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Journal of Organometallic Chemistry 690 (2005) 2790–2795
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

# The synthesis of functional derivatives of the $[1\text{-}CB_9H_{10}]^-$ anion by Brellochs reaction ☆

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Received 12 October 2004; accepted 14 January 2005
Available online 14 March 2005

**Abstract**

Reactions of decaborane with various aldehydes in alkaline media were studied. The reactions with HCOH and 2-$MeOC_6H_4$-CHO give the corresponding *arachno*-carboranes [6-R-*arachno*-$CB_9H_{13}]^-$ (R = H, $C_6H_4$-2-OMe), whereas the reactions with $C_6H_5CHO$, 4-$BrC_6H_4CHO$, 4-$MeCONHC_6H_4CHO$, and 2-$SC_4H_3CHO$ result in the *nido*-carboranes [6-R-*nido*-$CB_9H_{11}]^-$ (R = $C_6H_5$, $C_6H_4$-4-Br, $C_6H_4$-4-NHCOMe, 2-$SC_4H_3$). Both the *arachno*- and *nido*-carboranes can be easily oxidized with elemental iodine in an alkaline aqueous solution giving the corresponding *closo*-derivatives [2-R-*closo*-2-$CB_9H_9]^-$. These *closo*-2-isomers, under heating in solution, undergo rearrangement to more thermodynamically favorable *closo*-1-isomers [1-R-*closo*-1-$CB_9H_9]^-$. The structure of $(Bu_4N)$[1-(4-$BrC_6H_4$)-1-$CB_9H_9$] was determined using single crystal X-ray diffraction.


*Keywords:* 1-carba-*closo*-decaborate; Derivatives; Synthesis; X-ray structure

## 1. Introduction

The 1-carba-*closo*-decaborate anion [*closo*-1-$CB_9H_{10}]^-$ has been considered as a potential boron moiety for boron neutron capture therapy (BNCT) for cancer [2]. From the BNCT point of view, this boron cluster has two evident advantages over more commonly used and widely investigated compounds, based on dicarba-*closo*-dodecaboranes $C_2B_{10}H_{12}$ [3,4] and dodecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ [5]. The first advantage is that the numerous methods of functionalisation via the carbon atom that were developed for dicarboranes will be possible to apply to the $[1\text{-}CB_9H_{10}]^-$ anion. This open the way to the synthesis of various functional derivatives that might be able to accumulate selectively in tumor cells, which is one of the important requirements in BNCT. The second advantage is good solubility of the $[1\text{-}CB_9H_{10}]^-$ anion in water as the sodium salt [6]; this aspect is very important for the delivery of the BNCT agents to the tumor.

Despite these advantages, no attempt has been taken to use the [*closo*-1-$CB_9H_{10}]^-$ anion in the BNCT-related projects because a high-yield preparative method for its synthesis has not been found until recently. The synthesis of this anion was first reported by Knoth [7] as a product of the thermal disproportionation of the [*nido*-$CB_{10}H_{13}]^-$ anion (together with [*closo*-1-$CB_{11}H_{12}]^-$ as the second product), and it can also be obtained in low yield from the reductive deamination of [6-$Me_3N$-*nido*-$CB_9H_{11}$] with sodium metal [7]. Much later, a more convenient synthesis based on the reaction of [6-$Me_3N$-*nido*-

☆ Preliminary results of this study were reported at XI International Meeting on Boron Chemistry (IMEBORON-XI) in Moscow, 2002 [1].

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doi:10.1016/j.jorganchem.2005.01.052

$CB_9H_{11}$] with piperidine was proposed [8]. More recently, two new methods based on the deamination of [1-$Me_3N$-*closo*-1-$CB_9H_9$] [9] and [1-$H_3N$-*closo*-1-$CB_9H_9$] [10] were proposed. These findings have made the 1-carba-*closo*-decaborate anion more available and by now a number of its halogen derivatives were prepared [10–12].

However, all of these methods suffer from some experimental drawbacks, the principal of which is the necessity of using multi-step synthetic procedures which markedly decrease the yield of the desired product from the very expensive $^{10}B$-enriched decaborane $^{10}B_{10}H_{14}$. The solution of this problem was given by Brellochs [13] who reported an elegant route for the preparation of the ten-vertex monocarboranes [1-R-*closo*-1-$CB_9H_9$]$^-$ (R = H, Me, Ph). According to Brellochs, the reaction of decaborane with aldehydes in alkaline solution results in [6-R-*arachno*-6-$CB_9H_{13}$]$^-$, which can be easily oxidized to [2-R-*closo*-2-$CB_9H_9$]$^-$ that under heating undergoes rearrangement into the more stable [1-R-*closo*-1-$CB_9H_9$]$^-$ isomer.

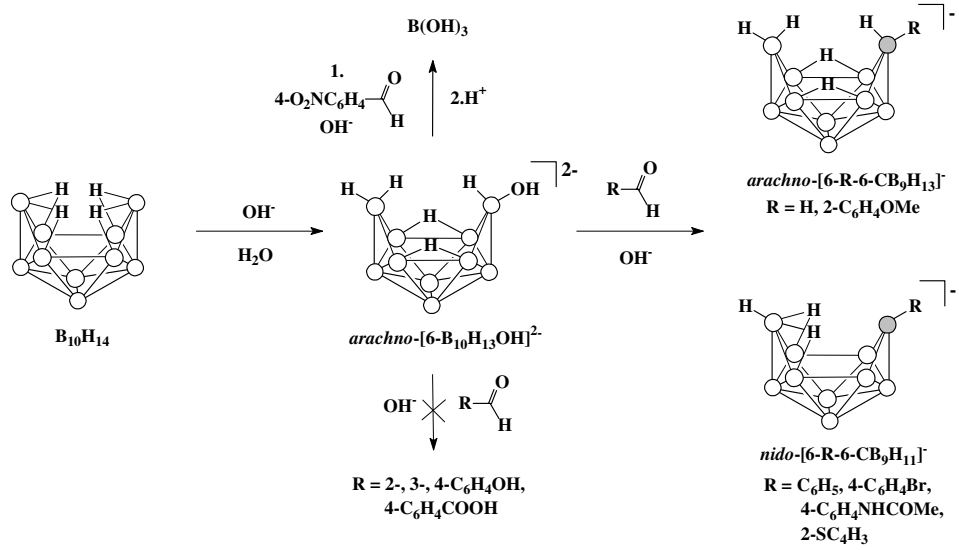
In our ongoing search for functional derivatives of the 1-carba-*closo*-decaborate anion applicable for synthesis BNCT agents, we have studied the Brellochs reaction with various functional aromatic and heteroaromatic aldehydes. Some results of this study are reported in the present paper.

## 2. Results and discussion

The Brellochs reaction is especially attractive for the synthesis of functional derivatives of the [1-$CB_9H_{10}$]$^-$ anion because of the commercial availability of aldehydes containing various functionalities. Here, we have studied reactions of decaborane with various functional aldehydes under the Brellochs reaction conditions. Unfortunately, the Brellochs original preliminary notice [13] contains no experimental details. However, during the initial phases of our study, two very useful communications concerning the first stage of the Brellochs reaction appeared [14,15]. More recently, the excellent review [16] and several papers [17–19], concerning the synthesis of various arylderivatives of the 1-carba-*closo*-decaborate anion were published. Unfortunately, most of these papers provide virtually no information regarding the experiment details.

To prepare functional derivatives of the 1-carba-*closo*-decaborate anion we studied reactions of decaborane with a series of various aldehydes, namely RC(O)H (R = H, $C_6H_5$, $C_6H_4$-4-COOH, $C_6H_4$-2-OH, $C_6H_4$-3-OH, $C_6H_4$-4-OH, $C_6H_4$-4-$NO_2$, $C_6H_4$-2-OMe, $C_6H_4$-4-NHCOMe, $C_6H_4$-4-Br, 2-$SC_4H_3$). It was found that reactions of decaborane with different aldehydes proceed in somewhat varied ways (Scheme 1). As reported initially by Brellochs [13] and verified later [14,19], the reaction with formaldehyde results in [*arachno*-6-$CB_9H_{14}$]$^-$. The reaction of decaborane with benzaldehyde gives [6-Ph-*nido*-6-$CB_9H_{11}$]$^-$ [15,17] rather than the *arachno* product [13]. No carborane products were obtained with aldehydes containing acidic functions, such as 2-, 3-, and 4-hydroxybenzaldehydes and 4-carboxybenzaldehyde.

The reaction with 2-methoxybenzaldehyde results in the *arachno* product [6-(2-$MeOC_6H_4$)-*arachno*-6-$CB_9H_{13}$]$^-$. The formation of the *arachno* product is unique in the series of arylaldehydes investigated. The reason for this exception is not clear, but one possible explanation is the stabilization of the *arachno* form via formation of an intramolecular hydrogen bond between the oxygen atom and the *endo*-hydrogen atom at position C(6) (five-member




Scheme 1.

cycle), or the terminal hydrogen atoms at positions B(5) and B(7) of the carborane cage (six-member cycle). The $^{1}$H NMR spectrum of [6-(2-$MeOC_6H_4$)-*arachno*-6-$CB_9H_{13}]^-$ in methanol-$d_4$ contains two sets of signals from the 2-methoxyphenyl substituent, which may correspond to existence of a mixture of hydrogen-bonded and non-bonded forms or (less probably) a mixture of two different hydrogen-bonded forms. The $^{11}$B NMR spectrum of [6-(2-$MeOC_6H_4$)-*arachno*-6-$CB_9H_{13}]^-$ demonstrates only the set of signals corresponding to the *arachno* structure. Unfortunately our attempts to grow crystals of this compound appropriate for X-ray study were unsuccessful.

In the case of 4-nitrobenzaldehyde, the reaction results in the complete destruction of the boron cage, giving boric acid after acidification of the reaction mixture. The reactions with 4-bromobenzaldehyde, 4-acetamidobenzaldehyde and 2-thiophenecarboxaldehyde, as in the case of unsubstituted benzaldehyde, gave the corresponding *nido* derivatives [6-R-*nido*-6-$CB_9H_{11}]^-$.

Both the *arachno*- and the *nido*-derivatives can be easily oxidized with elemental iodine in an alkaline aqueous solution to give the corresponding *closo*-derivatives [2-R-*closo*-2-$CB_9H_9]^-$. These *closo*-2-isomers, under heating in solution, undergo rearrangement to more thermodynamically favorable *closo*-1-isomers [1-R-*closo*-1-$CB_9H_9]^-$ (Scheme 2).

In the case of the acetamido derivative [2-(4-$MeCONHC_6H_4$)-*closo*-2-$CB_9H_9]^-$, the isomerization is accompanied by hydrolysis giving amine [1-(4-$H_2NC_6H_4$)-*closo*-1-$CB_9H_9]^-$ as a product. The synthesis of the last derivative as well as its further derivatization has been described recently in the literature [18] based on our outlined procedure [1a].

The crystal structure of $(Bu_4N)$[1-(4-$BrC_6H_4$)-1-$CB_9H_9$] was determined by method of single crystal X-ray diffraction. The molecular structure of the [1-(4-$BrC_6H_4$)-1-$CB_9H_9]^-$ anion is presented in Fig. 1 and the selected structural parameters are presented in Table 1.

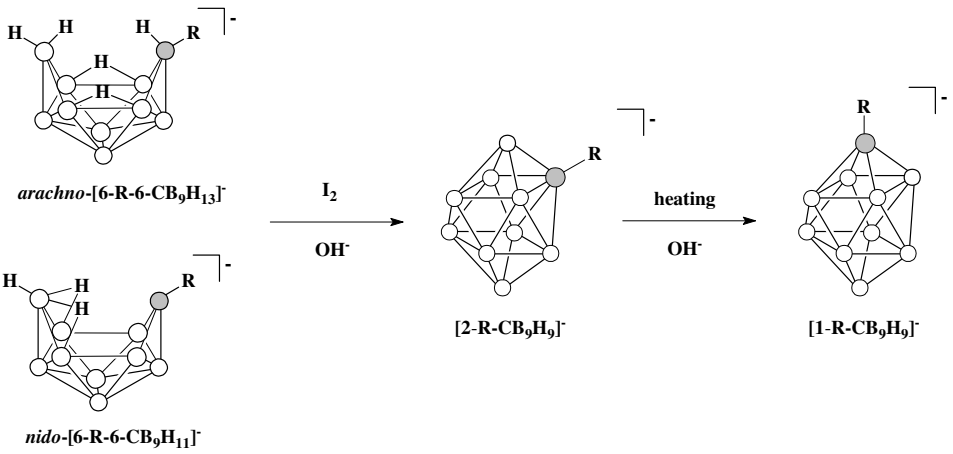
All the steps of the described synthetic pathway proceed with reasonably high yields opening a convenient route for the synthesis of functional derivatives of the [*closo*-1-$CB_9H_{10}]^-$ anion, which can be used for the development of BNCT agents, the construction of new materials.

## 3. Experimental

$^{1}$H, $^{13}$C, and $^{11}$B NMR spectra were collected using Varian Unity 400 and Bruker AMX 400 spectrometers. Chemical shifts were referenced to $SiMe_4$ = 0.00 ppm for $^{1}$H and $^{13}$C and to $Et_2O \cdot BF_3$ = 0.0 ppm for $^{11}$B. Elemental analyses were performed in the Laboratory of Microanalysis of the Institute of Organoelement Compounds (Moscow).

### 3.1. Synthesis of Cs[6-(2-$CH_3OC_6H_4$)-*arachno*-6-$CB_9H_{13}$]

1.22 g (10.0 mmol) decaborane(14) was dissolved in 60 ml of 10% aqueous solution of sodium hydroxide at 0 °C. 4.08 g (30.0 mmol) 2-methoxybenzaldehyde followed by 50 ml of ethanol were added and stirred for 3 h. EtOH was removed in vacuo and the residue was extracted three times with $Et_2O$ (3 × 50 ml). The organic layer was concentrated to 20 ml in vacuo at room temperature and treated with solution of 3.0 g (20.0 mmol) CsF in 5 ml of methanol. The precipitate formed was filtered, washed with 20 ml of $Et_2O$ and dried over $P_2O_5$, giving 1.92 g (53%) of the product. $^{1}$H NMR (methanol-$d_4$ ppm): minor isomer −7.33 (1H, dd), 7.23 (1H, dt), 6.93 (1H, d), 6.92 (1H, t) 3.82 (3H, s); major isomer −7.06 (1H, dd), 6.99 (1H, dt), 6.74 (1H, d), 6.73 (1H, t),




Scheme 2.

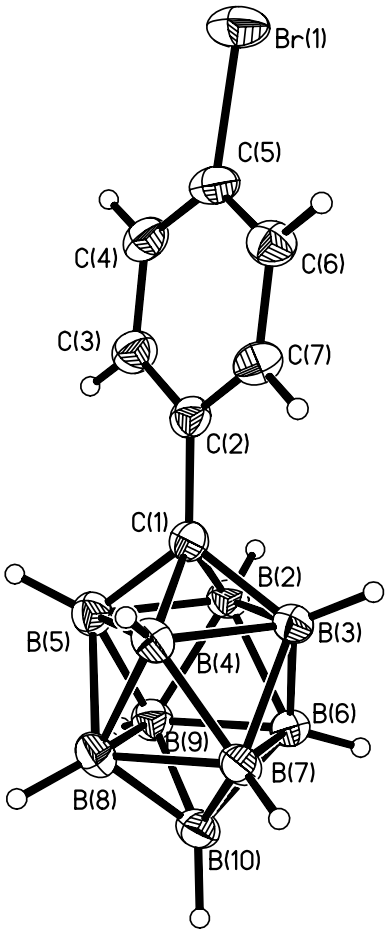



Fig. 1. Molecular structure of the $[1\text{-}(4\text{-}BrC_6H_4)\text{-}1\text{-}CB_9H_9]^-$ anion.

Table 1
Bond lengths (Å) for the $[1\text{-}(4\text{-}BrC_6H_4)\text{-}1\text{-}CB_9H_9]^-$ anion

| | | | |
|---|---|---|---|
| C(1)–B(2) | 1.612(3) | B(6)–B(7) | 1.833(4) |
| C(1)–B(3) | 1.607(3) | B(6)–B(9) | 1.826(3) |
| C(1)–B(4) | 1.605(3) | B(7)–B(8) | 1.837(3) |
| C(1)–B(5) | 1.600(3) | B(8)–B(9) | 1.832(3) |
| B(2)–B(3) | 1.824(4) | B(6)–B(10) | 1.683(3) |
| B(2)–B(5) | 1.838(4) | B(7)–B(10) | 1.697(4) |
| B(3)–B(4) | 1.833(3) | B(8)–B(10) | 1.703(4) |
| B(4)–B(5) | 1.841(4) | B(9)–B(10) | 1.691(3) |
| B(2)–B(6) | 1.797(3) | C(1)–C(2) | 1.494(3) |
| B(2)–B(9) | 1.802(3) | C(2)–C(3) | 1.393(3) |
| B(3)–B(6) | 1.796(3) | C(2)–C(7) | 1.383(3) |
| B(3)–B(7) | 1.818(3) | C(3)–C(4) | 1.388(3) |
| B(4)–B(7) | 1.809(3) | C(6)–C(7) | 1.394(3) |
| B(4)–B(8) | 1.819(3) | C(4)–C(5) | 1.389(3) |
| B(5)–B(8) | 1.804(3) | C(5)–C(6) | 1.372(3) |
| B(5)–B(9) | 1.818(4) | C(5)–Br | 1.908(2) |

3.78 (3H, s); 4.61 (1H, s), −0.24 (1H, s). $^{13}C$ NMR (methanol-$d_4$ ppm): 158.3, 134.6, 130.6, 129.6, 129.0, 128.9, 126.4, 121.4. 121.1, 111.2, 110.5, 62.2, 56.1, 55.7. $^{11}B$ NMR (methanol-$d_4$ ppm): −1.8 (1B, d, $J$ = 125 Hz), −9.0 (3B, d, $J$ = 143 Hz), −23.5 (1B, t, $J$ = 107 Hz), −28.5 (2B, d, $J$ = 125 Hz), −39.2 (2B, d, $J$ = 140 Hz). Anal. Calc. for $C_8H_{20}B_9CsO$: C, 26.51; H, 5.56; B, 26.84. Found: C, 26.32; H, 5.67; B, 27.02%.

### 3.2. Synthesis of $(Me_4N)[6\text{-}(4\text{-}CH_3CONHC_6H_4)\text{-}nido\text{-}6\text{-}CB_9H_{11}]$

0.61 g (5.0 mmol) decaborane(14) was dissolved in 30 ml of 10% aqueous solution of sodium hydroxide at 0 °C. 2.40 g (15.0 mmol) 4-acetylamidobenzaldehyde followed by 40 ml of ethanol were added and stirred for 4 h. The EtOH was removed in vacuo and the residue was extracted three times with $Et_2O$ (3 × 50 ml). The organic phase was concentrated almost to dryness in vacuo at room temperature, diluted with 5 ml of water and treated with solution of 1.5 g (10.0 mmol) $Me_4NBr$ in 5 ml of water. The precipitate formed was filtered, washed with cold water (2 × 10 ml) and diethyl ether (20 ml), and dried over $P_2O_5$, giving 1.05 g (64%) of the product. $^1H$ NMR (methanol-$d_4$ ppm): 7.29 (2H, d, $J$ = 8.6 Hz), 7.24 (2H, d, $J$ = 8.6 Hz), 3.11 (12H, s, $Me_4N^+$), 2.1 (3H, s), −3.42 (2H, br s). $^{13}C$ NMR (methanol-$d_4$ ppm): 171.3, 148.9, 136.0, 129.0, 120.6, 55.9 ($Me_4N^+$), 23.7. $^{11}B$ NMR (methanol-$d_4$ ppm): 1.1 (2B, d, $J$ = 134 Hz), −2.3 (1B, d, $J$ = 131 Hz), −4.9 (2B, d, $J$ = 128 Hz), −12.2 (2B, d, $J$ = 146 Hz), −25.9 (1B, d, $J$ = 146 Hz), −38.1 (1B, d, $J$ = 140 Hz). Anal. Calc. for $C_{13}H_{31}B_9N_2O$: C, 47.50; H, 9.51; N, 8.52; B, 29.60. Found: C, 47.13; H, 9.68; N, 8.79; B, 29.56%.

### 3.3. Synthesis of $(Et_4N)[1\text{-}(4\text{-}NH_2C_6H_4)\text{-}closo\text{-}1\text{-}CB_9H_9]$

1.22 g (10.0 mmol) decaborane(14) was dissolved in 60 ml of 10% aqueous solution of sodium hydroxide at 0 °C. 4.80 g (29.5 mmol) 4-acetylamidobenzaldehyde followed by 70 ml of ethanol were added and stirred for 4 h. The EtOH was removed in vacuo and the residue was extracted three times with $Et_2O$ (3 × 50 ml). The diethyl ether was pumped off, the residue was dissolved in a solution of 2.4 g sodium hydroxide in 50 ml of water and treated dropwise at room temperature with solution of 5.08 g (20.0 mmol) iodine in 150 ml of methanol and stirred for additional 1 h. To the obtained solution of $[2\text{-}(4\text{-}MeCONHC_6H_4)\text{-}closo\text{-}2\text{-}CB_9H_9]$ ($^{11}B$ NMR (acetone-$d_6$ ppm): 2.4 (1B, d, $J$ = 155 Hz,), −2.1 (1B, d, $J$ = 164 Hz), −20.3 (1B, d, $J$ = 140 Hz), −24.8 (2B, d, $J$ = 152 Hz), −27.5 (4B, d, $J$ = 136 Hz)) 10 g sodium hydroxide was added and heated under reflux for 20 h under N2 atmosphere. The solution was cooled to room temperature and neutralized by the addition of 1 M hydrochloric acid. The reaction mixture was evaporated to dryness, the residue was dissolved in 100 ml of water and treated with solution of 3.30 g (20.0 mmol) $Et_4NCl$ in 10 ml of water. The precipitate formed was filtered, washed with cold water (2 × 10 ml) and diethyl ether (50 ml), and dried

in vacuo, giving 2.65 g (78%) of the product. $^1$H NMR (acetone-$d_6$ ppm): 7.81 (2H, d, $J$ = 8.5 Hz), 7.63 (2H, d, $J$ = 8.5 Hz), 4.62 (2H, s), 3.44 (8H, q, $Et_4N^+$), 1.36 (12H, t, $Et_4N^+$). $^{11}$B NMR (acetonel-$d_6$ ppm): 30.2 (1B, d, $J$ = 150 Hz), −14.9 (4B, d, $J$ = 150 Hz), −23.0 (4B, d, $J$ = 138 Hz).

### 3.4. Synthesis of $(Bu_4N)[2\text{-}(4\text{-}BrC_6H_4)\text{-}closo\text{-}2\text{-}CB_9H_9]$

0.61 g (5.0 mmol) decaborane(14) was dissolved in 30 ml of 10% aqueous solution of sodium hydroxide at 0 °C. 2.80 g (15.0 mmol) 4-bromobenzaldehyde followed by 20 ml of ethanol were added and stirred for 3 h. The EtOH was removed in vacuo and the residue was extracted three times with $Et_2O$ (3 × 50 ml). The diethyl ether was pumped off, the residue containing Na[6-(4-$BrC_6H_4$)-*nido*-6-$CB_9H_{11}$] ($^{11}$B NMR (methanol-$d_4$ ppm): −0.3 (2B, d, $J$ = 133 Hz,), −3.5 (1B, d, $J$ = 159 Hz), −6.5 (2B, d, $J$ = 133 Hz), −14.0 (2B, d, $J$ = 137 Hz), −28.1 (1B, d, $J$ = 148 Hz), −39.7 (1B, d, $J$ = 144 Hz)) was dissolved in a solution of 1.2 g sodium hydroxide in 25 ml of water and treated dropwise at room temperature with solution of 2.54 g (10.0 mmol) iodine in 75 ml of methanol. The reaction mixture was stirred overnight, concentrated in vacuo and treated with solution of 8.05 g (25.0 mmol) $Bu_4NBr$ in 20 ml of water. The precipitate formed was filtered, washed with water and recrystallized from methanol, giving 2.17 g (84%) of the product.$^1$H NMR (acetone-$d_6$ ppm): 7.15 (2H, d, $J$ = 8.6 Hz), 6.81 (2H, d, $J$ = 8.6 Hz), 3.45 (8H, m, $Bu_4N^+$), 1.83 (8H, m, $Bu_4N^+$), 1.44 (8H, m, $Bu_4N^+$), 0.98 (12H, t, $Bu_4N^+$). $^{11}$B NMR (acetone-$d_6$ ppm): 2.1 (1B, d, $J$ = 153 Hz), −2.8 (1B, d, $J$ = 168 Hz), −20.8 (1B, d, $J$ = 143 Hz), −25.6 (2B, d, $J$ = 153 Hz), −28.2 (2B, d, $J$ = 125 Hz), −29.0 (2B, d, $J$ = 128 Hz).

### 3.5. Synthesis of $(Bu_4N)[1\text{-}(4\text{-}BrC_6H_4)\text{-}closo\text{-}1\text{-}CB_9H_9]$

1.55 g (3.0 mmol) $(Bu_4N)$[2-(4-$BrC_6H_4$)-*closo*-2-$CB_9H_9$] in 200 ml of ethanol was heated under reflux for 16 h. The reaction mixture was cooled to room temperature and concentrated to dryness in vacuo, giving 1.48 g (95%) of the product. $^1$H NMR (dmso-$d_6$ ppm): 7.73 (2H, d, $J$ = 8.2 Hz), 7.56 (2H, d, $J$ = 8.2 Hz), 3.15 (8H, m, $Bu_4N^+$), 1.54 (8H, m, $Bu_4N^+$), 1.30 (8H, m, $Bu_4N^+$), 0.93 (12H, t, $Bu_4N^+$). $^{11}$B NMR (dmso-$d_6$ ppm): 30.1 (1B, d, $J$ = 140 Hz), −14.5 (4B, d, $J$ = 148 Hz), −22.6 (4B, d, $J$ = 140 Hz). Anal. Calc. for $C_{23}H_{49}B_9BrN$: C, 53.45; H, 9.56; N, 2.71; B, 18.82. Found: C, 53.18; H, 9.78; N, 3.01; B, 19.02%.

### 3.6. Synthesis of $(Et_3NH)[1\text{-}(2\text{-}C_4H_3S)\text{-}closo\text{-}1\text{-}CB_9H_9]$

1.22 g (10.0 mmol) decaborane(14) was dissolved in 60 ml of 10% aqueous solution of sodium hydroxide at 0 °C. 2.8 ml (3.36 g, 30.0 mmol) 2-thiophene carboxaldehyde followed by 60 ml of ethanol were added and stirred for 5 h. The EtOH was removed in vacuo and the residue was extracted three times with $Et_2O$ (3 × 50 ml). The diethyl ether was pumped off, the residue containing Na[6-(2-$C_4H_3S$)-*nido*-6-$CB_9H_{11}$] ($^{11}$B NMR ($D_2O$, ppm): 1.6 (2B, d, $J$ = 135 Hz), −0.8 (1B, d, $J$ = 146 Hz), −4.2 (2B, d, $J$ = 137 Hz), −10.8 (2B, d, $J$ = 137 Hz), −22.9 (1B, d, $J$ = 148 Hz), −36.8 (1B, d, $J$ = 144 Hz)) was dissolved in solution of 2.4 g sodium hydroxide in 50 ml of water and treated dropwise at room temperature with solution of 5.08 g (20.0 mmol) iodine in 150 ml of methanol. The reaction mixture was stirred overnight and concentrated in vacuo to 50 ml. The solution containing Na[2-(2-$C_4H_3S$)-*closo*-2-$CB_9H_9$] ($^{11}$B NMR ($D_2O$, ppm): −0.8 (1B, d), −3.2 (1B, d), −21.6 (1B, d), −25.8 (4B, d), −28.4 (2B, d)) was heated under reflux for 24 h, cooled to room temperature, neutralized with 1 M HCl, concentrated to 15 ml and treated with solution of 2.10 g (15.0 mmol) of $[Et_3NH]Cl$ in 10 ml of water. The precipitate formed was filtered, washed with $Et_2O$ and dried in vacuo, giving 2.15 g (76%) of the product. $^1$H NMR (acetone-$d_6$ ppm): 7.38 (1H, dd, $J$ = 3.6, 1.2 Hz), 7.21 (1H, dd, $J$ = 5.2, 1.2 Hz), 7.00 (1H, dd, $J$ = 5.2, 3.6 Hz), 3.37 (6H, q, $J$ = 7.2 Hz, $Et_3NH^+$), 1.38 (9H, t, $J$ = 7.2 Hz, $Et_3NH^+$). $^{13}$C NMR (acetone-$d_6$ ppm): 148.6, 127.0, 125.9, 123.0, 47.7 ($Et_3NH^+$), 9.2 ($Et_3NH^+$). $^{11}$B NMR (acetone-$d_6$ ppm): 30.5 (1B, d, $J$ = 146 Hz), −14.8 (4B, d, $J$ = 150 Hz), −24.0 (4B, d, $J$ = 140 Hz). Anal. Calc. for $C_{11}H_{27}B_9NS$: C, 43.65; H, 8.99; N, 4.63; B, 32.14. Found: C, 43.37; H, 9.08; N, 4.99; B, 31.86%.

### 3.7. Crystal structure determination of $(Bu_4N)$-$[1\text{-}(4\text{-}BrC_6H_4)\text{-}1\text{-}CB_9H_9]$

Crystal data: $(Bu_4N)[1\text{-}(4\text{-}BrC_6H_4)\text{-}1\text{-}CB_9H_9]$, $C_{23}H_{49}B_9BrN$ ($M$ = 516.83), monoclinic, space group $P2_1/c$ (No. 14), $a$ = 15.400(2), $b$ = 10.912(1), $c$ = 19.047(2) Å, $\beta$ = 110.086(3)°, $V$ = 3006.0(6) Å$^3$, $Z$ = 4, $d_{calc}$ = 1.142 g cm$^{-3}$, $\mu$ = 1.380 mm$^{-1}$, $F(000)$ = 1096, crystal colourless size 0.30 × 0.45 × 0.55 mm.

Single-crystal X-ray diffraction experiment was carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å, $\omega$-scans with a 0.3° step in $\omega$ and 10 s per frame exposure, $2\theta < 58°$) at 120 K. The low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow $N_2$ gas cryostat. Reflection intensities were integrated using SAINT software [20] and semi-empirical method SADABS [21]. A total of 47,870 reflections were measured, 7881 ($R_{int}$ = 0.0503) independent reflections were used in further calculations and refinement. The structures were solved by direct method and refined by the full-matrix least-squares method against $F^2$ in anisotropic for

nonhydrogen atoms approximation. The hydrogen atoms of the carbadodecaborate anion were located from the difference Fourier syntheses and refined in isotropic approximation. The positions of hydrogen atoms for phenyl ring and the $Bu_4N^+$ cation were calculated from the geometrical point of view and were included in the final refinement using a rigid motion model. The final refinements were converged to $R_1 = 0.0443$ (from 4461 unique reflections with $I > 2\sigma$ s($I$)) and $wR_2 = 0.0943$ (from all 7881 unique reflections); the number of the refined parameters is 343. All calculations were performed on an IBM PC/AT using the SHELXTL software [22].

## 4. Supplementary material

Crystallographic data for $(Bu_4N)[1\text{-}(4\text{-}BrC_6H_4)\text{-}1\text{-}CB_9H_9]$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC-252434. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam. ac.uk).

## Acknowledgments

This work was supported in parts by the Carl Trygger Foundation for Scientific Research, the Swedish Cancer Foundation, Russian Foundation for Basic Research (05-03-32429, 03-03-32214), and Division of Chemistry and Material Science of Russian Academy of Sciences (05-07). I.B.S. gratefully acknowledges Russian Foundation for Basic Research for the EUROBORON-3 travel Grant (04-03-427973).

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