A General Preparative Route to Compounds Containing 10-Vertex *arachno*- and *nido*-Tricarbaborane Cages

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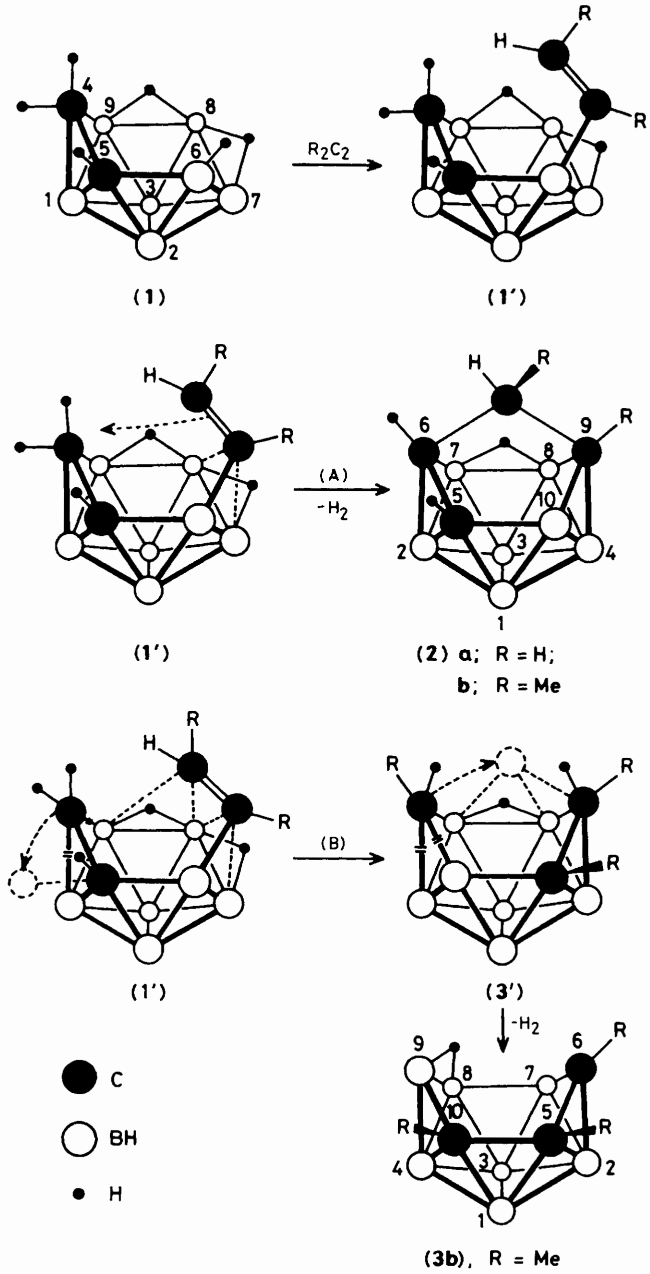
Two representatives of the 10-vertex family of tricarbaboranes, *arachno*-μ-6,9-RCH-9-R-5,6,9-$C_3B_7H_{11}$ (R = H or Me) and *nido*-5,6,10-Me_3-5,6,10-$C_3B_7H_8$, arise from two different modes of alkyne insertion (acetylene and but-2-yne) into the cage of *arachno*-4,5-$C_2B_7H_{13}$.

Only three types of neutral carbaboranes with a tricarborane framework have so far been fully characterized: the alkyl derivatives of *nido*-2,3,4-$C_3B_3H_7$[1] and two isomeric *arachno* compounds, μ-6,9-MeCH-5,6,10-Me_3-5,6,10-$C_3B_7H_9$ and μ-6,7-MeCH-5,6,10-Me_3-5,6,10-$C_3B_7H_9$.[2] The last two compounds, arising from degradative removal of one boron vertex from *nido*-$Me_4C_4B_8H_8$,[3] can be formulated alternatively as tetracarbon fragments of 13-vertex polyhedra. We now report our preliminary results on the development of a general synthetic route to new 10-vertex tricarbaboranes containing either a carbon bidentate *endo*-substituent bridging the 6,9-positions of the *arachno* tricarbadecaborane cage or a clean *nido* tricarbaborane framework.

Heating of *arachno*-4,5-$C_2B_7H_{13}$ (**1**)[4] with acetylene in hexane at 120 °C for 12 h resulted in the formation of a product mixture from which pure *arachno*-μ-6,9-CH_2-5,6,9-$C_3B_7H_{11}$



Scheme 1. Simplified representation of two characteristic modes (A and B) of the insertion of alkynes into the *arachno*-framework of 4,5-$C_2B_7H_{13}$.

(**2a**) was isolated in *ca.* 15% yield by column chromatography on silica gel in hexane. Additional tricarbaborane products have not yet been completely characterized and isolated.

Treatment of (**1**) with but-2-yne under the same conditions produced two main products, characterized as *arachno*-μ-6,9-MeCH-9-Me-5,6,9-Me-5,6,9-$C_3B_7H_{11}$ (**2b**) and *nido*-5,6,10-$C_3B_7H_8$ (**3b**), which were isolated in the pure state *via* preparative h.p.l.c. in hexane (yields *ca.* 30 and 15%, respectively).

The structures of all carbaboranes isolated are in agreement with their mass spectroscopic and ^1H, ^{13}C, ^{11}B, and 2-dimensional ^{11}B–^{11}B n.m.r. data.† The 2-dimensional measurements allow the ^{11}B resonances found in 1-dimensional spectra to be assigned to specific boron nuclei. All cross peaks expected for structures (**2a**), (**2b**), and (**3b**) shown in Scheme 1 were found in the 2-dimensional spectra except for those between boron atoms connected by bridging hydrogen atoms. These results clearly identified the boron networks in these compounds.

Even though no mechanistic data are available, the two different reaction pathways shown in Scheme 1 seem to account for the observed course of the insertion process. The reaction is consistent with the *cis*-hydroboration of the alkyne with the *endo*-hydrogen of the cage B(6)H_2 unit in (**1**). The *endo-cis*-6-RCH=CR– derivative (**1'**) (R = H or Me) thus formed then undergoes two modes (A and B) of C_2-insertion. Mode (A) suggests a clean C_2-insertion process *via* direct formation of a transmolecular C(6)–RCH–C(9) bridge, while pathway (B) is compatible with an insertion in which the least connected C(6)H_2 vertex has been expelled from the cage to form an Me substituent outside the cage. The suggested *arachno*-5,6,9-Me_3-5,6,9-$C_3B_7H_{10}$ intermediate (**3'**) is probably unstable under the conditions used, evolving dihydrogen and producing the *nido*-species (**3b**).

Compounds (**2a**) and (**2b**) are positional isomers of the previously reported[2] μ-6,9-MeCH-5,6,10-Me_3-5,6,10-$C_3B_7H_9$ and μ-6,7-MeCH$C_3B_7H_9$ compounds, which were preferably formulated as 11-vertex tetracarbaboranes. In this respect, compound (**2a**) is the second known parent tetracarbaborane and compound (**3b**) is the second known carbaborane with a clean tricarbaborane cage.

The C_2-insertion reactions of (**1**) reported here have proved to be a promising source of compounds containing polycarbon–borane frameworks. We are currently studying boron degradation and insertion reactions in this series including those leading to metallacarbaboranes.

Received, 20th March 1987; Com. 354

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† *Mass spectra* (high mass molecular cutoff, *m/z*): (**2a**) 138; (**2b**) 166; (**3b**) 166 (parent ions); ^1H n.m.r. spectra (200 MHz, $CDCl_3$): (**2a**), δ 4.19 (s, 1 H, H-5 or -6), 3.25 (s, 1 H, H-5 or -6), 2.03 (s, 1 H, μCH), 1.85 (d, 1 H, ^2J 11.5 Hz, μCH), 1.56 (s, 1 H, H-9), −2.14 (br.s, 1 H, μH); (**2b**), δ 3.71 (s, 1 H, H-5 or -6), 3.27 (s, 1 H, H-5 or 6), 2.29 (asym. q, 1 H, μCH), 1.15 (d, 3 H, ^2J 12.5 Hz, μMe), 1.34 (s, 3 H, Me-9), −1.59 (br.s, 1 H, μH); (**3b**), δ 2.10 (s, 6 H), 2.05 (s, 3 H), −2.22 (br.s, 1 H, μH), referenced to $SiMe_4$; ^{13}C n.m.r. spectrum (50.31 MHz, $CDCl_3$) of (**2a**), δ_C 64.68 (m, 1 C, μC), 53.07 (d, 1 C, J_{CH} 187 Hz, C-5 or -6), 41.61 (d, 1 C, 164, C-5 or -6), 29.12 (d, 1 C, 161, C-9), referenced to $SiMe_4$. ^{11}B n.m.r. spectra (64.18 MHz, $CDCl_3$); (**2a**), δ_B 7.65 (d, 1 B, $J_{BH}/^2J_{BH}$ 152/54 Hz, B-7), −1.66 (d, 2 B, 149, B-4, 8), −4.20 (d, 1 B, J 174, B-2), −12.96 (d, 1 B, 112, B-10), −13.99 (d, 1 B, 166, B-1), −42.52 (d, 1 B, 153, B-3); (**2b**), δ_B 10.40 (d, 1 B, 150/60, B-7), 0.40 (d, 1 B, 170, B-2), −2.46 (d, 2 B, 150, B-4,8), −13.00 (d, 1 B, 171, B-1), −13.82 (d, 1 B, 130, B-10), −43.80 (d, 1 B, 152, B-3); (**3b**), δ_B 4.30 (d, 1 B, 163/51, B-9), 2.82 (d, 1 B, 142, B-7), −0.44 (d, 1 B, 185, B-1), −6.05 (d, 1 B, 143, B-8), −10.27 (d, 2 B, 135, B-2,3), −40.74 (d, 1 B, 135, B-4) p.p.m., referenced to $BF_3 \cdot OEt_2$; assignments based on 2-dimensional ^{11}B–^{11}B spectra.