IMPROVED SYNTHESIS OF [*closo*-1-CB_9H_{10}]$^-$ ANION AND NEW C-SUBSTITUTED DERIVATIVES

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Dedicated to Professor Jaromír Plešek on the occasion of his 80th birthday in recognition of his major contributions to cluster borane chemistry.

The Brellochs method was utilized to gain access to the [*closo*-1-CB_9H_{10}]$^-$ anion (**1**). Previous work describing the details of the synthesis of **1** via the [*closo*-2-CB_9H_{10}]$^-$ anion (**2**) was brief and insufficient. Therefore, we report an optimized procedure for the synthesis of **1**, the preparation of the unknown C-halogenated series using *N*-halosuccinimides and bis(benzenesulfonyl)fluoroamine, and the unknown C-methylated product using CH_3I. NMR properties and regularities within the series were also investigated.

Keywords: Boranes; Carboranes; Monocarbaborane anions; Weakly coordinating and low nucleophilic anions; Brellochs reaction; Halogenations; Methylations.

Monocarbaborane anion [CB_9H_{10}]$^-$ (**1**)[1] belongs to the group of anions of general formula [CB_nH_{n+1}]$^-$, where the anionic charge is highly delocalized. These anions possess chemical, electrochemical and thermal stability; thus, they are useful in weakly coordinating and low- nucleophilic anion chemistry as were described by Reed and Strauss[2]. Out of this group, the [*closo*-1-$CB_{11}H_{12}$]$^-$ anion is the most studied[3] because of its easy accessibility. However, new synthetic breakthroughs produced monocarbaboranes via Brellochs reactions[4–6] of aldehydes with *nido*-$B_{10}H_{14}$, starting an accelerated expansion in sub-icosahedral monocarbaborane chemistry and revealing compounds with highly desirable characteristics.

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Suitably-substituted anions of this class are among the most stable compounds even to the most aggressive reagents. They are also highly lipophilic and can be extremely difficult to oxidize. This combination of properties makes these anions useful in applications as diverse as counterions for reactive cationic organometallic catalysts[7], electrolytes for non-aqueous solvents and electrical batteries[8], and solubilizers of cations in organics solvents[8].

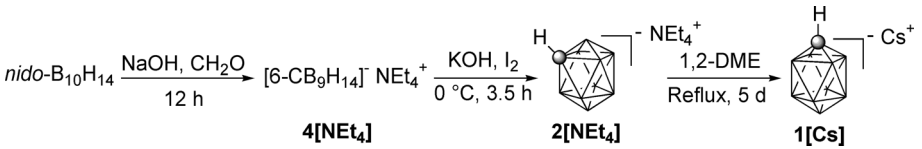
The Brellochs method[4–6] was utilized to gain access to [*closo*-1-CB_9H_{10}]$^-$ anion (**1**). Synthetic details previously described in the literature[4], acquired through the [*closo*-2-CB_9H_{10}]$^-$ anion (**2**), were brief and insufficient. Therefore, we report an optimized procedure for the synthesis of parent derivative **1**, the preparation of the unknown C-halogenated series, and the unknown C-methylated product. C-Halogenated derivatives, in particular [*closo*-1-CB_9H_9-1-I]$^-$ anion (**3a**) and [*closo*-1-CB_9H_9-1-Br]$^-$ anion (**3b**) may be suitable as building blocks for the production of molecular rod-type structures via various transition-metal coupling reactions. We also comment on NMR properties and regularities within the series.

RESULTS AND DISCUSSION

Synthesis

Optimization of the Brellochs Method

Starting from *nido*-$B_{10}H_{14}$, decaborane, parent derivative [*closo*-1-CB_9H_{10}]$^-$Cs$^+$ (**1**[Cs]) was prepared in three steps in 29% overall yield (Scheme 1).



SCHEME 1
Preparation of parent derivative [*closo*-1-CB_9H_{10}]$^-$Cs$^+$ (**1**[Cs])

[*arachno*-6-CB_9H_{14}]$^-$(NEt_4)$^+$ (**4**[NEt_4]) was prepared via literature precedence without any modifications[10]. The oxidation following the previously published synthesis[9] gave only half conversion to [*closo*-2-CB_9H_{10}]$^-$ anion (**2**) (along with an unknown impurity showing a ^{11}B NMR signal at 2 ppm). Performing the oxidation with 3.3 equivalents of I_2 at room temperature

gave anion **2** in only 30% yield. An impurity in the crude reaction mixture (appearing as a singlet at 0.7 ppm in the ^{1}H coupled ^{11}B NMR measured in D_2O) was observed, suggesting hydrolysis of the cluster. Minute formation of the thermodynamically stable [*closo*-1-CB_9H_{10}]$^-$ anion (**1**) was also observed.

Optimization was achieved by conducting the oxidation at 0 °C. This suggests that the formation of the hydrolysis product at 0.7 ppm is temperature-sensitive. Precipitation with (NEt_4^+)Br^- gave highly pure [*closo*-2-CB_9H_{10}]$^-$(NEt_4)$^+$ (**2**[NEt_4]) in >75% yield without formation of parent derivative **1**[NEt_4], and impurity at 0.7 ppm was no longer present in ^{11}B NMR.

Thermolysis of **2**[NEt_4] was achieved by refluxing in 1,2-dimethoxyethane (DME)[9]. Rearrangement was expected to be complete in 18 h; however, it was observed that the transformation was complete in 120 h. Rearrangement in refluxing CH_3CN was complete within the same time frame. This is in contrast to the [*closo*-2-CB_9H_9-2-COOH]$^-$ anion[11], where the isomerization is complete within 24 h. The difference in the energetics of the double-diamond-square-diamond (DDSD) mechanism[12] between the two systems may be explained by the electron-withdrawing ability of the carboxyl group, which reduces the electron density at the hypervalent carbon atom in the *closo*-1-CB_9 framework.

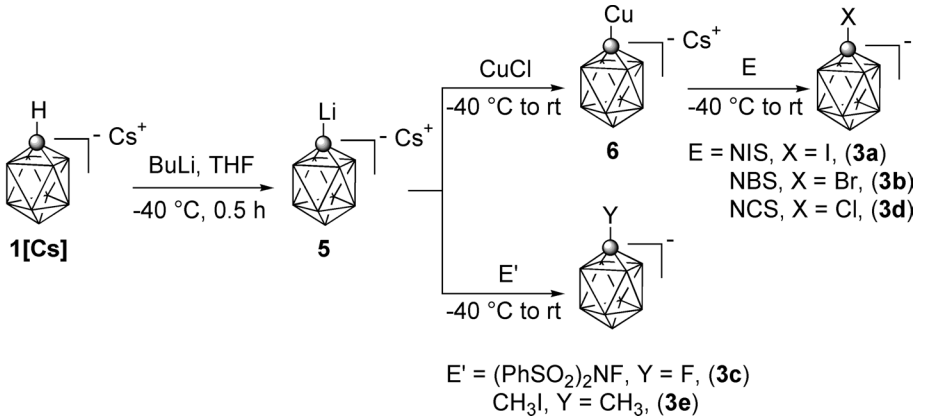
Parent derivative [*closo*-1-CB_9H_{10}]$^-$$Cs^+$ (**1**[Cs]) was soluble in larger volumes of H_2O. The Cs^+ counterion was desired to avoid complications with deprotonation during the halogenation and methylation steps. Evaporation of excess H_2O provided pure parent derivative **1**[Cs] in 74% yield.

Transformations at the Carbon Atom

Lithiation of parent derivative **1**[Cs] afforded reactive intermediate **5** (Scheme 2). Subsequently, bis(benzenesulfonyl)fluoroamine, *N*-chlorosuccimide (NCS), *N*-bromosuccimide (NBS), *N*-iodosuccimide (NIS), and iodomethane (CH_3I) were utilized as appropriate electrophilic reagents. CuCl was used to provide a more stable intermediate **6**. Reactions employing CuCl were attempted with NCS, NBS, and NIS. This methodology was employed in the synthesis of the C-halogenated series for [*closo*-1-$CB_{11}H_{12}$]$^-$ [13].

In the absence of CuCl, the halogenation reactions were clean affording only parent derivative **1** and C-substituted derivatives **3a**–**3e** with minimal formation of side-products (<10% of crude reaction mixture by ^{11}B NMR analysis). Fluorination under ambient temperature provided parent deriva-

tive **1** and fluorinated derivative **3c** in a 2:1 ratio. Chlorination proceeded slowly at room temperature. At reflux, the reaction gave parent derivative **1** and chlorinated derivative **3d** in a 1:1 ratio while iodination and bromination produced a 2:1 ratio of parent derivative **1** and halogenated derivative (iodinated derivative **3a** and brominated derivative **3b**, respectively) under the same conditions. Extended reaction times and additional portions of *n*-BuLi and the respective halogenating agent did not change the reaction course. Methylation provided parent derivative **1** and methyl derivative **3e** in the 3:7 ratio at ambient temperature. It is necessary to say that the [*closo*-1-CB_9H_9-1-CH_3]$^-$ anion (**3e**) was mentioned for the first time and probably prepared in 20% yield by the Brellochs reaction using acetaldehyde for insertion of the carbon atom into decaborane skeleton[14]. Furthermore, in Kennedy's article[14] the methyl derivative **3e** was characterized only by R_F.



SCHEME 2
C-Halogenated and C-methylated synthetic map

Reactions employing CuCl furnished improved starting-material-to-product ratios of 1:1, 1:1 and 3:5 for chlorination, bromination and iodination, respectively, with minimal side products (Table I). Employing CuCl is beneficial because reactive intermediate **6** is more stable than reactive intermediate **5**. This general improvement of the C-substitution reactions was also observed for the [*closo*-1-$CB_{11}H_{12}$-1-X]$^-$ halogenated series when CuCl was employed[13]. An alternative iodination procedure using I_2 produced a 4:1 ratio of parent derivative **1** and iodinated derivative **3a** by ^{11}B NMR analysis of the crude reaction mixture[15].

Precipitation of C-substituted derivatives **3a**–**3e** with $(HN(Et)_3)Cl$ or $(PhN(CH_3)_3)I$ gave oils that slowly crystallized. Precipitation with $(NEt_4)Br$ or $(NBu_4)Br$ gave C-substituted derivatives as crystalline solids. Moreover, $(NEt_4)Br$ or $(NBu_4)Br$ produced salts which allowed for tedious separation of iodinated derivative **3a**[NEt_4], brominated derivative **3b**[NEt_4], fluorinated derivative **3c**[NBu_4], chlorinated derivative **3d**[NEt_4], and methyl derivative **3e**[NBu_4] on silica gel using CH_2Cl_2 as eluent. Products were characterized by ^{11}B NMR, ^1H NMR, ^{13}C NMR, elemental analysis, and ESI-MS.

TABLE I
C-Halogenation and C-methylation of **1**[Cs]

Reaction conditions[a]	% 1-substitution[b]	% unreacted **1**[b]	Isolated yield[c]
$(PhSO_2)_2NF$	33 (**3c**)	66	23
1. CuCl, 2. NCS	50 (**3d**)	50	35
NCS	50 (**3d**)	50	na[e]
1. CuCl, 2. NBS	50 (**3b**)	50	34
NBS	33 (**3b**)	66	na[e]
1. CuCl, 2. NIS	60 (**3a**)	40	4[d]
NIS	33 (**3a**)	66	na[e]
CH_3I	70 (**3e**)	30	40

[a] Reactions were performed twice to verify reproducibility. [b] Ratios determined by ^{11}B NMR analysis of crude reaction mixture. [c] Yield after column chromatography (CH_2Cl_2, silica gel) and recrystallization ($EtOH/H_2O$). [d] See Experimental for comment. [e] Products were not isolated.

NMR Spectra

The availability of C-substituted [*closo*-1-CB_9H_{10}]$^-$ derivatives (**3a**–**3e**) provides an opportunity to summarize the effect of monohalogenation on the NMR shifts of the cage atoms in the ipso, ortho, meta, and para positions. The para position permits additional examination of Heřmánek's[16] antipodal effect[17–20]. In comparison with the icosahedral clusters ($[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^-$, $C_2B_{10}H_{12}$), there are insufficient data in the ten-vertex series ($[B_{10}H_{10}]^{2-}$, $[CB_9H_{10}]^-$, $C_2B_8H_{10}$), to efficiently study the influence of substituent position and identity throughout both types of clusters. Nevertheless, comparison of NMR shifts of C-halogenated [*closo*-1-CB_9H_{10}]$^-$ derivatives (**3a**–**3d**) with C-halogenated [*closo*-1-$CB_{11}H_{12}$]$^-$ derivatives[8] gives valuable results (Table II).

Table II and Fig. 1 summarize the shift increments (Δδ) in ^{11}B NMR and ^{13}C NMR of the halogenated and methylated derivatives **3a**–**3e** and compares them with the C-halogenated [*closo*-1-$CB_{11}H_{12}$]$^-$ anions. Figure 1 shows chemical shift changes at the ortho, meta, and para positions, as well as their correlation with Pauling's electronegativities[21] of halogens. The slope of these correlation lines (k_o, k_m, and k_p) may reflect the relative sensi-

TABLE II
Shift increments Δδ in ^{11}B NMR and ^{13}C NMR spectra for **3a**–**3e** (in parentheses Δδ for [*closo*-1-$CB_{11}H_{12}$]$^-$ anions[12]); parent refers to hydrogen as the substituent

Substituent	$\Delta\delta = \delta_{subst} - \delta_{parent}$			
	B_{para}	B_{meta}	B_{ortho}	B_{ipso}
F	–12.0 (–9.8)	–3.7 (–0.3)	0.0 (–3.4)	62.4 (61.1)
Cl	–4.0 (–4.9)	–0.7 (3.8)	4.3 (–0.3)	14.7 (18.3)
Br	–2.8 (–3.6)	0.0 (4.2)	5.0 (0.2)	–4.6 (–1.9)
I	–0.0 (–1.3)	0.8 (5.3)	6.0 (1.2)	–47.4 (–44.4)
CH_3	–4.5 (–4.4)	0.0 (3.5)	5.0 (0.3)	13.1 (15.9)

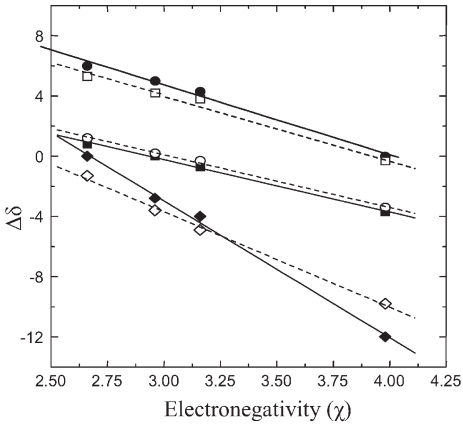


FIG. 1
Correlations between chemical shifts increments (Δδ) and electronegativity of halogen atoms (χ) in different positions. ● ortho position in **3a**–**3d**, ○ ortho position in [*closo*-1-$CB_{11}H_{11}$-1-X]$^-$, ■ meta position in **3a**–**3d**, □ meta position in [*closo*-1-$CB_{11}H_{11}$-1-X]$^-$, ◆ para position in **3a**–**3d**, ◇ para position in [*closo*-1-$CB_{11}H_{11}$-1-X]$^-$

tivities of the skeleton when compared with the halogen-substituted boron and carbon. Figure 2 demonstrates the dependence of ^{13}C NMR shift changes (ipso position) on the halogen electronegativity. Figures 1 and 2 depict a general linear dependence of the chemical shift changes on the electronegativity of the substituent, with the chemical shifts ($\Delta\delta$) for the ipso position becoming more positive as the halogen becomes more electronegative in the series I < Br < Cl < F. As ^{13}C NMR shifts[22] are generally sensitive to substituent effects, it is not surprising to observe large shifts over 100 ppm for ipso-substituted compounds found in both the [*closo*-1-CB_9H_{10}]$^-$ and [*closo*-1-$CB_{11}H_{12}$]$^-$ anion series[13] (see Fig. 2).

The chemical shifts in the more distant positions (ortho, meta, and para) are much smaller. Among them, the higher k_p shows higher sensitivity for the para position, which confirms Heřmánek's antipodal effect[22]. Furthermore, a higher k_p for [*closo*-1-CB_9H_9-1-X]$^-$ derivatives (**3a**–**3e**) in the para position than those anions in the [*closo*-1-$CB_{11}H_{11}$-1-X]$^-$ series demonstrates the general higher sensitivity of ten-vertex *closo* clusters compared with icosahedral clusters[20] in this position.

Finally, as predicted by the long-standing Williams empirical rule[23] which relates the chemical shifts and coordination numbers of boron atoms, the ^{13}C NMR chemical shifts of [*closo*-1-CB_9H_{10}]$^-$ anion (**1**) and [*closo*-2-CB_9H_{10}]$^-$ anion (**2**) illustrate the difference between the tetragonal

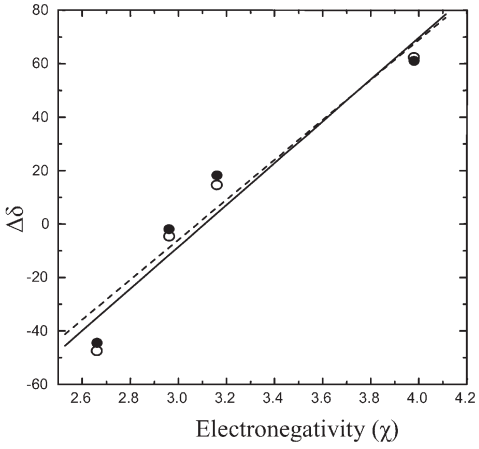


FIG. 2
Correlation between chemical shifts increments ($\Delta\delta$) and electronegativity of halogen atoms (χ): ○ for ipso position for halogenated derivatives **3a**–**3d** (fitted with dashed line), ● for ipso for [*closo*-1-$CB_{11}H_{11}$-1-X]$^-$ (fitted with solid line)

arrangement for C1 in anion **1** (53.01 ppm) and C2 in anion **2** (27.06 ppm). The rule was extended to the ^{13}C chemical shifts of skeletal carbon atoms by Todd[24] and are represented in the ten-vertex carborane, 1,6-$C_2B_8H_{10}$ (ref.[25]), where for C1 with connectivity four, δ 57.7, and for C6 with connectivity five, δ 35.4.

Unambiguous assignment of the C1 carbon in the halogenated samples was achieved by correlating the ortho BH protons with C1 via the two-bond coupling (H–B–C).

Conclusions

In short, we have reported an optimized procedure for the preparation of the parent derivative [*closo*-1-CB_9H_{10}]$^-$$Cs^+$ (**1**[Cs]) in 29% yield starting from $B_{10}H_{14}$ in three steps. We also reported the preparation and characterization of the previously unknown C-halogenated series (F, Cl, Br, and I) and C-methylated product of the [*closo*-1-CB_9H_{10}]$^-$ cluster. Analyzing the C-halogenated series **3a**–**3d**, as well by comparing **3a**–**3d** to the previously reported [*closo*-1-$CB_{11}H_{11}$-1-X]$^-$ series, we commented on the trends and regularities in the NMR spectra based on the ^{11}B and ^{13}C nuclei.

EXPERIMENTAL

General

All reactions were performed under standard vacuum and inert atmosphere techniques. Reaction work-up was performed in open air unless otherwise specified. Reagents were used as supplied by the manufacturer and added over a stream of inert gas in all cases. NMR spectra (δ, ppm; *J*, Hz) were recorded in acetone-d_6. THF was distilled over sodium in the presence of benzophenone. CuCl was stored and weighed under inert atmosphere in a glove bag. *n*-BuLi was titrated using menthol and 1,10-phenanthroline as the indicator in anhydrous THF. Removal of excess Et_2O in vacuo is defined as removing excess Et_2O at ambient temperature on a rotary evaporator followed by exposure to the reduced pressure of a high vacuum oil pump until bubbling of solution is no longer observed. Drying of crystalline products was performed using a high vacuum oil pump at room temperature.

Two-dimensional NMR experiments were performed at 11.75 tesla on a Varian Inova-500 NMR spectrometer equipped with two broadband channels for simultaneous pulse irradiation of ^{13}C and ^{11}B, while observing ^1H resonances. Broadband decoupling of ^{11}B was performed using the GARP decoupler modulation over a bandwidth greater than 15 kHz throughout the pulse-sequence and the acquisition time. 2D-gHMQC{^{13}C,^{11}B} (simultaneous ^{13}C and ^{11}B decoupling) and gHMBC{^{11}B} (^{11}B decoupling only) were performed using a Nalorac® triple-inverse probe. Other than the additional ^{11}B decoupling, standard Varian distribution pulse sequences were employed.

HPLC analysis was carried out using a Merck–Hitachi HPLC consisting of LaChrom Pump L 7100, Intelligent Autosampler L-7450, DAD Detector L-7450 and Interface D-7000. The system was equipped with ELSD Detector Altech ELSD 8000 in tandem arrangement. The chromatographic procedure is as follows: an isocratic ion-pair RP chromatographic method based on the modification of methods previously reported[26] for the separation of hydrophobic, borate anions. Column: stainless steel RP Separon SGX C18, 5 μm (250 × 4 mm ID, silica with chemically bonded octadecyl groups, endcapped) (Tessek Prague). Chromatographic conditions: solvent 4.5 mmol hexylamine acetate in 48% aqueous acetonitrile (Sigma–Aldrich, CHROMASOLV, for gradient elution), pH 5.6, flow rate 0.8 ml min^{-1}. ELSD detection: nebulising gas pressure 4.4 bar, drift tube temperature 85 °C, gain 8. DAD detection: UV range 210–235 nm, fixed wavelengths 210, 212, 215 and 222 nm; sensitivity range 2.0 A.U.F.S. Injection: 10 μl of samples of concentration approximately 1 mg ml^{-1} dissolved in the mobile phase or CH_3CN. The method allowed the resolution of most of the compounds from the real reaction mixtures and for purity assay and control. Capacity factor *k'* of the parent derivative [*closo*-1-CB_9H_{10}]$^-Cs^+$ (**1**[Cs]) was 1.41 under these conditions.

Electrospray negative ion mass spectra were measured in methanol solution using a Hewlett–Packard 5989 API/ES//MS instrument.

*Preparation of [closo-2-CB_9H_{10}]$^-(NEt_4)^+$ (**2**[NEt_4]).* To [*arachno*-6-CB_9H_{14}]$^-(NEt_4)^+$ (**4**[NEt_4]) (5.0 g, 19.7 mmol) cooled 10% HCl (250 ml) and Et_2O (50 ml) were added. The mixture was stirred under N_2 until all solid dissolved. The Et_2O layer was separated and the aqueous layer extracted with Et_2O (3 × 75 ml). The organic layers were combined, and cooled 1.0 M KOH (650 ml) was added. Et_2O was removed in vacuo at ambient temperature (no more than 35 °C). The aqueous layer was cooled to 0 °C in ice-bath. Elemental I_2 (33 g, 130 mmol) was added in three 11-g portions at 30 min intervals. Upon addition of the last portion, the reaction was further stirred at 0 °C for 2 h. If I_2 is added quickly, the solution may turn yellow, but the color eventually fades as the reaction progresses. The reaction mixture was filtered. (NEt_4)Br (4.5 g, 22 mmol) was added and, after brief stirring, a white crystalline solid precipitated. This solid was filtered, washed (H_2O), and dried in vacuo giving 3.6 g (73%) of [*closo*-2-CB_9H_{10}]$^-(NEt_4)^+$ (**2**[NEt_4]). Characterization data were consistent with literature results[12]. ^{13}C NMR: 27.06 C1 (CD_3CN).

*Preparation of parent derivative [closo-1-CB_9H_{10}]$^-Cs^+$ (**1**[Cs]).* To [*closo*-2-CB_9H_{10}]$^-(NEt_4)^+$ (**2**[NEt_4]) (14.4 g, 57.8 mmol) DME (300 ml) was added. The red solution was stirred at reflux for 120 h. After heating for 1 h, the red solution turned from yellow to clear. Once isomerization was complete (as detected by ^{11}B NMR), the DME was filtered and removed in vacuo. H_2O (500 ml), 10% aqueous HCl (500 ml), and Et_2O (250 ml) were added to the slightly yellow solid. Upon complete dissolution, the Et_2O layer was separated, and the aqueous layer was extracted with Et_2O (3 × 250 ml). The organic layers were combined, H_2O (300 ml) was added, and Et_2O was removed in vacuo. CsCl (9.8 g, 58 mmol) was added, and the mixture was concentrated in vacuo with heating. Upon concentration (~100 ml solution remaining), a crystalline solid precipitated, which was filtered, washed (cold H_2O), and dried. The solid was dissolved in acetone and filtered to remove remnant CsCl. Acetone was removed giving 10.7 g (74%) of parent derivative [*closo*-1-CB_9H_{10}]$^-Cs^+$ (**1**[Cs]) as an off-white solid. A second fraction (0.8 g) of 80% pure parent derivative **1** was collected from the aqueous filtrate via recrystallization from hot H_2O. Characterization data was consistent with literature result[12]. ^{13}C NMR (CD_3CN): 53.01 C1.

*Preparation of [closo-1-CB_9H_9-1-F]$^-(NBu_4)^+$ (**3c**[NBu_4]).* To a three-necked 50-ml round-bottom flask parent derivative [*closo*-1-CB_9H_{10}]$^-Cs^+$ (**1**[Cs]) (381 mg, 1.51 mmol) was added.

Under vacuum, the salt was heated briefly with a heat gun and then allowed to cool. After cooling, vacuum was removed and inert atmosphere maintained. Freshly distilled THF (5 ml) was added, and the solution was cooled to –40 °C. 1.5 M *n*-BuLi in hexanes (1.1 ml, 1.66 mmol) was added dropwise over 30 min. The solution was warmed to room temperature and further stirred for 2 h. During warming, a milky precipitate formed signifying the formation of reactive intermediate **5**. The suspension was cooled back to –40 °C, and bis(benzenesulfonyl)fluoroamine (523 mg, 1.66 mmol) was added. The reaction mixture slowly turned orange upon warming to room temperature and stirring continued for another 2 h. CH_3OH (3 ml) was added, and solvents were evaporated to dryness. 10% aqueous HCl (25 ml) and Et_2O (15 ml) were added to the residue, and the suspension was stirred for 2 h. The solution was extracted with additional Et_2O (3 × 15 ml), the organic layers were combined, and H_2O (20 ml) was added. The organic layer was removed in vacuo, the H_2O layer was filtered, and $(NBu_4)Br$ (520 mg, 1.6 mmol) was added. The precipitate was collected, washed (H_2O), and dried (490 mg). Recrystallization from EtOH/H_2O gave parent derivative **1**[NBu_4] and fluorinated derivative **3c**[NBu_4] in the 2:1 ratio (combined weight of 220 mg). This mixture of parent derivative **1**[NBu_4] and fluorinated derivative **3c**[NBu_4] was separated chromatographically (CH_2Cl_2, silica gel) giving 60 mg of fluorinated derivative **3c**[NBu_4]. The mother liquor from recrystallization was separated similarly, yielding a total of 130 mg (23%) of fluorinated derivative **3c**[NBu_4] as a white solid. An amount of 130 mg of parent derivative **1**[NBu_4] was recovered. ^{11}B NMR: 18.0 (d, J = 156, 1 B, B10), –19.2 (d, J = 147, 4 B, B2-5), –28.5 (d, J = 163, 4 B, B6-9). ^{1}H {^{11}B}NMR: 5.06 (s, 1 H, H10), 1.85 (s, 4 H, H2-5), 0.57 (s, 4 H, H6-9), 3.40 (t, 8 H), 1.86 (q, 8 H), 1.45 (q, 8 H), 1.00 (t, 12 H) (NBu_4^+). ^{13}C NMR: 115.41 (d, J_{CF} = 2, C1); 59.58, 26.26, 20.40, 15.24 (NBu_4^+). ^{19}F NMR (CD_3CN): 196.27. MS (ESI), *m/z*: 139. For $C_{17}H_{45}B_9FN$ (379.9) calculated: 53.75% C, 11.94% H; found: 53.98% C, 12.34% H.

*Preparation of [closo-1-CB_9H_9-1-Cl]$^-$(NEt_4)$^+$ (**3d**[NEt_4]), [closo-1-CB_9H_9-1-Br]$^-$(NEt_4)$^+$ (**3b**[NEt_4]), and [closo-1-CB_9H_9-1-I]$^-$(NEt_4)$^+$ (**3a**[NEt_4]) employing CuCl.* To a three-necked 50-ml round-bottom flask parent derivative [*closo*-1-$CB_9H_{10}]^-Cs^+$ (**1**[Cs]) (381 mg, 1.51 mmol) was added. Under vacuum, the salt was heated with a heat gun and then allowed to cool. After cooling, vacuum was removed and inert atmosphere maintained. Freshly distilled THF (5 ml) was added, and the solution was cooled to –40 °C. 1.5 M *n*-BuLi (1.1 ml, 1.66 mmol) was added slowly over 30 min. The solution was warmed to room temperature and further stirred for 2 h. During warming, a milky precipitate formed signifying the formation of reactive intermediate **5**. The suspension was cooled to –40 °C, CuCl (164 mg, 1.66 mmol) was added, and the light-brown solution was warmed to room temperature. The reaction mixture was cooled to –40 °C, and the appropriate halogenation reagent (1.66 mmol) was added. The reaction mixture turned dark green, and stirring continued at room temperature for 2 h. CH_3OH (3 ml) was added, and the solvents were evaporated to dryness. 10% aqueous HCl (25 ml) and Et_2O (15 ml) were added to the residue, and the suspension stirred for 2 h. The solution was extracted with additional Et_2O (3 × 15 ml), the organic layers were combined, and H_2O (20 ml) was added. The organic layer was removed in vacuo, the H_2O layer was filtered, and $(NEt_4)Br$ (340 mg, 1.6 mmol) was added. The precipitate was collected, washed (H_2O), and dried (333 mg of crude chlorinated derivative **3d**[NEt_4], 577 mg of crude brominated derivative **3b**[NEt_4], and 509 mg of crude iodinated derivative **3a**[NEt_4] were obtained). Recrystallization from EtOH/H_2O gave parent derivative **1**[NEt_4] and appropriate C-halogenated derivative (chlorinated **3d**[NEt_4], brominated **3b**[NEt_4], and iodinated **3a**[NEt_4]) in the same ratio shown in Table I for CuCl reactions (220 mg chlorinated derivative **3d**[NEt_4], 207 mg

brominated derivative **3b**[NEt_4], and 358 mg iodinated derivative **3a**[NEt_4]). Results of chromatographic separation (CH_2Cl_2, silica gel) are described below for both the recrystallized fraction and its mother liquor.

3d[NEt_4]. 150 mg (35%) as a white solid was obtained in total. 100 mg of parent derivative **1**[NEt_4] was recovered. ^{11}B NMR: 26.1 (d, *J* = 162, 1 B, B10), –15.0 (d, *J* = 156, 4 B, B2-5), –25.5 (d, *J* = 138, 4 B, B6-9). ^{1}H {^{11}B}NMR: 5.06 (s, 1 H, H10), 1.85 (s, 4 H, H2-5), 0.57 (s, 4 H, H6-9), 3.40 (q, 8 H), 1.40 (t, 12 H) (NEt_4^+). ^{13}C NMR: 67.74 (s, C1); 53.00, 7.65 (NEt_4^+). MS (ESI), *m/z*: 157. For $C_9H_{29}B_9ClN$ (284.1) calculated: 38.05% C, 10.29% H; found: 38.60% C, 10.84% H.

3b[NEt_4]. 170 mg (34%) as a white solid was obtained in total. 80 mg of parent derivative **1**[NEt_4] was recovered. ^{11}B NMR: 27.5 (d, *J* = 151, 1 B, B10), –14.5 (d, *J* = 156, 4 B, B2-5), –25.0 (d, *J* = 140, 4 B, B6-9). ^{1}H {^{11}B}NMR: 5.66 (s, 1 H, H10), 1.80 (s, 4 H, H2-5), 0.71 (s, 4 H, H6-9), 3.51 (q, 8 H), 1.41 (t, 12 H) (NEt_4^+). ^{13}C NMR: 48.42 (s, C1); 52.98, 7.74 (NEt_4^+). MS (ESI), *m/z*: 201. For $C_9H_{29}B_9BrN$ (328.6) calculated: 32.90% C, 8.90% H; found: 33.46% C, 9.38% H.

3a[NEt_4]. 20 mg (4%) as a white solid was obtained. Iodinated derivative **3a**[NEt_4] was eluted with a new compound of the same *m/z* ratio. Analysis by {^{11}B-^{11}B}-COSY NMR showed the presence of 8-I-CHB_9H_8. This isomer is probably a product of dynamic rearrangement hence the yield is low. ^{11}B NMR: 29.8 (d, *J* = 153, 1 B, B10), –13.6 (d, *J* = 153, 4 B, B2-5), –24.3 (d, *J* = 138, 4 B, B6-9). ^{1}H {^{11}B}NMR: 5.90 (s, 1 H, H10), 1.68 (s, 4 H, H2-5), 0.54 (s, 4 H, H6-9), 3.14 (q, 8 H), 1.18 (t, 12 H) (NEt_4^+). ^{13}C NMR: 5.6 (s, C1); 53.14, 7.74 (NEt_4^+). MS (ESI), *m/z*: 246. For $C_9H_{29}B_9IN$ (375.5) calculated: 28.79% C, 7.78% H; found: 28.94% C, 7.96% H.

*Preparation of [closo-1-CB_9H_9-1-CH_3]$^-$(NBu_4)$^+$ (**3e**[NBu_4]).* To a three-necked 50-ml round-bottom flask parent derivative [*closo*-1-CB_9H_{10}]$^-Cs^+$ (**1**[Cs]) (254 mg, 1.00 mmol) was added. Under vacuum, the salt was heated with a heat gun and allowed to cool. After cooling, the vacuum was removed and inert atmosphere maintained. Freshly distilled THF (5 ml) was added and the solution was cooled to –40 °C. 1.5 M *n*-BuLi (0.73 ml, 1.10 mmol) was added slowly over 30 min. The solution was warmed to room temperature and further stirred for 2 h. During warming, a milky precipitate formed signifying the formation of reactive intermediate **5**. The suspension was cooled to –40 °C before CH_3I (0.12 ml, 2.0 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirring continued for 2 h. CH_3OH (3 ml) was added, and the solvents were evaporated to dryness. 10% aqueous HCl (25 ml) and Et_2O (15 ml) were added to the residue and the suspension was stirred for 2 h. The solution was extracted with additional Et_2O (3 × 15 ml), the organic layers were combined, and H_2O (20 ml) was added. The organic layer was removed in vacuo, the H_2O layer was filtered, and (NBu_4)Br (0.350, 1.1 mmol) was added. The precipitate was collected, washed (H_2O), and dried (237 mg). Recrystallization from EtOH/H_2O gave parent derivative **1**[NBu_4] and methyl derivative **3e**[NBu_4] in the 3:7 ratio (combined weight of 156 mg). This mixture of parent derivative **1**[NBu_4] and methyl derivative **3e**[NBu_4] was separated chromatographically (CH_2Cl_2, silica gel) giving 120 mg of methyl derivative **3e**[NBu_4]. The mother liquor was separated similarly, and a total of 150 mg (40%) of methyl derivative **3e**[NBu_4] was obtained as a white solid. An amount of 50 mg of parent derivative **1**[NBu_4] was recovered. ^{11}B NMR: 25.6 (d, *J* = 152, 1 B, B10), –15.8 (d, *J* = 1150, 4 B, B2-5), –24.4 (d, *J* = 134, 4 B, B6-9). ^{1}H {^{11}B }NMR: 5.20 (s, 1 H, H10), 1.44 (s, 4 H, H2-5), 0.68 (s, 4 H, H6-9), 3.51 (d, 8 H), 1.41 (t, 12 H) (NEt_4^+). ^{13}C NMR: 66.6 (s, C1); 21.9 (s, CH_3); 59.36, 24.31,

20.40, 13.94 (NBu_4^+). MS (ESI), *m/z*: 135. For $C_{18}H_{48}B_9N$ (375.9) calculated: 57.52% C, 12.87% H; found: 57.02% C, 12.34% H.

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