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[15] A control experiment has shown that *i*$BuNH_3^+Cl^-$ is complexed in CD_2Cl_2 to a low extent by **2c**, and to nearly 100% after further addition of **3** (1 equiv). However, when **6a** (1 equiv) is added to the preformed supercation *i*$BuNH_3^+ \subset$ **2c**, the included *i*$BuNH_3^+$ ion is displaced by the better fitting *n*$BuNH_3^+$ ion.
[16] ^1H NMR spectra have shown **7** to be completely insolubile in CD_2Cl_2, either alone or admixed with one equivalent of **2c** or **3**.
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The [*closo*-2-CB_6H_7]$^-$ Ion: The First Representative of the 7-Vertex Monocarbaborane Series[**]

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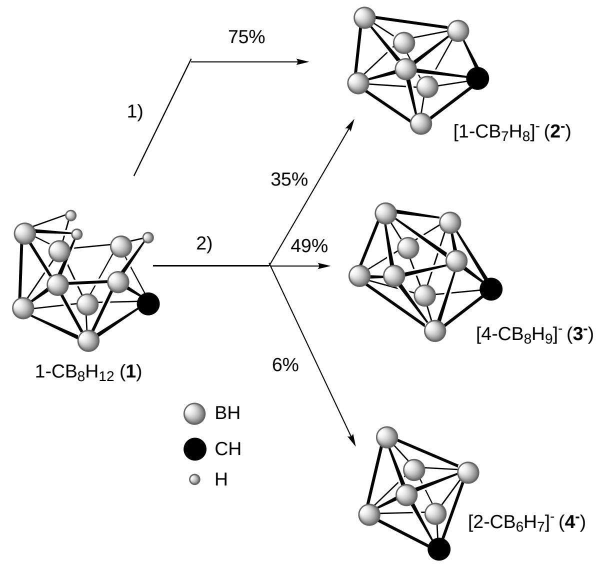
In contrast to the extensively explored area of dicarbaborane chemistry,[1] that of monocarbaboranes is much less represented, and many of the fundamental cluster types, namely those of the *nido* and *arachno* series, are unreported as yet. A typical and relatively well-developed field of monocarbaborane chemistry is that of the classically *closo* monocarbaborane anions of general formula $[CB_nH_{n+1}]^-$. Of these anions, thanks also to the recent discoveries of the $[CB_7H_8]^-$ and $[CB_8H_9]^-$ ions[2, 3] a complete series from $n = 7$ to 12 has already been isolated and structurally characterized, together with the 6-vertex ion $[CB_5H_6]^-$ and its conjugated acid CB_5H_7.[4] Nevertheless, the 7-vertex ion $[CB_6H_7]^-$ has so far remained elusive. At present, most studies in the area of *closo* monocarbaboranes focus on the substitution chemistry of the $[CB_9H_{10}]^-$ and $[CB_{11}H_{12}]^-$ ions.[1, 5] Currently, these anions attract much attention as so-called weakly coordinating anions because of their very low Lewis basicities.[6] Moreover, *closo* monocarbaboranes are studied as starting materials for borane-based liquid crystals.[7] We now report preliminary results on the isolation and structural characterization of the $[CB_6H_7]^-$ ion, a missing member of the 7-vertex *closo* monocarbaborane series.

Under strictly anaerobic conditions (deoxygenated Ar), the reaction between *nido*-1-CB_8H_{12} (**1**)[8] and two equivalents of Et_3N in dry toluene (reflux, 24 h) resulted in the isolation of previously reported[2] anion [*closo*-1-CB_7H_8]$^-$ (**2**$^-$), yield 75% [Eq. (1); Scheme 1 (path 1)].

$$\underset{\mathbf{1}}{1\text{-}CB_8H_{12}} + 2\ Et_3N \rightarrow \underset{(\mathbf{2}^-Et_3NH^+)}{[Et_3NH]^+[1\text{-}CB_7H_8]^-} + Et_3N\cdot BH_3 \tag{1}$$



Scheme 1.

In contrast, the reaction products are entirely different when the same reaction is carried out in an atmosphere containing N_2 with approximately 5% O_2 (Scheme 1, path 2)). The reaction then afforded a mixture of the known ions **2**$^-$ and [*closo*-4-CB_8H_9]$^-$ (**3**$^-$), together with a new ion [2-CB_6H_7]$^-$ (**4**$^-$; yields 35, 49, and 6%, respectively). Anion **4**$^-$ was finally isolated as a PPh_4^+ salt (**4**$^-$ PPh_4^+) by preparative TLC. The formation of **4**$^-$ 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**.

$$\underset{\mathbf{1}}{1\text{-}CB_8H_{12}} + 2\ Et_3N + O_2 + H_2O \rightarrow \underset{(\mathbf{4}^-Et_3NH^+)}{[Et_3NH]^+[2\text{-}CB_6H_7]^-} + Et_3N\cdot BH_3 + B(OH)_3 \tag{2}$$

Iodination of **4**$^-$ PPh_4^+ with I_2 (molar ratio 1:2.1) in CH_2Cl_2 in the presence of NEt_3 (HI scavenger) at ambient temperature resulted in the isolation of the diiododerivative [4,5-I_2-*closo*-2-CB_6H_5]$^-$[PPh_4]$^+$ (4,5-I_2-**4**$^-$ PPh_4^+) in 93% yield.

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[**] This work was supported by the Alexander-von-Humboldt Stiftung (FRG) (B.Š.), Deutsche Forschungsgemeinschaft (B. W., O.L.T.), Fonds der Chemischen Industrie (B.W.), and the Ministry of Education of Czech Republic (Project LN00A028). We also thank the Grant Agency of the Charles University (Grant No. 203/00/B-CH/PřF) and the Supercomputing Center of the Charles University in Prague for computer time.

The X-ray structure of anion $\mathbf{2}^-$ was already determined for its mono- and diiododerivatives[2] and that of the parent anion $\mathbf{3}^-$ was reported recently.[3] Although we were able to grow well-shaped crystals of $\mathbf{4}^-PPh_4^+$, the structure determination showed disorder between boron and carbon positions.

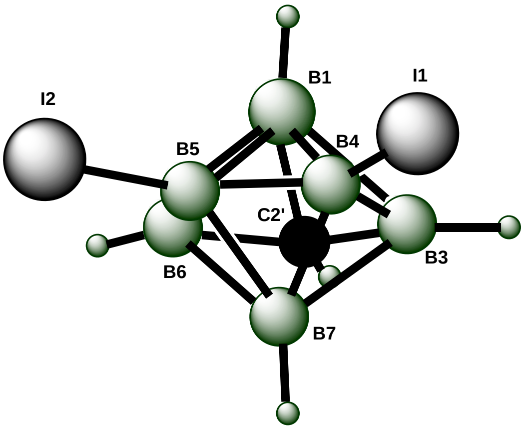

Figure 1. Representation of the crystallographically determined molecular structure of the $[4,5\text{-}I_2\text{-}\textit{closo}\text{-}2\text{-}CB_6H_5]^-$ anion ($4,5\text{-}I_2\text{-}\mathbf{4}^-$). Selected intracluster distances [Å]: B1-C2′ 1.708(11), B1-B3 1.818(10), B1-B4 1.792(8), B1-B5 1.822(11), 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).

Nevertheless, as shown in Figure 1, the structure of the 7-vertex *closo* cage was determined by single-crystal X-ray diffraction analysis of $4,5\text{-}I_2\text{-}\mathbf{4}^-PPh_4^+$.[9] The structure is entirely in agreement with the theoretically predicted pentagonal-bipyramidal C_s arrangement of the 7-vertex *closo* monocarbaborane cage in which the cage carbon occupies a low-coordinate cluster position.[10] This structure was found to be favored by 30.5 kcal mol^{-1} with respect to the $[1\text{-}CB_6H_7]^-$-ion minimum, with an overall symmetry of C_{5v}, as revealed from an ab initio study of the $[CB_6H_7]^-$ system performed by P. v. R. Schleyer and K. Najafian at a correlated level of theory (MP2) with the 6-31G* basis set.[11] In our work, this basis set and B3LYP/6-31G* (see Figure 2) geometries were used for GIAO calculations of the ^{11}B chemical shifts for $\mathbf{4}^-$ [12] to yield an excellent agreement between calculated and experimental data (maximum deviation 1 ppm).[13, 14, 15] the NMR spectra (see Table 1) of the parent ion $\mathbf{4}^-$ are also in accord with the calculated structure. The ^{11}B NMR spectrum shows 2:2:2 patterns of doublets and that of the diiododerivative $4,5\text{-}I_2\text{-}\mathbf{4}^-$ consists of two doublets and one singlet which integrate in the ratio 2:2:2. The ^1H and ^{13}C NMR spectra of both these CB_6 compounds show one CH singlet (with a triplet $^2J_{H,H}$ splitting in the ^1H spectrum for the diiododerivative). The $^1H\{^{11}B(\text{selective})\}$ NMR spectra[16] allowed for the assignment of all BH cage positions for both compounds.

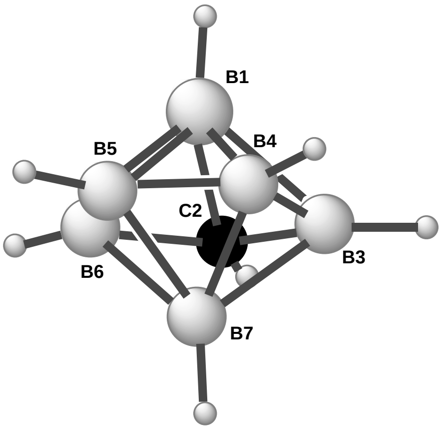

Figure 2. B3LYP/6-31G* optimized geometry of the parent $[\textit{closo}\text{-}2\text{-}CB_6H_7]^-$ ion ($\mathbf{4}^-$). Selected calculated bond lengths [Å], and angles [°]: C2-B1 1.734, B1-B3 1.826, B1-B4 1.803, C2-B3 1.551, B3-B4 1.647, B4-B5 1.647, B3-C2-B6 117.2, C2-B3-B4 104.1.

Table 1. NMR spectroscopic data measured in CD_2Cl_2.

Compound	Nucleus	δ [ppm]
$\mathbf{4}^-PPh_4^+$	^{11}B	3.9/4.6/4.8[a] (d, $^1J_{B,H}=151$ Hz, B 3,6), 0.2/0.4/0.5[a] (d, $J_{B,H}=138$ Hz, B 4,5), $-22.2/-21.4/-21.1$[a] (d, $^1J_{B,H}=150$ Hz, B 1,7)
	$^1H\{^{11}B\}$	5.37 (s, H 2), 3.96 (s, H 3,6), 3.37 (s, H 4,5), -0.72 (s, H 1,7)
	$^{13}C\{^1H\}$	78.6/72.9/73.8[b] (m, $^1J_{C,B}\sim 20$ Hz, C 2)
$4,5\text{-}I_2\text{-}\mathbf{4}^-PPh_4^+$	^{11}B	3.9 (d, $^1J_{BH}=158$ Hz, B 3,6), -3.8 (s, B 4,5), -20.3 (d, $^1J_{BH}=156$ Hz, B 1,7)
	$^1H\{^{11}B\}$	5.16 (t, $^2J_{H,H}=9.7$ Hz, H 2), 3.97 (d, $^2J_{H,H}=9.7$ Hz, H 3,6), -0.06 (s, H 1,7)
	$^{13}C\{^1H\}$	78.6 (m, $^1J_{C,B}\sim 20$ Hz, C 2)

[a] $\delta(^{11}B)_{exp}/\delta(^{11}B)_{calcd}$ (GIAO-SCF/II//MP2/6-31G*)/$\delta(^{11}B)_{calcd}$ (GIAO-SCF/II//B3LYP/6-31G*). [b] $\delta(^{13}C)_{exp}/\delta(^{13}C)_{calcd}$ (GIAO-SCF/II//MP2/6-31G*)/$\delta(^{13}C)_{calcd}$ (GIAO- SCF/II//B3LYP/6-31G*).

These results, allied with recent efficient routes from $B_{10}H_{14}$ to the starting monocarbaborane $\mathbf{1}$,[3, 17, 18] mean that the 8-vertex *closo* anion $\mathbf{2}^-$ and the recently reported[3] 9-vertex *closo* species $\mathbf{3}^-$ have now become the most readily accessible highly air-stabile *closo* carboranes. The long missing representative of the 7-vertex monocarbaborane family, the $[\textit{closo}\text{-}1\text{-}CB_6H_7]^-$ ion $\mathbf{4}^-$, 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 monocarborane systems. For example, these anions could act as weakly coordinating ligands to complement the $[CB_9H_{10}]^-$, $[CB_{11}H_{12}]^-$ ions, and their derivatives,[6] and they are also likely to be amenable to extensive substitution and metallacarborane chemistries.

Experimental Section

$\mathbf{4}^-PPh_4^+$: In an N_2 atmosphere, from which the contaminant O_2 was not removed, compound $\mathbf{1}$ (827 mg, 7.8 mmol) was added to a solution of Et_3N (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 $Et_3N\cdot BH_3$ 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 $\mathbf{2}^-[NEt_3H]^+$ and $\mathbf{3}^-[NEt_3H]^+$ (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

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[PPh$_4$]$^+$Cl$^-$ (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$_2$Cl$_2$ as the mobile phase (detection UV 254 nm). The second band, $R_f = 0.5$ was collected and washed out with MeCN. Evaporation of the solvent from combined fractions gave pure **4**$^-$PPh$_4^+$ (174 mg, 6%). White crystals were obtained by diffusion of Et$_2$O into a concentrated CH$_2$Cl$_2$ solution of **4**$^-$PPh$_4^+$. M.p. 350 °C, elemental analysis calcd (%) for C$_{25}$H$_{27}$B$_6$P: B 15.33; found B 14.82.

4,5-I$_2$-**4**$^-$PPh$_4^+$: A solution of **4**$^-$PPh$_4^+$ (35 mg, 0.083 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with several portions of solid I$_2$ (total 44 mg, 0.17 mmol) in the presence of NEt$_3$ (0.5 mL) under stirring at RT for 0.5 h. The mixture was extracted with 5% aqueous Na$_2$S$_2$O$_3$ (20 mL), the CH$_2$Cl$_2$ layer collected and filtered through a short column of silica gel. Evaporation of the filtrate gave pure 4,5-I$_2$-**4**$^-$PPh$_4^+$ (52 mg, 93%). White crystals were obtained by diffusion of Et$_2$O vapors into a concentrated CH$_2$Cl$_2$ solution of 4,5-I$_2$-**4**$^-$PPh$_4^+$. M.p. 210 °C; elemental analysis calcd (%) for C$_{25}$H$_{27}$B$_6$PI$_2$: B 9.62; found B 9.38.

Received: December 13, 2001 [Z18377]

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[9] a) Crystal structure data for C$_{25}$H$_{25}$B$_6$I$_2$P: $M_r = 675.08$, white crystal, size 0.2 × 0.18 × 0.10 mm^3, triclinic, space group $P\bar{1}$, $a = 7.9841(6)$, $b = 13.2428(9)$, $c = 13.5646(9)$ Å, $\alpha = 96.149(6)$, $\beta = 92.686(5)$, $\gamma = 92.994(6)°$, $V = 1422.02$ Å^3, $T = 293(2)$ K, $Z = 2$, $\rho_{calcd} = 1.577$ Mg m^{-3}, $F(000) = 652$, $\mu(\mathrm{Mo}_{K\alpha}) = 2.28$ mm^{-1}, Data collected with a Siemens P4 four-circle diffractometer (Mo$_{K\alpha}$ radiation $\lambda = 71.073$ pm, graphite monochromator); $\theta_{max} = 25°$. A total of 6152 reflections were measured, 4986 unique ($R_{int} = 0.0277$). Absorption correction empirical (by Ψ-scans), min./max. transmission coefficients 0.2453/0.2990, GoF on F^2 was 1.125, $R1$ ($I > 2\rho(I)$) = 0.0358, $wR2 = 0.0924$. Data/restrains/parameters 4956/0/308. Largest difference Fourier peak and hole 1.511 and −1.173 e Å^{-3}. Refinement used SHELXTL V.5.1 (G. M. Sheldrick, SHELXS-97, University of Göttingen, Göttingen (Germany), **1997**). b) CCDC-175525 (4,5-I$_2$-**4**$^-$PPh$_4^+$). contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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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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Peter Schell, and Peter H. Seeberger*

Glycosaminoglycans (GAGs), including heparin (**A**), are linear oligosaccharides that consist of amino sugars and uronic acids.[1] Many glycosaminoglycans are involved in vital biological functions[2] 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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[**] Financial support from the National Institutes of Health (HL-64799 and HL-62598), The Research Corporation (Research Innovation Award to P.H.S.), CaP CURE (Research Awards to P.H.S.), FOMEC (Postdoctoral Fellowship for H.A.O.), CNRI (Italian National Research Center, Postdoctoral Fellowship for A.B.), and the DAAD (German Academic Exchange Service, Postdoctoral Fellowship for P.S.) is gratefully acknowledged. Funding for the MIT-DCIF Varian 500 MHz NMR was provided by NSF (Award CHE-9808061). Funding for the MIT-DCIF Bruker 400 MHz NMR was provided by NIH (Award 1S10RR13886-01). Funding for the MIT-DCIF Varian 300 MHz was provided by NSF (Award DBI-9729592).

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