1-CARBA-*arachno*-PENTABORANE(10) DERIVATIVES

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Dedicated to Professor Jaromir Plesek on the occasion of his 70th birthday.

The formation of organo substituted 1-carba-*arachno*-pentaborane(10) derivatives is shown to proceed in high yield *via in situ* generated 1,1,1-tris(diethylboryl)propane (**2**) from diethyl(propyn-1-yl)-borane (**1**) by hydroboration with an excess of diethylborane (hydride bath). In the hydride bath, exchange reactions between **2** and other geminal bis(diethylboryl)alkanes take place until the carbaborane skeleton is formed. If tris(diethylboryl)methane is used under the same conditions, the corresponding 1-carba-*arachno*-pentaborane(10) derivatives **11** and **12** are formed in mixture with other unknown boranes or carboranes. ^{11}B and ^{13}C NMR data are presented to allow for straightforward identification of the 1-carba-*arachno*-pentaboranes(10).

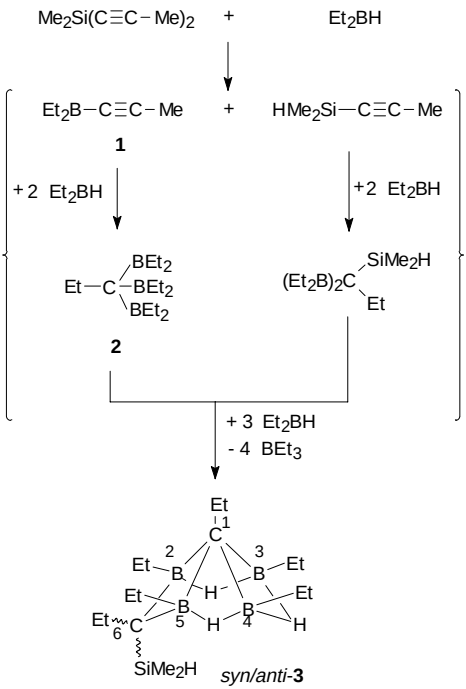
Key words: Carboranes; Boranes, propyn-1-yl, vinyl; Hydroboration; Exchange reactions, Et_2BH-catalyzed; NMR, ^{11}B, ^{13}C.

In the neighbourhood of electron-deficient boron atoms, an increase in the connectivity of the carbon atoms can be enforced, a situation typically encountered in carboranes[1]. Most synthetic routes to carboranes make use of reactions of polyhedral boranes with alkynes[1]. There are only few examples where simple organoboranes serve as starting materials[2,3]. However, these reactions have led to various organo substituted carboranes in high yields such as 1,5-dicarba-*closo*-pentaboranes(5) (ref.[2]) or 2,3,4,5-tetracarba-*nido*-hexaboranes(6) (ref.[3]) which are difficult to obtain by other procedures. In this context we have recently reported on the first examples of 1-carba-*arachno*-pentaboranes(10) (ref.[4]) according to Scheme 1; at the same time this type of carborane was also reported by two other groups[5,6].

The cleavage of the Si–C≡ bond as shown in Scheme 1 implies the synchronous formation of dimethyl(propyn-1-yl)silane and diethyl(propyn-1-yl)borane (**1**) which, in the presence of a large excess of Et_2BH* (ref.[7]) (hydride bath[4]), undergo fast hydroboration

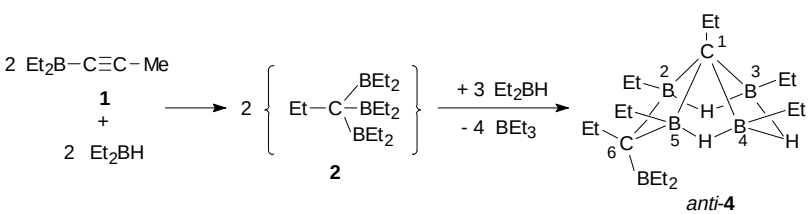
* The formula Et_2BH is used for simplicity: tetraethyldiborane(6) is usually obtained and used as a mixture with triethylborane and small amounts of other ethyldiboranes(6).

to give 1-dimethylsilyl-1,1-bis(diethylboryl)propane and 1,1,1-tris(diethylboryl)propane (**2**), followed by a number of Et_2BH-catalyzed exchange reactions leading to the 1-carba-*arachno*-pentaborane(10) derivatives **3** as a 45/55 mixture of *syn/anti* isomers. This mechanistic proposal[4] was supported later on by the finding that diethyl(propyn-1-yl)-borane (**1**) itself can be transformed to the 1-carba-*arachno*-borane(10) derivative **4** (ref.[8]) when **1** is added to the hydride bath as shown in Scheme 2.



SCHEME 1

In the present work, we want to present further evidence for the Et_2BH-catalyzed condensation of polyborylated alkanes to 1-carba-*arachno*-pentaborane(10) derivatives using trimethyl(propyn-1-yl)silane or diethyl(vinyl)borane together with diethyl(propyn-1-yl)borane or tris(diethylboryl)methane as starting materials.



SCHEME 2

EXPERIMENTAL

All experiments were carried out in an atmosphere of dry argon excluding oxygen and moisture. 1,2-Dimethoxyethane was dried over Na/K alloy, distilled and stored under argon. The following commercial compounds were used: triethylborane, boron trichloride, propyne, trimethylsilyl chloride, tributylstannyl chloride, butyllithium in hexane (1.6 mol l^{-1}), sodium tetrahydroborate. The following compounds were prepared according to literature procedures: diethylboron chloride[9], diethylborane[10], trimethyl(propyn-1-yl)silane[11], tributyl(propyn-1-yl)stannane[11].

For the characterization of the compounds and mixtures of compounds, the following NMR spectrometers were used: Jeol FX 90Q, Bruker ARX 250, Bruker AX 300. The chemical shifts δ are given in ppm, positive values indicate a shift to higher frequency (lower field) with respect to the reference. External references are: tetramethylsilane (^{1}H, ^{13}C, ^{29}Si NMR), boron trifluoride etherate (^{11}B NMR), tetramethylstannane (^{119}Sn NMR).

Diethyl(propyn-1-yl)borane (**1**)

Tributyl(propyn-1-yl)stannane (28.376 g, 86.22 mmol) was added dropwise over a period of 30 min at –40 °C to diethylboron chloride (9.023 g, 86.44 mmol). Then the solution was stirred for further 20 min to reach room temperature, and 8.346 g (89.6%) of compound **1** were condensed at 0.133 Pa into a liquid nitrogen-cooled trap. ^{1}H NMR spectrum (250.1 MHz, 25 °C, $CDCl_3$): 1.85 s, 3 H (≡C-C**H**$_3$); 1.25 q, 4 H (BC**H**$_2$CH$_3$); 1.00 t, 6 H (BCH$_2$C**H**$_3$). ^{11}B NMR spectrum (80.3 MHz, 25 °C, $CDCl_3$): 74.0. ^{13}C NMR spectrum (62.9 MHz, –30 °C, $CDCl_3$): 120.9 (≡**C**-CH$_3$); 89.6 (B-**C**≡); 21.6 br (B**C**H$_2$CH$_3$); 10.0 (BCH$_2$**C**H$_3$); 5.3 (≡C-**C**H$_3$).

1-(Diethylboryl)-1-(trimethylsilyl)prop-1-ene (**5**)

In an NMR tube, diethylborane (0.092 g, 1.22 mmol hydride) was added to a solution of trimethyl(propyn-1-yl)silane (0.137 g, 1.22 mmol) in 0.5 ml of $CDCl_3$ at –78 °C. After warming up to room temperature, the solution contained mainly 1-(diethylboryl)-1-(trimethylsilyl)prop-1-ene (**5**) (>80% purity according to ^{11}B NMR data). ^{1}H NMR spectrum (250.1 MHz, 25 °C, $CDCl_3$): 5.91 q, 1 H (=C**H**-); 1.85 d, 3 H, (=CH-C**H**$_3$); 1.16 q, 4 H (BC**H**$_2$CH$_3$); 0.91 t, 6 H (BCH$_2$C**H**$_3$); 0.12 s, 9 H ((C**H**$_3$)$_3$Si). ^{11}B NMR spectrum (80.3 MHz, 25 °C, $CDCl_3$): 83.5. ^{13}C NMR spectrum (62.9 MHz, –30 °C, $CDCl_3$): 153.5 br (=**C**); 136.0 (=**C**H-); 20.4 (=CH-**C**H$_3$); 20.6 br (B**C**H$_2$CH$_3$); 8.7 (BCH$_2$**C**H$_3$); 0.6 ((**C**H$_3$)$_3$Si). ^{29}Si NMR spectrum (17.9 MHz, 25 °C, $CDCl_3$): –13.1.

Diethyl(vinyl)borane (**7**)

Dibutyl(divinyl)stannane (19.804 g, 69.00 mmol) was added dropwise to diethylboron chloride (7.186 g, 68.8 mmol) over a period of 15 min at 0 °C. Then the solution was stirred for further 30 min at room temperature before 5.821 g (88.1%) of pure **7** were condensed at 0.133 Pa into a liquid nitrogen-cooled trap. ^{1}H NMR spectrum (250.1 MHz, 25 °C, $CDCl_3$): 6.64 dd, 6.11 dd, 6.02 dd, 3 H (**H**$_2$C=C**H**-); 1.31 q, 4 H (BC**H**$_2$CH$_3$); 1.03 t, 3 H (BCH$_2$C**H**$_3$). ^{11}B NMR spectrum (80.3 MHz, 25 °C, $CDCl_3$): 77.5. ^{13}C NMR spectrum (62.9 MHz, –30 °C, $CDCl_3$): 141.6 br (B**C**H=); 135.1 (=**C**H$_2$); 17.7 br (B**C**H$_2$CH$_3$); 8.6 (BCH$_2$**C**H$_3$).

1,1-Bis(diethylboryl)ethane (**8**)

Diethylborane (0.50 g, 6.3 mmol hydride) was added to diethyl(vinyl)borane (**7**) (0.521 g, 5.23 mmol) at –78 °C. The mixture was stirred for further 10 min at room temperature, and then all B–H bonds were converted into B–C bonds by saturating the solution with ethene for 2 h. Fractional distillation

under reduced pressure (b.p. 43–46 °C/1.6 kPa) gives 0.490 g (56.4%) of pure **8**. ^{1}H NMR spectrum (250.1 MHz, 25 °C, $CDCl_3$): 2.32 q, 1 H (C**H**); 1.05 d, 3 H (CH-C**H**$_3$); 1.19 q, 8 H (BC**H**$_2$CH$_3$); 0.94 t, 12 H (BCH$_2$C**H**$_3$). ^{11}B NMR spectrum (80.3 MHz, 25 °C, $CDCl_3$): 85.6. ^{13}C NMR spectrum (75.5 MHz, –30 °C, $CDCl_3$): 39.9 br (**C**H); 10.9 (CH-**C**H$_3$); 19.1 br (B**C**H$_2$CH$_3$); 8.5 (BCH$_2$**C**H$_3$).

syn-1,2,3,4,5-Pentaethyl-2,5-[1-(trimethylsilyl)propane-1,1-diyl]-1-carba-*arachno*-pentaborane(10) (**6**)

A solution of diethyl(propyn-1-yl)borane (**1**) (0.318 g, 2.95 mmol) in 20 ml of triethylborane was added dropwise to a solution of trimethyl(propyn-1-yl)silane (0.322 g, 2.96 mmol) in diethylborane (1.840 g, 24.4 mmol hydride) over a period of 2 h. After stirring for further 2 h, all volatile material was removed *in vacuo*. Fractional distillation under reduced pressure (b.p. 98–101 °C/0.003 Pa) gave 0.3105 g (33.1%) **6** (>80% purity from ^{11}B NMR data). ^{1}H NMR spectrum (250.1 MHz, 25 °C, $CDCl_3$): –2.03 br, 1 H (B(3)-**H**-B(4)); –1.35 br, 2 H (B(2)-**H**-B(3), B(4)-**H**-B(5)); 1.51 q, 2 H (C(1)C**H**$_2$CH$_3$); 1.05 t, 3 H (C(1)CH$_2$C**H**$_3$); 1.40 q, 2 H (C(6)C**H**$_2$CH$_3$); 0.94 t, 3 H (C(6)CH$_2$C**H**$_3$); 0.55 m, 0.60 m, 8 H (BC**H**$_2$CH$_3$); 0.97 t, 0.90 t, 12 H (BCH$_2$C**H**$_3$); 0.02 s, 9 H ((C**H**$_3$)$_3$Si). ^{13}C NMR spectrum (62.9 MHz, –30 °C, $CDCl_3$): 25.2 (C(6)**C**H$_2$CH$_3$); 15.8 (C(6)CH$_2$**C**H$_3$); 16.5 (C(1)**C**H$_2$CH$_3$); 16.4 (C(1)CH$_2$**C**H$_3$); 8.6 br, 8.0 br (B**C**H$_2$CH$_3$); 13.3, 13.2 (BCH$_2$**C**H$_3$); 1.2 ((**C**H$_3$)$_3$Si). ^{29}Si NMR spectrum (17.9 MHz, 25 °C, $CDCl_3$): 4.6.

syn/anti-1,2,3,4,5-Pentaethyl-2,5-(ethane-1,1-diyl)-1-carba-*arachno*-pentaborane(10) (**9**)

A solution of diethyl(propyn-1-yl)borane (**1**) (3.876 g, 35.89 mmol) in 30 ml of triethylborane was added dropwise to a solution of diethyl(vinyl)borane (**7**) (3.361 g, 35.01 mmol) in diethylborane (18.871 g, 250.3 mmol hydride) over a period of 2 h. After stirring for further 2 h, all volatile material was removed *in vacuo*. Fractional distillation under reduced pressure (b.p. 67–70 °C/0.133 Pa) gave 4.03 g (52.4%) of a mixture of *syn/anti*-**9** in a *ca* 1/2 ratio (^{1}H NMR data). *syn*-**9**: ^{1}H NMR spectrum (250.1 MHz, 25 °C, $CDCl_3$): –1.45 br, 1 H (B(3)-**H**-B(4)); 0.10 br, 2 H (B(2)-**H**-B(3), B(4)-**H**-B(5)); –0.68 m, 1 H (C(6)-**H**); 0.80 d, 3 H (C(6)-C**H**$_3$); 1.50 q, 2 H (C(1)C**H**$_2$CH$_3$); 0.80 t, 5 H (C(1)CH$_2$C**H**$_3$); 0.58 m, 0.52 m, 8 H (BC**H**$_2$CH$_3$); 0.97 t, 0.92 t, 12 H (BCH$_2$C**H**$_3$). ^{13}C NMR spectrum (62.9 MHz, –30 °C, $CDCl_3$): 17.2 (C(1)**C**H$_2$CH$_3$); 9.8 (C(1)CH$_2$**C**H$_3$); 14.4 (C(6)**C**H$_3$); 7.7 br, 2.6 br (B**C**H$_2$CH$_3$); 13.2, 12.2 (BCH$_2$**C**H$_3$). *anti*-**9**: ^{1}H NMR spectrum (250.1 MHz, 25 °C, $CDCl_3$): –1.56 br, 1 H (B(3)-**H**-B(4)); 0.15 br, 2 H (B(2)-**H**-B(3), B(4)-**H**-B(5)); –0.84 m, 1 H (C(6)-**H**); 0.73 d, 3 H (C(6)-C**H**$_3$); 1.53 q, 2 H (C(1)C**H**$_2$CH$_3$); 0.83 t, 3 H (C(1)CH$_2$C**H**$_3$); 0.62 m, 0.50 m, 8 H (BC**H**$_2$CH$_3$); 0.94 t, 0.88 t, 12 H (BCH$_2$C**H**$_3$). ^{13}C NMR spectrum (62.9 MHz, –30 °C, $CDCl_3$): 17.7 (C(1)**C**H$_2$CH$_3$); 14.1 (C(1)CH$_2$**C**H$_3$); 18.3 (C(6)**C**H$_3$); 10.6 br, 2.0 br (B**C**H$_2$CH$_3$); 13.3, 11.3 (BCH$_2$**C**H$_3$).

anti-2,3,4,5-Tetraethyl-2,5-(ethane-1,1-diyl)-1-carba-*arachno*-pentaborane(10) (**11**)

A solution of tris(diethylboryl)methane **10** (1.801 g, 8.19 mmol) in 30 ml of triethylborane was added dropwise to a solution of diethyl(vinyl)borane **7** (0.787 g, 8.20 mmol) in diethylborane (3.696 g, 49.02 mmol hydride) over a period of 4 h. After stirring for further 10 h all volatile material was removed *in vacuo*. Fractional distillation under reduced pressure (b.p. 43–47 °C/0.133 Pa) gave 0.35 g of a mixture with *anti*-**11** as the main component (*ca* 45%). ^{1}H NMR spectrum (250.1 MHz, 25 °C, $CDCl_3$): –1.61 br, 1 H (B(3)-**H**-B(4)); 0.00 br, 2 H (B(2)-**H**-B(3), B(4)-**H**-B(5)); –0.85 m, 1 H (C(6)-**H**); 0.71 d, 3 H (C(6)C**H**$_3$); 0.35 s, 1 H, ^1J(^{13}C,^{1}H) = 177 Hz (C(1)-**H**); 0.91 m, 0.67 m, 8 H (BC**H**$_2$CH$_3$); 0.95 t, 0.85 t, 12 H (BCH$_2$C**H**$_3$). ^{13}C NMR spectrum (62.9 MHz, –30 °C, $CDCl_3$): 18.0 (C(6)**C**H$_3$); 11.9 br, 2.5 br (B**C**H$_2$CH$_3$); 13.2, 10.7 (BCH$_2$**C**H$_3$).

syn-2,3,4,5-Tetraethyl-2,5-[(diethylboryl)methylene]-1-carba-*arachno*-pentaborane(10) (**12**)

In an NMR tube, diethylborane (0.173 g, 2.29 mmol hydride) was added to tris(diethylboryl)methane (**10**) (0.162 g, 0.737 mmol) in 0.4 ml of CD_2Cl_2. After 60 min, *ca* 10% of tris(diethylboryl)methane (**10**) have reacted to give *syn*-**12** without side products. However, the amount of side products increased rapidly with reaction time. ^{13}C NMR spectrum (62.9 MHz, –60 °C, CD_2Cl_2): 5.7 br, 3.0 br ($B\mathbf{C}H_2CH_3$); 13.7, n.o. ($BCH_2\mathbf{C}H_3$); 18.6 br ($B(\mathbf{C}H_2CH_3)_2$); 9.2 ($B(CH_2\mathbf{C}H_3)_2$).

RESULTS AND DISCUSSION

The electron count of the title compounds is in agreement with an *arachno* type structure derived from B_5H_{11} with a tetracoordinate bridging carbon atom C(6). Since the position of this bridging carbon atom is in the cluster area, C(6) could also be regarded as a cluster atom, and one would deal with derivatives of 1,6-dicarba-*arachno*-hexaborane(10), again with correct electron count. The concept of a simple predominant bridging function of C(6) is supported by calculated (see also ref.[6]) and experimental NMR data of another 1-carba-*arachno*-pentaborane(10) derivative, in which an *ortho*-phenylene moiety occupies the bridging position[5]. These ^{11}B and $^{13}C(1)$ NMR data are in very good agreement, given for the different substituent pattern, with the data of the compounds **3**, **4**, **6**, and **10–12** (Table I). If carbon atom C(6) would be an essential part of the cluster, it would have considerable influence on the electronic structure, and one would expect that the replacement of C(6) by the *ortho*-phenylene group should influence significantly the respective ^{11}B and $^{13}C(1)$ magnetic shielding, which is not the case.

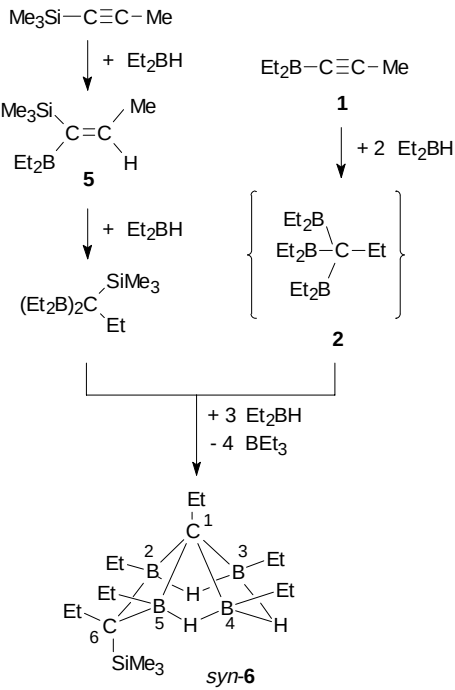
TABLE I
^{11}B (80.3 MHz, 25 °C, $CDCl_3$) and ^{13}C (62.9 MHz, –30 °C, $CDCl_3$) chemical shifts (ppm) of the skeleton atoms and the bridging carbon atoms

Compound	δC(1)	δB(2,5)	δB(3,4)	δC(6)
syn-**3**	6.2[a]	13.5[b]	–12.1[b]	–13.2[a]
anti-**3**	10.3[a]	14.9[b]	–12.1[b]	–6.8[a]
syn-**4**[f]	7.8[c]	13.3[d]	–12.1[d]	17.2[c]
anti-**4**	0.3[e]	10.0[d]	–11.1[d]	12.9[e]
syn-**6**	2.7	12.0	–11.0	–13.1
syn-**10**	7.3	12.9	–12.0	–14.6
anti-**10**	8.3	12.9	–12.5	–8.9
anti-**11**	1.2	12.9	–13.5	–10.8
syn-**12**	–4.8[c]	10.7[d]	–13.5[d]	n.o.

[a] –50 °C; [b] 160.5 MHz; [c] –60 °C, CD_2Cl_2; [d] CD_2Cl_2; [e] 75.5 MHz, –80 °C, CD_2Cl_2. [f] Ref.[12].

Reaction of Trimethyl(propyn-1-yl)silane with Et_2BH and Diethyl(propyn-1-yl)borane

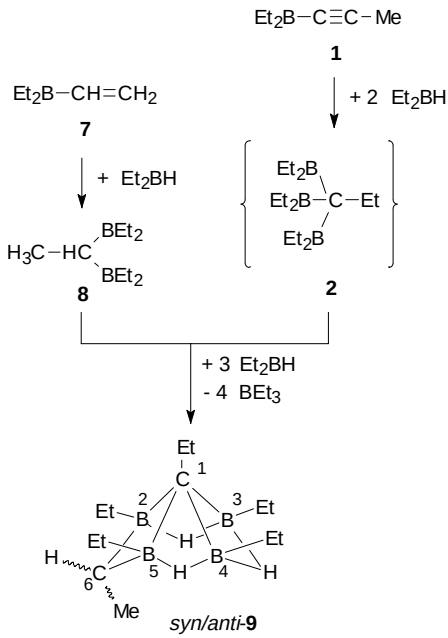
If the proposed mechanism shown in Scheme 1 is correct, hydroboration of trimethyl(propyn-1-yl)silane and diethyl(propyn-1-yl)borane with Et_2BH in excess (hydride bath) should lead to the 1-carba-*arachno*-pentaborane(10) derivatives **6**. The reaction proceeds in the expected way as shown in Scheme 3. In contrast to the previous findings for the ≈45/55 ratio of the *syn/anti* isomers (Scheme 1), the isomer *syn*-**6** is formed in a large excess. The identity of the carborane **6** is readily evident by inspection of the ^{11}B and ^{13}C NMR data (Table I).



SCHEME 3

Reaction of Diethyl(vinyl)borane with Et_2BH and Diethyl(propyn-1-yl)borane

The results obtained so far indicate that there is a general route to 1-carba-*arachno*-pentaborane(10) derivatives, using geminal bis(diethylboryl)alkanes and diethyl(propyn-1-yl)borane (**1**) in the presence of an excess of Et_2BH. This is demonstrated (Scheme 4) by the example of diethyl(vinyl)borane (**7**) which reacts with Et_2BH to give 1,1-bis(diethylboryl)ethane (**8**), and the addition of diethyl(propyn-1-yl)borane (**1**) to **8** in the hydride bath leads to the 1-carba-*arachno*-pentaborane(10) derivatives **9** (*syn/anti ca* 1/2). Again, the carboranes are readily identified by their ^{11}B and ^{13}C NMR data (Table I).



SCHEME 4

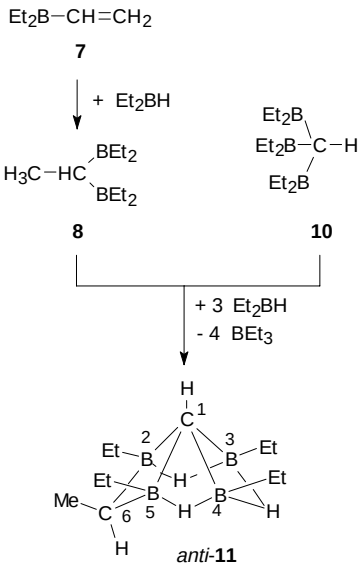
Reaction of Diethyl(vinyl)borane with Et_2BH and Tris(diethylboryl)methane

In contrast with 1,1,1-tris(diethylboryl)propane (**2**), which is generated *in situ*, tris(diethylboryl)methane (**10**) is accessible as a pure product[2b]. Treatment of diethyl(vinyl)borane (**8**) with an excess of Et_2BH and addition of tris(diethylboryl)methane (**10**) leads to a mixture of numerous compounds which could not be separated by fractional distillation. However, the main component (*ca* 45%) of this mixture was identified as the 1-carba-*arachno*-pentaborane(10) derivative **11** (Scheme 5) on the basis of typical ^{11}B and ^{13}C NMR data (Table I). The large magnitude of $^1J(^{13}C(1)^1H)$ = 177 Hz indicates unambiguously the apical position of this carbon atom. It appears that the formation of the isomeric *anti*-**11** is favoured.

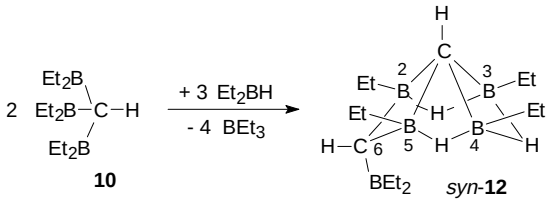
Reaction of Tris(diethylboryl)methane with Et_2BH

Since the *in situ* generated 1,1,1-tris(diethylboryl)propane (**2**) reacts with an excess of Et_2BH to give the 1-carba-*arachno*-pentaborane(10) derivative **4** in almost quantitative yield[8] (Scheme 2), it was of interest to study the behaviour of tris(diethylboryl)methane (10) under analogous reaction conditions (Scheme 6). This reaction proceeds in a much less straightforward way. A complex mixture of unknown boranes and carboranes is formed. However, it proved possible to identify the 1-carba-*arachno*-pentaborane(**10**)

derivative **12** by some characteristic NMR data (*e.g.* $^1J(^{13}C(1)^1H)$ = 185 Hz, Table I) as a minor product (*ca* 10%) in the reaction mixture.



SCHEME 5



SCHEME 6

CONCLUSIONS

1-Carba-*arachno*-pentaborane(10) derivatives are now readily available with ethyl groups as substituents in apical position and at the boron atoms. In the absence of the apical ethyl group, only complex mixtures are observed, although it was possible to identify the 1-carba-*arachno*-pentaboranes(10) as a major or minor product. The present results confirm the proposed mechanism, in which a large excess of Et_2BH (hydride bath[4]) plays an important role. As a result of B–C/B–H exchange, the $(Et_2B)_2C$ and $(Et_2B)_3C$ fragments are held together allowing for further intramolecular exchange reactions to take place, which lead to the 1-carba-*arachno*-pentaborane(10) skeleton. Clearly, these 1-carba-*arachno*-pentaborane(10) derivatives are of interest for further transformations. Thermally induced elimination of H_2, silanes or boranes[8,12] may lead

to other carbaboranes with a *closo*- or *nido*-structure, as has already been demonstrated in the case of borane elimination[8,12].

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