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A New Carborane Cage: Hexacarba-*arachno*-dodecaborane(12)

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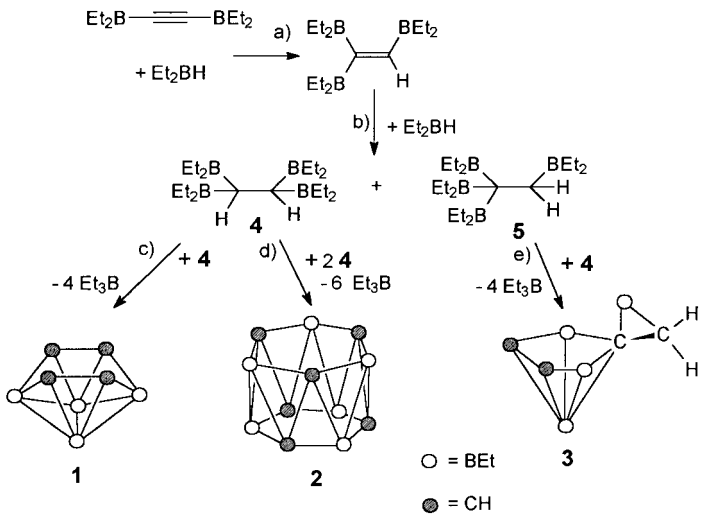
Dedicated to Professor Heinrich Nöth on the occasion of his 70th birthday

The multifaceted structural and synthetic chemistry of carboranes continues to diversify after more than thirty years.[1, 2] The reactions of various polyboranes with alkynes provides an access to a variety of carboranes;[1, 3, 4] however, with few exceptions, complex mixtures are obtained which may be difficult to separate. Transformations of simple organoboranes,[5, 6] mainly to B-alkylated derivatives, promise more specific entries into carborane chemistry. Thus, the hydroboration of 1-alkynyldiethylboranes under "hydride-bath" conditions (i.e., with a large excess of diethylborane Et_2BH[7]) gives access to new types of carboranes such as 1-carba-*arachno*-pentaborane(10),[8, 9] 2-carba-*nido*-pentaborane(8), or 2,4-dicarba-*nido*-hexaborane(8),[10, 11] and provides carboranes such as tetracarba-*nido*-octaborane(8)[12] (**1**) which were not readily accessible or well characterized before. Carborane **1** is a member of the family of carbon-rich carboranes on the borderline between classical and nonclassical structures. The known neutral carbon-rich carborane cages are all *nido* systems with a maximum of four skeleton carbon atoms: for example $C_4B_2R_6$,[13] $C_4B_4R_8$,[12] $C_4B_6R_{10}$,[4c, 14] and $C_4B_8R_{12}$.[15] There also are cationic *nido* carboranes with five carbon atoms: $[C_5BR_6]^+$.[16] We now report a carborane with six carbon and six boron atoms in the skeleton.

The reactions a – c shown in Scheme 1 provided the first straightforward route to the stable *nido*-C_4B_4 carborane **1**.[12] While all our attempts to improve the yield of **1** over 20% failed, these experiments revealed the nature of important



Scheme 1. Synthesis of **1** – **5**.

side products. The formation of **1** is accompanied by that of isomer **3**, which normally is destroyed (e.g. by oxidation) during the purification of **1**. As shown in Scheme 1 (reactions b and e), **3** results from Et_2BH-catalyzed condensation of **4** and **5**.[17] The spiro-carborane **3** is a new member of the still small family of 2,3,5-tricarba-*nido*-boranes(7).[18]

Other Et_2BH-catalyzed condensations are conceivable. Thus, the condensation of three molecules of 1,1,2,2-tetraborylethane (**4**) affords carborane **2** (Scheme 1, reaction e), which was isolated as a crystalline colorless solid. The simple NMR spectra of **2** (there are no appreciable changes between $-80\,^{\circ}C$ and ambient temperature) indicate either high symmetry or a highly fluxional structure. The one-dimensional $^1H-^{13}C$ heteronuclear shift correlation detected by ^1H NMR spectroscopy proves the presence of isolated H-C-C-H units by the splitting of the ^{13}C satellites ($^1J(^{13}C,^1H) = 152$ Hz) into doublets ($^3J(^1H,^1H) = 8.0$ Hz), and this suggests a rigid

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structure. In particular the ^{11}B NMR chemical shift at $\delta = +15.5$ supports a nonclassical structure for **2**, since trigonal-planar ^{11}B nuclei surrounded by carbon atoms should have quite different ^{11}B shifts ($\delta = +75 \pm 10$).[19]

^{11}B and ^{13}C chemical shifts calculated by ab initio methods have been proven to be very reliable[20] and extremely useful for determining the structures of carborane clusters.[11, 21] We applied the ab initio/GIAO/NMR method[20a] to confirm the proposed structure for **2**. Table 1 lists experimental ^{11}B and

Table 1. ^{11}B and ^{13}C NMR chemical shifts determined experimentally for $C_6H_6B_6Et_6$ (**2**) and calculated for the model compounds **2a**, **2b**, and **6**.

Compound	$\delta(^{11}B)$	$\delta(^{13}C)$
$C_6H_6B_6Et_6$ **2**[a]	15.5	33.7
$C_6H_6B_6H_6$ **2a**[b]	7.6	26.0
$C_6H_6B_6Me_6$ **2b**[b]	12.8	27.9
$C_6H_6B_6H_6$ (D_{3h}) **6**[b]	88.4	58.0

[a] Experimental values. [b] Calculated at the GIAO-SCF/6-31G*//MP2(fc)/6-31G* level of theory.

^{13}C NMR data of $C_6H_6B_6Et_6$ (**2**) together with computed chemical shifts (GIAO-SCF/6-31G*//MP2(fc)6-31G*)[22] of model compounds $C_6H_6B_6H_6$ (**2a**) and $C_6H_6B_6Me_6$ (**2b**). An alternative classical valence isomer (**6** is the parent compound) with a 2,5,7,10,11,12-hexabora-tetracyclo-[4,4,0,$1^{3,9}$,$1^{4,8}$]dodecane skeleton[23] (see Figure 1b) might also have been formed from the condensation reactions. However, **6** is not a minimum (HF/6-31G* computations on D_{3h} symmetry) and is 68.5 kcal mol^{-1} (MP2(fc)/6-31G* optimizations) less stable than the nonclassical isomer **2a**.

The agreement between theoretical and experimental NMR data (Table 1) is satisfactory for the D_3-symmetric clusters (**2a** and **2b**). In contrast, **6** is computed to show the expected low-field ^{11}B chemical shift ($\delta = 88.4$, see above). We conclude from these results that the computed geometry shown in Figure 1a closely resembles that of **2**. The drumlike

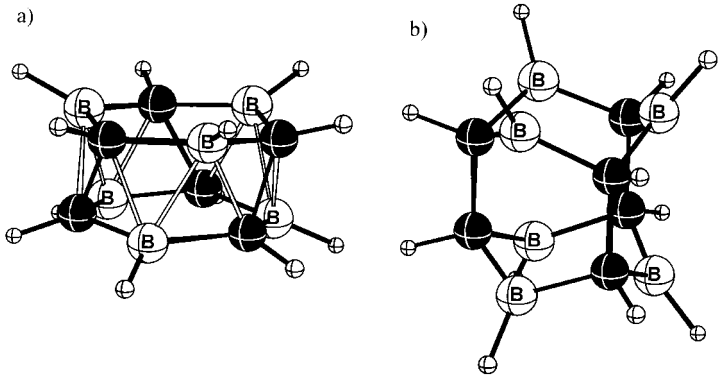

Figure 1. Geometries calculated at the MP2(fc)/6-31G* level of theory for a) **2a** (D_3, selected distances [Å]: C–C 1.619; C–B 1.590, 1.608 (open face), 1.736; B–B 1.863; for **2b**: C–C 1.617; C–B 1.591, 1.611 (open face), 1.744; B–B 1.891) and b) **6** (D_{3h}; C–C 1.610; C–B 1.57).

structure of **2**, a 12-vertex *arachno* cluster, is without precedent in carborane chemistry but can be derived from electron-counting[24] and structural recognition pattern rules.[25] The cage is a hexagonal antiprism in which the carbon atoms are separated as far as possible. Two highly coordinated vertices above the open faces would complete a closed 14-vertex deltahedron, which was predicted for the still elusive *closo*-$[B_{14}H_{14}]^{2-}$,[26,27] but are missing in the 12-vertex *arachno* compound.

There is great synthetic potential in the Et_2BH-catalyzed condensation of polyborylated alkanes. The new carborane **2**, with its two open hexagonal faces and doubly degenerate HOMO and LUMO, invites the addition of various fragments, in particular those which offer zero or two cage electrons.

Experimental Section

A solution of bis(diethylboryl)ethyne (3.57 g, 21.7 mmol) in Et_2BH (5.0 mL, 57.1 mmol hydride) was heated at 80 °C for 24 h. Then the solution was saturated with ethene to convert all reactive B–H bonds into B–Et bonds. Fractional distillation under reduced pressure first gave a mixture (0.97 g, 65:35) of **1** and **3** (b.p. 75–85 °C/7×10^{-5} hPa). The highly viscous residue was heated at 170–200 °C, and a colorless liquid (0.12 g, b.p. 160–165 °C/7×10^{-4} hPa) was collected containing more than 60% of **2**. On cooling the liquid to −20 °C, pure **2** crystallized as colorless prisms (0.067 g, m.p. 51–54 °C). ^1H NMR (250.1 MHz, 25 °C, $CDCl_3$): $\delta = 1.51$ (s, 6H, CH), 0.95 (m, 30H, BEt); ^{11}B NMR (80.3 MHz, 25 °C, $CDCl_3$): $\delta = 15.5$; ^{13}C NMR (62.9 MHz, −30 °C, $CDCl_3$): $\delta = 33.7$ (br, CH), 11.2 (br), 9.5 (BEt); EI-MS (70 eV): m/z (%) = 318 (60) [M^+], 289 (100) [$M^+ - Et$], 261 (30) [$M^+ - Et - C_2H_4$].

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Characterization of Hydrogen-Bonded Supramolecular Assemblies by MALDI-TOF Mass Spectrometry after Ag^+ Labeling**

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Synthesis based on the formation of noncovalent bonds provides a valuable alternative to the classical chemistry of covalent bonds. It has developed into an area of enormous interest for a wide variety of scientific and technological disciplines, ranging from materials science to molecular electronics.[1, 2] The identification of small hydrogen-bonded dimers[3] or metal-coordinated assemblies[4] is relatively simple. However, for large multicomponent assemblies held together by weak forces the characterization is far from straightforward and is currently one of the major challenges in this field.[5] Most studies primarily rely on NMR data of compounds in solution, which solely provide information on the stoichiometry of the assembly, in combination with data from vapor-pressure osmometry (VPO) and/or gel-permeation chromatography (GPC).[1, 6] The latter techniques give values for the average molecular weight with an error of up to 20%. Occasionally light- or neutron-scattering data[7] or single X-ray crystal structures are reported.[8] However, the characterization of weakly bound noncovalent assemblies by mass spectrometry, the only technique that provides quantitative data on the molecular composition, is still met with very limited success.[9] For hydrogen-bonded assemblies only two cases have been reported by Lehn et al. and Whitesides et al.,[10] but the ion-labeling methods they use either require covalent attachment of benzo[18]crown-6 moieties to one of the components or work only for extremely stable assemblies.

Here we describe a novel Ag^+-labeling technique for the mass spectrometric characterization of multicomponent hydrogen-bonded assemblies. The method is based on the remarkably high affinity of Ag^+ ions for a variety of aromatic π donors[11, 12] and cyano groups,[13] and it provides for a nondestructive way to generate positively charged hydrogen-bonded assemblies that can be easily detected by matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry.[14] The method is applicable to assemblies of both high (type **A**) and much lower thermodynamic stability (type **B**; Figure 1). Moreover, we show that the MALDI-TOF-MS data perfectly correlate with ^{1}H NMR

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