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Reductive Degradation of *nido*-1-CB_8H_{12} into Smaller-Cage Carborane Systems via New Monocarbaboranes [*arachno*-5-CB_8H_{13}]$^-$ and *closo*-2-CB_6H_8

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Abstract: Treatment of the *nido*-1-CB_8H_{12} (**1**) carborane with $NaBH_4$ in THF at ambient temperature led to the isolation of the stable [*arachno*-5-CB_8H_{13}]$^-$ ($\mathbf{2}^-$), which was isolated as $Na^+[5\text{-}CB_8H_{13}]^-\cdot 1.5\,THF$ and $PPh_4^+[5\text{-}CB_8H_{13}]^-$ in almost quantitative yield. Compound $\mathbf{2}^-$ underwent a boron-degradation reaction with concentrated hydrochloric acid to afford the *arachno*-4-CB_7H_{13} (**3**) carborane in 70% yield, whereas reaction between $\mathbf{2}^-$ and excess phenyl acetylene in refluxing THF gave the [*closo*-2-CB_6H_7]$^-$ ($\mathbf{4}^-$) in 66% yield. Protonation of the $Cs^+\mathbf{4}^-$ salt with concentrated H_2SO_4 or CF_3COOH in CH_2Cl_2 afforded a new, highly volatile 2-CB_6H_8 (**4**) carborane in 95% yield, the deprotonation of which with Et_3N in CH_2Cl_2 leads quantitatively to $Et_3NH^+[2\text{-}CB_6H_7]^-$ ($Et_3NH^+\mathbf{4}^-$). Both compounds $\mathbf{4}^-$ and **4** can be deboronated through treatment with concentrated hydrochloric acid in CH_2Cl_2 to yield the carbahexaborane *nido*-2-CB_5H_9 (**5**) in 60% yield. New compounds $\mathbf{2}^-$, **3**, and **4** were structurally characterised by the ab initio/GIAO/MP2/NMR method. The method gave superior results to those carried out using GIAO-HF when relating the calculated ^{11}B NMR chemical shifts to experimental data.

Keywords: boranes · boron degradation · carboranes · density functional calculations · monocarbaboranes

Introduction

Recent developments in the chemistry of monocarbaboranes, namely the degradative carbon insertion into decaborane(14),[1] have led to improved synthetic routes to the nine-vertex monocarbaboranes [*closo*-4-CB_8H_9]$^-$, *nido*-1-CB_8H_{12}, *arachno*-4-CB_8H_{14}, and their C-phenyl analogues.[2] Encouraged by these developments, we have just recently set for systematic studies in the chemistry of *nido*-1-CB_8H_{12}. Although this carborane has been known for thirty years,[3] not too much work on this interesting species has so far been reported. This compound has been used as a starting material for the synthesis of the *closo* anions [1-CB_6H_7]$^-$, [1-CB_7H_8]$^-$, and [4-CB_8H_9]$^-$ and ligand (L) derivatives 6-L-*arachno*-5-CB_8H_{12}.[1,4,5] In this work we report an extension of the 1-CB_8H_{12} chemistry that resulted in a high-yield preparation of new carboranes [*arachno*-5-CB_8H_{13}]$^-$ and *closo*-2-CB_6H_8 together with new syntheses of carboranes [*closo*-2-CB_6H_7]$^-$, *nido*-2-CB_5H_9, and *arachno*-4-CB_7H_{13}. The syntheses are based on reductive degradation of the 1-CB_8H_{12} cage and significantly extend the area of monocarbaborane chemistry.

Results and Discussion

Syntheses: Treatment of the *nido*-1-CB_8H_{12} (**1**) carborane[1,3] with $NaBH_4$ in THF at ambient temperature for 2 h, followed by evaporation of the volatile materials led to the isolation of a new, stable borane [*arachno*-5-CB_8H_{13}]$^-$ ($\mathbf{2}^-$, Scheme 1 path a), which was isolated as its sodium salt (THF solvate), $Na^+[5\text{-}CB_8H_{13}]^-\cdot 1.5\,THF$, ($Na^+\mathbf{2}^-\cdot 1.5\,THF$), in practically quantitative yield. Precipitation of the sodium salt with aqueous PPh_4Cl afforded $PPh_4^+[5\text{-}CB_8H_{13}]^-$ in 95% yield as a white solid. The formation of $\mathbf{2}^-$ is in agreement with the stoichiometry of Equation (1):

$$\underset{\mathbf{1}}{1\text{-}CB_8H_{12}} + BH_4^- + THF \rightarrow \underset{\mathbf{2}^-}{[5\text{-}CB_8H_{13}]^-} + THF\cdot BH_3 \quad (1)$$

The most probable mechanism of this simple reaction consists in the H^- attack at the B2 vertex in **1**, which results in

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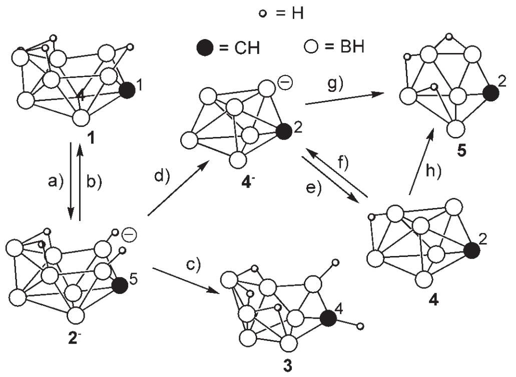

Scheme 1. Reductive degradation of the *nido*-1-CB_8H_{12} (**1**) cage. a) $NaBH_4$/THF, RT; b) conc. H_2SO_4/CH_2Cl_2, 0 °C; c) Na^+ salt, aq. HCl/CH_2Cl_2; d) excess PhC_2H/THF, reflux; e) Cs^+ salt, F_3CCOOH or conc. H_2SO_4/CH_2Cl_2; f) Et_3N/CH_2Cl_2; g) and h) aq. HCl/CH_2Cl_2.

opening of the μ-H2,3 bridge and formation of two BH_2 units in positions 2 and 4 (for numbering see Figure 1) of the cluster. The reaction in Equation (1) represents an example of *nido→arachno* conversion and is similar to that reported for the formation of the ligand derivatives 4-L-*arachno*-5-CB_8H_{12}.[5]

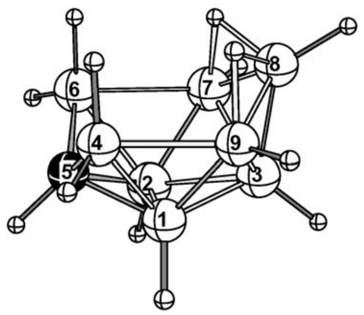

Figure 1. The structure of the [*arachno*-5-CB_8H_{13}]$^-$ ($\mathbf{2}^-$) as optimized at the RMP2(fc)/6-31G* level. Selected bond lengths [Å] and bond angles [°]: B4–C5 1.658, B4–B9 2.023, B8–B9 1.789, B4–C5–B6 114.3, C5–B4–B9 99.6, B7–B8–B9 105.2.

The acidification of $\mathbf{2}^-$ (Na^+ or PPh_4 salts) with concentrated H_2SO_4 in CH_2Cl_2 at 0 °C (Scheme 1 path b) resulted in hydrogen evolution and formation of carborane **1** in ≈90 % yield [Eq. (2)]:

$$\underset{\mathbf{2^-}}{[5\text{-}CB_8H_{13}]^-} + H^+ \rightarrow \underset{\mathbf{1}}{1\text{-}CB_8H_{12}} + H_2 \qquad (2)$$

In contrast to the reaction in Equation (2), similar treatment with concentrated aqueous HCl (Scheme 1 path c) afforded the previously reported[6] carborane *arachno*-4-CB_7H_{13} (**3**) in 70 % yield [Eq. (3)]:

$$\underset{\mathbf{2^-}}{[5\text{-}CB_8H_{13}]^-} + H_3O^+ + 2\,H_2O \rightarrow \underset{\mathbf{3}}{4\text{-}CB_7H_{13}} + B(OH)_3 + H_2 \qquad (3)$$

Scheme 1 suggests that the formation of the eight-vertex carborane **3** is consistent with hydrolytic removal of one BH_2 vertex (4 or 6) from structure $\mathbf{2}^-$. For further reactions, it is more convenient to use the CH_2Cl_2 solution of compound **3** as it is obtained from the synthesis, owing to relatively high volatility of this carborane. No doubt that this synthesis is much more convenient than the previously reported multistep procedure.[6]

The synthesis shown in path d) of Scheme 1 is very interesting and useful. The reaction between $\mathbf{2}^-$ (generated in situ in the reaction in Equation (1)) and excess phenyl acetylene in refluxing THF for 6 h, followed by evaporation, precipitation with aqueous PPh_4Cl, and crystallization gave the [*closo*-2-CB_6H_7]$^-$ ($\mathbf{4}^-$) [4] in 66 % yield [Eq. (4)]:

$$\underset{\mathbf{2^-}}{[5\text{-}CB_8H_{13}]^-} + 2\,PhC_2H \rightarrow \underset{\mathbf{4^-}}{[2\text{-}CB_6H_7]^-} + 2\,\underset{\text{not isolated}}{\{PhCH{=}CHBH_2\}} \qquad (4)$$

Mechanistically, the reaction is in agreement with removal of the B4 and B6 vertices from structure **2**, followed by closure of the rest of the skeleton through the connecting atom B5 with C7, B8, and B9. The two vertices are most probably removed as BH_3 groups via hydroboration of the phenyl acetylene,[7] but the {PhCH=CHBH$_2$} hydroboration product was not isolated and its fate was not further traced as it was unimportant for the isolation of $\mathbf{4}^-$. Nevertheless, the reaction in Equation (4) represents undoubtedly the best access to the so far hardly available[4] $\mathbf{4}^-$, and a considerable improvement of the recently published method.[7]

Protonation of the $Cs^+\mathbf{4}^-$ salt with concentrated H_2SO_4 or CF_3COOH in CH_2Cl_2 afforded the isolatable conjugated acid, a new carborane 2-CB_6H_8 (**4**, Scheme 1 path e), in a yield of 95 % as a highly volatile material. Here again, for further reactions with **4**, it is more convenient to use the CH_2Cl_2 solution of compound **4** obtained directly in the synthesis. Deprotonation of carborane **4** with Et_3N in CH_2Cl_2 (Scheme 1 path f) then leads quantitatively to Et_3NH^+ [2-CB_6H_7]$^-$ ($Et_3NH^+\mathbf{4}^-$).

Paths g) and h) of Scheme 1 show that neither the seven-vertex $\mathbf{4}^-$ nor the neutral **4** are stable towards acid hydrolysis. Reactions of both $Cs^+\mathbf{4}^-$ and **4** with concentrated hydrochloric acid in CH_2Cl_2 (RT, 4 h) resulted in the "decapitation" of the B1 vertex under the formation of the previously reported[8] carbahexaborane *nido*-2-CB_5H_9 (**5**) in 60 % yield as a sole product:

$$\underset{\mathbf{4^-}}{[2\text{-}CB_6H_7]^-} + H_3O^+ + 2\,H_2O \rightarrow \underset{\mathbf{5}}{2\text{-}CB_5H_9} + B(OH)_3 + H_2 \qquad (5)$$

The best preparation of carborane **5** thus far reported (19 % yield) is based on treatment of an anion obtained from the reaction between Me_4NBH_4 and *closo*-2,5-$C_2B_6H_8$ with HCl. The reaction also yields methylated derivatives of

5 and pure products must be isolated by gas chromatography.[8] In contrast, the procedure according to Equation (5) is clean and, therefore, improves substantially the access and availability to this carborane. Other procedures are much less convenient, e.g., just 2.4% of **5** originates from the pyrolysis of 1,2-dimethylpentaborane(9).[9]

NMR spectroscopy: The known compounds **3**, **4**$^-$, and **5** were identified by ^{11}B NMR spectroscopy[4,6,8] and the missing ^{1}H NMR data for carboranes **3** and **5** were completed and updated. All ^{11}B and ^{1}H NMR resonances were interrelated by [^{11}B–^{11}B]-COSY[10] and ^{1}H–{^{11}B(selective)}[11] NMR spectroscopy, which led to the complete assignments of all signals to individual BH cluster vertices. In accord with the C_s symmetry structure (see Scheme 1 and Figure 1), the ^{11}B NMR spectrum of **2**$^-$ consists of 2:1:2:1 patterns of doublets and one intensity 2 triplet as a result of the two equivalent BH_2 vertices at the B4,6 sites. The ^{11}B NMR spectrum of the C_s-symmetry compound **4** shows 2:2:2 patterns of doublets, of which the second, assigned to positions B4,5 associated with the bridging hydrogen atom, is markedly broadened owing to the coupling to this bridge. The spectrum shows notable similarity to that of **4**$^-$, the most remarkable difference is the upfield shift ($\approx$9 ppm) of the B4,5 resonance.

The ^{1}H–{^{11}B} NMR spectrum of **2**$^-$ shows four 2:1:2:1 singlets assigned to BH units in positions H7,9, H8, H1,2, and H3, one singlet of the cage CH5 unit, two singlets of intensity 2 attributed to *exo* and *endo* components of the two identical cage BH_2 groups in 4,6 positions together with one high-field singlet of intensity 2 owed to the two identical B–H–B bridges. The spectrum of the neutral carborane **4** exhibits one singlet of the cage CH unit, three singlets of intensity 2 assigned to BH units at the H3,6, H4,5, and H1,7 sites together with a broader singlet in an exceptionally low-field (4.10 ppm) owed to the bridging μ-H4,5 hydrogen.

Geometry optimization and magnetic property calculations: The optimized geometries of compounds **2**$^-$, **3**, and **4** at the at the RMP2(fc)/6-31G* level are shown in Figure 1, Figure 2, Figure 3. The RMP2(fc)/6-31G* geometry of **5** has been already reported.[12] The structure of **2**$^-$ is consistent with a C_s-symmetry nine-vertex *arachno* cluster containing two BH_2 vertices and two bridging hydrogen atoms symmetrically arranged along the symmetry plane intersecting the C5, B3, and B8 atoms and bisecting the B1–B2 bonding vector. The structure of compound **4** optimized as a C_s-symmetry cluster is similar to that of **4**$^-$,[4] but with boron atoms B4 and B5 spanned by a *conventional* hydrogen bridge. Comparison between the ^{11}B shifts calculated at the GIAO-MP2/II//RMP2(fc)/6-31G* level and the corresponding experimental data for all compounds[13] revealed a very good agreement (see the Experimental Section), which can be taken as a proof of correct structure design. The same comparison between experimental and calculated ^{13}C shifts is less satisfactory, but falls within usual limits.

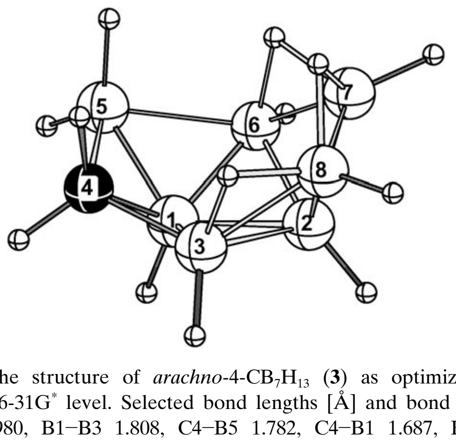

Figure 2. The structure of *arachno*-4-CB_7H_{13} (**3**) as optimized at the RMP2(fc)/6-31G* level. Selected bond lengths [Å] and bond angles [°]: B5–B6 1.980, B1–B3 1.808, C4–B5 1.782, C4–B1 1.687, B1–C4–B5 117.0, B8–B7–B6 108.7.

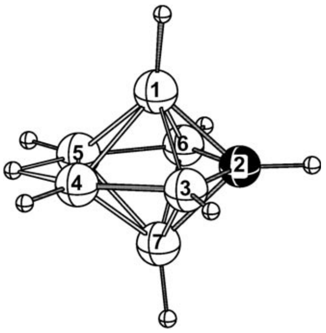

Figure 3. The structure of *closo*-2-CB_6H_8 (**4**) as optimized at the RMP2(fc)/6-31G* level. Selected bond lengths [Å] and bond angles [°]: B4–B5 1.701, B3–B4 1.664, C2–B3 1.528, C2–B1 1.696, B4–B5–B6 105.5, B6–C2–B3 115.7.

Conclusion

This paper is a targeted continuation the previously reported[1] boron-degradation sequence *nido*-$B_{10}H_{14}$→[*arachno*-6-CB_9H_{14}]$^-$→*arachno*-4-CB_8H_{14}→*nido*-1-CB_8H_{12}. We have now demonstrated that this system demolition game can be extended in the *nido*-1-CB_8H_{12}→[*arachno*-5-CB_8H_{13}]$^-$→ *arachno*-4-CB_7H_{13}→[*closo*-2-CB_6H_7]$^-$→*closo*-2-CB_6H_8→ *nido*-2-CB_5H_9 manner, with the overall loss of five boron atoms from the original decaborane cage. A key step in these syntheses is based on the reduction of 1-CB_8H_{12} to the new, stable [5-CB_8H_{13}]$^-$, which is isomeric with the previously reported,[3,19] [4-CB_8H_{13}]$^-$. An important aspect of the work is a relatively facile access to the so far hardly available[4,6,8] eight, seven and six-vertex carboranes 4-CB_7H_{13}, [2-CB_6H_7]$^-$, and 2-CB_5H_9. Moreover, two of the compounds of the series, [5-CB_8H_{13}]$^-$ and 2-CB_6H_8, are new carboranes, which demonstrates that there are still reasonable chances for the isolation of new-type skeletons in the area of cluster-boron chemistry. There is no doubt that the compounds isolated in this study will be employed soon by a vast community of chemists as substrates for substitution reactions and various metallacarborane syntheses. Of special importance might be the use of the now readily available *closo* [2-

$CB_6H_7]^-$ as a new ligand in the closely watched area of weakly coordinating anions.[20]

Experimental Section

General procedures: All reactions were carried out with the use of standard vacuum or inert-atmosphere techniques as described by Shriver,[14] although some operations, such as column LC, were carried out in air. The starting carborane **1** was prepared according to the literature.[1,3] THF was distilled over sodium diphenylketyl; dichloromethane and hexane were dried over CaH_2 and freshly distilled before use. Other chemicals were of reagent or analytical grade and were used as purchased. Analytical TLC was carried out on Silufol (silica gel on aluminum foil; detection by I_2 vapour, followed by 2% aqueous $AgNO_3$ spray). Low-resolution mass spectra were obtained by using a Finnigan MAT Magnum ion-trap quadrupole mass spectrometer equipped with a heated inlet option, as developed by Spectronex AG, Basel, Switzerland (70 eV, EI ionisation). ^{1}H and ^{11}B NMR spectroscopy was performed at 9.4 T by means of a Varian Mercury 400 instrument. The [^{11}B–^{11}B]-COSY[10] and ^{1}H–{^{11}B(selective)}[11] NMR experiments were made essentially as described earlier.[7] Chemical shifts are given in ppm to high-frequency (low field) of $\Xi = 32.083971$ MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm), $\Xi = 25.144$ MHz ($SiMe_4$) for ^{13}C (quoted ±0.5 ppm), and $\Xi = 100$ MHz ($SiMe_4$) for ^{1}H (quoted ±0.05 ppm), Ξ is defined as in ref. [15] and the solvent resonances were used as internal secondary standards.

Synthesis of [*arachno*-5-CB_8H_{13}]$^-$ (2^-): A solution of compound **1** (250 mg, 2.26 mmol) in THF (20 mL) was treated with $NaBH_4$ (100 mg, 2.64 mmol) under stirring at room temperature for 2 h. The mixture was filtered and the volatile materials were removed from the filtrate by evaporation. The residue was vacuum dried at ambient temperature for 12 h to obtain Na^+**2**$^-\cdot$1.5 THF (538 mg, 98%), which was analyzed by integrated NMR spectroscopy. The sodium salt can be converted into Cs^+ or PPh_4^+ salts (yields 90 and 95%, respectively) by dissolution in water and precipitation with aqueous CsCl or PPh_4·Cl. The white precipitates thus obtained were isolated by filtration, washed by water, and dried in vacuo.

*Analysis of PPh_4^+**2**$^-$*: R_f 0.22 (3% MeCN/CH_2Cl_2); m.p. 290°C; ^{11}B NMR (128.3 MHz, $CDCl_3$, 25°C): δ = 2.1 (d, ^{1}J(B,H) = 140 Hz, 2B; B7,9), −0.9 (d, ^{1}J(B,H) = 128 Hz, ^{1}J(B,B) = 18 Hz, 1B; B8), −6.1 (d, ^{1}J(B,H) = 143 Hz, 2B; B1,2), −27.0 (t, ^{1}J(B,H) = 119 Hz, 2B; B4,6), −57.2 ppm (d, ^{1}J(B,H) = 147 Hz, 1B; B3), all theoretical [^{11}B–^{11}B]-COSY cross-peaks observed, except for B7–B8 and B8–B9; δ(^{11}B)$_{calcd}$ (GIAO-MP2/II//RMP2(fc)/6-31G*) = 1.4 (B7,9), −2.5 (B8), −5.3 (B1,2), −26.8 (B4,6), −58.9 ppm (B3); ^{1}H–{^{11}B} NMR (400 MHz, $CDCl_3$, 25°C): δ = 3.17 (s, 1H; H8), 2.91 (s, 2H; H7,9), 2.31 (s, 2H; H1,2), 1.05 (s, 2H; *exo*-H4,6), 0.65 (s, 1H; H5), 0.51 (s, 2H; *endo*-H4,6), −0.89 (s, 1H; H3), −2.01 ppm (s, 2H; μH7,8/8,9); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 10.7 ppm; δ(^{13}C)$_{calcd}$ (GIAO-MP2/II//RMP2(fc)/6-31G*) = 13.6 ppm (C5); elemental analysis calcd (%) for $C_{25}H_{331}B_8P$ (451.04): C 66.57, H 7.37; found: C 65.38 H 7.02.

***Synthesis of arachno*-4-CB_7H_{13} (3)**: A mixture Na^+**2**$^-\cdot$1.5 THF (243 mg, 1 mmol) and CH_2Cl_2 (20 mL) was treated with conc. hydrochloric acid (2 mL) under stirring and cooling at 0°C for 2 h. The CH_2Cl_2 layer was separated, dried with $MgSO_4$, and filtered through a short layer of silica. Evaporation of the filtrate under high vacuum at −15°C gave 71 mg, (70%) of compound **3**, which was isolated as a semisolid white material. Owing to the relatively high volatility and air sensitivity of **3**, it is better to use the filtered CH_2Cl_2 solution of compound **3** for further use.

*Analysis of **3***: ^{11}B NMR (128.3 MHz, $CDCl_3$, 25°C): δ = 8.5 (d, ^{1}J(B,H) = 161 Hz, 1B; B7), 3.5 (d, ^{1}J(B,H) = 155 Hz, 1B; B6), −0.4 (d, ^{1}J(B,H) = 151 Hz, 1B; B3), −5.8 (d, ^{1}J(B,H) = ≈155 Hz 1B; B1), −6.6 (d, ^{1}J(B,H) = ≈155 Hz, 1B; B8), −15.0 (t, ^{1}J(B,H) = 131 Hz, 1B; B5), −55.3 ppm (d, ^{1}J(B,H) = 156 Hz, 1B; B2), all theoretical [^{11}B–^{11}B]-COSY cross-peaks observed, except for B3–B8; δ(^{11}B)$_{calcd}$ (GIAO-MP2/II//RMP2(fc)/6-31G*) = 9.2 (B7), 3.8 (B6), −1.2 (B3), −3.5 (B1), −7.0 (B8), −12.2 (B5), −55.4 ppm (B2); ^{1}H–{^{11}B} NMR (400 MHz, $CDCl_3$, 25°C): δ = 3.80 (s, 1H; H7), 3.53 (s, 1H; H5), 3.39 (s, 1H; H3), 2.99 (s, 1H; H1), 2.52 (s, 1H; H8), 2.18 (s, 2H; *exo* and *endo*-H5), 0.64 (s, 2H; *exo* and *endo*-H4), −0.35 (s, 1H; H2), −1.03 (s, 1H; μ-H3,8), −1.81 (s, 1H; μ-H6,7), −2.19 ppm (s, 1H; μ-H7,8); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25°C): δ = −16.8 ppm (C4); δ(^{13}C)$_{calcd}$ (GIAO-MP2/II//RMP2(fc)/6-31G*) = −12.2 ppm (C4).

Synthesis of [*closo*-2-CB_6H_7]$^-$ (4^-): Phenyl acetylene (1615 mg, 15.8 mmol) was added to the filtered THF solution of Na^+**2**$^-$ salt obtained in the first experiment and the mixture was heated at reflux for 72 h. The solvents were then evaporated and the residue digested with CH_2Cl_2 (20 mL) and water (20 mL) under cooling. The aqueous layer was then precipitated with CsCl (863 mg, 2.3 mmol) under cooling at 0°C to isolate (323 mg, 66% based on **1** used) of Cs^+**4**$^-$, which was dried in vacuo and identified by NMR spectroscopy as reported earlier.[4]

***Closo*-2-CB_6H_8 (4) and its re-conversion to 4^-**: A suspension of Cs^+**4**$^-$ (300 mg, 1.38 mmol) in CH_2Cl_2 (20 mL) was treated with F_3CCOOH (160 mg, 1.40 mmol) at 0°C for 2 h under stirring. The mixture was filtered through a short layer of silica and then fractionated between −78°C and −196°C traps. The −78°C trap contained 111 mg (95%) of compound **4**, which was isolated as a white semisolid material. Owing to the very high volatility and air sensitivity of **4**, it is better to use the filtered CH_2Cl_2 solution of compound **4** for further use. Treatment of this solution with a slight excess of triethylamine, followed by evaporation and drying in vacuo led to the isolation of Et_3NH^+**4**$^-$ (252 mg, 98%).

*Analysis of **4***: R_f (hexane) 0.1 ; ^{11}B NMR (128.3 MHz, $CDCl_3$, 25°C): δ = 3.5 (d, ^{1}J(B,H) = 187 Hz, 2B; B3,6), −9.4 (d, ^{1}J(B,H) = 143 Hz, 2B; B4,5), −22.8 ppm (d, ^{1}J(B,H) = 174 Hz, 2B; B1,7), all theoretical [^{11}B–^{11}B]-COSY cross-peaks observed; δ(^{11}B)$_{calcd}$ (GIAO-MP2/II//RMP2(fc)/6-31G*) = 3.2 (B3,6), −11.9 (B4,5), −23.2 ppm (B1,7); ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$, 25°C): δ = 5.39 (s, 1H; H2), 4.67 (s, 2H; H3,6), 4.45 (s, 2H; H4,5), 4.10 (s, 1H; μ-H4,5), −0.32 ppm (s, 2H; H1,7). MS: *m*/*z*: (%) = 86 (68, [*M*]$^+$), 85 (100, [*M*−H]$^+$); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 60.1 ppm (C2); δ(^{13}C)$_{calcd}$ (GIAO-MP2/II//RMP2(fc)/6-31G*) = 65.3 ppm (C2).

Synthesis of *nido*-2-CB_5H_9 (5): A suspension of Cs^+**4**$^-$ (300 mg, 1.38 mmol) in CH_2Cl_2 (20 mL) was treated with with conc. hydrochloric acid (2 mL) under stirring and cooling at 0°C for 4 h. The CH_2Cl_2 layer was separated, dried with $MgSO_4$ and filtered trough a short layer of silica. Fractionation between −78°C and −196°C traps gave 62 mg (60%) of compound **5** which was isolated as a white semisolid material from the −78°C trap. Owing to the very high volatility and air sensitivity of **5**, it is better to use the filtered CH_2Cl_2 solution of compound **5** for further use.

*Analysis of **5***: R_f (hexane) 0.15 ; ^{11}B NMR (128.3 MHz, $CDCl_3$, 25°C): δ = 15.7 (dd, ^{1}J(B,H) = 162 Hz, ^{1}J(B,μ-H) = 31 Hz, 2B; B3,6), −4.9 (dd, ^{1}J(B,H) = 156 Hz, ^{1}J(B,μ-H) = 22 Hz, ^{1}J(B,B) = 18 Hz, 2B; B4,5), −53.2 ppm (d, ^{1}J(B,H) = 165 Hz, 2B; B1), all theoretical [^{11}B–^{11}B]-COSY cross-peaks observed; δ(^{11}B)$_{calcd}$ (GIAO-MP2/II//RMP2(fc)/6-31G*) = 15.6 (B3,6), −4.8 (B4,5), −54.5 (B1); ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$, 25°C): δ = 5.43 (s, 1H; H2), 4.50 (s, 2H; H3,6), 3.46 (s, 2H; H4,5), −0.26 (s, 1H; μ-H4,5), −1.09 (s, 1H; H1), −2.16 ppm (s, 2H; μ-H3,4 and 5,6); ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 25°C): δ = 101.3 ppm (C2); δ(^{13}C)$_{calcd}$ (GIAO-MP2/II//RMP2(fc)/6-31G*) = 110.6 ppm (C2).

Geometry optimization and magnetic property calculations: Both initial geometry optimizations (under symmetry restrictions as mentioned above) of 2^-, **3**, and **4** and the corresponding frequency calculations were performed at a Hartree–Fock level of theory using a basis set of 6-31G*.[16] The latter calculations determined the nature of the stationary points. The minima were characterised with zero imaginary frequencies. The final geometry optimizations of these clusters were run at the RMP2(fc)/6-31G* level and the results are shown in Figure 1, Figure 2, Figure 3. The calculations used the Gaussian03 program package[17] and were performed on a Fujitsu–Siemens PC. The latter geometries were used for calculations of chemical shieldings. They were calculated first at a SCF level with the GIAO method and employed the II Huzinaga basis set.[18] The final level of the computations of chemical shieldings was GIAO-MP2 with the same basis set.

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[13] Interestingly, both calculated and experimental ^{11}B NMR spectra of **4**$^{-}$ and **4** are in good accord, with the exception of the B4,5 shifts. This pair of atoms in **4** exhibits an upfield shift of $\approx$10 ppm with respect to that in **4**$^{-}$, see ref. [4]. Conversely, "computational removal" of the B(7)-H-B(8) hydrogen bridge from [μ-6,9-O-*arachno*-5,10-$C_2B_8H_{11}$]$^{-}$ and subsequent GIAO-MP2/II//RMP2(fc)/6-31G* calculations on the resulting dianion provided entirely different ^{11}B NMR patterns as compared to those of the experimentally available monoanion. For an excellent agreement between the computed and measured chemical shifts of the latter anion see: D. Hnyk, J. Holub, *Dalton Trans.* **2006**, 2620–2622. References to other recent applications of this structural tool are given therein.

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