

pyrrole NH resonance as a probe to determine the molar fraction of complexed macrocycle.

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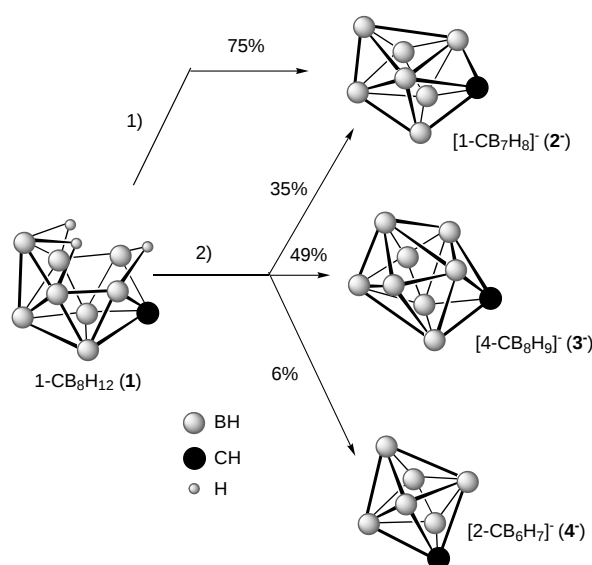
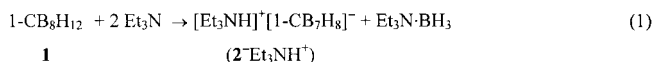
## The $[\text{closo-2-CB}_6\text{H}_7]^-$ Ion: The First Representative of the 7-Vertex Monocarbaborane Series\*\*

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In contrast to the extensively explored area of dicarbaborane chemistry,<sup>[1]</sup> that of monocarbaboranes is much less represented, and many of the fundamental cluster types, namely those of the *nido* and *arachno* series, are unreported as yet. A typical and relatively well-developed field of monocarbaborane chemistry is that of the classically *closo* monocarbaborane anions of general formula  $[\text{CB}_n\text{H}_{n+1}]^-$ . Of these anions, thanks also to the recent discoveries of the  $[\text{CB}_7\text{H}_8]^-$  and  $[\text{CB}_8\text{H}_9]^-$  ions<sup>[2, 3]</sup> a complete series from  $n = 7$  to 12 has already been isolated and structurally characterized, together with the 6-vertex ion  $[\text{CB}_5\text{H}_6]^-$  and its conjugated acid  $\text{CB}_5\text{H}_7$ .<sup>[4]</sup> Nevertheless, the 7-vertex ion  $[\text{CB}_6\text{H}_7]^-$  has so far remained elusive. At present, most studies in the area of *closo* monocarbaboranes focus on the substitution chemistry of the

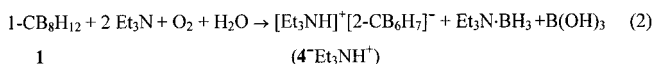
$[\text{CB}_9\text{H}_{10}]^-$  and  $[\text{CB}_{11}\text{H}_{12}]^-$  ions.<sup>[1, 5]</sup> Currently, these anions attract much attention as so-called weakly coordinating anions because of their very low Lewis basicities.<sup>[6]</sup> Moreover, *closo* monocarbaboranes are studied as starting materials for borane-based liquid crystals.<sup>[7]</sup> We now report preliminary results on the isolation and structural characterization of the  $[\text{CB}_6\text{H}_7]^-$  ion, a missing member of the 7-vertex *closo* monocarbaborane series.

Under strictly anaerobic conditions (deoxygenated Ar), the reaction between *nido*-1- $\text{CB}_8\text{H}_{12}$  (**1**)<sup>[8]</sup> and two equivalents of  $\text{Et}_3\text{N}$  in dry toluene (reflux, 24 h) resulted in the isolation of previously reported<sup>[2]</sup> anion  $[\text{closo-1-CB}_7\text{H}_8]^-$  (**2**<sup>−</sup>), yield 75 % [Eq. (1); Scheme 1 (path 1)].



Scheme 1.

In contrast, the reaction products are entirely different when the same reaction is carried out in an atmosphere containing  $\text{N}_2$  with approximately 5 %  $\text{O}_2$  (Scheme 1, path 2)). The reaction then afforded a mixture of the known ions **2**<sup>−</sup> and  $[\text{closo-4-CB}_8\text{H}_9]^-$  (**3**<sup>−</sup>), together with a new ion  $[\text{2-CB}_6\text{H}_7]^-$  (**4**<sup>−</sup>; yields 35, 49, and 6 %, respectively). Anion **4**<sup>−</sup> was finally isolated as a  $\text{PPh}_4^+$  salt (**4**<sup>−</sup>  $\text{PPh}_4^+$ ) by preparative TLC. The formation of **4**<sup>−</sup> seems to be in agreement with the side reaction given in Equation (2) and is consistent with the elimination of two BH vertices from structure **1**.



Iodination of **4**<sup>−</sup>  $\text{PPh}_4^+$  with  $\text{I}_2$  (molar ratio 1:2.1) in  $\text{CH}_2\text{Cl}_2$  in the presence of  $\text{NEt}_3$  (HI scavenger) at ambient temperature resulted in the isolation of the diiododerivative  $[\text{4,5-I}_2\text{-2-CB}_6\text{H}_5]^-[\text{PPh}_4]^+$  (**4,5-I}\_2\text{-4**<sup>−</sup>  $\text{PPh}_4^+$ ) in 93 % yield.

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The X-ray structure of anion **2**<sup>−</sup> was already determined for its mono- and diiododerivatives<sup>[2]</sup> and that of the parent anion **3**<sup>−</sup> was reported recently.<sup>[3]</sup> Although we were able to grow well-shaped crystals of **4**<sup>−</sup> PPh<sub>4</sub><sup>+</sup>, the structure determination showed disorder between boron and carbon positions.

Nevertheless, as shown in Figure 1, the structure of the 7-vertex *closo* cage was determined by single-crystal X-ray diffraction analysis of 4,5-I<sub>2</sub>-**4**<sup>−</sup> PPh<sub>4</sub><sup>+</sup>.<sup>[9]</sup> The structure is

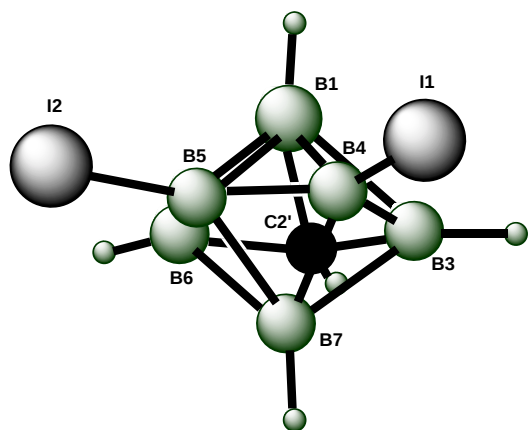


Figure 1. Representation of the crystallographically determined molecular structure of the [4,5-I<sub>2</sub>-*closo*-2-CB<sub>6</sub>H<sub>5</sub>]<sup>−</sup> anion (4,5-I<sub>2</sub>-**4**<sup>−</sup>). Selected intra-cluster distances [Å]: B1-C2' 1.708(11), B1-B3 1.818(10), B1-B4 1.792(8), B1-B5 1.822(11), B1-B6 1.832(13), C2'-B3 1.539(11), B3-B4 1.617(9), B4-B5 1.639(8), B5-B6 1.624(9), C2'-B7 1.705(13), B3-B7 1.804(15), B4-B7 1.790(10), B5-B7 1.799(9), B6-B7 1.819(10), B4-I1 2.160(6), B5-I2 2.162(7).

entirely in agreement with the theoretically predicted pentagonal-bipyramidal C<sub>s</sub> arrangement of the 7-vertex *closo* monocarbaborane cage in which the cage carbon occupies a low-coordinate cluster position.<sup>[10]</sup> This structure was found to be favored by 30.5 kcal mol<sup>−1</sup> with respect to the [1-CB<sub>6</sub>H<sub>7</sub>]<sup>−</sup> ion minimum, with an overall symmetry of C<sub>5v</sub>, as revealed from an ab initio study of the [CB<sub>6</sub>H<sub>7</sub>]<sup>−</sup> system performed by P. v. R. Schleyer and K. Najafian at a correlated level of theory (MP2) with the 6-31G\* basis set.<sup>[11]</sup> In our work, this basis set and B3LYP/6-31G\* (see Figure 2) geometries were used for GIAO calculations of the <sup>11</sup>B chemical shifts for **4**<sup>−</sup><sup>[12]</sup> to yield an excellent agreement between calculated and experimental data (maximum deviation 1 ppm).<sup>[13, 14, 15]</sup> the NMR spectra (see Table 1) of the parent ion **4**<sup>−</sup> are also in accord with the calculated structure. The <sup>11</sup>B NMR spectrum shows 2:2:2 patterns of doublets and that of the diiododerivative 4,5-I<sub>2</sub>-**4**<sup>−</sup> consists of two doublets and one singlet which integrate in the ratio 2:2:2. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of both these CB<sub>6</sub> compounds show one CH singlet (with a triplet <sup>2</sup>J<sub>H,H</sub> splitting in the <sup>1</sup>H spectrum for the diiododerivative). The <sup>1</sup>H{<sup>11</sup>B} (selective) NMR spectra<sup>[16]</sup> allowed for the assignment of all BH cage positions for both compounds.

These results, allied with recent efficient routes from B<sub>10</sub>H<sub>14</sub> to the starting monocarbaborane **1**,<sup>[3, 17, 18]</sup> mean that the 8-vertex *closo* anion **2**<sup>−</sup> and the recently reported<sup>[3]</sup> 9-vertex *closo* species **3**<sup>−</sup> have now become the most readily accessible highly air-stable *closo* carboranes. The long missing repre-

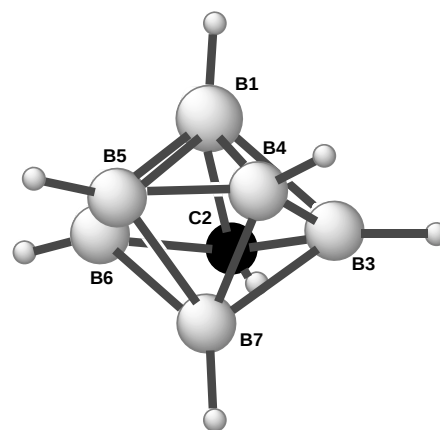


Figure 2. B3LYP/6-31G\* optimized geometry of the parent [*closo*-2-CB<sub>6</sub>H<sub>7</sub>]<sup>−</sup> ion (**4**<sup>−</sup>). Selected calculated bond lengths [Å], and angles [°]: C2-B1 1.734, B1-B3 1.826, B1-B4 1.803, C2-B3 1.551, B3-B4 1.647, B4-B5 1.647, B3-C2-B6 117.2, C2-B3-B4 104.1.

Table 1. NMR spectroscopic data measured in CD<sub>2</sub>Cl<sub>2</sub>.

| Compound                                                                 | Nucleus                          | δ [ppm]                                                                                                                                                                                                                                              |
|--------------------------------------------------------------------------|----------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>4</b> <sup>−</sup> PPh <sub>4</sub> <sup>+</sup>                      | <sup>11</sup> B                  | 3.9/4.6/4.8 <sup>[a]</sup> (d, <sup>1</sup> J <sub>BH</sub> = 151 Hz, B 3,6),<br>0.2/0.4/0.5 <sup>[a]</sup> (d, <sup>1</sup> J <sub>BH</sub> = 138 Hz, B 4,5),<br>−22.2/−21.4/−21.1 <sup>[a]</sup> (d, <sup>1</sup> J <sub>BH</sub> = 150 Hz, B 1,7) |
|                                                                          | <sup>1</sup> H{ <sup>11</sup> B} | 5.37 (s, H 2), 3.96 (s, H 3,6), 3.37 (s, H 4,5), −0.72 (s, H 1,7)                                                                                                                                                                                    |
|                                                                          | <sup>13</sup> C{ <sup>1</sup> H} | 78.6/72.9/73.8 <sup>[b]</sup> (m, <sup>1</sup> J <sub>CB</sub> ~ 20 Hz, C 2)                                                                                                                                                                         |
| 4,5-I <sub>2</sub> - <b>4</b> <sup>−</sup> PPh <sub>4</sub> <sup>+</sup> | <sup>11</sup> B                  | 3.9 (d, <sup>1</sup> J <sub>BH</sub> = 158 Hz, B 3,6), −3.8 (s, B 4,5),<br>−20.3 (d, <sup>1</sup> J <sub>BH</sub> = 156 Hz, B 1,7)                                                                                                                   |
|                                                                          | <sup>1</sup> H{ <sup>11</sup> B} | 5.16 (t, <sup>2</sup> J <sub>H,H</sub> = 9.7 Hz, H 2),<br>3.97 (d, <sup>2</sup> J <sub>H,H</sub> = 9.7 Hz, H 3,6), −0.06 (s, H 1,7)                                                                                                                  |
|                                                                          | <sup>13</sup> C{ <sup>1</sup> H} | 78.6 (m, <sup>1</sup> J <sub>CB</sub> ~ 20 Hz, C 2)                                                                                                                                                                                                  |

[a] δ(<sup>11</sup>B)<sub>exp</sub>/δ(<sup>11</sup>B)<sub>calcd</sub> (GIAO-SCF/II//MP2/6-31G\*)/δ(<sup>11</sup>B)<sub>calcd</sub> (GIAO-SCF/II//B3LYP/6-31G\*). [b] δ(<sup>13</sup>C)<sub>exp</sub>/δ(<sup>13</sup>C)<sub>calcd</sub> (GIAO-SCF/II//MP2/6-31G\*)/δ(<sup>13</sup>C)<sub>calcd</sub> (GIAO-SCF/II//B3LYP/6-31G\*).

sentative of the 7-vertex monocarbaborane family, the [*closo*-1-CB<sub>6</sub>H<sub>7</sub>]<sup>−</sup> ion **4**<sup>−</sup>, is also very stable in air and its chemistry will now contribute substantially to the development of carborane chemistry. We are currently working on the optimization of its synthesis and on the development of other chemistry of all these new 7–9-vertex monocarbaborane systems. For example, these anions could act as weakly coordinating ligands to complement the [CB<sub>6</sub>H<sub>10</sub>]<sup>−</sup>, [CB<sub>11</sub>H<sub>12</sub>]<sup>−</sup> ions, and their derivatives,<sup>[6]</sup> and they are also likely to be amenable to extensive substitution and metal-lacarborane chemistries.

### Experimental Section

**4**<sup>−</sup> PPh<sub>4</sub><sup>+</sup>: In an N<sub>2</sub> atmosphere, from which the contaminant O<sub>2</sub> was not removed, compound **1** (827 mg, 7.8 mmol) was added to a solution of Et<sub>3</sub>N (1616 mg, 16 mmol) in toluene (100 mL). The mixture was heated at reflux for 24 h and then evaporated in vacuum at ambient temperature. The residual semi-liquid materials were heated in vacuum (heating gun) to remove Et<sub>3</sub>N·BH<sub>3</sub> by distillation, which was collected in a trap at 0 °C (404 mg, 45%). The residue was then extracted several times with hot water (ca. 70 °C), the combined aqueous extracts were evaporated to dryness and the residue was recrystallized twice from a minimum of hot water to give 1343 mg of a mixture of **2**<sup>−</sup> [NEt<sub>3</sub>H]<sup>+</sup> and **3**<sup>−</sup> [NEt<sub>3</sub>H]<sup>+</sup> (molar ratio 1:1.4, as determined from the integrated NMR spectrum) as a white crystalline material, which was not separated further. A solution of

[PPh<sub>4</sub>]<sup>+</sup>Cl<sup>−</sup> (300 mg, 0.8 mmol) in water (20 mL) was added to the mother liquor from this crystallization and a white precipitate was formed and collected by filtration, washed with water (2 × 10 mL), and dried in vacuum at RT to give 277 mg of an anionic mixture. This mixture was separated by multiple preparative TLC on silica gel, using 3% MeCN/CH<sub>2</sub>Cl<sub>2</sub> as the mobile phase (detection UV 254 nm). The second band, *R*<sub>f</sub> = 0.5 was collected and washed out with MeCN. Evaporation of the solvent from combined fractions gave pure 4<sup>−</sup>PPh<sub>4</sub><sup>+</sup> (174 mg, 6%). White crystals were obtained by diffusion of Et<sub>2</sub>O into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution of 4<sup>−</sup>PPh<sub>4</sub><sup>+</sup>. M.p. 350 °C, elemental analysis calcd (%) for C<sub>25</sub>H<sub>27</sub>B<sub>6</sub>P: B 15.33; found B 14.82.

4,5-I<sub>2</sub>-4<sup>−</sup>PPh<sub>4</sub><sup>+</sup>: A solution of 4<sup>−</sup>PPh<sub>4</sub><sup>+</sup> (35 mg, 0.083 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was treated with several portions of solid I<sub>2</sub> (total 44 mg, 0.17 mmol) in the presence of NEt<sub>3</sub> (0.5 mL) under stirring at RT for 0.5 h. The mixture was extracted with 5% aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (20 mL), the CH<sub>2</sub>Cl<sub>2</sub> layer collected and filtered through a short column of silica gel. Evaporation of the filtrate gave pure 4,5-I<sub>2</sub>-4<sup>−</sup>PPh<sub>4</sub><sup>+</sup> (52 mg, 93%). White crystals were obtained by diffusion of Et<sub>2</sub>O vapors into a concentrated CH<sub>2</sub>Cl<sub>2</sub> solution of 4,5-I<sub>2</sub>-4<sup>−</sup>PPh<sub>4</sub><sup>+</sup>. M.p. 210 °C; elemental analysis calcd (%) for C<sub>25</sub>H<sub>27</sub>B<sub>6</sub>PI<sub>2</sub>: B 9.62; found B 9.38.

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the same basis set as used in ref. [11] and analogous GIAO-calculations of the shielding tensor of 4<sup>−</sup> were performed. Both geometries performed almost equally well (maximum deviation from experimental *δ*(<sup>11</sup>B) data ± 1 ppm). b) Coordinates for the B3LYP/6-31G\* structure of 4<sup>−</sup> are available from the authors (e-mail: hnyk@iic.cas.cz).

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## Conformational Locking of the Glycosyl Acceptor for Stereocontrol in the Key Step in the Synthesis of Heparin\*\*

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Glycosaminoglycans (GAGs), including heparin (**A**), are linear oligosaccharides that consist of amino sugars and uronic acids.<sup>[1]</sup> Many glycosaminoglycans are involved in vital biological functions<sup>[2]</sup> but still, little is known about the molecular mechanisms responsible for their action. Much progress toward the synthesis of heparin fragments has been reported

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