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Regioselective Monoiodination of Carba-*closo*-dodecaborates: M[7-I-12-X-*closo*-$CB_{11}H_{10}$] (M = Cs^+, $[Et_4N]^+$; X = F, Cl, Br, OH)

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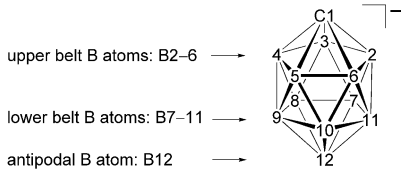
Selective monoiodination of a series of carba-*closo*-dodecaborates with a halogen atom or a hydroxy substituent bonded to the antipodal boron atom resulted in salts of the novel anions [7-I-12-X-*closo*-$CB_{11}H_{10}$]$^-$ [X = F (**1**), Cl (**2**), Br (**3**), OH (**4**)]. These anions were isolated as $[Et_4N]^+$ salts and converted into the Cs^+ salts. The novel compounds were studied by multi NMR spectroscopy, mass spectrometry (MALDI), and elemental analysis. The solid-state structure of Cs[7-I-12-HO-*closo*-$CB_{11}H_{10}$]·$(CH_3)_2CO$ was determined by single-crystal X-ray diffraction. The assignment of the NMR spectroscopic data and the discussion of structural properties was supported by the results of the DFT calculations.

Introduction

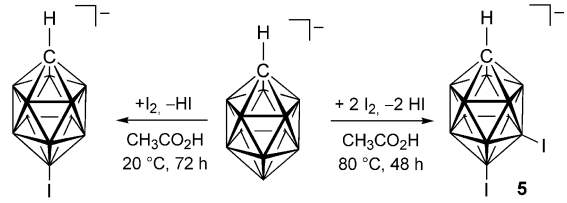
Selective functionalization of the carba-*closo*-dodecaborate anion [*closo*-$CB_{11}H_{12}$]$^-$ (Scheme 1) is of growing interest because the resulting anions are attractive building blocks for new compounds with many possible applications,[1] for example in medicine,[2,3] material sciences,[4–6] and catalysis.[7]



Scheme 1. Numbering of the vertices of the [*closo*-$CB_{11}H_{12}$]$^-$ anion.

An especially attractive class of carba-*closo*-dodecaborate anions are partially iodinated [*closo*-$CB_{11}H_{12}$]$^-$ anions, because they are valuable starting materials for the further derivatization of the {*closo*-CB_{11}} cluster, in particular for Pd-catalyzed Kumada-type cross-coupling reactions resulting in anions with boron–carbon bonds,[1,5,8,9] e.g. [12-CH_3-*closo*-$CB_{11}H_{11}$]$^-$.[5] The first examples of mono- and diiodinated carba-*closo*-dodecaborate anions [12-I-*closo*-$CB_{11}H_{11}$]$^-$ and [7,12-I_2-*closo*-$CB_{11}H_{10}$]$^-$, respectively, were reported in 1986.[10] Furthermore, {*closo*-CB_{11}} clusters with a higher iodine content,[1,11] for example [1-R-*closo*-$CB_{11}I_{11}$]$^-$ and [1-R-2,3,4,5,6-H_5-*closo*-$CB_{11}I_6$]$^-$ (R = H, H_2N),[3,12] have been described. Some of the iodine-rich anions were used as weakly coordinating anions[13] or were discussed as X-ray contrast agents.[3]

Single and double iodination of the [*closo*-$CB_{11}H_{12}$]$^-$ anion is achieved in glacial acetic acid using elemental iodine as shown in Scheme 2. At room temperature only monoiodination takes place resulting in the highly regioselective formation of the 12-substituted isomer.[5,10] Some substituted carba-*closo*-dodecaborate anions, for example [1-R-*closo*-$CB_{11}H_{11}$]$^-$ (R = Me,[5] Ph,[8]), were monoiodinated using elemental iodine as well. The [7,12-I_2-*closo*-$CB_{11}H_{10}$]$^-$ anion (**5**) is formed at 80 °C.[10]



Scheme 2. Mono- and diiodination reaction of [*closo*-$CB_{11}H_{12}$]$^-$.[5,10]

The regioselective monoiodination in the 12-position of the [*closo*-$CB_{11}H_{12}$]$^-$ anion is a typical reaction for the carba-*closo*-dodecaborate anion, since electrophilic substitution occurs at the antipodal boron atom in general (Scheme 1). In most cases, minor amounts of the respective 7-substituted isomer are formed. Further examples are the reactions of [*closo*-$CB_{11}H_{12}$]$^-$ with anhydrous hydrogen fluoride, *N*-chlorosuccinimide, *N*-bromosuccinimide, and sulfuric acid that produce the anions [12-X-*closo*-$CB_{11}H_{11}$]$^-$ (X = F,[14] Cl,[15] Br,[15] OH[16]), respectively (Scheme 3).

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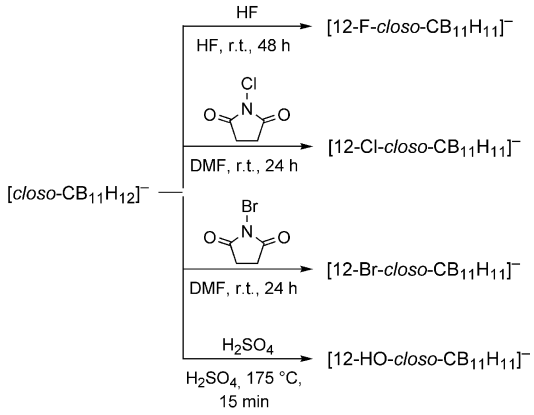
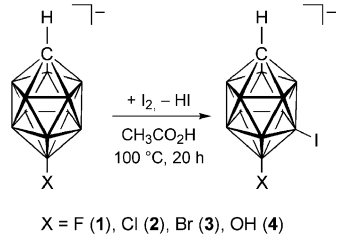


Scheme 3. Selective substitutions of [*closo*-$CB_{11}H_{12}]^-$ in the antipodal position resulting in [12-F-*closo*-$CB_{11}H_{11}]^-$,[14] [12-Cl-*closo*-$CB_{11}H_{11}]^-$,[15] [12-Br-*closo*-$CB_{11}H_{11}]^-$,[15] and [12-HO-*closo*-$CB_{11}H_{11}]^-$.[16]

In this contribution the synthesis of a series of monoiodinated carba-*closo*-dodecaborates with the iodine substituent in the 7-position of the cluster, [7-I-12-X-*closo*-$CB_{11}H_{10}]^-$ [X = F (**1**), Cl (**2**), Br (**3**), OH (**4**)], are reported. The salts were characterized by ^{11}B, ^1H, and ^{13}C NMR spectroscopy, by MALDI mass spectrometry, and elemental analysis. A single crystal of Cs[7-I-12-HO-*closo*-$CB_{11}H_{10}]\cdot(CH_3)_2CO$ was investigated by single-crystal X-ray diffraction.

Results and Discussion

As outlined in the introduction, monoiodination of the parent carba-*closo*-dodecaborate anion occurs in a highly regioselective reaction at the antipodal boron atom of the 12-vertex cluster (Scheme 1). Hence, a different strategy has to be used for a selective iodination at one of the lower belt boron atoms. One possibility is the protection of the 12-position with an inert substituent. Regioselective monoiodination at the 7-position of the carba-*closo*-dodecaborate anions [12-X-*closo*-$CB_{11}H_{11}]^-$ (X = F, Cl, Br, OH), whose syntheses are depicted in Scheme 3, is accomplished as presented in Scheme 4. The tetraethyl ammonium salts of the novel anions [7-I-12-X-*closo*-$CB_{11}H_{10}]^-$ are isolated in a yield of approximately 90%. The reaction conditions, elemental I_2, glacial acetic acid, and a reaction temperature of 100 °C, are similar to those used for the preparation of the diiodinated anion [7,12-I_2-*closo*-$CB_{11}H_{10}]^-$ (Scheme 2).[10] The progress of the reactions is checked after 6 h periodically by $^{11}B\{^1H\}$ NMR spectroscopy to ensure completion of the reaction. Prolonged treatment with iodine at 100 °C results in iodination of more than one BH vertex; according to NMR spectroscopic data solely at the lower belt boron atoms (Scheme 1). Hence, minor amounts of [Et_4N][7,8-I_2-12-X-*closo*-$CB_{11}H_9$] and [Et_4N][7,9-I_2-12-X-*closo*-$CB_{11}H_9$] are obtained along with the salts of the monoiodinated anions.



Scheme 4. Preparations of [7-I-12-X-*closo*-$CB_{11}H_{11}]^-$ [X = F (**1**), Cl (**2**), Br (**3**), OH (**4**)].

The $[Et_4N]^+$ salts of [7-I-12-X-*closo*-$CB_{11}H_{10}]^-$ [X = F (**1**), Cl (**2**), Br (**3**), OH (**4**)] are extracted into diethyl ether as H^+(solv) salts by treatment with aqueous HCl. Addition of an aqueous solution of CsCl yields the respective Cs^+ salts. These salts can be further purified by precipitation from a concentrated acetone solution by addition of chloroform.

NMR Spectroscopy

The carba-*closo*-dodecaborate anions [7-I-12-X-*closo*-$CB_{11}H_{10}]^-$ [X = F (**1**), Cl (**2**), Br (**3**), I (**5**), OH (**4**)] were characterized by multi-NMR spectroscopy. The assignments of the ^{11}B and ^1H NMR signals (Figure 1) are mostly based on data derived from $^{11}B\{^1H\}$-$^1H\{^{11}B\}$ 2D[17] and

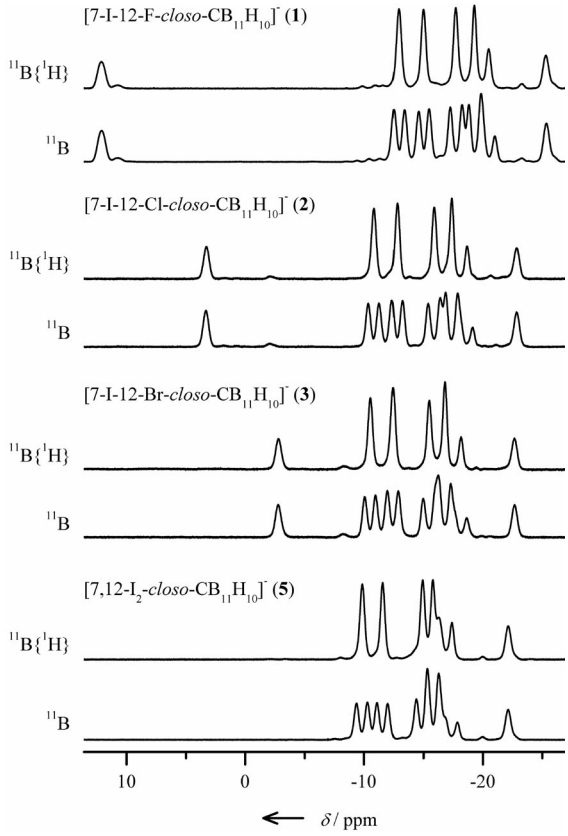


Figure 1. ^{11}B and $^{11}B\{^1H\}$ NMR spectra of the anions [7-I-12-X-*closo*-$CB_{11}H_{10}]^-$ [X = F (**1**), Cl (**2**), Br (**3**), I (**5**)].

Table 1. Experimental and calculated ^{11}B and ^{13}C NMR chemical shifts of [7-I-12-F-*closo*-$CB_{11}H_{10}]^-$ (**1**), [7-I-12-Cl-*closo*-$CB_{11}H_{10}]^-$ (**2**), [7-I-12-Br-*closo*-$CB_{11}H_{10}]^-$ (**3**), [7,12-I_2-*closo*-$CB_{11}H_{10}]^-$ (**5**), and [7-I-12-HO-*closo*-$CB_{11}H_{10}]^-$ (**4**).[a,b]

	$\delta(^{13}C)$				$\delta(^{11}B)$											
	1		2/6		3/5		4		7		8/11		9/10		12	
Anion	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.
1	38.2	40.7	–17.7	–20.9	–19.2	–23.3	–20.2	–24.3	–25.3	–6.6	–12.9	–15.1	–15.0	–17.3	12.1	11.7
2	44.7	47.1	–15.9	–19.5	–17.4	–21.2	–18.7	–22.6	–22.8	–2.0	–10.8	–13.0	–12.8	–14.7	3.3	5.3
3	46.7	48.6	–15.5	–18.5	–16.8	–21.1	–18.2	–22.4	–22.6	–6.2	–10.5	–13.2	–12.4	–14.6	–2.8	5.6
5	50.2	47.9	–14.9	–18.8	–15.8	–22.4	–17.4	–23.8	–22.1	–3.5	–9.9	–11.9	–11.6	–14.1	–16.3	2.5
4	38.6	41.1	–17.3	–21.4	–18.8	–22.3	–20.0	–23.8	–23.6	–3.8	–12.3	–13.3	–14.4	–16.5	9.6	8.5

[a] Chemical shifts in ppm. [b] NMR solvent: CD_3CN.

$^{11}B\{^1H\}$-$^{11}B\{^1H\}$ COSY[18] experiments and aided by the results of DFT calculations (Table 1).

The {*closo*-CB_{11}} clusters of the anions [7-I-12-X-*closo*-$CB_{11}H_{10}]^-$ [X = F (**1**), Cl (**2**), Br (**3**), I (**5**), OH (**4**)] possess C_s symmetry, hence, seven signals are observed in the ^{11}B NMR spectra (Table 1). In Figure 1 the ^{11}B and $^{11}B\{^1H\}$ NMR spectra of the homologous anions [7-I-12-X-*closo*-$CB_{11}H_{10}]^-$ [X = F (**1**), Cl (**2**), Br (**3**), I (**5**)] are depicted, and in Table 1 the experimental chemical shifts are compared to $\delta(^{11}B)$ derived from DFT calculations. In the ^{11}B NMR spectra of the anions the signal with the lowest resonance frequency is assigned to the B7 nucleus. The signal of the ^{11}B nucleus of the B12 atom is shifted from +12.1 (B–F, **1**) to –16.3 ppm (B–I, **5**) within the series. A similar trend is found for the related anions [12-X-*closo*-$CB_{11}H_{10}]^-$ (X = F,[14] Cl,[15] Br,[15] I[10]) (Table 2). $\delta(^{13}C)$ of the cluster carbon atom increases from 38.2 to 50.2 ppm on changing the halogen substituent from fluorine to iodine (Table 1).

Table 2. Experimental and calculated[a] ^{11}B NMR chemical shifts of [12-F-*closo*-$CB_{11}H_{11}]^-$, [12-Cl-*closo*-$CB_{11}H_{11}]^-$, [12-Br-*closo*-$CB_{11}H_{11}]^-$, [12-I-*closo*-$CB_{11}H_{11}]^-$, and [12-HO-*closo*-$CB_{11}H_{11}]^-$.[a,b]

	2–6		7–11		12	
Anion	Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.
[12-F-*closo*-$CB_{11}H_{11}]^-$	–19.2	–22.3	–15.0	–16.7	13.6	12.7
[12-Cl-*closo*-$CB_{11}H_{11}]^-$	–17.7	–20.7	–12.9	–14.4	3.7	5.6
[12-Br-*closo*-$CB_{11}H_{11}]^-$	–17.2	–20.4	–12.9	–14.0	–3.5	5.3
[12-I-*closo*-$CB_{11}H_{11}]^-$	–16.1	–20.4	–11.7	–14.0	–17.7	0.5
[12-HO-*closo*-$CB_{11}H_{11}]^-$	–18.6	–22.0	–14.5	–15.8	9.1	11.0

[a] Chemical shifts in ppm. [b] NMR solvent: CD_3CN.

The ^{11}B and ^{13}C NMR chemical shifts of the [7-I-12-HO-*closo*-$CB_{11}H_{10}]^-$ (**4**) anion are relatively close to those of the fluorinated anion [7-I-12-F-*closo*-$CB_{11}H_{10}]^-$ (**1**) (Table 1).

Solid-State Structure of Cs[7-I-12-HO-*closo*-$CB_{11}H_{10}$]·$(CH_3)_2CO$ [Cs^+**4**·$(CH_3)_2CO$]

Cs[7-I-12-HO-*closo*-$CB_{11}H_{10}$] crystallizes, with one molecule of acetone, in the triclinic space group $P\bar{1}$ (no. 2) with two formula units in the unit cell. A model of the [7-I-12-HO-*closo*-$CB_{11}H_{10}]^-$ anion in the crystal is depicted in Figure 2. The experimental and calculated [B3LYP/6-311++G(d,p)] bond lengths and angles are in good agreement (Table 3). A part of the crystal structure of Cs[7-I-12-HO-*closo*-$CB_{11}H_{10}$]·$(CH_3)_2CO$ is shown in Figure 3 and the shortest Cs–O and Cs–I distances are listed in the figure caption.

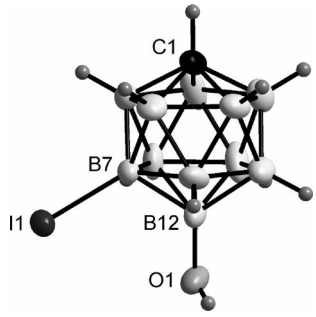


Figure 2. The [7-I-12-HO-*closo*-$CB_{11}H_{10}]^-$ anion in the crystal of Cs^+**4**·$(CH_3)_2CO$ (displacement ellipsoids are at the 40% probability level).

Table 3. Selected experimental and calculated bond lengths in Å of the [7-I-12-HO-*closo*-$CB_{11}H_{10}]^-$ anion (**4**).

	Exp.	Calcd.
Symmetry	C_1	C_s
B7–I1	2.19(1)	2.221
B12–O1	1.43(1)	1.420
C1–B2/B3/B4/B5/B6[a]	1.70(2)	1.707
B2–B3/B3–B4/B4–B5/B5–B6/B6–B2[a]	1.77(2)	1.781
B2–B7/B3–B7/B3–B8/···/B2–B11[a]	1.77(2)	1.771
B7–B8/B8–B9/B9–B10/B10–B11/B11–B7[a]	1.77(2)	1.784
B7–B12	1.77(2)	1.789
B8–B12/B11–B12[a]	1.80(2)	1.816
B9–B12/B10–B12[a]	1.80(2)	1.796

[a] Mean value.

The B–O bond length in [7-I-12-HO-*closo*-$CB_{11}H_{10}]^-$ (**4**) of 1.43(1) Å is comparable to the length of *d*(B–O) in related carba-*closo*-dodecaborate anions: [Ph_3MeP][1-H-2,3,4,5,6-$(HO)_5$-*closo*-$CB_{11}Br_6$]·$3H_2O$ [1.395(5) Å],[19] [H_7O_3][Ph_3MeP][1-H-2,3,4,5,6-$(HO)_5$-*closo*-$CB_{11}Br_6]_2$·$3H_2O$ [1.397(5) Å],[19] and [Ph_4P][2-Cl$(CH_2)_4$O-*closo*-$CB_{11}H_{11}$] [1.409(3) Å].[20] Comparable B–O bond lengths were also reported for the related [HO-*closo*-$B_{12}H_{11}]^{2-}$ anion with different countercations (1.40–1.43 Å).[21] In

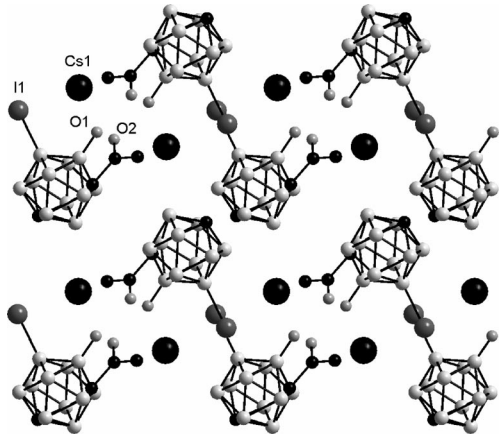


Figure 3. Part of the crystal structure of Cs[7-I-12-HO-*closo*-$CB_{11}H_{10}$]·$(CH_3)_2CO$ [Cs^+**4**·$(CH_3)_2CO$]; view along [010] (hydrogen atoms and the split positions of the Cs^+ cation and the I atom with minor occupation are omitted for clarity). Selected interatomic distances in Å: Cs1···O1 2.986(8), Cs1···O1′ 3.109(7), Cs1···O2 3.194(8), Cs1···I1 4.115(4), Cs1···I1′ 4.017(3).

contrast, in the oxonium derivative 12-{$O(CH_2CH_2)_2$}-*closo*-$CB_{11}H_{11}$ a longer B–O bond was observed [1.520(1) Å].[16] Similar to *d*(B–O), the B–I bond length in anion **4** of 2.19(1) Å compares well to related boron–iodine bond lengths in other {*closo*-CB_{11}} clusters, e.g. in the [1-H-*closo*-$CB_{11}I_{11}]^-$ anion in its [nBu$_3$NH]$^+$ salt [$d(B–I)_{average}$ = 2.149(5) Å].[22] The average inner-cluster boron–boron [1.78(2) Å] and carbon–boron bond lengths [1.70(2) Å] are similar to values reported for the [*closo*-$CB_{11}H_{12}]^-$ anion.[15,23]

Conclusions

The selective monoiodination in the 7-position of the {*closo*-CB_{11}} cluster (Scheme 1), achieved by protection of the 12-position using an inert substituent, results in salts of the anions [7-I-12-X-*closo*-$CB_{11}H_{10}]^-$ [X = F (**1**), Cl (**2**), Br (**3**), OH (**4**)]. The cesium salts of the novel, monoiodinated anions **1**–**4** are valuable starting materials for Kumada-type cross-coupling reactions, resulting in {*closo*-CB_{11}} clusters with a substituent bonded through carbon to the boron atom in the 7-position. Recently, the alkynyl-substituted derivatives [Et_4N][7-PhCC-12-X-*closo*-$CB_{11}H_{10}$] (X = F, Cl, Br) and [Et_4N][7-Me_3SiCC-12-F-*closo*-$CB_{11}H_{10}$], which are promising candidates for a further derivatization of the carba-*closo*-dodecaborate anion, were reported by us.[24]

Experimental Section

General Remarks: ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were recorded at room temperature in CD_3CN with a Bruker Avance DRX-500 spectrometer operating at 500.13, 125.76, 470.59, and 160.46 MHz for ^{1}H, ^{13}C, ^{19}F, and ^{11}B nuclei, respectively. NMR signals were referenced against TMS (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), and BF_3·OEt_2 in CD_3CN (^{11}B) as external standards. Matrix-assisted laser desorption/ionization (MALDI) mass spectra in the negative-ion mode were recorded with a Bruker Ultraflex TOF spectrometer. Elemental analysis (C, H, N) were performed with a Euro EA3000 instrument (HEKA-Tech, Germany). The values of the elemental analyses for some of the compounds are slightly beyond the commonly accepted differences from theory. These deviations are mainly attributed to the general problem in obtaining correct elemental analyses of boron rich compounds, as reported by others earlier.[25]

Chemicals: All standard chemicals were obtained from commercial sources. Cesium carba-*closo*-dodecaborate was synthesized from [Me_3NH][$B_{11}H_{14}$][26] following an improved protocol[6] of a literature procedure.[27] Cs[7,12-I_2-*closo*-$CB_{11}H_{10}$] (Cs^+**5**) was prepared in a similar manner to published procedures starting from Cs[*closo*-$CB_{11}H_{12}$] and elemental iodine in glacial acetic acid.[10] The Cs^+ salts of the anions [12-Cl-*closo*-$CB_{11}H_{11}]^-$ and [12-Br-*closo*-$CB_{11}H_{11}]^-$ were obtained from Cs[*closo*-$CB_{11}H_{12}$] by treatment with *N*-chlorosuccinimide and *N*-bromosuccinimide in dimethylformamide,[15] Cs[12-F-*closo*-$CB_{11}H_{11}$] was obtained by reacting Cs[*closo*-$CB_{11}H_{12}$] with anhydrous HF,[14] and Cs[12-HO-*closo*-$CB_{11}H_{11}$] was prepared by the treatment of the parent cesium carba-*closo*-dodecaborate with H_2SO_4.[16]

[Et_4N][7-I-12-F-*closo*-$CB_{11}H_{10}$] ([Et_4N]$^+$1): A 250 mL round-bottomed flask equipped with a magnetic stirring bar was charged with Cs[12-F-*closo*-$CB_{11}H_{11}$] (1.04 g, 3.5 mmol), elemental iodine (2.7 g, 10.6 mmol), and glacial acetic acid (60 mL). The flask was equipped with a reflux condenser and the reaction mixture was heated to 95–100 °C for 16 h. After 10 h the progress of the reaction was checked every 2 h by ^{11}B NMR spectroscopy. The reaction mixture was cooled to room temperature and Na_2SO_3 (500 mg) was added while stirring. The solvent was removed at 60 °C using a rotary evaporator. The solid residue was dissolved in water (100 mL) and a solution of [Et_4N]Br (2 g) in water (50 mL) was added while stirring. A white precipitate immediately formed, which was isolated by filtration. The isolated [Et_4N]$^+$**1** contained approximately 5% of a mixture of the [Et_4N]$^+$ salts of the two isomers [7,8-I_2-12-F-*closo*-$CB_{11}H_9]^-$ and [7,9-I_2-12-F-*closo*-$CB_{11}H_9]^-$ as deduced from ^{11}B{^{1}H} NMR spectroscopy and in agreement with the MALDI mass spectrum; yield 1.23 g (3.0 mmol, 85%). $C_9H_{30}B_{11}FIN$ (417.17): calcd. C 25.91, H 7.25, N 3.36; found C 24.75, H 7.05, N 3.31. ^{1}H{^{11}B} NMR (CD_3CN): δ = 2.28 (m, 1 H, CH), 1.96 (s, 2 H, BH-8 and BH-11), 1.94 (s, 2 H, BH-2 and BH-6), 1.80 (s, 1 H, BH-4), 1.72 (s, 2 H, BH-9 and BH-10), 1.53 (s, 2 H, BH-3 and BH-5) ppm. ^{13}C{^{1}H} NMR (CD_3CN): δ = 38.2 (br. s, 1 C) ppm. ^{11}B NMR (CD_3CN): δ = 12.1 (s, 1 B, B-12), –12.9 [d, $^1J(^{11}B,^1H)$ = 142 Hz, 2 B, B-8 and B-11], –15.0 [d, $^1J(^{11}B,^1H)$ = 143 Hz, 2 B, B-9 and B-10], –17.7 [d, $^1J(^{11}B,^1H)$ = 158 Hz, 2 B, B-2 and B-6], –19.2 [d, $^1J(^{11}B,^1H) \approx$ 160 Hz, 2 B, B-3 and B-5], –20.5 [d, $^1J(^{11}B,^1H) \approx$ 160 Hz, 1 B, B-4], –25.3 (s, 1 B; B-7) ppm. ^{19}F NMR (CD_3CN): δ = –190.7 [q, $^1J(^{19}F,^{11}B)$ = 58 Hz, 1 F] ppm. MS (MALDI): *m*/*z* (isotopic abundance) calcd. for **1** ([$CH_{10}B_{11}FI]^-$): 282 (1), 283 (3), 284 (13), 285 (37), 286 (74), 287 (100), 288 (81), 289 (30); found 282 (<1), 283 (1), 284 (10), 285 (40), 286 (75), 287 (100), 288 (85), 289 (29).

[Et_4N][7-I-12-X-*closo*-$CB_{11}H_{10}$] {X = Cl ([Et_4N]$^+$2), Br ([Et_4N]$^+$3), OH ([Et_4N]$^+$4)}: The tetraethylammonium salts of the anions **2**–**4** were synthesized according to the method described for [Et_4N]$^+$**1**. Analogously to [Et_4N]$^+$**1** these salts also contain small amounts of diiodinated (ca. 5%) carba-*closo*-dodecaborates: [Et_4N][7,8-I_2-12-X-*closo*-$CB_{11}H_9$] and [Et_4N][7,9-I_2-12-X-*closo*-$CB_{11}H_9$] (X = Cl, Br, OH).

[Et$_4$N][7-I-12-Cl-*closo*-CB$_{11}$H$_{10}$] ([Et$_4$N]$^+$2): Yield 0.74 g (1.7 mmol, 87%). $C_9H_{30}B_{11}ClIN$ (433.62): calcd. C 24.93, H 6.97, N 3.23; found C 25.28, H 7.18, N 3.37. $^1H\{^{11}B\}$ NMR (CD_3CN): δ = 2.42 (m, 1 H, CH), 2.07 (s, 2 H, BH-2 and BH-6), 2.00 (s, 2 H, BH-8 and BH-11), 1.95 (s, 1 H, BH-4), 1.84 (s, 2 H, BH-9 and BH-10), 1.66 (s, 2 H, BH-3 and BH-5) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 44.7 (br. s, 1 C) ppm. ^{11}B NMR (CD_3CN): δ = 3.3 (s, 1 B, B-12), –10.8 [d, $^1J(^{11}B,^1H)$ = 143 Hz, 2 B, B-8 and B-11], –12.8 [d, $^1J(^{11}B,^1H)$ = 143 Hz, 2 B, B-9 and B-10], –15.9 [d, $^1J(^{11}B,^1H)$ = 152 Hz, 2 B, B-2 and B-6], –17.4 [d, $^1J(^{11}B,^1H)$ = 158 Hz, 2 B, B-3 and B-5], –18.7 [d, $^1J(^{11}B,^1H) \approx$ 160 Hz, 1 B, B-4], –22.8 (s, 1 B; B-7) ppm. MS (MALDI): *m*/*z* (isotopic abundance) calcd. for **1** ([$CH_{10}B_{11}ClI]^-$): 298 (1), 299 (3), 300 (12), 301 (34), 302 (70), 303 (100), 304 (94), 305 (56), 306 (24), 307 (9); found 298 (1), 299 (5), 300 (16), 301 (41), 302 (80), 303 (100), 304 (97), 305 (66), 306 (30), 307 (13).

[Et$_4$N][7-I-12-Br-*closo*-CB$_{11}$H$_{10}$] ([Et$_4$N]$^+$3): Yield 0.63 g (1.3 mmol, 91%). $C_9H_{30}B_{11}BrIN$ (478.07): calcd. C 22.61, H 6.33, N 2.93; found C 22.29, H 6.22, N 2.71. $^1H\{^{11}B\}$ NMR (CD_3CN): δ = 2.58 (m, 1 H, CH), 2.12 (s, 2 H, BH-2 and B-6), 2.05 (s, 2 H, BH-8 and B-11), 1.96 (s, 1 H, BH-4), 1.93 (s, 2 H, BH-9 and BH-10), 1.70 (s, 2 H, BH-3 and BH-5) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 46.7 ppm. ^{11}B NMR (CD_3CN): δ = –2.8 (s, 1 B, B-12), –10.5 [d, $^1J(^{11}B,^1H)$ = 145 Hz, 2 B, B-8 and B-11], –12.4 [d, $^1J(^{11}B,^1H)$ = 143 Hz, 2 B, B-9 and B-10], –15.5 [d, $^1J(^{11}B,^1H)$ = 156 Hz, 2 B, B-2 and B-6], –16.8 [d, $^1J(^{11}B,^1H)$ = 157 Hz; 2 B, B-3 and B-5], –18.2 [d, $^1J(^{11}B,^1H) \approx$ 160 Hz, 1 B, B-4], –22.6 (s, 1 B, B-7) ppm. MS (MALDI): *m*/*z* (isotopic abundance) calcd. for **1** ([$CH_{10}B_{11}BrI]^-$): 343 (2), 344 (9), 345 (26), 346 (57), 347 (89), 348 (100), 349 (83), 350 (52), 351 (19); found 343 (5), 344 (15), 345 (45), 346 (70), 347 (92), 348 (100), 349 (85), 350 (45), 351 (12).

[Et$_4$N][7-I-12-HO-*closo*-CB$_{11}$H$_{10}$] ([Et$_4$N]$^+$4): Yield 0.31 g (0.7 mmol, 90%). $C_9H_{31}B_{11}INO$ (415.17): calcd. C 26.04, H 7.53, N 3.37; found C 27.45, H 7.95, N 3.40. $^1H\{^{11}B\}$ NMR (CD_3CN): δ = 2.21 (m, 1 H, CH), 1.94 (s, 2 H, BH-2 and BH-6), 1.91 (s, 2 H, BH-8 and BH-11), 1.80 (s, 1 H, BH-4), 1.69 (s, 2 H, BH-9 and BH-10), 1.53 (s, 2 H, BH-3 and BH-5) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN): δ = 38.6 ppm. ^{11}B NMR (CD_3CN): δ = 9.6 (s, 1 B, B-12), –12.3 [d, $^1J(^{11}B,^1H)$ = 139 Hz, 2 B, B-8 and B-11], –14.4 [d, $^1J(^{11}B,^1H)$ = 136 Hz, 2 B, B-9 and B-10], –17.3 [d, $^1J(^{11}B,^1H)$ = 152 Hz, 2 B, B-2 and B-6], –18.8 [d, $^1J(^{11}B,^1H)$ = 156 Hz, 2 B, B-3 and B-5], –20.0 [d, $^1J(^{11}B,^1H)$: overlapped, 1 B, B-4], –23.6 (s, 1 B, B-7) ppm. MS (MALDI): *m*/*z* (isotopic abundance) calcd. for **1** ([$CH_{11}B_{11}IO]^-$): 280 (1), 281 (3), 282 (13), 283 (37), 284 (74), 285 (100), 286 (81), 287 (30), 288 (1); found 280 (<1), 281 (2), 282 (15), 283 (35), 284 (72), 285 (100), 286 (80), 287 (30), 288 (<1).

Cs[7-I-12-F-*closo*-CB$_{11}$H$_{10}$] (Cs$^+$1): In a 250 mL Erlenmeyer flask [Et$_4$N]$^+$**1** (1.05 g, 2.5 mmol) was suspended in aqueous hydrochloric acid (30 mL, 10% v/v) and diethyl ether (150 mL) was added. The mixture was stirred until all solid material dissolved. The ether layer was separated and the aqueous phase was extracted twice more with Et_2O (2 × 50 mL). The combined ether solutions were dried with $MgSO_4$, filtered, and most of the solvent was removed. The residue was treated with a solution of CsCl (0.7 g) in water (10 mL). All volatiles were removed under reduced pressure and the solid residue was extracted with acetone (100 mL). The acetone was evaporated and the semi-solid residue was treated with $CHCl_3$ (300 mL). The mixture was stored in a refrigerator for 5 h. The white solid was isolated by filtration. According to ^{11}B NMR spectroscopy the purity is >95%; yield 0.64 g (1.5 mmol, 61%). $CH_{10}B_{11}CsFI$ (419.81): calcd. C 2.86, H 2.40; found C 2.97, H 2.45. Evaporation of the filtrate and drying in vacuo gave a second crop with a higher content of impurities: diiodinated monofluorocarba-*closo*-dodecaborates; yield 0.27 g (0.7 mmol, 26%).

Cs[7-I-12-Cl-*closo*-CB$_{11}$H$_{10}$] (Cs$^+$2): Two fractions of Cs$^+$**2** were obtained in a similar manner to that described for Cs$^+$**1**. First crop: yield 0.34 g (0.8 mmol, 66%). $CH_{10}B_{11}ClCsI$ (436.27): calcd. C 2.75, H 2.31; found C 3.09, H 2.68. Second crop: yield 0.10 g (0.2 mmol, 20%).

Cs[7-I-12-Br-*closo*-CB$_{11}$H$_{10}$] (Cs$^+$3): Two fractions of Cs$^+$**3** were obtained using a method similar to the one described for Cs$^+$**1**. First crop: yield 0.35 g (0.7 mmol, 63%). $CH_{10}B_{11}BrCsI$ (480.72): calcd. C 2.50, H 2.10; found C 2.62, H 2.61. Second crop: yield 0.12 g (0.2 mmol, 21%).

Cs[7-I-12-HO-*closo*-CB$_{11}$H$_{10}$] (Cs$^+$4): The preparation of Cs$^+$**4** was performed in the same manner as described for its halogenated congeners. The only exception is that Cs$^+$**4** could not be precipitated from the acetone solution by addition of chloroform. Hence, the solution containing the cesium salt was evaporated to dryness and only one fraction of Cs$^+$**4** was isolated; yield 0.21 g (0.5 mmol, 81%). $CH_{11}B_{11}CsIO$ (417.82): calcd. C 2.87, H 2.65; found C 3.01, H 3.26.

Crystal Structure Determination of Cs[12-HO-*closo*-CB$_{11}$H$_{11}$]·(CH$_3$)$_2$CO: Colorless crystals of Cs$^+$**4**·$(CH_3)_2CO$ suitable for X-ray diffraction were obtained from acetone by slow evaporation of the solvent. A crystal was investigated with an imaging plate diffraction system (IPDS, Stoe & Cie) using Mo-K_α radiation (λ = 0.71073 Å) at 150 K. The salt crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with Z = 2, and cell dimensions of a = 8.896(5) Å, b = 8.968(4) Å, c = 10.837(7) Å, α = 87.74(7)°, β = 76.80(8)°, γ = 89.73(6)°, and V = 841.0(8) Å^3; $\rho_{calcd.}$ = 1.650 Mg m^{-3}, μ(Mo-K_α) = 4.020 mm^{-1}, F(000) = 440. Face-indexed absorption corrections were applied. A total of 13011 reflections were collected ($1.0 < \theta_{max} < 25.1°$). The structure was solved by direct methods[28] and refinement based on full-matrix least-squares calculations on F^2 with 2989 independent reflections [2049 independent reflections with $I > 2\sigma(I)$], 195 variables, and 2 restraints.[29] The positions of the H atoms were located from ΔF-synthesis with the hydroxy H atom being the only exception. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined using idealized bond lengths as well as angles, and their isotropic displacement parameters were kept equal to 140% for the methyl H atoms and the H atom of the OH substituent and equal to 130% for the H atoms bonded to boron. The positions of the cesium and the iodine atom were split. The occupancies for both positions of each atom were refined with identical anisotropical displacement parameters for cesium and iodine as 86 and 14%, respectively. These occupancy factors were fixed and then the anisotropical displacement parameters were allowed to refine without any restraints. The final refinement resulted in $R_1[F_o^2 > 2\sigma(F_o^2)]$ = 0.050, wR_2 = 0.129 (all data), $w = 1/[\sigma^2(F_o^2) + (0.059P) + 3.250P]$, with $P = (F_o^2 + 2F_c^2)/3$, S = 1.016, $\Delta\rho_{max}/\Delta\rho_{min}$ = +1.676 and –0.859 e Å^{-3}.

The molecular structure diagram was drawn with the program Diamond 3.1.[30] CCDC-705476 contains the supplementary crystallographic data for Cs$^+$**4**·$(CH_3)_2CO$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum Chemical Calculations: Density functional calculations (DFT)[31] were carried out using Becke's three-parameter hybrid functional and the Lee–Yang–Parr correlation functional (B3LYP).[32] Geometries were optimized, and energies were calculated with the 6-311++G(d,p) basis set for all atoms except iodine. Diffuse functions were incorporated because improved energies are

obtained for anions.[33] For the core electrons of iodine the relativistic effective large-core potential denoted ECP46MDF[34] was used and for the valence electrons the 6-311G(d) basis set was applied.[35] Test calculations on HI, I_2, and BI_3 showed that the combination of basis sets used for iodine and the lighter atoms used in this study results in reliable predictions for the structural parameters. All structures represent true minima with no imaginary frequency on the respective hypersurface. All calculations were carried out using the Gaussian 03 program suite.[36] DFT-GIAO[37] NMR shielding constants $\sigma(^{11}B)$, $\sigma(^{13}C)$, and $\sigma(^{19}F)$ were calculated at the B3LYP/6-311++G(2d,p) [iodine: ECP46MDF + 6-311G(d)] level of theory using the geometries computed as described. The ^{11}B, ^{13}C, and ^{19}F NMR shielding constants were calibrated to the respective chemical shift scale $\delta(^{11}B)$, $\delta(^{13}C)$, and $\delta(^{19}F)$ using predictions on diborane(6), Me_4Si, and $CFCl_3$ with chemical shifts of –16.6 ppm for B_2H_6[38] and 0 ppm for Me_4Si as well as for $CFCl_3$.[39]

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