New Ways to a Series of Parent Representatives of the Eight-, Nine-, and Ten-Vertex Monocarbaborane Family

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The conditions for a reaction between *nido*-$B_{10}H_{14}$ (**1**) and aqueous formaldehyde in an alkaline solution have been optimized, which resulted in the isolation of the [*arachno*-6-CB_9H_{14}]$^-$ anion (**2**) in 52% yield. Anion **2** was used as a convenient source for the synthesis of a series of basic monocarbaborane compounds. Thus, oxidation of **2** (Et_4N^+ salt) with I_2 in CH_2Cl_2 in the presence of Et_3N at room temperature afforded the [*nido*-6-CB_9H_{12}]$^-$ anion (**3**). Acidification of anion **2** (generated in situ from borane **1**) with hydrochloric acid, in the presence of both $FeCl_3{\cdot}6H_2O$ and CH_2O, led to the formation of *arachno*-4-CB_8H_{14} (**4**), from which *nido*-1-CB_8H_{12} (**5**) was obtained by dehydrogenation at 200 °C in quantitative yield. Compound **4** can easily be converted into the [*closo*-1-CB_7H_8]$^-$ anion (**6**) in 71% yield via reaction with Et_3N and I_2 in THF at –78 °C. Anion **6** is also formed in 75% yield by treatment of carborane **5** with Et_3N in refluxing toluene. The [*closo*-1-CB_8H_9]$^-$ anion (**7**) was isolated by iodination of carborane **5** in the presence of Et_3N (yield 81%) or by the heating of the $PPh_4{}^+$ salt of anion **2** at 220 °C (yield 95%). The structure of anion **2** was determined by an X-ray diffraction study and the structures of compounds **2**, **4**, **5**, and **7** were geometry optimized at the RMP2(fc)/6-31G* level. The NMR spectroscopic measurements are in some cases complemented by unpublished ^{13}C NMR spectroscopic data. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Until recently, the syntheses of the eight-, nine- and ten-vertex monocarbaboranes have been a rather difficult task[1] as the procedures for the preparation of the parent (unsubstituted) representatives of these families were based on multistep reaction sequences starting from *nido*-decaborane(14), $B_{10}H_{14}$. A new, simple synthesis of the previously reported[2] [*arachno*-6-CB_9H_{14}]$^-$ anion and some of its C-substituted derivatives is a straightforward breakthrough into the area of monocarbaborane chemistry. The work also includes facile routes to the isomeric *closo* anions [2-CB_9H_{10}]$^-$ and [1-CB_9H_{10}]$^-$ developed by one of the authors.[3] Based on these results, experimental details of the synthesis of [*arachno*-6-CB_9H_{14}]$^-$ and *arachno*-4-CB_8H_{14} have been communicated in a preliminary fashion[4] and a few of the authors immediately started investigating further consequences of this chemistry, especially those relating to the C-phenyl and other substituted monocarbaborane derivatives of designed cluster shapes.[5] We report here on the optimization of the new synthesis of the [*arachno*-6-CB_9H_{14}]$^-$ anion[2] together with new routes to the basic parent monocarbaboranes [*nido*-6-CB_9H_{12}]$^-$,[6] *arachno*-4-CB_8H_{14},[6,7] *nido*-1-CB_8H_{12},[6b,8] [*closo*-1-CB_7H_8]$^-$,[9] and [*closo*-4-CB_8H_9]$^-$.[4] Even though most of these compounds have been previously reported, the methods outlined in this paper dramatically improve access to most of these monocarbaborane species and make them generally available. The numbering systems used for compounds discussed in this work are in Scheme 1.

Results and Discussion

Syntheses

It has previously been communicated[3,4] that the reaction of *nido*-decaborane(14), $B_{10}H_{14}$ (**1**), with an aqueous NaOH solution, followed by the addition of aqueous formal-

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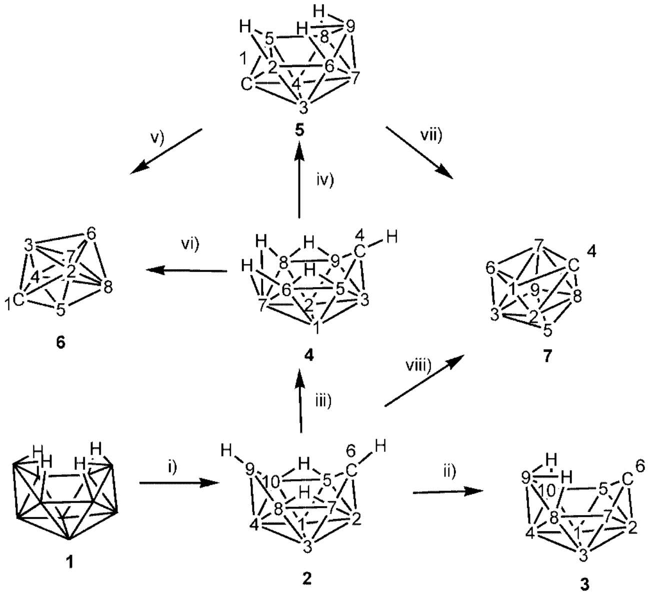


Scheme 1. Syntheses of carboranes from the [*arachno*-6-CB_9H_{14}]$^-$ (**2**) anion. i) aq. NaOH, CH_2O, r.t., 6 h. ii) I_2/Et_3N, CH_2Cl_2, room temp. iii) aq. HCl, aq. $FeCl_3$, hexane or aq. HCl, aq. CH_2O, hexane. iv) heating at 200 °C. v) Et_3N, toluene, reflux 6 h. vi) I_2/Et_3N, THF, −78 °C. vii) I_2/Et_3N, THF, −78 °C. viii) PPh_4^+ salt, 220 °C (the structures in schemes are presented in a simplified manner: calcd. C=CH and unmarked vertices of individual polyhedra stand for BH cluster units)

dehyde, generates the [*arachno*-6-CB_9H_{14}]$^-$ anion (**2**) (see path i) of Scheme 1]. The reaction may reasonably be predicted to proceed via the long-known[10] [*arachno*-6-$B_{10}H_{13}OH$]$^{2-}$ anion as in Equation (1) and Equation (2) and the overall reaction is then represented by Equation (3).

$$B_{10}H_{14} + 2\,OH^- \rightarrow [6\text{-}B_{10}H_{13}OH]^{2-} + H_2O \qquad (1)$$

$$[6\text{-}B_{10}H_{13}OH]^{2-} + CH_2O + 2\,H_2O \rightarrow [6\text{-}CB_9H_{14}]^- + B(OH)_4^- + H_2 \qquad (2)$$

$$B_{10}H_{14} + 2\,OH^- + CH_2O + H_2O \rightarrow [6\text{-}CB_9H_{14}]^- + B(OH)_4^- + H_2 \qquad (3)$$

It was found, however, that the reaction of Equation (3) did not give the best yields of anion **2** using a 1:1 molar ratio of **1**/CH_2O. The reaction was in fact accompanied by a side formation of the previously reported[6] [*nido*-6-CB_9H_{12}]$^-$ anion (**3**) as in Equation (4).

$$[6\text{-}CB_9H_{14}]^- + CH_2O \rightarrow [6\text{-}CB_9H_{12}]^- + CH_3OH \qquad (4)$$

Reaction 3 was therefore examined at variable **1**/CH_2O ratios, using 10% NaOH as the reaction medium at room temperature. The reaction was quenched after 5 h by precipitation with NEt_4Cl and the reaction products were analyzed by ^{11}B NMR spectroscopy. The results are shown in Table 1, from which it can be inferred that excess CH_2O promotes the side formation of anion **3**. Optimum reaction conditions for the formation of anion **2**, given in the Exp. Sect., are at molar ratios of 1:3.05. Anion **2** is then removed from the reaction mixture by extraction with Et_2O, followed by precipitation with a suitable countercation in water. The yield of **2,** prepared in this manner in several experiments, is approximately 50%; this one-pot procedure surpasses the previously reported method[2] in all aspects. Mechanistically, the formation of anion **2** is consistent with a unique subrogation of the B6H(OH) vertex in [*arachno*-6-$B_{10}H_{13}OH$]$^{2-}$ with the formaldehyde CH_2 unit.

Table 1. Products and yields of reactions 3 and 4

Molar ratio **1**/CH_2O[a]	Overall yield (%)[b]	**2**[c]	**3**[c]
1:1.05	43	90	10
1:2.05	45	90	10
1:3.05	58	95	−
1:4.5	76	67	33
1:6.5	68	72	20

[a] In 10% NaOH, room temp., 5 h, then precipitated with NEt_4Cl. [b] Sum of yields of NEt_4^+**2** and NEt_4^+**3**. [c] Content of anions **2** and **3** (in molar%) in the anionic mixture isolated (estimated from ^{11}B NMR spectra).

Anion **2** has become a multipurpose reagent for the preparation of the whole series of monocarbaborane compounds (see Scheme 1). As outlined in path ii) of Scheme 1, a room temperature reaction between Et_4N^+[*arachno*-6-CB_9H_{14}]$^-$ (Et_4N^+**2**) and elemental I_2 in CH_2Cl_2 in the presence of NEt_3 (proton scavenger) resulted in the oxidation of **2** and quantitative formation of the [*nido*-6-CB_9H_{12}]$^-$ anion,[6] which was isolated as its Et_4N^+ salt, Et_4N^+[*nido*-6-CB_9H_{12}]$^-$ (Et_4N^+**3**). The reaction is consistent with the stoichiometry as in Equation (5).

$$[6\text{-}CB_9H_{14}]^- + 2\,Et_3N + I_2 \rightarrow [6\text{-}CB_9H_{12}]^- + 2\,Et_3N{\cdot}HI \qquad (5)$$

Anion **2** has also been found to be a very convenient source of the nine-vertex carborane *arachno*-4-CB_8H_{14} (**4**). A room temperature reaction of Na^+**2** with hydrochloric acid and $FeCl_3{\cdot}6H_2O$ in an aqueous medium in the presence of hexane (extraction medium) results in almost quantitative isolation of carborane **4** [see path iii) of Scheme 1 and Equation (6)]. Another, equally effective alternative, is the use of CH_2O in place of the iron trichloride as in Equation (7). Both reactions are carried out more conveniently in one pot from decaborane via in situ generation of anion **2** with typical yields in the range of 45−50% (based on the use of **1**). The formation of carborane **4** is obviously associated with a hydrolytic removal of the B9 vertex in **2**.

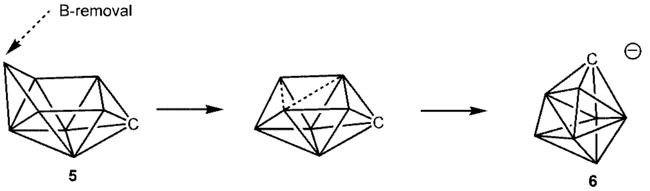
$$6\text{-}CB_9H_{14}^- + Fe^{3+} + 3\,H_2O \rightarrow 4\text{-}CB_8H_{14} + Fe^{2+} + B(OH)_3 + 3/2\,H_2 \qquad (6)$$

$$6\text{-}CB_9H_{14}^- + CH_2O + H_3O^+ + 2\,H_2O \rightarrow 4\text{-}CB_8H_{14} + CH_3OH + B(OH)_3 + H_2 \qquad (7)$$

Carborane **4** was converted quantitatively into *nido*-1-CB_8H_{12} (**5**) by heating in vacuo for 6 h at 200 °C (path iv) of Scheme 1) via lower-temperature modification of the previously reported method (sublimation through a hot tube at 350 °C).[6b] Compound **5** was then conveniently used for generating other important compounds of the eight- and nine-vertex monocarbaborane family. As shown in path v) of Scheme 1, treatment of carborane **5** with Et_3N in refluxing toluene led to the isolation of the [*closo*-1-$CB_7H_8]^-$ anion (**6**),[9] the reaction being consistent with the stoichiometry of Equation (8).

$$1\text{-}CB_8H_{12} + 2\,Et_3N \rightarrow Et_3NH^+[1\text{-}CB_7H_8]^- + Et_3N{\cdot}BH_3 \qquad (8)$$

The anion **6** was then isolated in 75% yield as its PBu_4^+ salt, PBu_4^+**6**, upon treatment with aqueous NaOH and precipitation with PBu_4Cl. Salts of anion **6,** with any arbitrary countercation, may be similarly prepared. The reaction is consistent with the elimination of the B9 vertex in **5**, followed by closure of the rest of the carborane cage (see Scheme 2). As shown in path vi) of Scheme 1 [see also Equation (9)], anion **6** can also be generated in 71% yield via reaction between the *arachno* carborane **4** and I_2 in the presence of Et_3N in THF at −78 °C.



Scheme 2. Proposed formation of the [*closo*-1-$CB_7H_8]^-$ (**6**) anion via removal of the B9 vertex from *nido*-1-CB_8H_{12} (**7**); extra hydrogen atoms omitted for clarity

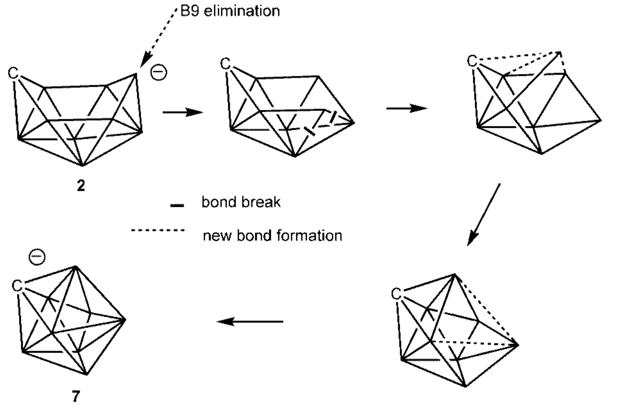
$$\begin{aligned}&4\text{-}CB_8H_{14} + 4\,Et_3N + I_2 \rightarrow\\ &\qquad Et_3NH^+[1\text{-}CB_7H_8]^- + Et_3N{\cdot}BH_3 + 2\,Et_3N{\cdot}HI\end{aligned} \qquad (9)$$

The reaction may be explained by removing the B6 vertex in **4**, followed by oxidative closure of the remaining CB7 skeleton. A similar mechanism was proposed earlier for the formation of anion **6** from 6-Me_3N-*arachno*-4-CB_8H_{12}.[9] The Et_3NH^+ salt was again converted into PBu_4^+**6** as in the preceding case. Both procedures of Equations (8) and (9) are very simple and anion **6** now becomes one of the best available compounds of monocarbaborane chemistry. The same applies to the nine-vertex anion [*closo*-4-$CB_8H_9]^-$ (**7**) which was reported in a preliminary communication.[4] One method for the preparation of **7** is based on treatment of compound **5** with I_2 in the presence of Et_3N in THF at −78 °C [Equation (10) and path vii) of Scheme 1].

$$1\text{-}CB_8H_{12} + 3\,Et_3N + I_2 \rightarrow Et_3NH^+[4\text{-}CB_8H_9]^- + 2\,Et_3N{\cdot}HI \qquad (10)$$

$$[6\text{-}CB_9H_{14}]^- \rightarrow [4\text{-}CB_8H_9]^- + [BH_3] + H_2 \qquad (11)$$

The Et_3NH^+ salt was again converted in situ into PBu_4^+**7** (yield 81%) in an alkaline solution by precipitation with PBu_4Br. Other salts with suitable countercations can be isolated in a similar manner. The formation of **7** can be classified as a clean *nido* → *closo* conversion in which the original B2, B5 and B9 vertices in **5** are interconnected via oxidation to **7**. A very simple access to anion **7** is also the heating of PPh_4^+**2** at 220 °C [see Equation (11) and path viii) of Scheme 1]. The reaction provides PPh_4^+**7** in 95% yield as a single product and is associated with a clean elimination of the B9 vertex from anion **2** followed by cage closure. The process is probably associated with the rearrangement of one of the boron vertices as suggested in Scheme 3. This method is much more convenient than a similar heating of Cs^+**2**[4] (maximum yield of **7** 60%), which is associated with the side formation of other anions.



Scheme 3. Proposed formation of the [*closo*-1-$CB_8H_9]^-$ (**7**) anion via removal of the B9 vertex from the [*arachno*-6-$CB_9H_{14}]^-$ (**2**) cage; extra hydrogen atoms omitted for clarity

Structural Studies

The structures of anions **6** (I_2 and 1-Ph derivatives)[5b][5e,9] and **7**[4] have already been determined crystallographically and those of anions **6**,[11] and **7**[4,11] have been geometry-optimized. In this work these studies are complemented by an X-ray diffraction study of anion **2** (see Figure 1) and the geometries of compounds **2**, **3**, **4**, and **5** optimized at the RMP2(fc)/6-31G* level (see Figure 2).

The crystallographic structure of PPh_3Me^+**2**, depicted in Figure 1, is in agreement with the earlier proposed structure.[2] The anionic part contains one CH_2 and one BH_2 unit in the apical positions and two hydrogen bonds in the open hexagonal face. The longest bond lengths in the open face are those attached to B9, followed by the "bridging" B−B distances and C−B separations. The B8−B9−B10 angle is significantly (10.7°) smaller than B5−C6−B7. Other intracluster C−B and B−B distances are within usual limits. Comparisons between experimental and calculated bond lengths for anion **2** show good agreement, which reflects the accuracy of the calculations.

In the *nido* anion **3**, the calculated B5−B10 distance is 0.068 Å longer than the corresponding "bridged" B5−B10 separation in its *arachno* counterpart **2**. The B5−B10 dis-

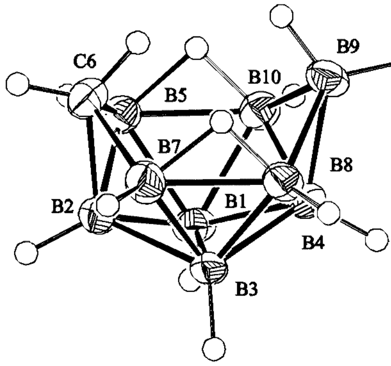


Figure 1. ORTEP representation of the crystallographically determined molecular structure of $PMePh_3^+$[*arachno*-6-CB_9H_{14}]$^-$ ($PMePh_3^+$**2**) (cationic part omitted); displacement ellipsoids are drawn at 50% probability level; selected bond lengths (Å) and angles (°): B1−B2 1.736(2), B1−B3 1.809(2), B1−B4 1.787(2), B1−B5 1.779(2), B1−B10 1.768(2), B2−B3 1.746(2), B2−B5 1.782(2), B2−C6 1.668(2), B2−B7 1.775(2), B3−B4 1.792(2), B4−B8 1.747(2), B4−B9 1.731(2), B4−B10 1.741(2), B5−C6 1.729(2), B5−B10 1.850(2), C6−B7 1.728(2), B7−B8 1.877(2), B8−B9 1.894(2), B9−B10 1.915(2), B5−C6−B7 112.66(10), B8−B9−B10 102.24(9)

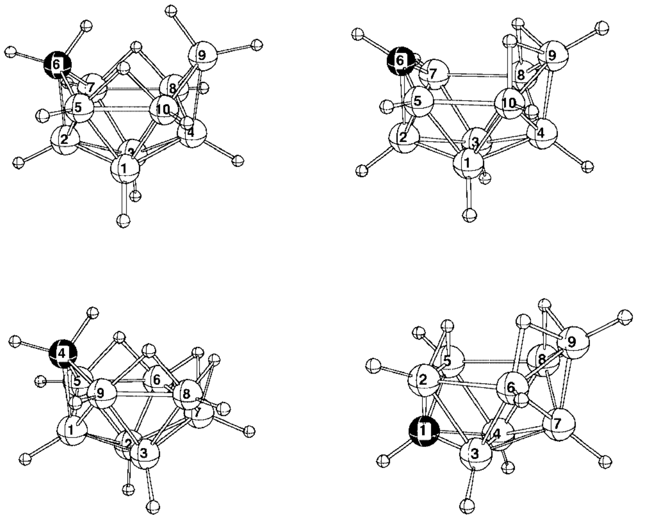
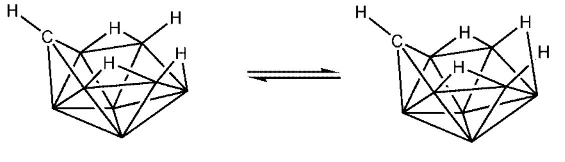


Figure 2. Geometry-optimized structures of [*arachno*-6-CB_9H_{14}]$^-$ (**2**), [*nido*-6-CB_9H_{12}]$^-$ (**3**), *arachno*-4-CB_8H_{14} (**4**), and *nido*-1-CB_8H_{12} (**5**) at the RMP2(fc)/6-31G* level; selected bond lengths (Å) and angles (°): **2** B1−B2 1.734, B1−B3 1.810, B1−B4 1.788, B1−B5 1.772, B1−B10 1.770, B2−B5 1.774, B2−C6 1.671, B4−B9 1.735, B4−B10 1.737, B5−C6 1.7233, B5−B10 1.849, B8−B9 1.913, B−H (mean) 1.199, B5-μH5,10 1.358, B10-μH5,10 1.284, C6−H (mean) 1.088, B5−C6−B7 112.2, B8−B9−B10 101.5; **3** B1−B2 1.749, B1−B3 1.809, B1−B4 1.804, B1−B5 1.765, B1−B10 1.765, B2−B5 1.793, B2−C6 1.696, B4−B9 1.710, B4−B10 1.777, B5−C6 1.539, B5−B10 1.917, B8−B9 1.762, B−H (mean) 1.198, B8-μH8,9 1.315, B9-μH8,9 1.338, C6−H 1.093, B5−C6−B7 118.1, B8−B9−B10 104.1; **4** B1−B2 1.798, B1−B3 1.733, B1−B5 1.799, B1−B6 1.720, B1−B7 1.816, B3−B4 1.669, B3−B5 1.762, B4−B9 1.720, B5−B6 1.827, B9−B7 1.837, B8−B9 1.827, B−H (mean) 1.189, B5-μH5,6 1.368, B6-μH5,6 1.290, C4−H (mean) 1.087, B6-μH6,7 1.246, B7-μH6,7 1.526, B5−C4−B9 114.6, B6−B7−B8 127.3; **5** C1−B2 1.592, C1−B3 1.608, B2−B5 1.891, B2−B6 1.937, B3−B4 1.817, B6−B7 1.799, B7−B9 1.696, B8−B9 1.775, B−H (mean) 1.189, B2-μH2,5 1.331, B6-μH6,9 1.315, B9-μH6,9 1.337, C1−H 1.087, B8−B9−B6 100.5

tance in **3** is also 0.155 Å longer than the "bridged" B8−B9 bond length. Further comparisons suggest that the B5−C6−B7 and B8−B9−B10 angles in **3** are 5.9 and 2.6° larger, respectively, than those in **2** and the B5−C6−B7 angle in **3** is also 14° larger than B8−B9−B10. This means than the open hexagonal faces in both anions **2** and **3** are rather irregular and more open in the area around the carbon vertices.

Calculations on the neutral carborane **4** at both the MP2/6-31G* and B3LYP/6-31G* levels characterized the C_s structure shown in Figure 2 as a minimum. Comparison of computed chemical shifts for this structure to experimental data leaves no doubt that the solution spectra are due to a static structure (C_s symmetric) and not time averaging of rapidly rearranging C_1 structures shown in Scheme 4. The *C*s structure contains two pairs of asymmetrical hydrogen bonds; the B5-μH5,6 distance is 0.078 Å longer than B6-μH5,6 and the B6-μH6,7 separation is 0.28 Å shorter than B7-μH6,7, which at 1.526 Å is extremely long. Comparison of the calculated open-face C−B (1.720/1.733 Å) and the bridging B−B (1.827/1.849 Å) distances and the B−C−B angles (114.6/112.2°) in anions **4** and **2**, respectively, suggests that the C4−B5−B6−B8−B9 section in **4** is very similar to the corresponding B5−C6−B7−B8−B10 part of the molecule of **2**. This corresponds to the fact that the two molecules are related by removing one boron vertex. Comparison of the bridging B−B distances in **4** shows that the B6−B7 separation is only slightly (0.01 Å) longer than the B5−B6 distance. In the *nido* compound **5**, the B2−B6 separation is significantly (0.162 Å) longer than the bridging B6−B9 distance and the other bridging B2−B5 separation is 0.116 Å longer than B6−B9. The B6−B9−B8 angle is at 100.5°, which is similar to the B8−B9−B10 angle in the *nido* anion **3** (cf. 104°) (Scheme 4).



4 (C_1) **4** (C_1)

Scheme 4. Time averaging between two C_1 structures for compound **4**; averaged ^{11}B NMR shifts computed for this process at the IGLO-HF/DZ level are: 4.3 (B1), −39.8 (B2,3), 9.2 (C4), −9.6 (B5,9), −25.8 (B6,8), 26.8 (B7)

The ^{11}B and ^{1}H NMR spectroscopic data for all compounds encountered in this work have mostly been reported previously, in some cases we have added the data for anions with different countercations. The work is supplemented by the unpublished ^{13}C NMR shifts of the cage CH or CH_2 units for selected compounds. The optimized geometries have been used as a basis for the calculation of theoretical ^{11}B and ^{13}C NMR chemical shifts. A comparison between calculated and experimental shifts (see Exp. Sect.) is generally in good agreement.

Conclusions

The efficient route from $B_{10}H_{14}$ to the starting monocarbaborane anion **2** has improved the yield of this anion by about five times, in comparison with the original procedure.[2] This means that the eight-, nine- and ten-vertex species prepared in this work are now one of the most readily accessible monocarbaboranes. Their chemistry should now contribute substantially to the development of carborane science. For example, the *closo* anions **6** and **7**, together with the recently reported [*closo*-CB_6H_7]$^-$ anion,[12] could act as "weakly coordinating anions" to complement [CB_9H_{10}]$^-$ and [$CB_{11}H_{12}$]$^-$, and their derivatives.[13] The compounds are also likely to be amenable to extensive substitution and metallacarborane chemistries. We are currently developing these areas with the aim of extending the knowledge of the chemistry of monocarbaboranes with less than ten cluster atoms.

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 compound **1** was sublimed in vacuo at 80 °C using an apparatus equipped with a water-cooled sublimation finger. THF was distilled from sodium diphenyl ketyl, dichloromethane and hexane were dried over CaH_2 and freshly distilled before use. Other chemicals were reagent or analytical grade and were used as purchased. The purity of the individual compounds was checked by analytical TLC on Silufol (silica gel on aluminum foil; detection by iodine vapors, followed by 2% aqueous $AgNO_3$ spray). Melting points were measured in sealed capillaries under argon and are uncorrected. Multinuclear (^{1}H, ^{11}B, and ^{13}C) NMR spectroscopy was performed essentially with the instrumentation described in other related papers from our laboratories.[15] The ^{11}B and ^{13}C chemical shifts are given in the following manner: δ(exp.)/δ(calcd., IGLO-HF/DZ), δ(calcd., GIAO-HFII), δ(calcd., GIAO-B3LYP/II).

Salts of [*arachno*-6-CB_9H_{14}]$^-$ (2) (Optimized Procedure): A solution of compound **1** (1.24 g, 10 mmol) in 20 mL of hexane was treated with 10% aqueous NaOH (70 mL) whilst stirring and cooling at 0 °C. The cooling was continued and 2.5 g of an aqueous CH_2O solution (37%, w/w, stabilized with methanol) (ca. 31 mmol of CH_2O) diluted with 10 mL of water was added over a period of 1 h. The stirring was continued at ambient temperature for 12 h. The hexane layer was separated and the aqueous solution was extracted by three 10-ml portions of Et_2O and the combined extracts were evaporated with water (30 mL) to remove the diethyl ether. The remaining aqueous solution (solution A) was precipitated alternatively with solid $Et_4N^+Cl^-$ (1.7 g, 10 mmol), $PPh_4{}^+Cl^-$ (3.75 g, 10 mmol), and $Ph_3PMe^+Cl^-$ (3.15 g, 10 mmol). The white precipitates were isolated by filtration, the solids were washed with cold water (2 × 10 mL) and vacuum dried for 12 h to give pure Et_4N^+ (1.3 g, 51%), $PPh_4{}^+$ (2.6 g, 56%), and Ph_3PMe^+ (2.1 g, 52%) salts of anion **2**, respectively. The salts were recrystallized by diffusion of hexane vapors into solutions of CH_2Cl_2. M.p. 348 °C (decomp.). ^{11}B NMR (128.3 MHz, CD_3CN, 295 K): δ = −1.4/ 3.2, 5.4, −2.7 [d, ^1J(B,H) = 129 Hz, 1 B, B4], −10.3/−8.3, −5.6, −13.2 (d, ^1J(B,H) ≈160 Hz, 1 B, B2), −12.9/−14.2, −11.2, −17.3 [d, ^1J(B,H) = 154 Hz, 2 B, B5,7], −23.3/−21.1, −21.4, −25.5 [t, ^1J(B,H) = 106 Hz, 1 B, B9], −28.8/−28.6, −26.9, −32.1 [d, ^1J(B,H) = 128 Hz, 2 B, B8,10], −39.8/−41.4, −38.9, −44.4 [d, ^1J(B,H) = 138 Hz, 2 B, B1,3]. ^{13}C{^{1}H } NMR [100.6 MHz, $(CD_3)_2SO$, 295 K]: δ = −4.8/−1.4, −12.5, −2.0 (s br., 1 C, C6). $C_9H_{42}B_9N$ (253.75): calcd. C 42.60, H 16.68; found C 43.20, H 15.62.

Et_4N^+[*nido*-6-CB_9H_{12}]$^-$ (Et_4N^+3): Triethylamine (0.5 mL) was added to a solution of Et_4N^+**2** (381 mg, 1.5 mmol) in CH_2Cl_2 (20 mL) and the mixture was treated with solid I_2 (381 mg, 1.5 mmol) in several portions over a period of 2 h whilst stirring at room temperature. The mixture was then shaken with 5% aqueous $Na_2S_2O_3$ (20 mL) and water (20 mL). The bottom layer was separated, evaporated and the residual solid was vacuum dried at ambient temperature for 12 h to give pure Et_4N^+**3**. M.p. 298 °C (decomp.). ^{11}B NMR (128.3 MHz, CD_2Cl_2, 295 K): δ = 1.7/2.5.4.7, −1.1 [d, ^1J(B,H) = 135 Hz, 2 B, B5,7], −1.8/−3.0, −0.9, −10.0 [d, ^1J(B,H) ≈ 150 Hz, 1 B, B9], −4.6/−3.1, 1.7, −5.7 [d, ^1J(B,H) = 134 Hz, 2 B, B1,3], −12.5/−13.5, −9.6, −15.0 [d, ^1J(B,H) = 140 Hz, 2 B, B8,10], −30.7/−34.5, −31.2, −33.8 [d, ^1J(B,H) = 147 Hz, 1 B, B2], −37.9/−41.4, −38.4, −43.4 [d, ^1J(B,H) = 142 Hz, 1 B, B4]. ^{13}C NMR [100.6 MHz, $(CD_3)_2SO$, 295 K]: δ = 126.4/129.9, 124.7, 140 (d, $^1J_{C,H}$ = 144 Hz, 1 C, C6). $C_9H_{40}B_9N$ (251.73): calcd. C 42.94, H 16.02; found C 41.15, H 15.38.

***arachno*-4-CB_8H_{14} (4):** a) Solution A from the preparation of anion **2** (containing ca. 5.2 mmol of Na^+**2**) was added dropwise to a stirred mixture of aqueous HCl (ca. 4.5 M, 35 mL), $FeCl_3$·$6H_2O$ (6.5 g) and hexane (30 mL) and the stirring was continued for 6 h (hydrogen evolution). The hexane layer was separated, evaporated and the residue sublimed at 50 °C (bath temperature) to obtain compound **4** (540 mg, 48%, based on **1** used), which was identified by NMR spectroscopy. ^{11}B NMR: δ = 17.0/16.3, 18.8, 12.6 (B7), −3.7/−2.9, 1.3, −6.5 (B1), −6.3/−7.8, −4.7, −9.7 (B5,9), −34.9/−36.4, −34.5, −42.8 (B6,8), −41.1/−47.1, −44.4/−49.6 (B2,3), experimental data from ref.[6a] ^{13}C NMR (125.8 MHz, $CDCl_3$, 295 K): δ = −10.8/−13.1, −16.4, −10.0 (t, $^1J_{C,H}$ = 134 and 162 Hz, 1 C, C4). b) Hexane (40 mL) and an aqueous solution of CH_2O (37%, w/v, stabilized with methanol) (1.6 g, ca. 20 mmol of CH_2O) were added to solution A from the preparation of anion **2** whilst stirring and cooling to 0 °C (bath temperature). The mixture was then treated dropwise with aqueous HCl (ca. 4.5 M, 35 mL) at 0 °C for 1 h, and the stirring was then continued for 6 h at room temperature (hydrogen evolution). The hexane layer was separated and pure compound **4** (563 mg, 50% based on **1**) was isolated as in the preceding experiment.

***nido*-1-CB_8H_{12} (5):** Freshly sublimed compound **4** (500 mg, 4.44 mmol) was placed in a 250-mL Pyrex tube equipped by a break seal and sealed in vacuo under cooling liquid nitrogen. The tube was then heated at 200 °C for 6 h and opened into a vacuum manifold under cooling with liquid nitrogen. The solid residue was then sublimed into a −78 °C trap to obtain pure compound **7** (495 mg, 99%), which was identified by spectroscopy. ^{11}B NMR: δ = 7.6/6.4, 8.9, 2.0 (B9), −3.3/−0.3, 0.2, −5.4 (B3,4), −11.5/−12.6, −9.3, −14.2 (B6,8), −26.5/−26.0, −24.7, −31.2 (B2,5), −53.3/−54.4, −52.6, −58.8 (B7), experimental data from ref.[16] ^{13}C NMR (125.8 MHz, $CDCl_3$, 295 K): δ = 31.1/29.5, 19.6, 35.7 (d, $^1J_{C,H}$ = 199 Hz, 1 C, C1).

[*closo*-1-CB_7H_8]$^-$ Anion (6): a) NEt_3 (1.6 mL) was added to a solution of compound **4** (260 mg, 2.31 mmol) in THF (20 mL) and the mixture was treated with a solution of I_2 (1175 mg, 4.62 mmol) in THF (30 mL) under vigorous stirring and cooled to −78 °C over a period of 1 h. The volatiles were then evaporated, the residual materials dried in vacuo for 1 h and then treated with a mixture of 5% KOH (20 mL) and CH_2Cl_2 (20 mL) under shaking. The CH_2Cl_2 layer, containing $NEt_3{\cdot}BH_3$ (identified via ^{11}B NMR), was discarded and the aqueous layer treated with solid PBu_4Cl (681 mg, 2.31 mmol). The precipitate was isolated by filtration and dried under vacuum for 2 h at room temperature. Crystallization by diffusion of hexane vapors into a CH_2Cl_2 solution gave white crystals (586 mg, 71%) which were identified by ^{11}B NMR spectroscopy[9] as PBu_4^+**6**. $^{13}C\{^{11}B\}$ NMR [100.6 MHz, $(CD_3)_2CO$, 295 K]: $\delta = 60.1$ (s, 1 C, C1). b) Under strictly anaerobic conditions (deoxygenated Ar), a solution of compound **5** (300 mg, 2.71 mmol) in toluene (30 mL) was treated with NEt_3 (1 mL) and then heated at reflux for 6 h. The mixture was then cooled to ambient temperature and extracted with two 10-ml portions of 5% KOH. The aqueous layer was treated with solid PBu_4Cl (800 mg, 2.71 mmol) and then extracted with CH_2Cl_2 (20 mL). The organic layer was placed onto a silica gel column (2.5 × 20 cm) and elution with 5% MeCN in CH_2Cl_2 gave the main fraction of $R_f = 0.23$. This was evaporated to dryness and the residue crystallized by diffusion of hexane vapors into a CH_2Cl_2 solution to isolate white crystals of PBu_4^+**6** (681 mg, 75%).

[*closo*-4-CB_8H_9]$^-$ Anion (7): a) A solution of freshly sublimed compound **5** (150 mg, 1.36 mmol) in THF (10 mL) was treated with Et_3N (0.5 mL) whilst stirring and cooling to −78 °C and solid I_2 (346 mg, 1.36 mmol) was then added in several portions over a period of 1 h. The THF was evaporated and the residual solid treated with 5% aqueous KOH while shaking and cooling. The Et_3N thus evolved was evaporated and the residual solution filtered. The filtrate was treated with PBu_4Br (462 mg, 1.36 mmol) and extracted with CH_2Cl_2 (20 mL). The CH_2Cl_2 extract was mounted onto a silica gel column (2.5 × 20 cm) and elution with 5% MeCN in CH_2Cl_2 gave a pure fraction of $R_f = 0.2$. This was evaporated and the residual solid crystallized by diffusion of hexane vapors into a CH_2Cl_2 solution to isolate the white crystals of PBu_4^+**7** (405 mg, 81%). Other salts of anion **7** can be obtained by precipitation of the aqueous filtrate with a suitable countercation. ^{11}B NMR (160.4 MHz, $CDCl_3$, 25 °C): $\delta = 12.8$ [d, $^1J(B,H) = 145$ Hz, 2 B, B5,6], -14.3 [d, $^1J(B,H) = 148$ Hz, 4 B, B1,2,7,8], -20.3 [d, $^1J(B,H) = 136$ Hz, 1 B, B3,9], all theoretical [^{11}B-^{11}B]-COSY crosspeaks observed. $^1H\{^{11}B\}$ NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 4.37$ (s, 2 H, H5,6), 4.13 (s, 1 H, H4), 1.47 (s, 4 H, H1,2,7,8), 0.64 (s, 2 H, H3,9). ^{13}C NMR (125.8 MHz, $CDCl_3$, 25 °C): $\delta = 44.5$ (br.d, $^1J_{C,H} = 182$ Hz, 1 C, C4). b) Solid PPh_4^+**2** (926 mg, 2 mmol) was heated for 2 h at 220 °C. The residual solid was dissolved in CH_2Cl_2 (10 mL) and the solution was carefully covered by hexane (20 mL). The white crystals that separated on standing for 3 days were identified by NMR spectroscopy as pure PPh_4^+**9** (849 mg, 95%).

Computational Details: The GAUSSIAN94 program package[17] was used for calculations, which were performed on the Power Challenge XL computer of the Supercomputing Center of the Charles University in Prague. The structures proposed on the basis of experimental ^{11}B and ^1H NMR spectroscopy were optimized first at RHF/6-31G* within the given symmetry restriction. Frequency calculations, carried out at the same level, determined the nature of the stationary points. Minima are characterized by zero imaginary frequency (NIMAG = 0). Further optimizations at RMP2(fc)/6-31G* included the effect of electron correlation. Selected geometry parameters are given in Figure 2. For MP2/6-31G* optimized geometries the chemical shieldings were calculated at a SCF level using both the IGLO (invariant gauge for localized orbitals) and GIAO (gauge-invariant atomic orbital) method. In addition the B3LYP density functional theory level was applied using GIAO, the latter being incorporated in the GAUSSIAN94. NMR shift calculations employed Huzinaga basis sets:[18] DZ (double zeta) and II well-designed for magnetic properties calculations.[19]

X-ray Crystallographic Study: Crystals of PPh_3Me^+**2** were grown by slow diffusion of hexane vapors into a CH_2Cl_2 solution. The crystal was mounted on a glass fiber with epoxy cement and measured on a four-circle diffractometer Nonius KappaCCD equipped with a CCD area detector at 150(2)K with Mo-K_α radiation ($\lambda = 0.71073$ Å, graphite-monochromated). The structure was solved by the direct method (SIR97)[20] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-97).[21] All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms of the carborane cage were located on difference Fourier maps and refined isotropically; remaining hydrogen atoms of PPh_3Me^+ were on calculated positions and refined applying the riding model with assigned temperature factors either $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or $H_{iso}(H) = 1.5\ U_{eq}$(pivot atom) for the methyl moiety.
Crystal data: $C_{20}H_{32}B_9P$, a colorless block of dimensions 0.70 × 0.45 × 0.4 mm crystallizes in the monoclinic space group $P2_1/c$ with the lattice parameters $a = 11.7370(2)$, $b = 15.0650(2)$, $c = 14.0740(2)$ Å, $\beta = 107.8960(8)°$, $V = 2368.13(6)$ Å^3, $Z = 4$, $\mu = 0.122\ mm^{-1}$; 39627 reflections collected in the range $2° \le 2\theta \le 55°$, 5417 reflections independent ($R_{int} = 0.029$), 4824 assigned to be observed [$I > 2\sigma(I)$], full-matrix least-squares refinement against F^2 with 328 parameters converged at $wR(F^2) = 0.0990$ ($R[F^2 > 2\sigma(F^2)] = 0.0356$, $w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.6888P]$ where $P = F_o^2 + 2F_c^2)/3$) and the max./min. residual electron density was $0.309/-0.303$ e·Å^{-3}. CCDC-230897 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] B. Štíbr, *Chem. Rev.* **1992**, *92*, 225−250.

[2] [2a] B. Štíbr, T. Jelínek, J. Plešek, S. Heřmánek, *J. Chem. Soc., Chem. Commun.* **1987**, 963−964. [2b] K. Nestor, T. Jelínek, X. L. R. Fontaine, J. D. Kennedy, M. Thornton-Pett, K. Baše, B. Štíbr, *J. Chem. Soc., Dalton Trans.* **1990**, 2887−2894.

[3] B. Brellochs in *Contemporary Boron Chemistry* (Eds.: M. G. Davidson, A. K. Hughes, K. Wade), Royal Society of Chemistry, Cambridge, UK, **2000**, pp. 212−214.

[4] T. Jelínek, B. Štíbr, J. Holub, M. Bakardjiev, D. Hnyk, D. L. Ormsby, C. A. Killner, M. Thornton-Pett, H.-J. Schanz, B. Wrackmeyer, J. D. Kennedy, *Chem. Commun.* **2001**, 1756−1757; B. Štíbr, B. Wrackmeyer. *J. Organomet. Chem.* **2002**, *657*, 3−8.

[5] [5a] T. Jelinek, C. A. Kilner, M. Thornton-Pett, J. D. Kennedy, *Chem. Commun.* **2001**, 1790−1791. [5b] A. Franken, C. A.

Kilner, M. Thornton-Pett, J. D. Kennedy, *Collect. Czech. Chem. Commun.* **2002**, *67*, 869−912. [5c] T. Jelinek, M. Thornton-Pett, J. D. Kennedy, *Collect. Czech. Chem. Commun.* **2002**, *67*, 1035−1050. [5d] A. Franken, C. A. Kilner, M. Thornton-Pett, J. D. Kennedy, *J. Organomet. Chem.* **2002**, *657*, 176−179. [5e] A. Franken, C. A. Kilner, M. Thornton-Pett, J. D. Kennedy, *J. Organomet. Chem.* **2002**, *657*, 180−186. [5f] A. Franken, C. A. Kilner, M. Thornton-Pett, J. D. Kennedy, *Inorg. Chem. Commun.* **2002**, *5*, 581−584. [5g] A. Franken, C. A. Kilner, M. Thornton-Pett, J. D. Kennedy, *Chem. Commun.* **2002**, 2048−2049. [5h] N. J. Bullen, A. Franken, C. A. Kilner, J. D. Kennedy, *Chem. Commun.* **2003**, 1684−1685. [5i] A. Franken, C. A. Kilner, J. D. Kennedy, *Inorg. Chem. Commun.* **2003**, *6*, 1104−1108. [5j] S. L. Renard, A. Franken, C. A. Kilner, J. D. Kennedy, M. A. Halcrow, *New. J. Chem.* **2003**, *26*, 1634−1637.

[6] [6a] B. Štíbr, K. Baše, S. Heřmánek, J. Plešek, *J. Chem. Soc., Chem. Commun.* **1976**, 150−151. [6b] K. Baše, B. Štíbr, J. Dolanský, J. Duben, *Collect. Czech. Chem. Commun.* **1981**, *46*, 2345−2353.

[7] A. E. Wille, J. Plešek, J. Holub, B. Štíbr, P. J. Carroll, L. G. Sneddon, *Inorg. Chem.* **1996**, *35*, 5342−5346.

[8] [8a] K. Baše, S. Heřmánek, B. Štíbr, *Chem. Ind. (London)* **1977**, 951−952. [8b] S. Heřmánek, J. Fusek, B. Štíbr, J. Plešek, T. Jelínek, *Polyhedron* **1986**, *5*, 1873−1879.

[9] [9a] J. Plešek, T. Jelínek, B. Štíbr, S. Heřmánek, *J. Chem. Soc., Chem. Commun.* **1988**, 348−349. [9b] T. Jelínek, B. Štíbr, J. Plešek, J. D. Kennedy, M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.* **1995**, 431−437.

[10] E. L. Muetterties, F. Klanberg, *Inorg. Chem.* **1966**, *5*, 315−316.

[11] P. v. R. Schleyer, K. Najafian, *Inorg. Chem.* **1998**, *7*, 3454−3470.

[12] B. Štíbr, O. L Tok, W. Milius, M. Bakardjiev, J. Holub, D. Hnyk, B. Wrackmeyer, *Angew. Chem. Int. Ed.* **2002**, *41*, 2126−2128.

[13] [13a] C. Reed, *Acc. Chem. Res.* **1998**, *31*, 133−139. [13b] S. Strauss, *Chem. Rev.* **1993**, *93*, 927−942.

[14] D. F. Shriver, M. A. Drezdon, *Manipulation of Air Sensitive Compounds*, 2nd ed., Wiley, New York, **1986**.

[15] B. Štibr, J. Holub, M. Bakardjiev, I. Pavlík, O. L. Tok, I. Císarová, B. Wrackmeyer, M. Herberhold, *Chem. Eur. J.* **2003**, *9*, 2239−2244.

[16] J. H. Jones, B. Štíbr, J. D. Kennedy, A. D. Lawrence, M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.* **1993**, 1269−1274.

[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petterson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zahrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkra, M. Challacombe, C. Y. Peng, P. Y. Ayala, Y. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomprets, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, L. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, J. A. Pople, *GAUSSIAN94*, Revision B.2. Gaussian Inc., Pittsburg, PA, **1995**.

[18] S. Huzinaga, *Approximate Atomic Wave Functions*, University of Alberta, Edmonton, Canada, **1971**.

[19] W. Kutzelnigg, M. Schindler, U. Fleischer, *NMR, Basic Principles and Progress*, Springer-Verlag, Berlin, New York, **1990**; Vol. 23.

[20] A. Altomore, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Molinerni, G. Polidori, R. Spagna, *J. Appl. Crystalogr.* **1999**, *32*, 115−119.

[21] G. M. Sheldrick, *SHELX97*, *Program for Crystal Structure Refinement* from Diffraction Data, University of Göttingen, Germany, **1997**.

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