Condensation Route from 1,1,1-Tris(diethylboryl)propane to Pentaethyl-1,5-dicarba-*closo*-pentaborane(5) *via arachno*-CB₄(10) and *nido*-C₂B₄(8) Carbaboranes

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Diethyl(prop-1-ynyl)borane **1** reacts, in the presence of a large excess of tetraethyldiborane(6), to give the new substituted 1-carba-*arachno*-pentaborane(10) **4** as the first intermediate which can be isolated; **4** rearranges *via* the *nido*-C₂B₄(8) carbaboranes **A** and **B** to the known pentaethyl-1,5-dicarba-*closo*-pentaborane(5) **5** which is characterized by single crystal X-ray analysis.

Although both synthesis and properties of polyboranes have been intensively studied since the pioneering work of Alfred Stock,[1] mechanisms of formation, explaining the condensation of boron hydrides, are still debatable. This is also true for many of the small carbaboranes which are accessible in low yield from the reactions between tetraborane(10) or pentaborane(9) and alkynes,[2] and by dehalogenations of alkylboron halides with alkali metals,[3] preventing any firm mechanistic conclusions. In contrast, the formation of C,B-alkylated 1,5-dicarba-*closo*-pentaboranes(5) from condensation of two equivalents of 1,1,1-tris(dialkylboryl)alkanes of the type **3**, *via* [>BH]-catalysed elimination of trialkylborane, appears to be a straightforward route.[4,5] These smallest *closo*-carbaboranes deserve particular interest, since their structure and bonding may be described as being midway between classical and non-classical.[6] They have already served as starting materials for the synthesis of peralkylated hexaboraadamantanes and their non-classical valence isomers, the fluxional *nido*-C₄B₆(10) carbaboranes.[7] Stimulated by the recent synthesis of relatively stable alkyl-substituted 1-carba-*arachno*-pentaborane(10) derivatives,[8] potential precursors of *nido*- and *closo*-carbaboranes, we have now re-investigated the complete hydroboration of diethyl(prop-1-ynyl)borane **1**[9] in the presence of a large excess of tetraethyldiborane(6)† ('hydride bath'), Scheme 1. By this, a new route to pentaethyl-1,5-dicarba-*closo*-pentaborane(5) **5** was elucidated, and for the first time, the molecular structure of a *closo*-C₂B₃(5) carbaborane was determined by single crystal X-ray diffraction analysis.

By monitoring the reactions shown in Scheme 1, using ¹¹B NMR, it becomes evident that the hydroboration proceeds *via*
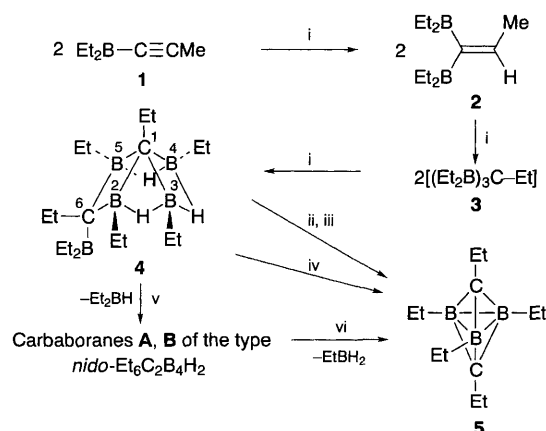

Scheme 1 *Reagents and conditions*: i, tetraethyldiborane(6)† serves as the solvent, −78 °C to room temp., 1 h; ii, in tetraethyldiborane(6) at room temp. for 20 d, or after 4 h at 100 °C; iii, C₆D₆ solution in the presence of pyridine or 4-methylpyridine, several days; iv, 110 °C, 24 h, no solvent; v, 110 °C, 10⁻⁴ Torr, 1 h, collected in a trap at 0 °C, see text; vi, 150 °C, 1 h

1,1-bis(diethylboryl)but-1-ene **2** (δ¹¹B 76.4). However, the next product which can be detected is not the 1,1,1-tris-(diethylboryl)propane **3**[4,5] but the new 1-carba-*arachno*-pentaborane(10) derivative **4**[8] which is most likely formed by [>BH]-catalysed condensation of two molecules of **3**, a typical function of the 'hydride bath'.[8] The structure of **4** follows conclusively from its consistent NMR data,‡ in agreement with ¹H, ¹¹B and ¹³C NMR data for analogous compounds in which the Et₂B group in **4** is replaced by a Me₂HSi group.[8]

If **4** is kept in the 'hydride bath', the rearrangement to **5** is complete after 20 days at room temp., or after 4 h at 100 °C. Addition of Lewis bases such as pyridine to solutions of **4** also induces the conversion to **5** at room temp. After heating compound **4** to 110 °C for 24 h without a solvent, an essentially quantitative rearrangement to **5** is observed, by elimination of Et₃B and ethyldiboranes(6), as shown by ¹¹B NMR. If **4** is heated to 110 °C *in vacuo* for 1 h, a mixture of volatile compounds can be collected in a trap cooled to 0 °C. According to the ¹¹B NMR spectra, this mixture contains small amounts of both *arachno*-CB₄(10) **4** and *closo*-C₂B₃(5) carbaboranes **5**, in addition to two other presumably *nido*-C₂B₄(8) carbaboranes **A** and **B** as major products (ratio *ca.* 3:1) with three ¹¹B NMR signals for **A** (δ¹¹B 39.4, 17.9, 12.4 and −27.8 in a 1:1:1 ratio with cross peaks in the 2D ¹¹B–¹¹B COSY spectrum) and one ¹¹B NMR signal for **B** (δ¹¹B −11.1). The structure of the final product **5**§ [δ¹¹B 13.8;[5] δ¹³C 106.3, C(1,5)[10]] requires that the bridging carbon atom C(6) in **4** becomes part of the carbaborane framework during the course of further condensation leading to **A** and **B**, accompanied by elimination of Et₂BH. All known neutral *nido*-C₂B₄(8) carbaboranes have the two skeleton carbon atoms adjacent to each other, and their δ¹¹B values[11] are not at all compatible with those for **A** or **B**, suggesting that *nido*-structures of **A** and **B** must be constructed without C–C bonds. Both **A** and **B** are precursors of **5**, since the mixture of **A** and **B** is transformed into **5** by heating to 150 °C for 1.5 h.

The molecular structure of **5**¶ is shown in Fig. 1. It possesses C_1 symmetry in contrast to the parent *closo*-C₂B₃H₅ carbaborane with D_{3h} symmetry, as determined by electron diffraction.[12] The B–B distances [1.853(2) Å] are longer, and the B–C distances within the cage [1.556(2) Å] are shorter, resulting in a shortening of the C(1)···C(5) distance [2.261(3) Å], in comparison with the parent carbaborane.[12] At first sight, the geometry of **5** is compatible with a classical description of the bonding situation. However, the small endocyclic angles at the boron and carbon atoms suggest multicentre bonding[6] at the faces of the cage.‖

This study shows that the formation of 1-carba-*arachno*-pentaborane(10) derivatives of type **4** appears to be a general phenomenon if a 'hydride bath' is used for generating 1,1,1-tris(dialkylboryl)alkanes **3**.[8] The protection of terminal functions at the boron atoms by ethyl groups enables one to follow various cage rearrangements more readily than in the case of the binary boron hydrides. The *arachno*-CB₄(10) carbaboranes should be ideal starting points for studying the condensation to *nido*- and *closo*-cage structures, depending on
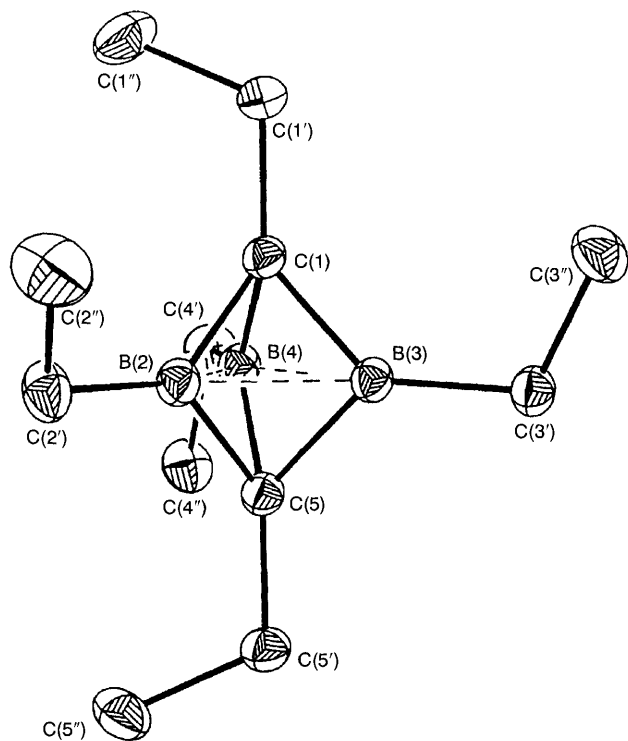
Fig. 1 Molecular structure of 5 as determined by X-ray analysis. Distances (Å) and selected bond angles (°): C(1)···C(5) 2.275(1), C(1)–B(2) 1.577(1), C(1)–B(3) 1.561(1), C(1)–B(4) 1.573(1), C(1)–B(4) 1.573(1), C(5)–B(2) 1.571(1), C(5)–B(3) 1.574(1), B(5)–B(4) 1.567(1), B(2)–B(3) 1.873(1), B(3)–B(4) 1.872(1), B(2)–B(4) 1.882(2), C(1)–C(1') 1.508(1), C(5)–C(5') 1.534(1), B(2)–C(2') 1.580(1), B(3)–C(3') 1.575(1), B(4)–C(4') 1.575(2), C(1)–C(1'') 1.526(1), C(2')–C(2'') 1.521(2), C(3)–C(3'') 1.535(1), C(4')–C(4'') 1.528(2), C(5')–C(5'') 1.534(1); B(2)–C(1)–B(3) 73.3(1), B(2)–C(1)–B(4) 73.4(1), B(3)–C(1)–B(4) 73.3(1), B(2)–C(5)–B(3) 73.1(1), B(2)–C(5)–B(4) 73.7(1), B(3)–C(5)–B(4) 73.2(1), C(1)–B(2)–C(5) 92.6(1), C(1)–B(3)–C(5) 93.0(1), C(1)–B(4)–C(5) 92.8(1), C(1)–C(1')–C(1'') 112.8(1), C(5)–C(5')–C(5'') 113.4(1), B(2)–C(2')–C(2'') 113.9(1), B(3)–C(3')–C(3'') 115.0(1), B(4)–C(4')–C(4'') 116.5(1).

the nature of the substituents and on the reaction conditions; this field is currently under investigation.

Footnotes

† Lewis-base free tetraethyldiborane(6) is present in a mixture with Et₃B and minor amounts of other ethyldiboranes(6); the hydride content can be determined by volumetric analysis of H₂ evolved by hydrolysis in diethyl ether[13] or by ^{11}B NMR.[8]

‡ Compound 4 is obtained as a yellowish, viscous liquid (NMR data suggest the endo-structure) in 23% yield and > 90% purity after all volatile material [^{11}B NMR analysis shows the presence of Et₃B, ethyldiboranes(6) and a significant amount of 5] had been removed in vacuo for 4 h at room temp. and then for 1 h at 70 °C. Selected data: v(BHB) 2080m cm⁻¹; ¹H NMR

(300 MHz, 25 °C, CD₂Cl₂) δ −1.00 [br, 2 H, B(2,4)–H–B(3,5)], −1.44 [br, 1 H, B(3)–H–B(4)], 1.64 (q), 0.95 [t, 5 H, C(1)–Et], 1.63 (q), 0.94 [t, 5 H, C(6)–Et], 0.61 (m), 0.63 (m), 0.95 (t), 1.07 [t, 20 H, B(2,3,4,5)–Et]; 1.13 (m), 0.97 (t, 10 H, BEt₂); ^{11}B NMR (80.3 MHz, CD₂Cl₂) δ 79.9 ($v_{1/2}$ 800 Hz, BEt₂), 10.0 [$v_{1/2}$ = 230 Hz, B(2,5)], −11.1 [$v_{1/2}$ 120 Hz, B(3,4)]; ^{13}C NMR (75.5 MHz, −80 °C, CD₂Cl₂) δ 0.3 [br C(1)], 12.9 [br, C(6)], 15.0, 9.0 [C(1)–Et], 25.2, 16.4 [C(6)–Et], 8.5 (br), 2.3 (br), 13.0, 12.9 [B(2,3,4,5)–Et], 14.8 (br) 14.1 (BEt₂).

§ Compound 5 is obtained as described[4] as a colourless liquid. Selected data: bp 84–86 °C (9 Torr); ¹H NMR (250 MHz, 25 °C, C₆D₆) δ 2.42 (q, 4 H), 1.21 [t, 6 H, C(1,5)–Et], 0.95 [br, 15 H, B(2,3,4)–Et], ^{11}B NMR (80.3 MHz, 25 °C, C₆D₆) δ 13.8; ^{13}C NMR (62.5 MHz, 25 °C, C₆D₆) δ 106.3 [br, C(1,5)], 18.7, 15.3 [C(1,5)–Et], 4.1 (br), 9.8 [B(2,3,4)–Et].

¶ Crystal data for 5: The crystal was grown by in situ crystallization with an IR laser beam producing a molten zone in a Lindemann capillary (0.3 mm diameter) at −80 °C (below the melting point of −61.5 °C⁵), thus performing a miniature zone refinement[14] from the neat material. C₁₂H₂₅B₃, M = 201.8, monoclinic, space group $P2_1/c$ (no. 14), a = 9.219(2), b = 20.669(7), c = 7.842(2) Å, β = 111.97(2)°, V = 1385.8 Å³, Z = 4, F(000) = 448, D_c = 0.967 Mg m⁻³, colourless, cylindric crystal, 0.3 mm diameter. Data were collected and processed using a Siemens R3m/V diffractometer (graphite-monochromized Mo-Kα radiation), T = 120 K; $2\theta_{max}$ = 90°, index ranges −18 ⩽ h ⩽ 15, −17 ⩽ k ⩽ 41, −2 ⩽ l ⩽ 15; 8842 intensities measured, 6898 independent (R_{int} = 0.0333), 5696 observed [F_o ⩾ 4.0 σ(F)]. The structure was solved and refined using direct methods (SHELXTL PLUS program package), full-matrix least squares on $\Sigma w(F_o − F_c)^2$; extinction correction X = 0.0065(13), where F^* = $F[1 + 0.002 X F^2/\sin(2\theta)]^{-1/4}$, weighting scheme w^{-1} = $\sigma^2(F) + 0.0021F^2$, hydrogen atoms isotropic without constraints, all other atoms anisotropic, 237 refined parameters, data-to-parameter ratio 24.0 : 1, R, R_w = 0.0556, 0.062, S = 1.1751; maximum residual electron density 0.31 e Å⁻³. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‖ A detailed discussion of the bonding situation together with the X–X experimental electron density distribution and MO calculations will be published elsewhere.[15]

References

1 A. Stock, Hydrides of Boron and Silicon, Cornell University Press, Ithaca, New York, 1993, pp. 51–85.

2 R. N. Grimes, Carboranes, Academic, London, 1970.

3 R. Köster, G. Benedikt and M. A. Grassberger, Justus Liebigs Ann. Chem., 1968, 719, 187.

4 R. Köster and G. W. Rotermund, Tetrahedron Lett., 1964, 1667.

5 R. Köster, H.-J. Horstschäfer, P. Binger and P. K. Mattschei, Liebigs Ann. Chem., 1975, 1339.

6 T. Onak and K. Fuller, in Electron Deficient Boron and Carbon Clusters, ed. G. A. Olah, K. Wade and R. E. Williams, Wiley, New York, 1991, pp. 183–194.

7 R. Köster, G. Seidel and B. Wrackmeyer, Angew. Chem., 1985, 97, 317; Angew. Chem., Int. Ed. Engl., 1985, 24, 326; R. Köster, G. Seidel, B. Wrackmeyer, D. Bläser, R. Boese, M. Bühl and P. v. R. Schleyer, Chem. Ber., 1991, 124, 2715.

8 R. Köster, G. Seidel and B. Wrackmeyer, Angew. Chem., 1994, 106, 2380; Angew. Chem., Int. Ed. Engl., 1994, 33, 2294.

9 R. Köster, H.-J. Horstschäfer and G. Seidel, Inorg. Synth., 1992, 29, 77.

10 R. Köster and B. Wrackmeyer, Z. Naturforsch., Teil B, 1981, 36, 704.

11 A. R. Siedle, Annu. Rep. NMR Spectrosc., 1982, 12, 177.

12 F. A. McNeill, K. L. Gallaher, F. R. Scholer and S. H. Bauer, Inorg. Chem., 1973, 12, 1208.

13 R. Köster and P. Binger, Inorg. Synth., 1974, 15, 141.

14 R. Boese and M. Nussbaumer, in Correlations, Transformations, and Interactions in Organic Crystal Chemistry, IUCr Crystallographic Symposia, ed. D. W. Jones and A. Katrusiak, Oxford University Press, Oxford, 1994, vol. 7, pp. 20–37.

15 D. Boese and D. Blaser, unpublished work.