-CB$_4$H$_8$, and B-Me-1-3-Bu-1-CB$_4$H$_8$ were either obtained in very small amounts or were completely absent. The differences in the yields of the products obtained from 3-Bu≡C=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$_2$B$_3$H$_8$ derivatives have been synthesised from reactions of B$_4$H$_{10}$ with various alkynes, the unknown derivative nido-2,3-3-Bu$_2$-2,3-C$_2$B$_3$H$_{10}$ was not obtained from B$_4$H$_{10}$ and 3-Bu≡C≡CBu. A minor volatile product, identified as the known basket compound 2,4-(µ-BuCH=CH)$_2$B$_4$H$_8$, is probably formed from 2,2-dimethyl-3-butyne and B$_4$H$_{10}$ present during the reaction. The bridged carbaborane 1-3-Bu-2,5-µ-CH$_2$-1-CB$_4$H$_8$ 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$_4$H$_8$ compounds discussed here – an observation that is consistent with the higher

![Figure 3](image)

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

<table>
<thead>
<tr>
<th>1-R-1,2-C$_2$B$<em>3$H$</em>{10}$</th>
<th>2-R-1,2-C$_2$B$<em>3$H$</em>{10}$</th>
<th>1,2-C$_2$B$_3$H$_8$ type (1,2,7,8)</th>
<th>2,3-C$_2$B$_3$H$_8$ type (3,9)</th>
<th>2,5-µ-CH$_2$-1-CB$_4$H$_8$ type (4,5,10,11,12)</th>
<th>1-CB$<em>4$H$</em>{10}$ type (6,13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeC≡CH</td>
<td>25 : 75</td>
<td>52 [7%]</td>
<td>11 [1.5%]</td>
<td>15 [2%]</td>
<td>7 [1%]</td>
</tr>
<tr>
<td>EtC≡CH</td>
<td>35 : 65</td>
<td>56 [8%]</td>
<td>11 [1.5%]</td>
<td>10 [1.5%]</td>
<td>12 [1.5%]</td>
</tr>
<tr>
<td>*PrC≡CH</td>
<td>40 : 60</td>
<td>56 [8%]</td>
<td>14 [2%]</td>
<td>3 [0.5%]</td>
<td>14 [2%]</td>
</tr>
<tr>
<td>*BuC≡CH</td>
<td>45 : 55</td>
<td>59 [12%]</td>
<td>0.5 [0.1%]</td>
<td>35 [7%]</td>
<td>0.5 [0.1%]</td>
</tr>
<tr>
<td>MeC≡Me</td>
<td>-</td>
<td>39 [6%]</td>
<td>20 [3%]</td>
<td>26 [4%]</td>
<td>7 [1%]</td>
</tr>
<tr>
<td>etC≡Me</td>
<td>65 : 35</td>
<td>45 [7%]</td>
<td>19 [3%]</td>
<td>26 [4%]</td>
<td>6 [1%]</td>
</tr>
<tr>
<td>MeSi≡SiCH</td>
<td>100 : 0</td>
<td>100 [12%]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HC≡CH</td>
<td>-</td>
<td>90% [25%]</td>
<td>0.5% [0.1%]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$C≡C=CH$_2$</td>
<td>-</td>
<td>-</td>
<td>0.5% [0.1%]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HC≡CH</td>
<td>-</td>
<td>-</td>
<td>0.5% [0.1%]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$C≡C=CH$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>89% [11%]</td>
<td>7% [1%]</td>
</tr>
</tbody>
</table>

*For 1-Et-2-Me-1,2-C$_2$B$_3$H$_8$ (7b): 1-Me-2-Et-1,2-C$_2$B$_3$H$_8$ (8b), Reference 19 1,2-C$_2$B$_3$H$_8$, 2,3-C$_2$B$_3$H$_8$, Reference 34 4a,5a,6a
yield obtained for the butyl derivative.

Products from the quenched reactions of B₄H₁₀ 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-CB₃H₄ is the minor isomer and is the only exo-isomer of the 1-R-2,5-µ-R’CH-1-CB₃H₄ type that is positively identified here and supported by computations reported elsewhere. 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 Me₅Si≡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 (Me₅Si⁺). This product was identified by NMR spectroscopy as 1-Me₅Si-1,2-C₂B₃H₆ for which the B(4) peak value differs little from that of the parent carbaborane, 1,2-C₂B₃H₄; thus no “trans” effect is observed. The other possible isomer, 2-Me₅Si-1,2-C₂B₃H₆, 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 B₄H₁₀ with ethyne and with allene are included for comparison. Whereas ethyne gives the nido-carbapentaborane C₂B₃H₄ as the major product and nido-dicarbahexaborane C₂B₆H₁₀ as a minor product on reaction with B₄H₁₀, allene affords only bridged and fluxional arachno-carbapentaboranes as volatile carbaboranes. The reactions of B₄H₁₀ 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 [B₄H₆] and H₂. With ethenes, B₄H₁₀ gives high yields of ‘basket’ compounds 2,4-µ-(RCHCHR’)/B₄H₆, via the subsequent reaction of [B₄H₆] with RCH=CHR’, The mechanisms were corroborated by theoretical computations on the proposed reaction pathways. Minor basket products were also present in which a second ethene molecule appears to have been hydroborated by B₄H₁₀ to form an alkyl group –RCH₂R, since the basket compound formed initially does not give such products with ethenes.

The low yields of the volatile carbaborane products from reactions of B₄H₁₀ and ethynes reported here, in contrast to high yields of the basket products from B₄H₁₀ with ethenes, suggest that many pathways to different carbaborane products exist. From the results of Grimes’s gas-phase kinetic study on the thermolysis of B₄H₁₀ with ethyne it seems likely that [B₄H₆] formed initially from B₄H₁₀ then reacts with an ethyne molecule to yield an intermediate C₂B₄H₁₀. Depending on the path taken, C₂B₄H₁₀ may

1. lose a [BH₃] intermediate to give C₂B₃H₄,
2. lose H₂ to form C₂B₃H₆ or
3. react with a second ethyne molecule to give an intermediate C₂B₃H₁₁.

An alternative route to C₂B₃H₄ from the reaction of [B₄H₆] and ethyne was proposed by McKee in the first of his theoretical investigations into the complex reaction pathways of tetraborane(10) with unsaturated hydrocarbons. However, on the basis of experimental work, [B₄H₆] is not considered to be present in the initial stages of the thermolysis of B₄H₁₀. The triborane carbonyl B₄H₁₀CO, a precursor to [B₄H₆], gives a high energy ‘flash’ reaction at -20°C with ethyne, resulting in several closo-carbaborane products from which C₂B₃H₄ may well be formed as an intermediate. McKee’s second theoretical paper supports the formation of [C₂B₃H₁₀] from the reaction of [B₄H₆] and ethyne and also the removal of [BH₃] from [C₂B₄H₁₀] to give C₂B₃H₄.
The quenched reaction of $\text{B}_4\text{H}_{10}$ with allene to give two distinct *arachno*-monocarbapentaboranes (bridged and fluxional) resembles the reaction of $\text{B}_4\text{H}_{10}$ with ethene, in that reactions of $\{\text{B}_4\text{H}_6\}$ and of $\text{B}_4\text{H}_{10}$ 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 $\text{B}_4\text{H}_{10}$ 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.

Both distinct mechanisms in the reactions of $\text{B}_4\text{H}_{10}$ with ethyne and of $\text{B}_4\text{H}_{10}$ with allene probably occur in the quenched reactions reported here of $\text{B}_4\text{H}_{10}$ with alkyl ethynes. The initial intermediate $\{\text{RR'}\text{C}_2\text{B}_4\text{H}_6\}$ formed from $\{\text{B}_4\text{H}_6\}$ and $\text{RR'}\text{C} \equiv \text{CR'}$ may follow four distinct pathways.

a) lose a $\{\text{BH}_3\}$ intermediate to give $\text{RR'}\text{C}_2\text{B}_4\text{H}_6$

b) lose H$_2$ to form $\text{RR'}\text{C}_2\text{B}_4\text{H}_6$

c) cleave the triple bond during rearrangement into the bridging *arachno* carbaborane 1-R-2,5-CHR'-1-CB$_4$H$_7$ or

d) react with a second ethyne molecule to give an intermediate $\{\text{RR'}\text{R'}\text{C}_2\text{B}_4\text{H}_6\}$

Two observations suggest that pathway (d) may well be dominant. Firstly, for all gas-phase reactions reported here at 70°C (for which the alkyn: $\text{B}_4\text{H}_{10}$ ratio was 2:1) the alkyn is used up before the $\text{B}_4\text{H}_{10}$. 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-$\text{CH}_2$R'-1-R-1-CB$_4$H$_7$ is presumably formed by hydroboration of $\text{B}_4\text{H}_{10}$ with RC≡CR' to give an intermediate $\{\text{RR'}\text{C}_2\text{B}_4\text{H}_6\}$ 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$_2$Si-1,2-C$_2$B$_4$H$_{10}$, was obtained from the quenched gas-phase reaction of $\text{B}_4\text{H}_{10}$ and Me$_2$Si≡C=CH. Interestingly, the time needed for the Me$_2$Si≡C=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$_2$Si≡C=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$_2$Si-2,5-µ-CH$_2$-1-CB$_4$H$_7$ and B-CH$_2$-1-Me$_2$Si-1-CB$_4$H$_6$ and the known carbaborane 2-Me$_2$Si-2,3-C$_2$B$_4$H$_8$) are not observed.

The observation of only one isomer of Me$_2$SiC≡CH$_2$B$_4$H$_6$ from the reaction of Me$_2$Si≡C=CH with $\text{B}_4\text{H}_{10}$ contrasts with the observation of a mixture of RC≡CR' isomers from the alkyl ethynes RC≡CH listed in Table 1. More intriguing is the fact that the 1-isomer is identified for Me$_2$SiC$_2$B$_4$H$_6$, whereas the major components in all RC≡CR' compounds are identified as the 2-isomers. The pentaboranes Me$_2$SiB$_4$H$_7$ and MeB$_4$H$_8$ (closely related to Me$_2$SiC$_2$B$_4$H$_6$ and MeC$_2$B$_4$H$_8$, respectively) have been reported to undergo thermal rearrangements. The 2-isomer of Me$_2$SiB$_4$H$_8$ rearranges at 145°C to a 4:1 mixture of 1- and 2-isomers. The 1-isomer of MeB$_4$H$_8$ rearranges at 200°C to a 9:1 mixture of the 2- and 1-isomers. 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), B₄H₁₀, with alkyl ethylenes have been carried out for the first time and shown to give the first C-alkyl derivatives of the *nido*-dicarbapentaborane 1,2-C₅B₆H₆ as the major volatile products. Both isomers of 1-R-2′-1,2-C₅B₆H₆ 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 B₄H₁₀ with ethyne. Two types of *arachno*-monocarbapentaboranes of formula 1-C₅B₆H₁₀ 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 B₄H₁₀ with trimethylsilyl ethylene, Me₃SiC=CH, afforded just one volatile product, 1-Me₃Si-1,2-C₅B₆H₆. 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 but with a capillary connected at the exit of the column to the mass spectrometer. B₄H₁₀ was produced from NMe₃B₄H₁₀ (Alfa Products) and BF₃ (Camber Gas) using a literature procedure. Ethyne (B.O.C.), propyne (Camber Gas), 2-butenyl (Lancaster) and other alkynes were obtained commercially. The partially deuterated propyne MeCD=CD was made from MeC=CH with D₂O and NaOH.

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 ¹³B decoupling facility and high-field spectra were obtained at 9.4 Tesla (400 MHz ¹H; 128 MHz ¹¹B; 100 MHz ¹³C) on a Bruker AM-400 instrument. Subtracted ¹H¹¹B selective] and line-narrowed 2D ¹¹B-¹¹B COSY experiments were carried out as described in literature elsewhere, 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_BH and J_BH° coupling constants were obtained by resolution enhancements.

General Procedure

The alkylene (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 alkylene 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=CM (m/z 68) at 25, EtC=CH (m/z 54) at 25, PrC=CH (m/z 68) at 22, BuC=CH (m/z 82) at 30 and Me₃SiC=CH at 35. For comparison, a period of 40 minutes was needed for H≡C=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 ¹¹B 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_BH and J_BH° coupling constants were obtained by resolution enhancements.

Products from B₄H₁₀ and MeC=CH:

1-Me-1,2-C₅B₆H₁₀ 1a; δ(¹H) -11.3 (2B; dd, J_BH= 169, J_BH°= 42; B3, B5), -13.1 (1B; dt; B4); δ(¹¹B) 2.50 (1H; s; B4H), 2.26 (1H; s; C2H), 2.20 (2H; s; B3H, B5H), 1.70 (3H; s; C(CH₃)), -1.60 (2H; s; H₆); δ(¹³C) 65.1, C1; 10.0, C1H; -12.0, C2.

2-Me-1,2-C₅B₆H₁₀ 2a; δ(¹H) -13.5 (2B; dd, J_BH= 169, J_BH°= 47; B3, B5), -19.4 (1B; dt, J_BH= 169, J_BH°= 43; B4); δ(¹¹B) 2.26 (1H; s; B4H), 2.18 (2H; s; B₃H, B₅H), 1.41 (3H; s; C₂CH₂), 1.08 (1H; sext, J_BHCH₃ = 3.7; C1H), -1.99 (2H; s; H₆); δ(¹³C) 73.4, C2; 14.6, CH₃; -15.4, C1.

2-Me-2,3-C₅B₆H₁₀ 3a; δ(¹H) 0.1 (1B, d, J_BH= 160; B5), -2.6 (1B, dd, J_BH= 160, J_BH°= 55; B4), -3.1 (1B, dd, J_BH= 156, J_BH°= 53; B6), -49.9 (d, J_BH= 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; CH₃), -0.98 (1H; s; B1H), -2.12 (1H; s; H₆g, s); -2.13 (1H; s; H₆a).

1-Me-2,5-CH₂-1,2-C₅B₆H₁₀ 4a; δ(¹H) 1.6 (2B, d, J_BH= -145; B₂, B₅), -20.1 (2B, ddd, J_BH= 165, J_BH₂,2,3,4,5,6 = 63, J_BH₂,2,3,4,5 = 37; B₃, B₄); 3.25 (2H; s; B₂, B₅H), 2.23 (2H; s; B₃, B₄H), 1.61 (3H; s; CH₃), 0.68 (2H; s; H₂,2,3,4,5,6), -0.95 (1H; m, J_BH= 16, J_BH°= 4; CH₃); -1.40 (1H, m, J_BH= 16, J_BH°= 6; CH₃), -2.26 (1H; s; H₆a, s), 2.5-endo-MeCH-C₁B₆H₁₀ 5a; 1.6 (2B; B₂, B₅), -21.8 (2B, ddd, J_BH= 169, J_BH₂,2,3,4,5,6 = 64, J_BH₂,2,3,4,5 = 37; B₃, B₄), 0.68 (3H; d, J_HH= 8; CH₃), -0.27 (2H; s; H₂,2,3,4,5,6), -0.80 (1H; CH₃); 1.8Me-2,1-C₅B₆H₁₀ 6a; δ(¹H) 6.6 (1B; sext, J_BHend= ~ 31; B2), 1.6 (1B; d of sextets, J_BH= 132, J_BHend= ~ 33; B₄), -1.3 (2B; d of sextets, J_BH= 142, J_BHend= ~ 30; B₃, B₅); 2.90 (1H; s; B₄H), 2.55 (2H; s; B₃, B₅H), 1.35 (5H; s; H₆), 1.29 (3H; s; C₂CH₂), 0.49 (3H; B₇H₆).

Products from B₄H₁₀ and EtC=CH:

1-Et-1,2-C₅B₆H₁₀ 1b; δ(¹H) -12.1 (2B; dd, J_BH= 171, J_BH°= 44; B3, B5), -13.8 (1B; dt; B4); δ(¹¹B) 2.47 (1H; s; B₄H), 2.29 (1H; s; C₂H), 2.19 (2H; s; B₃H, B₅H), 2.04 (2H; q, J_BH= 7; C₁CH₂), 0.95 (3H; t, J_HH= 7; CH₃), -1.67 (2H; s; H₆).

1-Et-1,2-C₅B₆H₁₀ 2b; δ(¹H) -13.8 (2B; dd, J_BH= 168, J_BH°= 41; B3, B₅), -19.4 (1B; dt, J_BH= 168, J_BH°= 49; B₄); δ(¹¹B)
Products from B$_8$H$_{10}$ and PrC$_6$H$_4$:

1-Pr,1-2-C$_6$H$_5$-1c, 2e, $\delta^1$B) -11.8 (2B; dd, $J_{BB} = 170$, $J_{BB} = 44$; B3, B5), -1.35 (15; dd, B4); $\delta^2$H$_{11}$) -1.61 (1H; s; B3, B5). 3.24 (2H; s; B2,5H), 2.40 (2H; s; B3,4H), 1.02 (9H, s, C12H). 1.15 (8H; m, C12H), 0.46 (3H; B3H).

Products from B$_8$H$_{10}$ and Me$_3$C$_6$Me:

1,2,3-endo-3-C$_6$H$_5$ Me 7a, $\delta^1$B) -11.8 (2B; dd, $J_{BB} = 169$, $J_{BB} = 47$; B3, B5). -17.2 (1B; dt, $J_{BB} = 168$, $J_{BB} = 47$; B4); $\delta^2$H$_{11}$). 2.42 (1H; s; H4), 2.02 (2H; s; B3,5H), 1.60 (3H; s; C12H), 1.39 (3H; s; C22H), -1.59 (2H; s; H6). 2.3-Me-2,3-C$_6$H$_5$ 7b, $\delta^1$B) -1.8 (1B, d, $J_{BB} = 169$; B5). -3.8 (2B, dd, $J_{BB} = 155$, $J_{BB} = 51$; B4, B6). -46.9 (d, $J_{BB} = 181$; B1); $\delta^2$H$_{11}$) 3.44 (s; B5H), 3.19 (s; B4H, B6H), 2.05 (s; CH$_2$H), -0.95 (s; B1H), -2.14 (s; H4). 2-Me-2,5-endo-Me$_3$C$_6$H$_5$ 7c, $\delta^1$B) 4.3 (2B; dd, $J_{BB} = 146$; B2), -2.04 (2B, ddd, $J_{BB} = 169$, $J_{BB} = 23,4,5$; B5, B6, B3,4Me), 0.63 (3H; d, $J_{BB} = 6$; endo CH$_3$), 0.05 (2H; H$_{3,2}$). 0.58 (1H; m; CH$_3$), -2.14 (s; H6). 2-Me-2,5-exo-Me$_3$C$_6$H$_5$ 7d, $\delta^1$B) 2.8 (2B; B2,5), -19.7 (2B, ddd, $J_{BB} = 173$, $J_{BB} = 23,4,5$, 64, $J_{BB} = 37$; B3,4); $\delta^2$H$_{11}$) 3.26 (2H; s; B2,5H), 2.24 (2H; s; B3,4H), 1.60 (3H; s; C12H), 0.63 (3H; d, $J_{BB} = 6$; endo CH$_3$), 0.05 (2H; H$_{3,2}$). 0.58 (1H; m; CH$_3$), -2.14 (s; H6). 2-Me-B-Et-C$_6$H$_5$ 7e, $\delta^1$B) 8.2 (1B; sextet, $J_{BB} = 6$; B2), 1.0 (1B; d of sextets, $J_{BB} = 132$, $J_{BB} = 35$; B4). -1.8 (2B of d sets, $J_{BB} = 140$, $J_{BB} = 32$; B3,4); $\delta^2$H$_{11}$) 2.90 (1H; s; B4H), 2.58 (2H; s; B3,5H), 1.32 (5H; s; H$_{p,endo}$), 1.22 (3H; m; C12H), 1.11 (2H; q; B2CH), 1.00 (3H; t; CH$_2$CH).
2-Et-3-Me-2,3-C$_2$B$_{10}$H$_{10}$b $^{9b}$ $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}$B $^{11}