The Parent Hexacarbaborane *arachno*-$C_6B_6H_{12}$ and a Methylated Pentacarbaborane *arachno*-$CH_3C_5B_7H_{12}$: Domains of Incipient Hydrocarbon Behavior within Borane Clusters**

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Hydrocarbons have as a structural basis domains of the diamond or graphite lattice, or combinations thereof, with peripheral bonds to hydrogen. The structural basis of boron hydrides are hollow triangulated polyhedral clusters, the surfaces of which consist of boron-linked BH units. Mixed hydrides will have intermediate structures, and there is considerable interest in which type of structure will emerge or be suppressed as the carbon-to-boron ratio varies. Will there be a sudden jump from borane cluster to hydrocarbon skeleton behavior with increasing carbon content, or will separate domains of hydrocarbon and borane behavior gradually emerge in the same compound? Such crossover behavior might be expected when the carbon-to-boron ratio is approximately unity.

Recently, the highly substituted carborane $C_6B_6H_6Et_6$ (**1**) was reported to have the twelve-vertex polyhedral drum structure **I**.[1] This is formally an *arachno* structure derived by the removal of two polar six-connectivity vertices from the closed fourteen-vertex 1:6:6:1 D_{6d} stack **II**. By contrast, we now report that the unsubstituted parent species $C_6B_6H_{12}$ (**2**) has a quite different μ-6,9-(CH=CH)-*arachno*-5,6,8,10-$C_4B_6H_{10}$ structure (Figure 1), in which an *arachno* ten-vertex C_4B_6 polyhedral cluster domain is bridged by an ethylene group with hydrocarbon character (structure **III**). This is also formally a twelve-vertex *arachno* polyhedral structure, and it can be derived from an alternative closed fourteen-vertex structure, namely, the 2:2:2:4:2:2 C_{2v} stack **IV**, by the removal of two six-connectivity vertices.

Compound **2** was obtained, along with the previously reported tetracarbaboranes[2] and other carboranes, as a product of the reaction of acetylene with 4,5-$C_2B_7H_9$ in Et_2O in the presence of 0.1 equivalents of 1,8-di(methylamino)-naphthalene under forcing conditions (repeated supply of acetylene, 120 °C, 48 h). This contrasts to the room-temperature reaction with methyl propionate which led to ten-vertex tricarbaboranes.[3] The constitution of **2** was established by comparison of its NMR spectroscopic data with ab initio/IGLO calculations at the II/IGLO/MP2/6-31G* level.[4, 5] Other structures, including asymmetrical drum polyhedra analogous to **I**, did not match. The compound is an example of an unsubstituted, parent *arachno*-$C_6B_6H_{12}$ carborane. Other isomers may be feasible. The contrast between structures **I** and **III** illustrates that the structural crossover is critically dependent on the cluster substituents and the boron-to-carbon ratio of the skeleton. It will also depend on the relative positioning of the boron and carbon atoms.

A second new twelve-vertex product isolated from the reaction, namely, the first cluster pentacarbaborane $CH_3C_5B_7H_{12}$ (**3**), is in accord with these perceptions. The structure of **3** (Figure 2) was also established by comparison of its NMR data with ab initio/IGLO calculations at the II/IGLO/MP2/6-31G* level.[4, 5] Compound **3** has a lower

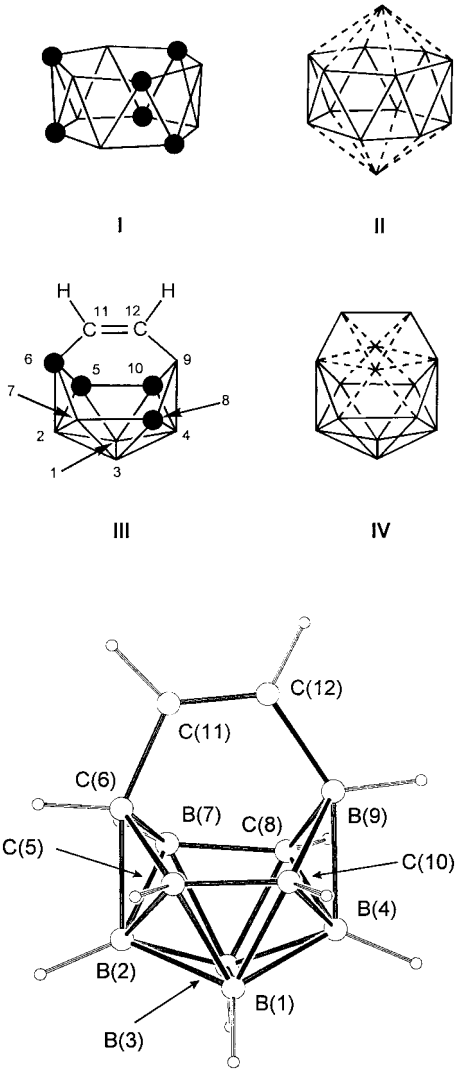

Figure 1. MP2/6-31G* energy-minimized molecular structure of **2**. Selected interatomic distances [Å]: C(5)–C(6) 1.551, C(6)–B(7) 1.773, B(7)–C(8) 1.576, C(8)–B(9) 1.760, B(9)–C(10) 1.739, C(10)–C(5) 1.497, C(6)–C(11) 1.507, B(9)–C(12) 1.575, C(11)–C(12) 1.337.

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[**] Contribution no. 73 from the Řež-Leeds Anglo-Czech Polyhedral Collaboration (ACPC). We thank Dr. Christoph van Wüllen and Dr. Mike Schmidt for the provision of free computational software. The support of the Grant Agency of the Czech Republic (grant no. 203/97/0060), the UK EPSRC (grant nos. GR/F/43215 and GR/J/56929) and the Royal Society (London) are greatly appreciated, as is the assistance of Simon Barrett with NMR spectroscopy.

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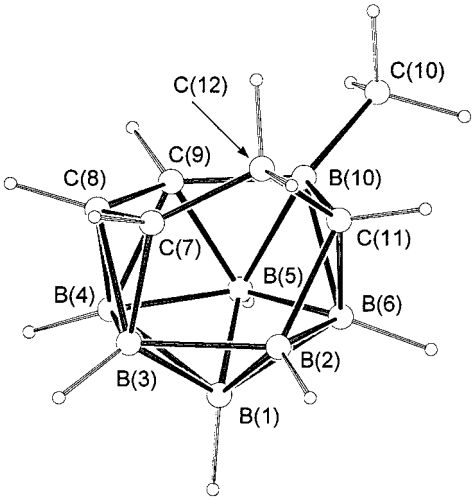
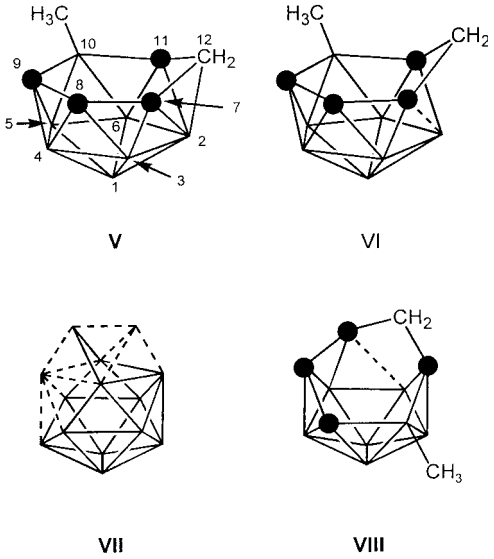


Figure 2. MP2/6-31G* energy-minimized molecular structure of **3**. Selected interatomic distances [Å]: C(7)–C(8) 1.484, C(8)–C(9) 1.531, C(9)–B(10) 1.630, B(10)–C(11) 1.650, C(11)–C(12) 1.532, C(12)–C(7) 1.505, B(2)–C(12) 2.304, B(2)–C(7) 2.222.

skeletal carbon-to-boron ratio than the hexacarbaborane **2** and one substituent bound to boron, and the cluster concomitantly has more polyhedral character. It resembles the twelve-vertex structure **V**, but is perhaps better regarded as 10-CH_3-μ-7,11-(CH_2)-*arachno*-7,8,9,11-$C_4B_6H_{10}$, an eleven-vertex *arachno*-C_4B_7 cluster with a CH_2 bridge as in **VI**; that is, the hydrocarbon domain consists of the one-carbon CH_2 unit rather than the two-carbon C_2H_2 unit of **2**. In principle the skeleton of **3** is also of twelve-vertex *arachno* geometry and is derived from the 2:2:2:4:2:2 C_{2v} stack by the removal of two nonadjacent atoms, as in **VII**. However, there is also some additional connectivity lengthening (hatched lines in **VI** and **VIII**), and the B(2)–C(7) separation is long (2.22 Å), so that B(2)-B(3)-C(7)-C(12)-C(11) is effectively an incipient five-membered open face (Figure 2).

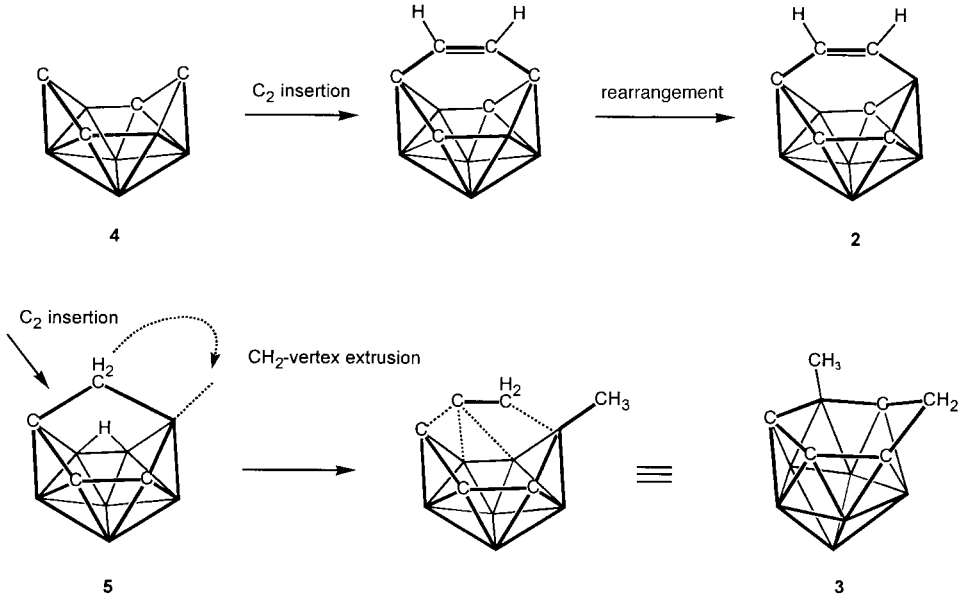
The alternative view **VIII** and the $C_6B_6H_{12}$ structure **III** represent successive stages in the emergence of the dicarbon hydrocarbon domain as the skeletal carbon-to-boron ratio increases. Conversely, the progression from **III** to **VIII** represents successive stages in the incorporation of an acetylenic unit into a borane framework and may have mechanistic implications. As suggested in Scheme 1, the products may result from C_2 insertion into the ten- and eleven-vertex carboranes **4** and **5**, which are present in the reaction mixture. The formation of **3** would involve extrusion of the original CH_2 vertex into an exoskeletal position.

Compounds **2** and **3** are the first unsubstituted hexacarbaborane and the first twelve-vertex cluster pentacarbaborane, respectively, and they illustrate new aspects of the crossover between open hydrocarbon skeletons and closed borane-type clusters. Attempts to isolate the other high-carbon carboranes that are present in trace quantities as reaction products are underway.



Experimental Section

arachno-4,5-$C_2B_7H_{13}$ (5 mmol) was treated with 1,8-di(methylamino)naphthalene (0.5 mmol) and an excess of acetylene in 30 mL of Et_2O (stainless steel vessel, 120 °C, repeated supply of acetylene, 48 h), followed by filtration, evaporation of the solvent, and extraction of the residue with a mixture of 5% aqueous HCl (20 mL) and hexane (30 mL). The hexane layer was evaporated, and the residue subjected to repeated preparative HPLC separation in hexane. The separation of this complex carborane mixture resulted in the isolation of a large number of fractions. The following carboranes have so far been isolated in pure form: *nido*-$C_4B_6H_{10}$ (1%),[2] *nido*-$C_4B_7H_{11}$ (2%),[2] **2** (3%), *arachno*-$C_4B_7H_{13}$ (10%),[2] and **3** (4%) (in order of increasing k' values); they were identified by NMR spectroscopy. The new carboranes **2** and **3** were isolated as white waxy solids that are stable under nitrogen.



Scheme 1. Proposed mechanisms for the formation of **2** and **3**.

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NMR data for **2**: experimental ($CDCl_3$, 294–297 K): $\delta(^{11}B)$ ($\delta(^1H)$; $^1J_{B,H}$): BH(1) −30.5 (+1.20; 164 Hz), BH(2) +0.4 (+3.17; 171 Hz), BH(3) −29.6 (+1.74; 165 Hz), BH(4) +4.5 (+2.75; 156 Hz), BH(7) +3.8 (+3.53; 170 Hz), BH(9) −22.8 (+2.28; 121 Hz); CH signals at $\delta(^1H) = +7.12$, +6.82, +2.92 (2H, accidental coincidence), +2.75, +2.49, and +2.13; calculated (II/IGLO//MP2/6-31G*):[4, 5] $\delta(^{11}B)$ ($\Delta\delta$): B(1) −29.8 (−0.7), B(2) +2.4 (+2.0), B(3) −31.6 (+2.0), B(4) +8.5 (−4.0), B(7) +5.7 (−1.9), and B(9) −24.1 (+1.3); IR (KBr): $\tilde{\nu} = 3059$, 2987 cm^{-1} (CH=CH ?); MS (70 eV): m/z (%): 150 (25) [M^+], 148 (100) [$M^+ - H_2$].

NMR data for **3**: experimental ($CDCl_3$, 294–297 K): $\delta(^{11}B)$ ($\delta(^1H)$; $^1J_{B,H}$): BH(1) −39.7 (+0.52; 148 Hz, BH(2) +32.4 (+5.04; 170 Hz), BH(3) −31.1 (+0.61; 160 Hz), BH(4) +0.4 (+3.53; 170 Hz), BH(5) −5.5 (+2.70; *J* not measurable due to overlap), BH(6) −7.9 (+1.81; 157 Hz), BCH_3(10) −5.2 (CH_3 at +0.28); CH signals at $\delta(^1H) = +3.05$, +2.90, +2.67, +1.87, +1.39 and +1.25; calculated (II/IGLO//MP2/6-31G*):[4, 5] $\delta(^{11}B)$ ($\Delta\delta$): B(1) −42.1 (−2.4), B(2) +33.9 (+1.5), B(3) −31.5 (−0.4), B(4) −2.5 (+2.1), B(5) −5.3 (−0.2), B(6) −4.4 (−3.5), B(10) −7.8 (−2.6); MS (70 eV): m/z (%): 164 (38) [M^+], 162 (100) [$M^+ - H_2$].

Received: December 1, 1998 [Z 12735 IE]
German version: *Angew. Chem.* **1999**, *111*, 1922–1924

Keywords: ab initio calculations · boron · carboranes · NMR spectroscopy

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DNA-Based Assembly of Gold Nanocrystals**

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The ability to generate assemblies of metallic, magnetic, or semiconducting nanocrystals, in which the relative spatial arrangement of two or more distinct nanocrystals is controlled, would allow for a systematic investigation of the physical properties of these novel structures.[1] A number of reports have described methods for organizing nanocrystals into arrays using small molecules,[2] nano-patterned templates,[3] and crystallization.[4] Recently, methods that use biopolymers to assemble nanocrystals have appeared in the literature.[5] For example, Au nanocrystals derivatized with complementary single-stranded DNAs (ssDNAs) can be hybridized to each other to form periodic arrays.[6] In a preliminary report, we showed that nanocrystals modified with ssDNA could be arranged into homodimeric and homotrimeric assemblies.[7] We now report the synthesis of heterodimeric and heterotrimeric "nanocrystal molecules" in which Watson–Crick base-pairing interactions are used to control the relative spatial arrangement of Au nanocrystals that are 5 and 10 nm in diameter. A preliminary characterization of the optical properties of these assemblies is also reported.

DNA is an ideal template for the formation of nanocrystal molecules due to its ability to form well-defined secondary and tertiary structures and its similarity in size to nanocrystals. To use DNA in this capacity, nanocrystals must first be complexed with ligands that stabilize them in aqueous buffers. Secondly, ssDNA must be site-specifically modified with moieties that covalently bind to the complexed nanocrystals such that the resulting conjugates effectively hybridize to complementary ssDNA. In addition, methods for purifying the nanocrystal molecules from their synthetic precursors or undesired larger assemblies are likely to be needed.

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[**] A.P.A. and P.G.S. would like to acknowledge support by the U.S. Department of Energy under Contract No. DE-ACO3-76SF00098. P.G.S. would like to acknowledge support by the Office of Naval Research, Order No. N0001498F0402. P.G.S. is an HHMI investigator. C.J.L. is grateful to the HHMI for a predoctoral fellowship. W.B.C. would like to acknowledge an Alexander Hollaender Postdoctoral Fellowship sponsored by the DOE and administered by the Oak Ridge Institute for Science and Education.

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  1433-7851/99/3812-1808 $ 17.50+.50/0