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Microwave-Assisted Alkylation of $[CB_{11}H_{12}]^-$ and Related Anions

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A total of 19 permethylated derivatives of substituted $[CB_{11}H_{12}]^-$ anions have been prepared using alkylation with microwave assistance. The reactions proceed much faster and more cleanly than under ordinary conditions. Microwave assistance is especially convenient for the permethylation of carborane anions carrying electron-withdrawing groups in positions 1 and/or 12. Even $[1\text{-F-}CB_{11}H_{11}]^-$ can be undecamethylated, whereas under ordinary heating, it has only been hexamethylated.

Introduction

Many derivatives of the $[CB_{11}H_{12}]^-$ anion[1] have been reported over the years,[2−6] and polyalkylated anions have been of particular interest in our laboratory.[7,8] Highly alkylated carborane anions have remarkable properties, related to their high lipophilicity. They have a striking solubilizing ability for large organic[9] and "naked" alkali-metal[10] cations in solvents of low polarity. In poorly ligating solvents, their lithium salts strongly catalyze pericyclic reactions[11] and the radical-induced polymerization of terminal alkenes, such as isobutylene.[12,13]

The relatively electron-rich nature of the BH vertices in $[CB_{11}H_{12}]^-$ and similar anions, particularly in position 12 and only a little less in positions 7−11, is reflected in their reactivity toward electrophilic reagents. Methyl triflate,[7,8] methyl bromide,[14] or a trimethylaluminum/methyl iodide mixture[15] are capable of replacing all boron-bound hydrogen atoms with methyl substituents. However, alkylation of these anions with alkyl triflates often proceeds very slowly at room temperature[16] and yields triflyloxylated byproducts at higher temperatures. We now report that microwave heating permits a much easier synthesis of several known highly methylated carborate anions and affords previously inaccessible ones.

Results

The carborane anions **1a**−**19a** were converted to the permethylated anions **1b**−**19b** by the standard methylation procedure with methyl triflate in sulfolane in the presence of CaH_2,[17] but with microwave assistance (Scheme 1 and Table 1). The base is needed to neutralize the triflic acid byproduct, which would otherwise tend to protonate the methyl groups to produce methane, placing triflyloxy substituents on the cage.

The permethylation of $[1\text{-I-}CB_{11}H_{11}]^-$ (**3a**) illustrates the difference between the conventional thermal (Figure 1) and microwave (Figure 2) conditions. Ordinary methylation of this anion proceeds very slowly at room temperature and is only complete after 6 weeks.[16] We now find that increasing the temperature to 70 °C shortens the reaction time to 4 days, and microwave-assisted reaction under the same reaction conditions, including temperature, provides the fully methylated product in 90 min.

The methylation reaction employed a smaller excess of the methylation agent than was found desirable in earlier work (20 equiv per 1 equiv of the carborate anion). The time needed for permethylation depends on the substituents X and Y present in positions 1 and 12 of the CB_{11} cage, respectively (Scheme 1). Permethylation proceeds best for carborane

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Scheme 1

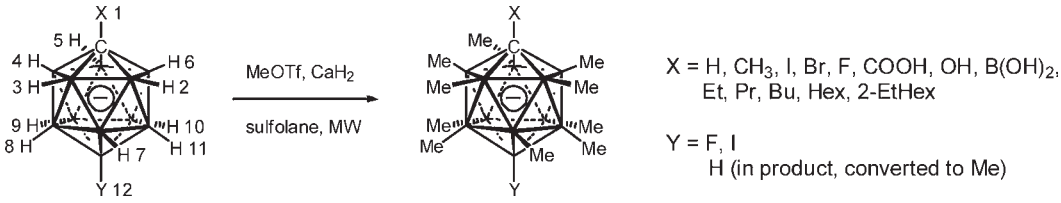

Table 1. Microwave-Assisted Permethylation (see Scheme 1)

starting material $[1\text{-X-12-Y-CB}_{11}\text{H}_{10}]^-$					product $[1\text{-X-12-Y-CB}_{11}\text{Me}_{10}]^-$			
no.	X	Y	scale (mmol)	MW heating[a] (min/deg)	no.	X	Y	isolated yield (%)
1a	H	H	0.4−1.5	30/60, 20/100	**1b**	H	Me	82
2a	Me	H	0.3−1.5	30/60, 30/100	**2b**	Me	Me	83
3a	I	H	0.3−1.8	20/60, 30/80, 10/100	**3b**	I	Me	76
4a	Br	H	0.2−1.6	20/60, 30/80, 10/100	**4b**	Br	Me	83
5a	F	H	0.2−1.1	30/60, 45/90, 60/100	**5b**	F	Me	78
6a	COOH	H	1.2	30/70, 30/100	**6b**	COOMe	Me	86
7a	OH	H	0.1−1.0	60/60, 30/70, 60/80	**7b**	OMe	Me	78
8a	$B(OH)_2$	H	0.5	30/50, 10/60, 10/80	**8b**	$B(OH)_2$	Me	79
9a	H	I	0.6	30/60, 20/80, 10/100	**9b**	H	I	74
10a	Me	I	0.5−2.0	30/60, 20/80, 10/100	**10b**	Me	I	80
11a	Et	I	0.5	120/80	**11b**	Et	I	78
12a	Pr	I	0.3	150/80	**12b**	Pr	I	57
13a	Bu	I	0.5	150/80	**13b**	Bu	I	77
14a	Hex	I	2.0	150/80	**14b**	Hex	I	73
15a	2-EtHex	I	0.5	120/60, 300/80	**15b**	2-EtHex	I	69
16a	COOH	I	0.6	20/45, 20/50, 20/60, 20/70, 10/75	**16b**	COOMe	I	70
17a	H	F	2.0	30/50, 60/70	**17b**	H	F	80
18a	Me	F	0.4−1.3	30/60, 30/80, 30/90, 30/100	**18b**	Me	F	81
19a	Hex	F	0.4−1.0	30/60, 30/80, 90/90	**19b**	Hex	F	52

[a] A sequence of microwave heating regimes. For instance, "30/60, 20/100" means heating for 30 min at 60 °C, followed by heating for 20 min at 100 °C.

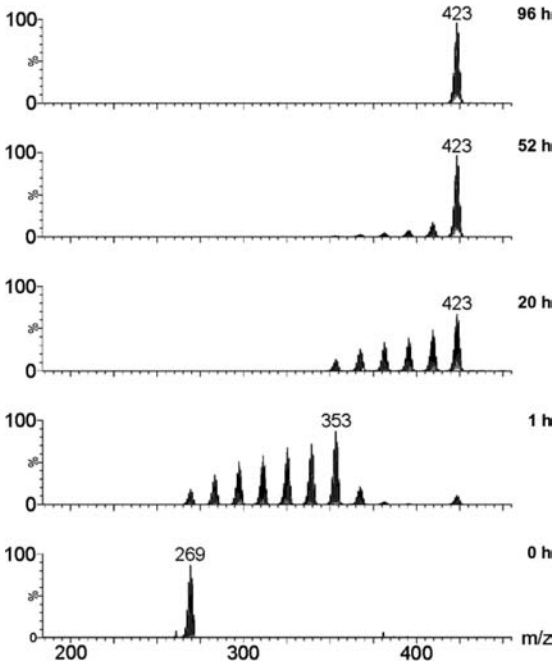

Figure 1. Methylation of $[1\text{-I-CB}_{11}\text{H}_{11}]^-$ with methyl triflate under conventional heating to 70 °C: ESI(−)-MS of samples withdrawn at the times specified.

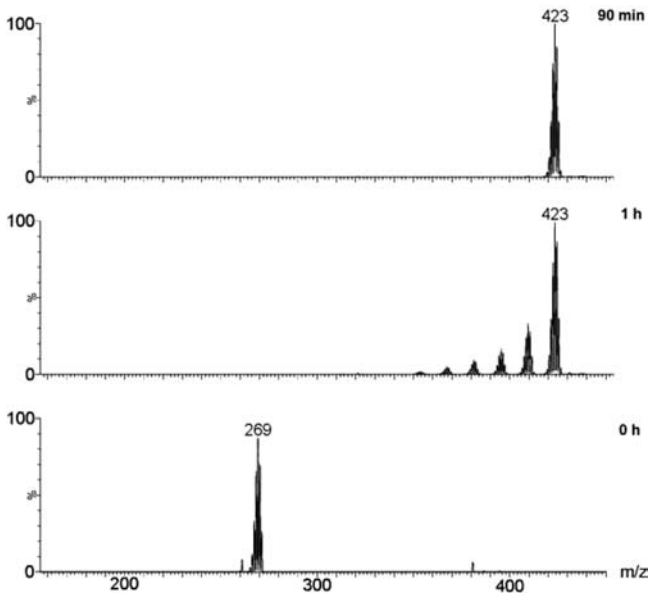

Figure 2. Methylation of $[1\text{-I-CB}_{11}\text{H}_{11}]^-$ with methyl triflate under microwave heating to 70 °C: ESI(−)-MS of samples withdrawn at the times specified.

anions carrying electron-withdrawing groups in these positions (Table 1; **3a**−**6a** and **16a**−**19a**). The 1-fluoro anion **5a** is undecamethylated under microwave assistance, whereas it was only hexamethylated under conventional conditions.[16]

When position 1 carries an alkyl or another electron-donating group, the reaction is faster but it yields mixtures containing substantial amounts of triflyloxylated carborane anion byproducts. The unwanted triflyloxy substitution is suppressed when an iodine substituent is present in position 12 (Table 1; **9a**−**16a**). The 12-iodo anions are permethylated smoothly and without significant side reactions.

Table 2. NMR Chemical Shifts δ in [1-X-12-Y-CB11Me10]$^-$ in Acetone-d_6

	[1-X-12-Y-$CB_{11}Me_{10}$]$^-$		^{1}H NMR			^{13}C NMR				^{11}B NMR		
entry	X	Y	CH_3(2−6)	CH_3(7−11)	CH_3(12)	C(1)	CH_3(2−6)	CH_3(7−11)	CH_3(12)	B(2−6)	B(7−11)	B(12)
1b[a]	H	Me	−0.17	−0.40	−0.52	61.08	−2.00	−3.90	−3.10	−11.17	−7.79	0.33
2b[a]	Me	Me	−0.32	−0.39	−0.50	51.55	−3.30	−3.30	−2.50	−10.00	−7.90	0.18
3b[a]	I	Me	−0.17	−0.36	−0.50	43.94	−1.30	−3.30	−3.00	−9.21	−8.19	1.07
4b[a]	Br	Me	−0.18	−0.37	−0.50	63.74	−1.80	−3.30	−3.30	−9.60	−8.56	−0.04
5b	F	Me	−0.20	−0.39	−0.52	104.50	−4.40	−3.90	−3.70	−11.71	−10.56	−4.75
6b	COOMe	Me	−0.11	−0.38	−0.46	64.65	−2.25	−3.45	−2.30	−8.76	−6.99	−4.29
7b	OMe	Me	−0.10	−0.41	−0.53	93.61	−2.80	−3.80	−3.40	−10.40	−9.71	−3.83
8b	$B(OH)_2$	Me	−0.07	−0.39	−0.48	55.95	−2.20	−3.50	−2.40	−9.27	−6.01	4.37
11b	Et	I	−0.15	−0.25		61.54	−2.10	−0.70		−9.75	−7.99	−4.12
12b	Pr	I	−0.15	−0.25		61.40	−2.15	−0.65		−9.76	−8.02	−4.16
13b	Bu	I	−0.15	−0.25		61.30	−2.25	−0.75		−9.74	−8.01	−4.07
14b	Hex	I	−0.15	−0.25		61.39	−1.90	−0.60		−9.74	−8.01	−4.11
15b	2-EtHex	I	−0.13	−0.24		62.51	−2.10	−0.60		−9.68	−7.93	−3.93
16b	COOMe	I	−0.07	−0.21		66.60	−1.90	−0.75		−9.11	−7.58	−1.60
17b	H	F	−0.17	−0.30		53.38	−3.00	−4.85		−13.81	−9.85	12.89
18b	Me	F	−0.34	−0.30		48.24	−4.00	−4.55		−12.29	−9.96	12.70
19b	Hex	F	−0.19	−0.31		50.78	−2.80	−4.40		−11.84	−9.56	13.23
21	COOH	Me	−0.07	−0.38	−0.47	64.59	−2.40	−3.65	−2.65	−8.76	−7.09	−4.15
22	COOH	H	−0.08	−0.24		70.65	−1.50	−1.50		−8.77	−7.60	0.84

[a] Less complete NMR data have already been reported.[6,8]

Many of the same microwave-assisted reactions were attempted with additional alkyl triflates (EtOTf, BuOTf, R^fCH_2-OTf), milder and cheaper alkylation reagents (Me_2SO_4, $(MeO)_2CO$, MeI, EtI, EtBr, AllylBr), solvents (sulfolane, CH_2Cl_2, $(EtO)_3PO$, $(MeO)_3PO$, CH_3NO_2, neat), and bases (CaH_2, NaH, DMAP, DTBPy, DTBMP), but all of these reactions produced mixtures instead of pure single products. The situation was again best with electron-withdrawing substituents in positions 1 and 12.

Interesting observations were made during the attempted reduction of the [1-CH_3OCO-$CB_{11}Me_{11}$]$^-$ anion (**6b**) to the [1-$HOCH_2$-$CB_{11}Me_{11}$]$^-$ anion. The reduction of the ester by conventional methods using $LiAlH_4$ or $LiEt_3BH$ at room temperature or at reflux failed, and the starting material was recovered. Ester reduction was achieved only when the carborane cage was not methylated. The [1-CH_3OCO-$CB_{11}H_{11}$]$^-$ anion (**6a**) was reduced slowly under harsh conditions to the desired [1-$HOCH_2$-$CB_{11}H_{11}$]$^-$ anion (**20**), but subsequent microwave-assisted methylation of **20** only produced mixtures.

Similarly, hydrolysis of the ester **6b** to [1-HOCO-$CB_{11}Me_{11}$]$^-$ (**21**) by conventional methods using KOH, *tert*-BuOK, MeONa, Li_2Se, or BBr_3 at room temperature or at reflux also failed. However, we noticed that the removal of the iodine substituent in the ester [1-CH_3OCO-12-I-$CB_{11}Me_{10}$]$^-$ (**16b**) by Na/NH_3 reduction was accompanied by cleavage of the ester group and yielded the [1-HOCO-12-H-$CB_{11}Me_{10}$]$^-$ anion (**22**). We then applied similar reducing conditions to the conversion of **6b** into the free acid **21** and found that the reaction was accomplished easily.

The availability of a series of variously substituted analogues of the [$CB_{11}Me_{12}$]$^-$ anion offered an opportunity to characterize substituent effects on the ^{11}B and ^{13}C NMR chemical shifts. We have used 2D NMR techniques to assign all signals unambiguously and collect the results in Table 2.

Discussion

The use of microwave heating greatly facilitates the synthesis of polymethylated derivatives of the [$CB_{11}H_{12}$]$^-$ anion. The mechanism of acceleration is not clear, but it appears likely that it is related to the specific delivery of kinetic energy to charged particles, possibly enhancing the anion reactivity by dissociating ion aggregates or tight ion pairs. Combined with the recent discovery that triflyloxy substituents can be replaced with methyls[18] or hydrogens,[19] the present results make a variety of polymethylated CB_{11} anions readily accessible.

A clear pattern regarding the effect of substituents in positions 1 and 12 has now emerged in the methylation reaction with methyl triflate. Electron-donating alkyl substituents accelerate methylation but also promote the side reaction that introduces triflyloxy substituents. Curiously, methyl is not nearly as detrimental in this regard as the longer alkyls. Electronegative substituents slow down methylation and suppress triflyloxylation entirely.

In spite of this synthetic advance, permethylation of general substituted CB_{11} anions still faces serious restrictions, as the vigorous conditions of the methylation reaction severely limit the range of organic structures that can be tolerated. Multiple bonds, aromatic rings, and groups with lone pairs cannot be present, and such substituents must be introduced only after the methylation step.

Clean peralkylation with groups other than methyl remains an unsolved synthetic problem. Under conditions that we tried, mixtures of incompletely alkylated anions and/or anions carrying triflyloxy substituents were obtained. Subsequent treatment with trialkylaluminum reagents or with KC_8 would allow a replacement of the triflyloxy groups with alkyls[18] or hydrogens,[19] respectively, but in most instances, poorly separable mixtures would still result. This may be immaterial if the purpose of alkylation is to enhance the solubility of lithium salts in nonpolar solvents in order to use them as catalysts,[18] but it will be a problem whenever pure substances are required for further work.

The NMR chemical shifts listed in Table 2 complement previously reported data.[6] Substitution in positions 1 and 12 of the carborane cage has little effect on the chemical shift of the methyl protons but affects the ^{13}C and ^{11}B NMR chemical shifts profoundly. The chemical shift of the cage

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carbon, C(1), is determined by the electronic nature of the substituent. An attachment of an electron-withdrawing substituent results in a downfield shift, whereas electron-donating substituents induce an upfield shift relative to the parent $[HCB_{11}Me_{11}]^-$. The ^{13}C chemical shifts of $CH_3(7-11)$ reflect substitution at vertex 12. These carbons resonate in the range −3.90 to −3.30 ppm for the 12-Me anions, from −0.75 to −0.60 ppm for the 12-I anions, and from −4.85 to −4.40 ppm for the 12-F anions. The opposite effects of the fluoro and iodo substituents are presumably due to the different relative importance of the σ and π effects of these substituents.

^{11}B NMR spectra reflect the antipodal effect,[20] and the chemical shift of B(12) is very sensitive to substitution not only in position 12 but also in position 1. The effects of the fluorine substituent in these two positions are opposite, presumably again reflecting its dual short-range σ-withdrawing and long-range π-donating nature.

Finally, we point out the remarkable degree of steric hindrance introduced into position 1 by the presence of methyl groups in the surrounding five positions and possibly also by the buttressing effect of groups present elsewhere on the carborane cage. The successful conversion of the methoxycarbonyl group into a carboxyl group under reducing conditions may have a general significance in that it could be a general reaction for cleaving bonds that are "benzylic" to the CB_{11} cage.

The extreme difficulties observed in our attempts to perform reactions on the methoxycarbonyl group of the methylated 1-MeOCO-substituted anions suggest that substitution with highly alkylated CB_{11}^- groups may provide a uniquely high protection for otherwise extremely reactive moieties.

Experimental Part

Materials. All experimental manipulations were carried out under an inert atmosphere. Sulfolane (reagent grade, Aldrich) was vacuum-distilled from CaH_2 or dried with molecular sieves (4 Å). Tetrahydrofuran (THF) was dried and distilled from $LiAlH_4$. CaH_2 and methyl triflate (Aldrich) were reagent grade and used as purchased (Aldrich). $[Me_3NH][CB_{11}H_{12}]$ (**1a**) was purchased from Katchem Ltd. (Elišky Krásnohorske 6, 1 Prague 110 00, Czech Republic). The compounds **2a**,[8,17] **3a**,[16] **4a**,[16] **5a**,[21] **7a**,[22] **9a**,[22] **10a**,[8] **11a**,[18] **12a**,[18] **13a**,[18] **14a**,[18] and **15a**[18] were prepared according to published procedures.

Equipment and Measurements. NMR spectra were measured in acetone-d_6, and the following referencing was used: ^1H, residual signal of acetone-d_6 (δ = 2.05 ppm); ^{13}C, signal of acetone-d_6 for a deuteriomethyl group (δ = 29.80 ppm); ^{11}B, signal of $BF_3 \cdot Et_2O$ as an external standard in a coaxial capillary (δ = 0.00 ppm); ^{19}F, signal of hexafluorobenzene as an external standard in a coaxial capillary (δ = −163.00 ppm). ^1H and ^{13}C NMR spectra were recorded with Bruker Avance 500 and 600 spectrometers working at 500.0, 499.8, and 600.1 MHz for ^1H NMR and 125.7 and 150.9 MHz for ^{13}C NMR, respectively. $^1H\{^{11}B\}$, ^{11}B, $^{11}B\{^1H\}$, ^{19}F, $^{19}F\{^1H\}$, and $^{19}F\{^{11}B\}$ NMR spectra were recorded with a Bruker Avance 500 spectrometer working at 499.8 MHz for ^1H NMR, 160.4 MHz for ^{11}B NMR, and 470.3 MHz for ^{19}F NMR, respectively. Boron signals were assigned using $^{11}B-^{11}B$ COSY. Carbon signals of C-1 and methyl groups attached to boron are not directly detectable because of $^{11}B-^{13}C$ coupling, and therefore H,C-HSQC and H,C-HMBC techniques were used for the assignment of ^{13}C NMR resonances. The methyl groups in positions 2−6 were identified by a H,C-HMBC experiment that showed cross-peaks between their protons and that at C-1. Electrospray ionization mass spectrometry (ESI-MS) spectra were recorded with a Waters Micromass ZQ spectrometer. IR spectra were recorded with a Bruker EQUINOX 55 (IFS 55) spectrometer in KBr pellets or in CCl_4 (0.1 mm cell). Elemental analyses were obtained using a Perkin-Elmer PE 2400 Series II analyzer. All microwave experiments were performed in a CEM Discover S-class or Biotage AB Initiator EXP Microwave synthesis system in septum-capped 10, 20, or 35 mL microwave tubes with magnetic stirring. The temperature was measured by an IR camera, and the power was usually about 1 W/10 °C. Open-vessel experiments were performed in the CEM system. Because of hydrogen evolution, the sealed vessels become pressurized during the reaction. The CEM system allows work in the open-vessel mode, which was used in some cases and is recommended.

General Procedure for Cation Exchange from $NHMe_3^+$ to Cs^+. A $NHMe_3^+$ salt of the carborate (10 mmol) was suspended in 30 mL of water (high-performance liquid chromatography, HPLC), and a solution of $CsOH \cdot H_2O$ (30 mmol) in 30 mL of water (HPLC) was added. This solution was stirred for 30 min and then was evaporated to dryness. The solid was again treated with water (80 mL) and concentrated to ∼15 mL. The suspension was extracted with diethyl ether (3 × 150 mL). The combined organic phase was dried over Cs_2CO_3. Diethyl ether was evaporated, and the solid cesium salt was dried at 10^{-2} mbar and 120−140 °C.

Trimethylammonium 1-Carba-*closo*-dodecaborate-1-carboxylic Acid (6a). This salt was prepared by modification of a literature procedure.[22] $Cs[CB_{11}H_{12}]$ (**1a**; 1.0 g, 3.6 mmol) was placed in a dry Schlenk flask. The flask was charged with argon, and THF (50 mL, freshly distilled from $LiAlH_4$) was added. The solution was cooled to −78 °C and degassed. A solution of *n*-BuLi (4.4 mL, 1.6 M in hexane, 7.0 mmol) was added at once, and the mixture was stirred for an additional 10 min at −78 °C. The flask was then placed into the ice bath and stirred for 1 h. A white precipitate of $Li[1\text{-}Li\text{-}CB_{11}H_{11}]$ formed during this period. Powdered CO_2 (excess) was added at −78 °C, and the reaction mixture was allowed to warm up to room temperature. Stirring was continued for another 2 h, and completion of the reaction was checked by ESI-MS. Water was added slowly, and the reaction mixture was evaporated to dryness. The residue was purified by partitioning between water and Et_2O. The ether layer contained unreacted $[CB_{11}H_{12}]^-$, and the water layer contained a salt of the pure desired product. The water layer was removed and acidified by the addition of HCl (20%) to pH ∼2. The product was precipitated as the $NHMe_3^+$ salt by the addition of $NHMe_3Cl$. The white solid was filtered off, washed with water and pentane, and dried under vacuum (10^{-2} mbar/120 °C) to obtain 710 mg of pure $NHMe_3[1\text{-}HOCO\text{-}CB_{11}H_{11}]$ (**6a**) as a white solid in 80% yield. $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 1.62 (bs, 5H, H-7,8,9,10,11), 1.79 (bm, 1H, H-12), 1.98 (bs, 5H, H-2,3,4,5,6), 3.19 (s, 9H, CH_3N). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 46.02 (CH_3N), 68.59 (C-1), 168.24 (COO). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −13.17 (bs, 5B, B-2,3,4,5,6), −12.31 (bs, 5B, B-7,8,9,10,11), −5.52 (bs, 1B, B-12). IR (KBr pellet): ν 3178 (m) and 3145 (s, ν(NH), TMA), 2750 and 2707 (w, ν(OH), dimer), 2594 (s), 2568 and 2538 (vs, ν(B−H)), 1698 (s, ν(C=O), dimer), 1472, 1455, and 1445 (m, $\nu_{as}(CH_3)$, TMA), 1433 (m) and 1313 (s, ν(C−O), β(COH)), 1414 (m, $\delta_s(CH_3)$, TMA), 1392 (w, δ(NH), TMA), 1249 and 1229 (w, $\delta_{as}(CH_3)$), 1030 (m), 1050 (m), 731 (w) and 719 (m, δ(B−H)), 975 (m; ν_{as}(CN), TMA), 836 and 813 (w, ν_s(CN), TMA) cm^{-1}. ESI(−)-MS: *m*/*z* 187, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{26}H_{32}B_{11}O_2P$: C, 59.32; H, 6.13. Found: C, 59.46; H, 6.07.

Trimethylammonium 1-Carba-*closo*-dodecaborate-1-boronic Acid (8a). **1a** (600 mg, 2.2 mmol) was placed in a dry Schlenk flask. The flask was charged with argon, and THF (40 mL, freshly distilled from $LiAlH_4$) was added. The solution was cooled to −78 °C and degassed. A solution of *n*-BuLi (2.8 mL, 1.6 M in

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hexane, 4.5 mmol) was added at once, and the mixture was stirred for an additional 10 min at −78 °C. The flask was then placed into an ice bath and stirred for 1 h. A white precipitate of Li[1-Li-$CB_{11}H_{11}$] formed during this period. Trimethyl borate (520 mg, 5 mmol) was added at −78 °C, and the reaction mixture was allowed to warm to room temperature. Stirring was continued for another 20 h, and completion of the reaction was checked by ESI-MS. Water was added slowly, and the reaction mixture was evaporated to dryness. The residue was dissolved in hot water, and the product was precipitated as an $NHMe_3^+$ salt by the addition of $NHMe_3Cl$. The white solid was filtered off, washed with water and pentane, and dried under vacuum (10^{-2} mbar/120−140 °C) to obtain 337 mg of pure $NHMe_3$[1-$(HO)_2$B-$CB_{11}H_{11}$] (**8a**) as a white solid in 62% yield. $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 1.64 (bs, 5H, H-7,8,9,10,11), 1.74 (bs, 5H, H-2,3,4,5,6), 1.80 (bm, 1H, H-12), 3.14 (s, 9H, CH_3N), 5.93 (bs, 2H, $B(OH)_2$). ^{13}C NMR (150.9 MHz, acetone-d_6): δ 45.84 (CH_3N), 58.34 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −13.57 (bs, 5B, B-2,3,4,5,6), −11.12 (bs, 5B, B-7,8,9,10,11), −4.47 (bs, 1B, B-12), 29.22 (bs, 1B, $B(OH)_2$). IR (KBr pellet): ν 3555, 3533, and 3412 (bm, ν(OH)), 3180 (m, $\nu(Me_3N^+$-H)), 2541 (vs, ν(B−H)), 1478, 1469, and 1453 (m, $\delta_{as}(CH_3)$, TMA), 1414 (m, $\delta_{as}(CH_3)$, TMA), 1403 (m, $\delta(Me_3N^+$-H)), 1367 (m), 1330 (m) and 1309 (s, ν(B−OH)), 1251 and 1231 (w, r(CH_3), TMA), 1051 (m), 1023 (m), 974 (m, ν_{as}(CN), TMA), 852 and 808 (w, ν_s(CN), TMA), 725 (m, δ(B−H)) cm^{-1}. ESI(−)-MS: *m*/*z* 187, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{25}H_{33}B_{12}O_2P$: C, 57.06; H, 6.32. Found: C, 57.15; H, 6.36.

Trimethylammonium 12-Iodo-1-carba-*closo*-dodecaborate-1-carboxylic Acid (16a). 6a (0.3 g, 1.2 mmol) was dissolved in glacial acetic acid (20 mL), and iodine was added (610 mg, 2.4 mmol). The reaction mixture was heated for 48 h at 60 °C. The progress of the reaction was checked by ESI-MS. After completion, the solution of Na_2SO_3 (20%) was added to remove excess iodine. The reaction mixture was evaporated to dryness by azeotropic distillation in the presence of toluene and dried under vacuum. The residue was dissolved in a minimum amount of water, and the product was precipitated by the addition of $NHMe_3Cl$. The white solid was filtered off, washed with water and pentane, and dried under vacuum (10^{-2} mbar/120−140 °C) to obtain 363 mg of pure $NHMe_3$[1-HOCO-12-I-$CB_{11}H_{10}$] (**16a**) as a white solid in 81% yield. $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 1.97 (bs, 5H, H-2,3,4,5,6), 2.05 (bs, 5H, H-7,8,9,10,11), 3.04 (s, 9H, CH_3N). ^{13}C NMR (150.9 MHz, acetone-d_6): δ 44.74 (CH_3N), 66.78 (C-1), 168.79 (COO). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −15.86 (bs, 1B, B-12), −13.04 (bs, 5B, B-2,3,4,5,6), −10.92 (bs, 5B, B-7,8,9,10,11). IR (KBr pellet): ν 3175, 3108, and 3024 (m, ν(NH), TMA), 2568 and 2549 (vs, ν(B−H)), 1746 (w), 1728 (m) and 1703 (m, ν(CO)), 1477, 1467, and 1452 (m, $\nu_{as}(CH_3)$, TMA), 1414 (w, $\delta_s(CH_3)$, TMA), 1371 (m, δ(NH), TMA), 1264 and 1253 (m, ν(C−O), β(COH)), 1037 (w), 727 (m) and 715 (m, δ(B−H)), 976 (m, ν_{as}(CN), TMA), 824 (w, ν_s(CN), TMA), 806 (m, ν(B−I)), 461 (vw, δ_s(CN), TMA) cm^{-1}. ESI(−)-MS: *m*/*z* 313, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{26}H_{31}B_{11}IO_2P$: C, 47.87; H, 4.79. Found: C, 47.98; H, 4.63.

General Procedure A (Fluorination of [1-X-12-H-$CB_{11}H_{10}$]$^-$ in Position 12). A 120 mL PFA reactor (Savillex) equipped with a magnetic stirring bar was charged with Cs[1-X-12-H-$CB_{11}H_{10}$] (5 mmol) and liquid anhydrous HF (70 mL) at −78 °C. [***Caution!*** *HF is extremely hazardous and should only be handled by trained personnel!*] The PFA reactor was capped and stirred for 4−14 days at 25 °C. After removal of HF under reduced pressure, a white solid remained in the reactor. The residue was dissolved in excess water (HPLC), neutralized with NH_4OH (15%), and filtered on a glass frit, and the filtrate was concentrated with a rotary evaporator to 60−80 mL. This solution was treated with trimethylammonium chloride (30%). The precipitate was filtered off, washed with water and then pentane, and vacuum-dried to provide the product [1-X-12-F-$CB_{11}H_{10}$]$^-$.

Trimethylammonium 12-Fluoro-1-carba-*closo*-dodecaborate (17a).[23]**.** The desired product was prepared according to the general procedure A, starting from **1a** (2 g, 7.25 mmol) in liquid anhydrous HF (100 mL) after 4 days. $NHMe_3$[12-F-$CB_{11}H_{11}$] (**17a**) was isolated as a white solid (1.25 g, 78% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 1.46 (bs, 5H, H-2,3,4,5,6), 1.67 (bs, 5H, H-7,8,9,10,11), 1.96 (bm, 1H, H-1), 3.17 (s, 9H, CH_3N). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 36.08 (C-1), 46.02 (CH_3N). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −18.56 (bs, 5B, B-2,3,4,5,6), −14.14 (bs, 5B, B-7,8,9,10,11), 14.51 (bs, 1B, B-12). $^{19}F\{^{11}B\}$ NMR (470.3 MHz, acetone-d_6): δ −192.85. IR (KBr pellet): ν 3209 (s, ν(NH), TMA), 2568, 2544, and 2512 (vs, ν(B−H)), 1478 (m), 1468 (m), 1454 (w, $\nu_{as}(CH_3)$, TMA), 1416 (w, $\delta_s(CH_3)$, TMA), 1386 (w, δ(NH), TMA), 1253 and 1232 (vw, $\delta_{as}(CH_3)$, TMA), 1180 (w), 1157 (m) and 1143 (w, ν(B−F)), 1012 (m) and 731 (m, δ(B−H)), 977 (m, ν_{as}(CN), TMA), 824 (w, ν_s(CN), TMA) cm^{-1}. ESI(−)-MS: *m*/*z* 161, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{25}H_{31}B_{11}FP$: C, 60.00; H, 6.24. Found: C, 60.11; H, 6.27.

Trimethylammonium 12-Fluoro-1-methyl-1-carba-*closo*-dodecaborate (18a). The desired product was prepared according to the general procedure A, starting from Cs[1-Me-$CB_{11}H_{11}$][7,8,17] (**2a**; 800 mg, 2.76 mmol) in liquid anhydrous HF (50 mL) after 6 days. $NHMe_3$[1-Me-12-F-$CB_{11}H_{10}$] (**18a**) was isolated as a white solid (573 mg in 88% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 1.56 (s, 3H, CH_3), 1.62 (bs, 5H, H-2,3,4,5,6), 1.73 (bs, 5H, H-7,8,9,10,11), 3.18 (s, 9H, CH_3N). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 24.62 (CH_3), 45.27 (CH_3N), 49.76 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −14.53 (bs, 5B, B-2,3,4,5,6), −13.54 (bs, 5B, B-7,8,9,10,11), 13.03 (bs, 1B, B-12). $^{19}F\{^{11}B\}$ NMR (470.3 MHz, acetone-d_6): δ −204.10. IR (KBr pellet): ν 3190 (s, ν(NH), TMA), 2559, 2539, and 2525 (vs, ν(B−H)), 1478 (m), 1471 (m), 1455 (m, $\nu_{as}(CH_3)$, TMA), 1416 (w, $\delta_s(CH_3)$, TMA), 1403 (w, δ(NH), TMA), 1382 (w, $\delta_s(CH_3)$), 1255 and 1233 (w, $\delta_{as}(CH_3)$, TMA), 1178, 1145, and 1123 (m, ν(B−F)), 1027 (m), 1006 (s) and 733 (m, δ(B−H)), 976 (m, ν_{as}(CN), TMA), 828 (w, ν_s(CN), TMA), 461 (vw, δ_s(CN), TMA) cm^{-1}. ESI(−)-MS: *m*/*z* 175, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{26}H_{33}B_{11}FP$: C, 60.70; H, 6.47. Found: C, 60.82; H, 6.41.

Trimethylammonium 12-Fluoro-1-hexyl-1-carba-*closo*-dodecaborate (19a). The desired product was prepared according to the general procedure A, starting from Cs[1-Hex-$CB_{11}H_{11}$][18] (500 mg, 1.39 mmol) in liquid anhydrous HF (40 mL) after 14 days at 40 °C. $NHMe_3$[1-Hex-12-F-$CB_{11}H_{10}$] (**19a**) was isolated and purified by column chromatography on SiO_2 (100 g) in the gradient of dichloromethane/methyl cyanide equal to 8−5:1. After evaporation and drying, the product was obtained as a white solid (199 mg in 47% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.84 (t, 3H, J_{vic} = 7.1 Hz, $CH_3(CH_2)_4CH_2$), 1.14 (m, 2H, $CH_3CH_2CH_2CH_2$-CH_2CH_2), 1.21 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.26 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.29 (m, 2H, $CH_3CH_2CH_2CH_2CH_2$-CH_2), 1.62 (bs, 5H, H-2,3,4,5,6), 1.73 (bs, 5H, H-7,8,9,10,11), 1.84 (m, 2H, $CH_3(CH_2)_4CH_2$), 3.17 (s, 9H, CH_3N). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 14.25 ($CH_3(CH_2)_4CH_2$), 23.19 ($CH_3CH_2CH_2$-$CH_2CH_2CH_2$), 29.80 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 31.71 (CH_3-$CH_2CH_2CH_2CH_2CH_2$), 32.38 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 37.96 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 45.99 (CH_3N), 56.15 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −15.52 (bs, 5B, B-2,3,4,5,6), −13.93 (bs, 5B, B-7,8,9,10,11), 13.79 (bs, 1B, B-12). $^{19}F\{^{11}B\}$ NMR (470.3 MHz, acetone-d_6): δ −202.38. IR (KBr pellet): ν 3190 (s, ν(NH), TMA), 2928 (w, $\nu_{as}(CH_2)$), 2874 (m, $\nu_s(CH_3)$), 2855 (m, $\nu_s(CH_2)$), 2556 (vs, ν(B−H)), 1479 (m) and 1471 (m, $\nu_{as}(CH_3)$, TMA), 1464 (m, $\beta_s(CH_2)$), 1457 (m, $\delta_s(CH_3)$), 1419 (w, $\delta_s(CH_3)$, TMA), 1404 (w, δ(NH), TMA), 1374 (w, $\delta_s(CH_3)$), 1366 (w, $\gamma_s(CH_2)$), 1253 and 1232 (w, $\delta_{as}(CH_3)$, TMA), 1146 (m, ν(B−F)),

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1025 (m), 1005 (s) and 736 (m, δ(B−H)), 976 (m, ν_{as}(CN), TMA), 828 (w, ν_s(CN), TMA), 460 (vw, δ_s(CN), TMA) cm^{-1}. ESI(−)-MS: *m*/*z* 245, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{31}H_{43}B_{11}FP$: C, 63.69; H, 7.41. Found: C, 63.94; H, 7.59.

General Procedure B (Microwave-Assisted Methylation of BH Vertices in [1-X-12-Y-$CB_{11}H_{10}$]$^-$). Calcium hydride (40 mmol) was added to a solution of [1-X-12-Y-$CB_{11}H_{10}$]$^-$ (1 mmol) in sulfolane (15 mL) in a 35 mL microwave tube capped with a rubber septum under an argon atmosphere. The tube was evacuated under reduced pressure and refilled with argon three times. The suspension was stirred at 25 °C for 30 min, methyl triflate (20 mmol) was added, and the rubber septum was quickly replaced with a microwave tube cap. The reaction mixture was placed into the MW system and heated. The reaction was monitored by withdrawing a small aliquot from the tube and checking by ESI-MS to ensure the reaction was complete prior to workup. The reaction mixture was diluted with methylene chloride (50 mL), and the remaining CaH_2 was removed by vacuum filtration and washed with methylene chloride (2 × 50 mL). The filtrate was neutralized with aqueous NH_4OH (25%) under vigorous stirring, and methylene chloride was evaporated. The oily residue was poured onto an excess of crushed ice, the precipitate was formed, and after 30 min, the reaction mixture was extracted with Et_2O (3 × 60 mL). The collected organic layer was washed with CsCl (20%, 3 × 60 mL), and the cesium wash was extracted with Et_2O again. The combined ether solution was dried with Cs_2CO_3, filtered, and evaporated. The resulting solid was a 1:1 complex of the carborane cesium salt and sulfolane. After recrystallization from water and hot filtration, residual sulfolane was distilled off (10^{-3} mbar/120−140 °C) to provide pure Cs[1-X-12-Y-$CB_{11}Me_{10}$]. The procedure was used to prepare the known anions **1b**,[8] **2b**,[7,8,17] **3b**,[16] **4b**,[16] **9b**,[8] and **10b**[8] and several new ones described below. NMR data of the known anions **1**−**4b** were revised and completely assigned by 2D NMR techniques.

Cesium (2−12)-Undecamethyl-1-carba-*closo*-dodecaborate (1b). ^{1}H NMR (500.0 MHz, acetone-d_6): δ −0.52 (bs, 3H, CH_3-12), −0.40 (bs, 15H, CH_3-7,8,9,10,11), −0.17 (bs, 15H, CH_3-2,3,4,5,6), 1.08 (bs, 1H, H-1). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −3.90 (CH_3-7,8,9,10,11), −3.10 (CH_3-12), −2.00 (CH_3-2,3,4,5,6), 61.08 (C-1). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −11.17 (bs, 5B, B-2,3,4,5,6), −7.79 (bs, 5B, B-7,8,9,10,11), 0.33 (bs, 1B, B-12).

Cesium (1−12)-Dodecamethyl-1-carba-*closo*-dodecaborate (2b). ^{1}H NMR (500.0 MHz, acetone-d_6): δ −0.50 (bs, 3H, CH_3-12), −0.39 (bs, 15H, CH_3-7,8,9,10,11), −0.32 (bs, 15H, CH_3-2,3,4,5,6), 0.81 (bs, 3H, CH_3-1).

Cesium 1-Fluoro-(2−12)-undecamethyl-1-carba-*closo*-dodecaborate (5b). The desired product was prepared according to the general procedure B, starting from $NHMe_3$[1-F-$CB_{11}H_{11}$][21] (**5a**; 250 mg, 1.13 mmol), CaH_2 (2.1 g, 50 mmol), and MeOTf (3.77 g, 23 mmol) in sulfolane (15 mL). Cs[1-F-$CB_{11}Me_{11}$] (**5b**) was isolated as a white solid (395 mg in 78% yield). ^{19}F NMR (470.3 MHz, acetone-d_6): δ −191.28. IR (KBr pellet): ν 2931 (s) and 2895 (vs, ν_{as}(CH_3)), 2828 (s, ν_s(CH_3)), 1434 (w, δ_{as}(CH_3)), 1306 (vs, δ_s-(CH_3)), 1151 (m, ν(C−F)), 919 (m, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: *m*/*z* 315, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{36}H_{53}B_{11}FP$: C, 66.04; H, 8.16. Found: C, 66.23; H, 8.01.

Cesium 1-(Methoxycarbonyl)-(2−12)-undecamethyl-1-carba-*closo*-dodecaborate (6b). The desired product was prepared according to the general procedure B, starting from **6a**[22] (300 mg, 1.21 mmol), CaH_2 (2.5 g, 60 mmol), and MeOTf (3.94 g, 24 mmol) in sulfolane (15 mL). Cs[1-MeOCO-$CB_{11}Me_{11}$] (**6b**) was isolated as a white solid (474 mg in 86% yield). ^{1}H NMR (500.0 MHz, acetone-d_6): δ −0.46 (bs, 3H, CH_3-12), −0.38 (bs, 15H, CH_3-7,8,9,10,11), −0.11 (bs, 15H, CH_3-2,3,4,5,6), 3.45 (s, 3H, CH_3O). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −3.45 (CH_3-7,8,9,10,11), −2.30 (CH_3-12), −2.25 (CH_3-2,3,4,5,6), 50.69 (CH_3O); 64.65 (C-1), 167.62 (COO). IR (KBr pellet): ν 2932 and 2896 (s, ν_{as}(CH_3)), 2829 (s, ν_s(CH_3)), 1704 and 1701 (vs, ν(C═O)), 1434 (m, δ_s(CH_3), δ_{as}(CH_3)), 1308 (s), 1303 (s) and 1290 (m, δ_s(CH_3)), 1267 (vs, ν(C−O)), 915 (m, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: *m*/*z* 355, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{38}H_{56}B_{11}O_2P$: C, 65.69; H, 8.12. Found: C, 65.76; H, 8.07.

Cesium 1-Methoxy-(2−12)-undecamethyl-1-carba-*closo*-dodecaborate (7b). The desired product was prepared according to the general procedure B, starting from Cs[1-HO-$CB_{11}H_{11}$][22] (**7a**; 150 mg, 0.51 mmol), CaH_2 (1 g, 24 mmol), and MeOTf (1.67 g, 10.2 mmol) in sulfolane (12 mL). Cs[1-MeO-$CB_{11}Me_{11}$] (**7b**) was isolated as a white solid (183 mg in 78% yield). ^{1}H NMR (499.8 MHz, acetone-d_6): δ −0.53 (bs, 3H, CH_3-12), −0.41 (bs, 15H, CH_3-7,8,9,10,11), −0.10 (bs, 15H, CH_3-2,3,4,5,6), 3.29 (s, 3H, CH_3O). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −3.80 (CH_3-7,8,9,10,11), −3.40 (CH_3-12), −2.80 (CH_3-2,3,4,5,6), 57.79 (CH_3O), 93.61 (C-1). IR (KBr pellet): ν 2929 (s) and 2895 (vs, ν_{as}(CH_3)), 2827 (s, ν_s(CH_3)), 1434 (w, δ_{as}(CH_3)), 1304 (vs, δ_s(CH_3)), 1201 (m, ν_{as}(COC)), 1023 (m, ν_s(COC)), 915 (m, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: *m*/*z* 327, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{37}H_{56}B_{11}OP$: C, 66.65; H, 8.47. Found: C, 66.76; H, 8.39.

Cesium (2−12)-Undecamethyl-1-carba-*closo*-dodecaborate-1-boronic Acid (8b). The product was prepared according to the general procedure B, starting from **8a** (210 mg, 0.85 mmol), CaH_2 (1.5 g, 36 mmol), and MeOTf (2.79 g, 17 mmol) in sulfolane (9 mL). Cs[1-$(HO)_2$B-$CB_{11}Me_{11}$] (**8b**) was isolated as a white solid (318 mg in 79% yield). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −9.27 (bs, 5B, B-2,3,4,5,6), −6.01 (bs, 5B, B-7,8,9,10,11), 4.37 (bs, 1B, B-12), 29.77 (bs, 1B, B$(OH)_2$)). IR (KBr pellet): ν 3630 (m, ν(OH)), 2928 (s) and 2894 (vs, ν_{as}(CH_3)), 2830 (s, ν_s(CH_3)), 1448, 1435, and 1412 (w, δ_{as}(CH_3)), 1358 and 1332 (s, ν(B−OH)), 1308 and 1289 (vs, δ_s(CH_3)), 918 (m), 909 (m) and 890 (w, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: *m*/*z* 341, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{36}H_{55}B_{12}O_2P$: C, 63.54; H, 8.15. Found: C, 63.69; H, 8.23.

Cesium 1-Ethyl-12-iodo-(2−11)-decamethyl-1-carba-*closo*-dodecaborate (11b). The product was prepared according to the general procedure B, starting from Cs[1-Et-12-I-$CB_{11}H_{10}$][18] (**11a**; 200 mg, 0.47 mmol), CaH_2 (784 mg, 18.63 mmol), and MeOTf (1.53 g, 9.32 mmol) in sulfolane (12 mL). Cs[1-Et-12-I-$CB_{11}Me_{10}$] (**11b**) was isolated as a white solid (207 mg in 77% yield). ^{1}H NMR (600.1 MHz, acetone-d_6): δ −0.25 (bs, 15H, CH_3-7,8,9,10,11), −0.15 (bs, 15H, CH_3-2,3,4,5,6), 0.83 (t, 3H, J_{vic} = 7.8 Hz, C$H_3$$CH_2$), 1.60 (bq, 2H, J_{vic} = 7.8 Hz, CH_3CH_2). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −2.10 (CH_3-2,3,4,5,6), −0.70 (CH_3-7,8,9,10,11), 13.10 (CH_3CH_2), 25.28 (CH_3CH_2), 61.54 (C-1). IR (KBr pellet): ν 2937 and 2896 (s, ν_{as}(CH_3), CB), 2972 (w, ν_{as}(CH_3), Et), 2830 (m, ν_s(CH_3)), 1459 (w, δ_{as}(CH_3), β_s(CH_2), Et), 1449, 1432, and 1413 (w, δ_{as}(CH_3), CB), 1377 (vw, δ_s(CH_3), Et), 1309 and 1290 (vs, δ_S(CH_3), CB), 1278 (m), 1255 (m), 1165 (m), 1144 (s, B-CH_3), 1109 (s, B-CH_3), 1086 (w), 1048 (vw), 1033 (w), 920 (w) and 907 (m, ν(B-CH_3), r(CH_3)), 835 (w), 814 (w, ν(B−I)), 736 (w), 688 (vw), 571 (m), 440 (m) cm^{-1}. ESI(−)-MS: *m*/*z* 437, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{37}H_{55}B_{11}IP$: C, 57.22; H, 7.14. Found: C, 57.34; H, 7.07.

Cesium 1-Propyl-12-iodo-(2−11)-decamethyl-1-carba-*closo*-dodecaborate (12b). The product was prepared according to the general procedure B, starting from Cs[1-Pr-12-I-$CB_{11}H_{10}$][18] (**12a**; 123 mg, 0.28 mmol), CaH_2 (470 mg, 11.17 mmol), and MeOTf (914 mg, 5.57 mmol) in sulfolane (10 mL). Cs[1-Pr-12-I-$CB_{11}Me_{10}$] (**12b**) was isolated as a white solid (92 mg in 56% yield). ^{1}H NMR (600.1 MHz, acetone-d_6): δ −0.25 (bs, 15H, CH_3-7,8,9,10,11), −0.15 (bs, 15H, CH_3-2,3,4,5,6), 0.71 (t, 3H, J_{vic} = 7.3 Hz, C$H_3$$CH_2$$CH_2$), 1.31 (m, 2H, CH_3C$H_2$$CH_2$), 1.46 (m, 2H, CH_3CH_2CH_2). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −2.15 (CH_3-2,3,4,5,6), −0.65 (CH_3-7,8,9,10,11), 15.34 ($CH_3CH_2CH_2$), 21.28 ($CH_3CH_2CH_2$), 35.26 ($CH_3CH_2CH_2$), 61.40 (C-1). IR (KBr pellet): ν 2933 and 2897 (s, ν_{as}(CH_3), CB), 2967 (m, ν_{as}(CH_3), Pr), 2870 (m, ν_s(CH_3), Pr), 2830 (m, ν_s(CH_3), CB), 1450, 1437, and

1410 (w, $\delta_{as}(CH_3)$, CB), 1376 (vw, $\delta_s(CH_3)$, Pr), 1308 and 1292 (vs, $\delta_s(CH_3)$, CB), 1278 (m), 1256 (m), 1170 (w), 1147 (s, B-CH_3), 1111 (s, B-CH_3), 1086 (w), 1032 (w), 947 (w), 921 (w), 909 (m) and 895 (w, ν(B-CH_3), r(CH_3)), 832 (w), 810 (m, ν(B−I)), 735 (w), 686 (vw), 571 (m), 439 (m) cm^{-1}. ESI(−)-MS: *m*/*z* 451, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{38}H_{57}B_{11}IP$: C, 57.72; H, 7.27. Found: C, 57.90; H, 7.36.

Cesium 1-Butyl-12-iodo-(2−11)-decamethyl-1-carba-*closo*-dodecaborate (13b). The desired product was prepared according to the general procedure B, starting from Cs[1-Bu-12-I-$CB_{11}H_{10}$][18] (**13a**; 250 mg, 0.55 mmol), CaH_2 (920 mg, 21.86 mmol), and MeOTf (1.80 g, 10.96 mmol) in sulfolane (20 mL). Cs[1-Bu-12-I-$CB_{11}Me_{10}$] (**13b**) was isolated as a white solid (251 mg in 76% yield). ^{1}H NMR (600.1 MHz, acetone-d_6): δ −0.25 (bs, 15H, CH_3-7,8,9,10,11), −0.15 (bs, 15H, CH_3-2,3,4,5,6), 0.82 (t, 3H, J_{vic} = 7.3 Hz, C$H_3$$CH_2CH_2CH_2$), 1.10 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.30 (bm, 2H, $CH_3CH_2CH_2CH_2$), 1.50 (bm, 2H, $CH_3CH_2CH_2CH_2$). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −2.25 (CH_3-2,3,4,5,6), −0.75 (CH_3-7,8,9,10,11), 14.15 ($CH_3CH_2CH_2CH_2$), 24.44 ($CH_3CH_2CH_2CH_2$), 30.14 ($CH_3CH_2CH_2CH_2$), 32.45 ($CH_3CH_2CH_2CH_2$), 61.30 (C-1). IR (KBr pellet): ν 2934 and 2899 (s, $\nu_{as}(CH_3)$, CB), 2957 (m, $\nu_{as}(CH_3)$, Bu), 2870 (m, $\nu_s(CH_3)$, Bu), 2855 (m, $\nu_s(CH_2)$, Bu), 2832 (m, $\nu_s(CH_3)$, CB), 1464 (w, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, Bu), 1448, 1435, and 1412 (w, $\delta_{as}(CH_3)$, CB), 1377 (vw, $\delta_S(CH_3)$, Bu), 1308 and 1299 (vs, $\delta_s(CH_3)$, CB), 1277 (m), 1256 (m), 1146 (s, B-CH_3), 1110 (s, B-CH_3), 1085 (w), 1046 (w), 1032 (w), 989 (w), 920 (w) and 907 (m, ν(B-CH_3), r(CH_3)), 835 (w), 814 (w, ν(B−I)), 734 (w), 688 (vw), 569 (m), 440 (m) cm^{-1}. ESI(−)-MS: *m*/*z* 465, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{39}H_{57}B_{11}IP$: C, 58.21; H, 7.39. Found: C, 58.42; H, 7.48.

Cesium 1-Hexyl-12-iodo-(2−11)-decamethyl-1-carba-*closo*-dodecaborate (14b). The product was prepared according to the general procedure B, starting from Cs[1-Hex-12-I-$CB_{11}H_{10}$][18] (**14a**; 1 g, 2.06 mmol), CaH_2 (3.47 g, 82.44 mmol), and MeOTf (6.76 g, 41.19 mmol) in sulfolane (35 mL). Cs[1-Hex-12-I-$CB_{11}Me_{10}$] (**14b**) was isolated as a white solid (940 mg in 73% yield). ^{1}H NMR (600.1 MHz, acetone-d_6): δ −0.25 (bs, 15H, CH_3-7,8,9,10,11), −0.15 (bs, 15H, CH_3-2,3,4,5,6), 0.85 (t, 3H, J_{vic} = 7.1 Hz, CH_3-$(CH_2)_4CH_2$), 1.10 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.21 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.26 (m, 4H, $CH_3CH_2CH_2CH_2$-CH_2CH_2), 1.31 (m, 4H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.50 (m, 2H, $CH_3(CH_2)_4CH_2$). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −1.90 (CH_3-2,3,4,5,6), −0.60 (CH_3-7,8,9,10,11), 14.26 ($CH_3(CH_2)_4CH_2$), 23.24 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 27.86 ($CH_3CH_2CH_2CH_2CH_2$-CH_2), 31.18 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 32.30 ($CH_3CH_2CH_2$-$CH_2CH_2CH_2$), 32.79 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 61.39 (C-1). IR (KBr pellet): ν 2927 and 2896 (vs, $\nu_{as}(CH_3)$, CB), 2957 (s, $\nu_{as}(CH_3)$, Hex), 2854 (s, $\nu_s(CH_2)$, Hex), 2829 (s, $\nu_s(CH_3)$, CB), 1466 and 1459 (w, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, Hex), 1432 (w, $\delta_{as}(CH_3)$, CB), 1370 (vw, $\delta_s(CH_3)$, Hex), 1309 and 1300 (vs, $\delta_s(CH_3)$, CB), 1290 (m), 1149 (m, B-CH_3), 1117 (m, B-CH_3), 1046 (w), 927 (m) and 916 (m; ν(B-CH_3), r(CH_3)), 832 (w), 812 (w, ν(B−I)), 734 (vw), 689 (vw), 574 (vw), 439 (vw) cm^{-1}. ESI(−)-MS: *m*/*z* 493, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{41}H_{63}B_{11}IP$: C, 59.13; H, 7.63. Found: C, 59.35; H, 7.76.

Cesium 1-(2-Ethylhexyl)-12-iodo-(2−11)-decamethyl-1-carba-*closo*-dodecaborate (15b). The product was prepared according to the general procedure B, starting from Cs[1-(2-EtHex)-12-I-$CB_{11}H_{10}$][18] (**15a**; 260 mg, 0.51 mmol), CaH_2 (860 mg, 20.43 mmol), and MeOTf (1.67 g, 10.18 mmol) in sulfolane (20 mL). Cs[1-(2-EtHex)-12-I-$CB_{11}Me_{10}$] (**15b**) was isolated as a slightly brown solid (228 mg in 68% yield). ^{1}H NMR (600.1 MHz, acetone-d_6): δ −0.24 (bs, 15H, CH_3-7,8,9,10,11), −0.13 (bs, 15H, CH_3-2,3,4,5,6), 0.75 (t, 3H, J_{vic} = 7.4 Hz, C$H_3$$CH_2$CH), 0.88 (t, 3H, J_{vic} = 7.2 Hz, C$H_3$$CH_2CH_2CH_2$CH), 1.11−1.32 (m, 8H, $CH_3CH_2CHCH_2CH_2$-CH_2CH_3), 1.40 (dd, 1H, J_{gem} = 15.8 Hz, J_{vic} = 4.4 Hz, CCH_aH_b-CH), 1.45 (dd, 1H, J_{gem} = 15.8 Hz, J_{vic} = 4.3 Hz, CCH_aH_bCH), 1.65 (m, 1H, CCH_2CH). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −2.10 (CH_3-2,3,4,5,6), −0.60 (CH_3-7,8,9,10,11), 10.27 (CH_3CH_2-CH), 14.42 ($CH_3CH_2CH_2CH_2CH$), 23.91 ($CH_3CH_2CH_2CH_2$-CH), 27.42 (CH_3CH_2CH), 28.96 ($CH_3CH_2CH_2CH_2CH$), 34.52 ($CHCH_2C$), 34.54 ($CH_3CH_2CH_2CH_2CH$), 37.07 ($CHCH_2C$), 62.51 (C-1). IR (KBr pellet): ν 2931 and 2900 (vs, $\nu_{as}(CH_3)$, CB), 2958 (s, $\nu_{as}(CH_3)$, 2-EtHex), 2873 (s, $\nu_s(CH_3)$, 2-EtHex), 2859 (s, $\nu_s(CH_2)$, 2-EtHex), 2831 (s, $\nu_s(CH_3)$, CB), 1460 (m, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, 2-EtHex), 1440 (m) and 1413 (w, $\delta_{as}(CH_3)$, CB), 1379 (w, $\delta_s(CH_3)$, 2-EtHex), 1312 and 1294 (vs, $\delta_s(CH_3)$, CB), 1277 (m), 1256 (w), 1166 (m), 1147 (s, B-CH_3), 1111 (m, B-CH_3), 1085 (w), 1049 (w), 990 (vw), 939 (w) and 914 (m, ν(B-CH_3), r(CH_3)), 835 (vw), 810 (w, ν(B−I)), 774 (w), 734 (w), 687 (vw), 568 (w), 439 (w) cm^{-1}. ESI(−)-MS: *m*/*z* 521, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{43}H_{67}B_{11}IP$: C, 60.00; H, 7.85. Found: C, 60.27; H, 7.69.

Cesium 1-(Methoxycarbonyl)-12-iodo-(2−11)-decamethyl-1-carba-*closo*-dodecaborate (16b). The product was prepared according to the general procedure B, starting from **16a** (200 mg, 0.54 mmol), CaH_2 (925 mg, 22 mmol), and MeOTf (1.81 g, 11 mmol) in sulfolane (15 mL). Cs[1-MeOCO-12-I-$CB_{11}Me_{10}$] (**16b**) was isolated as a white solid (227 mg in 70% yield). ^{1}H NMR (500.0 MHz, acetone-d_6): δ −0.21 (bs, 15H, CH_3-7,8,9,10,11), −0.07 (bs, 15H, CH_3-2,3,4,5,6), 3.48 (s, 3H, CH_3O). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −1.90 (CH_3-2,3,4,5,6), −0.75 (CH_3-7,8,9,10,11), 51.05 (CH_3O), 66.60 (C-1), 167.30 (COO). IR (KBr pellet): ν 2941 and 2900 (m, $\nu_{as}(CH_3)$), 2833 (m, $\nu_s(CH_3)$), 1705 (vs, ν(C═O)), 1434 (m, $\delta_s(CH_3)$), 1449 (w), 1434 (m) and 1413 (w, $\delta_{as}(CH_3)$), 1312 (s), 1305 (s) and 1296 (s, $\delta_s(CH_3)$), 1273 (vs, ν(C−O)), 918 and 911 (w, ν(B-CH_3)), 812 (w, ν(B−I)) cm^{-1}. ESI(−)-MS: *m*/*z* 467, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{37}H_{53}B_{11}IO_2P$: C, 55.09; H, 6.62. Found: C, 55.20; H, 6.71.

Cesium 12-Fluoro-(2−11)-decamethyl-1-carba-*closo*-dodecaborate (17b). The product was prepared according to the general procedure B, starting from **17a** (500 mg, 2.3 mmol), CaH_2 (3.9 g, 93 mmol), and MeOTf (7.55 g, 46 mmol) in sulfolane (18 mL). Cs[1-H-12-F-$CB_{11}Me_{10}$] (**17b**) was isolated as a white solid (799 mg in 80% yield). ^{1}H NMR (499.8 MHz, acetone-d_6): δ −0.30 (bs, 15H, CH_3-7,8,9,10,11), −0.17 (bs, 15H, CH_3-2,3,4,5,6), 0.84 (bs, 1H, H-1). ^{19}F{^{11}B} NMR (470.3 MHz, acetone-d_6): δ −208.15. IR (KBr pellet): ν 2931 (s) and 2896 (vs, $\nu_{as}(CH_3)$), 2830 (s, $\nu_s(CH_3)$), 1436 (w, $\delta_{as}(CH_3)$), 1307 (vs, $\delta_s(CH_3)$), 1179 and 1147 (m, ν(B−F)), 917 (m, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: *m*/*z* 302, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{35}H_{51}B_{11}$-FP: C, 65.61; H, 8.02. Found: C, 65.75; H, 8.13.

Cesium 1-Methyl-12-fluoro-(2−11)-decamethyl-1-carba-*closo*-dodecaborate (18b). The product was prepared according to the general procedure B, starting from **18a** (300 mg, 1.28 mmol), CaH_2 (2.15 g, 51 mmol), and MeOTf (4.27 g, 26 mmol) in sulfolane (20 mL). Cs[1-Me-12-F-$CB_{11}Me_{10}$] (**18b**) was isolated as a white solid (465 mg in 81% yield). ^{1}H NMR (600.1 MHz, acetone-d_6): δ −0.34 (bs, 15H, CH_3-2,3,4,5,6), −0.30 (bs, 15H, CH_3-7,8,9,10,11), 0.80 (bs, 3H, CH_3-1). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −4.55 (CH_3-7,8,9,10,11), −4.00 (CH_3-2,3,4,5,6), 12.67 (CH_3-1), 48.24 (C-1). ^{19}F{^{11}B} NMR (470.3 MHz, acetone-d_6): δ −209.13. IR (KBr pellet): ν 2934 (s) and 2898 (vs, $\nu_{as}(CH_3)$), 2831 (s, $\nu_s(CH_3)$), 1437 (m, $\delta_{as}(CH_3)$), 1384 (w, $\delta_s(CH_3)$, C−CH_3), 1311 (vs, $\delta_s(CH_3)$), 1151 (s) and 1060 (m, ν(B−F)), 914 (s, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: *m*/*z* 316, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{36}H_{53}B_{11}FP$: C, 66.04; H, 8.16. Found: C, 66.20; H, 8.04.

Cesium 1-Hexyl-12-fluoro-(2−11)-decamethyl-1-carba-*closo*-dodecaborate (19b). The product was prepared according to the general procedure B, starting from **19a** (100 mg, 0.26 mmol), CaH_2 (550 g, 13.2 mmol), and MeOTf (870 mg, 5.3 mmol) in sulfolane (10 mL). Cs[1-Hex-12-F-$CB_{11}Me_{10}$] (**19b**) was isolated as a white solid (70 mg in 52% yield). ^{1}H NMR (600.1 MHz, acetone-d_6): δ −0.31 (bs, 15H, CH_3-7,8,9,10,11), −0.19 (bs, 15H, CH_3-2,3,4,5,6), 0.86 (t, 3H, J_{vic} = 7.0 Hz, C$H_3(CH_2)_4CH_2$), 1.10 (m, 2H, CH_3CH_2-$CH_2CH_2CH_2CH_2$), 1.22 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$),

1.26 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.32 (m, 2H, CH_3CH_2-$CH_2CH_2CH_2CH_2$), 1.54 (m, 2H, $CH_3(CH_2)_4CH_2$). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −4.40 (CH_3-7,8,9,10,11), −2.80 (CH_3-2,3,4,5,6), 14.29 ($CH_3(CH_2)_4CH_2$), 23.28 ($CH_3CH_2CH_2CH_2CH_2$-CH_2), 28.09 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 31.33 ($CH_3CH_2CH_2$-$CH_2CH_2CH_2$), 32.14 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 32.38 (CH_3-$CH_2CH_2CH_2CH_2CH_2$), 50.78 (C-1). ^{19}F{^{11}B} NMR (470.3 MHz, acetone-d_6): δ −208.27. IR (KBr pellet): ν 2930 and 2902 (vs, $\nu_{as}(CH_3, CH_2)$, B−Me, Hex), 2873 (m, $\nu_s(CH_3)$), 2857 (m, $\nu_s(CH_2$, $CH_3)$, B−Me, Hex), 2834 (s, $\nu_s(CH_3)$, B−Me), 1465 (m, $\beta_s(CH_2)$), 1457 (m, $\delta_s(CH_3)$), 1439 (m, $\delta_{as}(CH_3)$, B−Me), 1376 (w, $\delta_s(CH_3)$), 1366 (w, $\gamma_s(CH_2)$), 1310 (vs, $\delta_s(CH_3)$, B−Me), 1147 (m, ν(B−F)), 915 (s, ν(B−Me)) cm^{-1}. ESI(−)-MS: m/z 385, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{41}H_{63}B_{11}FP$: C, 67.94; H, 8.76. Found: C, 68.21; H, 8.89.

Cesium 1-(Hydroxymethyl)-1-carba-*closo*-dodecaborate (20). **6a** (300 mg, 1.2 mmol) was placed in a dry Schlenk flask. The flask was charged with argon, and THF (20 mL, freshly distilled from $LiAlH_4$) was added. The solution was cooled to −78 °C and degassed. A solution of $LiEt_3BH$ (3 mL, 1 M in THF, 3 mmol) was added dropwise, followed by the addition of $LiAlH_4$ (150 mg, 4 mmol). The reaction mixture was stirred for 1 h at room temperature and then refluxed for another 20 h. Completion of the reaction was checked by ESI-MS. The reaction mixture was cooled to 0 °C, and the excess of hydrides was quenched by the slow addition of MeOH and evaporated to dryness. The residue was dissolved in water, acidified by the addition of HCl (20%) to pH 1−2, and extracted with diethyl ether (3 × 80 mL). The combined organic phase was then washed with a 20% solution of CsCl (2 × 20 mL) and then water (2 × 20 mL), dried over Cs_2CO_3, and evaporated to dryness. The residue was recrystallized from water, filtered off, washed with water and pentane, and dried under vacuum (10^{-2} mbar/120−140 °C) to obtain 195 mg of pure Cs[1-$HOCH_2$-$CB_{11}H_{11}$] (**20**) as a slightly yellow solid in 53% yield. ^{1}H{^{11}B} NMR (499.8 MHz, acetone-d_6): δ 1.58 (bs, 5H, H-7,8,9,10,11), 1.65 (bm, 1H, H-12), 1.76 (bs, 5H, H-2,3,4,5,6), 3.59 (bs, 2H, CH_2O). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 68.57 (CH_2O), 72.75 (C-1). ^{11}B{^{1}H} NMR (160.4 MHz, acetone-d_6): δ −13.61 (bs, 5B, B-2,3,4,5,6), −12.39 (bs, 5B, B-7,8,9,10,11), −8.22 (bs, 1B, B-12). IR (KBr pellet): ν 3580 and 3434 (m, ν(OH)), 2945 (w, $\nu_{as}(CH_2)$), 2887 (w, $\nu_s(CH_2)$), 2600 (m), 2570 (s), 2556 (s), 2533 (vs), 2509 (s) and 2495 (vs, ν(B−H)), 1399 (m, $\beta_s(CH_2)$), 1054 (w, ν(C−OH)), 1028 (s, β(B−H)), 726 (m, γ(B−H)) cm^{-1}. ESI(−)-MS: m/z 173, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{26}H_{34}B_{11}OP$: C, 60.94; H, 6.69. Found: C, 61.20; H, 6.52.

Cesium (2−12)-Undecamethyl-1-carba-*closo*-dodecaborate-1-carboxylic Acid (21). Sodium (0.2 g, 8.7 mmol) was dissolved in liquid ammonia (10 mL) in a dry Schlenk flask at −78 °C. **6b** (100 mg, 0.2 mmol) was dissolved in a minimum amount of dry THF (1 mL) and added dropwise to the solution under vigorous stirring, which was continued for an additional 2 h. A small aliquot was taken out and checked by ESI-MS to ensure that the reaction was complete prior to workup. When the reaction was complete, the flask was taken out of the dry ice bath, and the remaining sodium was then carefully quenched with methanol until the dark-blue color disappeared. The reaction was allowed to warm to room temperature, and liquid ammonia was evaporated. Residual solvents were evaporated in a vacuum, and the solid was treated with water (10 mL). The solution was acidified with HCl (10%) and extracted with diethyl ether (3 × 50 mL). The solution was then washed with a 20% solution of CsCl (2 × 30 mL), and the combined CsCl wash was then extracted with diethyl ether (3 × 20 mL). The combined organic phase was dried over molecular sieves (4 Å), evaporated to dryness, and recrystallized from water. The white crystals were filtered off, washed with water and pentane, and vacuum-dried to provide 76 mg of the pure product Cs[1-HOCO-$CB_{11}Me_{11}$] (**21**) in 80% yield. ^{1}H NMR (499.8 MHz, acetone-d_6): δ −0.47 (bs, 3H, CH_3-12), −0.38 (bs, 15H, CH_3-7,8,9,10,11), −0.07 (bs, 15H, CH_3-2,3,4,5,6). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −3.65 (CH_3-7,8,9,10,11), −2.65 (CH_3-12), −2.40 (CH_3-2,3,4,5,6), 64.59 (C-1), 168.28 (COO). IR (KBr pellet): ν 3422 (s, ν(OH)), 2932 and 2899 (s, $\nu_{as}(CH_3)$), 2832 (s, $\nu_s(CH_3)$), 1715 (vs, ν(C=O)), 1437 (m, $\delta_{as}(CH_3)$), 1310 (vs, $\delta_s(CH_3)$), 1139 (m, ν(C−O)), 914 (m, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: m/z 341, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{37}H_{54}B_{11}O_2P$: C, 65.28; H, 8.00. Found: C, 65.41; H, 8.10.

Cesium (2−11)-Decamethyl-1-carba-*closo*-dodecaborate-1-carboxylic Acid (22). Sodium (0.2 g, 8.70 mmol) was dissolved in liquid ammonia (10 mL) in a dry Schlenk flask at −78 °C. **16b** (100 mg, 0.17 mmol) was dissolved in a minimum amount of dry THF (1 mL) and added dropwise to the solution under vigorous stirring, which was continued for an additional 2 h. A small aliquot was taken out and checked by ESI-MS to ensure that the reaction was complete prior to workup. When the reaction was complete, the flask was taken out of the dry ice bath, and the remaining sodium was then carefully quenched with methanol until the dark-blue color disappeared. The reaction mixture was allowed to warm to room temperature, and liquid ammonia was evaporated. Residual solvents were evaporated under reduced pressure, and the solid was treated with water (10 mL). The solution was acidified with 10% HCl and extracted with diethyl ether (3 × 60 mL). The solution was then washed with a 20% solution of CsCl (2 × 30 mL), and the combined CsCl wash was then extracted with diethyl ether (3 × 20 mL). The combined organic phase was dried over molecular sieves (4 Å), evaporated to dryness, and recrystallized from water. The white crystals were filtered off, washed with water and pentane, and vacuum-dried to provide 59 mg of the pure product Cs[1-HOCO-12-H-$CB_{11}Me_{10}$] (**22**) in 76% yield. ^{1}H{^{11}B) NMR (499.8 MHz, acetone-d_6): δ −0.24 (s, 15H, CH_3-7,8,9,10,11), −0.08 (s, 15H, CH_3-2,3,4,5,6), 1.45 (s, 1H, H-12). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −1.50 (CH_3-2,3,4,5,6,7,8,9,10,11), 70.65 (C-1), 169.81 (COO). IR (KBr pellet): ν 3434 (s, ν(OH)), 2928 and 2899 (s, $\nu_{as}(CH_3)$), 2830 (m, $\nu_s(CH_3)$), 2452 (w, ν(B−H)), 1716 and 1703 (w, ν(C=O)), 1433 (w, $\delta_{as}(CH_3)$), 1305 (s, $\delta_s(CH_3)$), 918 (w, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: m/z 327, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{36}H_{52}B_{11}O_2P$: C, 64.86; H, 7.86. Found: C, 64.99; H, 7.80.

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