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Preparation of Undecamethylated and Hexamethylated 1-Halocarba-*closo*-dodecaborate Anions

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ABSTRACT: *We report an improved synthesis of 1-halocarba-closo-dodecaborate anions 1-Hal–$CB_{11}H_{11}^-$ and their efficient conversion to the undecamethylated anions 1-Hal–$CB_{11}Me_{11}^-$ (Hal = Cl, Br, I) and the hexamethylated anions 1-Hal-(7–12)-$(CH_3)_6$–$CB_{11}H_5^-$ (Hal = F, Cl) by treatment with methyl triflate in sulfolane in the presence of calcium hydride to remove the triflic acid byproduct*. © 2006 Wiley Periodicals, Inc. Heteroatom Chem 17:217–223, 2006; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20224

INTRODUCTION

The salts of polyalkylated derivatives of the 12-vertex *closo* carborate anion $CB_{11}H_{12}^-$ (**1**) [1–4], especially the lithium salt, have remarkable properties [5]. They are highly lipophilic and dissolve well in nonpolar and weakly coordinating solvents. The lithium cations contained in these solutions are so poorly solvated that they act as strong Lewis acids and catalyze pericyclic [6] and radical [7] reactions. The cation–anion pairs appear to be partially dissociated, since the solution of Li^+ $CB_{11}(CH_3)_{12}^-$ in benzene conducts electricity sufficiently for electrochemical measurements [8]. The nature of cation solvation in these solutions is suggested by crystal structures of alkali metal salt solvates with aromatics, in which the cation interacts with the aromatic π face [9].

The chemical reactivity of these alkylated anions is remarkable as well. Reversible one-electron oxidation of $CB_{11}(CH_3)_{12}^-$ yields an isolable neutral radical, a strong oxidant that can be used to produce $CB_{11}(CH_3)_{12}^-$ salts of metal cations by cleavage of metal–metal and metal–carbon bonds [10]. Several such salts of main-group [11,12] and transition [13] metals have been prepared and investigated. The metal cation acts as a strong Lewis acid and interacts with one or more of the methyl groups of the anion. When the strength of the interaction becomes excessive, the cation abstracts a methide anion from the methylated carborate anion to yield a "boronium ylide" with a naked icosahedral vertex, which can be trapped with nucleophiles [14–16]. It has been isolated and is stable below about −60 °C [16]. Remarkably, a species whose reactivity matches that expected for an isomeric "carbonium ylide" with a naked carbon vertex on the

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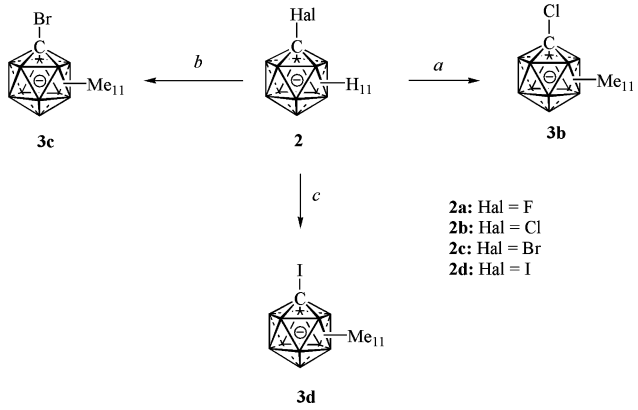
icosahedron is also formed readily, by Grob fragmentation of $BrCH_2CH_2$-$CB_{11}(CH_3)_{11}^-$ and similar anions [17]. The $-CB_{11}(CH_3)_{11}^-$ substituent appears to be an excellent leaving group that resembles a proton or a silyl substituent in its eagerness to depart without the electrons of the bond through which it is attached. Unlike a proton or a silyl group, however, it leaves as a neutral ylide without requiring the assistance of a nucleophile, and the rate of its departure is zero order in the nucleophile [17]. Apparently, the assistance that a departing proton or silyl cation obtains from the lone electron pair of a solvent or added base is provided internally by the electrons of the delocalized negative charge of the carborate anion. Indeed, it has been argued, at first hesitantly [16] and then with conviction [17], that the negative cage charge in the "carbonium ylide" is actually mostly localized on the carbon vertex, making the electronic structure resemble that of a singlet carbene more than that of a carbocation [16,17]. We have recently found that this is actually reflected in the reactivity of the "ylide" toward aromatic substrates [18].

Given the variety of interesting properties exhibited by alkylated carborane anions, the utility of methods for their introduction into organic structures is obvious. The standard procedure takes advantage of the acidity of the CH vertex in the $CB_{11}H_{12}^-$ anion for deprotonation and alkylation [19], followed by the introduction of methyl or other alkyl groups onto the boron vertices of the $-CB_{11}H_{11}^-$ substituent under conditions originally developed [20–23] for the preparation of the salts of $CB_{11}(CH_3)_{12}^-$. This involves treatment with an alkyl triflate in the presence of a base that removes triflic acid, which is formed as a byproduct of alkylation. This reaction has been used for the preparation of the undecamethylated anion $HCB_{11}(CH_3)_{11}^-$ [13,24] and many other polymethylated derivatives of the $CB_{11}H_{12}^-$ anion [25]. A cheaper methylation procedure using an alkyl bromide in a pressure vessel instead of triflate has been described [26], but we have not been able to reproduce the results.

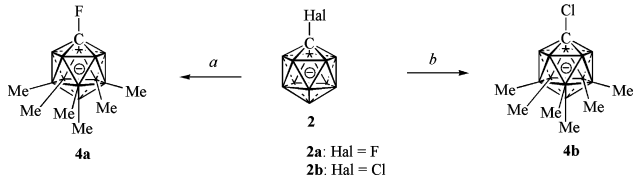
Although alkylation on carbon followed by methylation with methyl triflate was recently successfully used for the synthesis of a large number of organic structures containing the $-CB_{11}(CH_3)_{11}^-$ substituent in a project ultimately aimed at the preparation of ion-conducting polymers [17], it is not very satisfactory. The vigorous conditions of the alkylation reaction severely limit the range of organic structures that are tolerated, and multiple bonds, aromatic rings, and groups with lone pairs cannot be present. It would be far better to perform the alkylation of the carborane first and to introduce



SCHEME 1 Syntheses of permethylated 1-halocarborate anions. (a) CaH_2, MeOTf, sulfolane, RT, 18 days. (b) CaH_2, MeOTf, sulfolane, RT, 3.5 weeks, (c) CaH_2, MeOTf, sulfolane, RT, 6 weeks.

the prefabricated $-CB_{11}(CH_3)_{11}^-$ or similar alkylated carboranyl substituent into the organic structure second. Unfortunately, the acidity of the CH vertex in $HCB_{11}(CH_3)_{11}^-$ is much lower than that of the CH vertex in $CB_{11}H_{12}^-$, and we have been unable to find a base strong enough to be useful. Even in the presumably less deactivated (7–12)-$(CH_3)_6$-$CB_{11}H_5^-$ anion the CH vertex is not deprotonated with *tert*-butyllithium [27]. Our initial attempts to obviate the problem by methylating the 1-iodo derivative 1-I-$CB_{11}H_{11}^-$ and then performing a metal–halogen exchange on the anion 1-I-$CB_{11}(CH_3)_{11}^-$ were thwarted by difficulties in driving the methylation process to completion [24].

We have since managed to overcome the obstacles and presently describe an efficient conversion of the four known [28] 1-Hal-$CB_{11}H_{11}^-$ anions **2a–2d** (Scheme 1) into three fully methylated 1-Hal-$CB_{11}(CH_3)_{11}^-$ anions (**3b–3d**, Hal = Cl, Br, I, respectively) and two hexamethylated 1-Hal-(7–12)-$(CH_3)_6$-$CB_{11}H_5^-$ anions (**4a** and **4b**, Hal = F and Cl, respectively) (Scheme 2). These results promise to open a superior synthetic route toward compounds carrying the $-CB_{11}(CH_3)_{11}^-$ anion and similar substituents.



SCHEME 2 Syntheses of hexamethylated 1-halocarborate anions. (a) CaH_2, MeOTf, sulfolane, RT, 6 h. (b) CaH_2, MeOTf, sulfolane, 10 °C, 6 days.

RESULTS AND DISCUSSION

Preparation of the 1-Hal-$CB_{11}H_{11}^-$ Anions **2**

The yields of the published halogenation [28] of the $CB_{11}H_{12}^-$ anion (**1**) on carbon to yield the 1-halocarborate anions **2b–2d** have been improved by minor modifications such as the use of lower temperatures in the initial lithiation process and the use of 1,2-dichloroethane, 1,2-dibromoethane, and 1,2-diiodoethane or iodine as halogenation agents.

Preparation of the 1-Hal-$CB_{11}(CH_3)_{11}^-$ Anions **3b–3d**

The permethylated 1-halocarborate anions **3b–3d** were prepared by the methylation of the cesium salts of **2b–2d** in sulfolane with methyl triflate in the presence of CaH_2 as the base. Considerable patience was the key to success, as the reactions go to completion very slowly: 18 days for **2b**, 25 days for **2c**, and 42 days for **2d**. Best results were achieved by using freshly prepared methyl triflate and distilled sulfolane. The conversion was straightforward, and clean product was obtained in high isolated yield. Attempts to accelerate the reaction by heating were thwarted by the formation of byproducts. Already at 35 °C, a considerable amount of a trifloxy substituted species was formed.

The 1-chloro anion **3b** had been prepared previously by a circuitous route involving the trapping of the carbonium ylide $CB_{11}(CH_3)_{11}$ with the chloride anion [17].

In the case of the fluoro derivative **2a**, the methylation reaction stopped after six methyl groups were introduced, and we were unable to produce the permethylated product **3a**. In the case of the chloro derivative **2b**, the first six methyls entered quite fast to yield **4b**, and further methylation to **3b** was considerably slower. Such clear differentiation was not observed with the bromo and iodo anions **2c** and **2d**, and we were unable to steer the methylation toward the production of **4c** and **4d**.

Preparation of the 1-Hal-(7–12)-$(CH_3)_6$-$CB_{11}H_5^-$ Anions **4a** *and* **4b**

Hexamethylation of **2a** was complete after 6 h at room temperature. Only traces of the starting material were left, and the principal side product was the heptamethylated compound, present in a small amount. These impurities were separated by reverse phase chromatography.

We were able to take advantage of the higher reactivity of positions 7–12 in **2b** relative to positions 2–6 to produce pure **4b** in a 63% yield after 6 days by running the reaction at 10 °C. A single crystallization afforded an analytically pure sample and no separation by chromatography was necessary.

The location of the six methyl groups in the two anions **4** in positions 7–12 was proven using ^{11}B NMR spectroscopy. Under ^1H decoupling, both anions showed three boron signals with 1:5:5 intensity ratios. The weak peak was assigned to B12; one of the strong peaks is due to B2–B6 and the other to B7–B11. Without the decoupling, the peak due to the BH vertices was split into a doublet, while that due to BCH_3 vertices remained a singlet. In a 2D COSY spectrum, the BH and BCH_3 peaks were cross-correlated, but only the latter was cross-correlated with the peak of B12. The higher reactivity of the 7–12 positions is not surprising as they are generally more reactive in electrophilic substitution reactions on **1** [19,29,30]. Moreover, the electronegative halogens in position 1 probably deactivate their boron neighbors in positions 2–6 the most.

Methyl Carbon Assignment in NMR

2-D NMR was also used successfully to resolve and assign the ^{13}C resonances of the methyl groups in **3** and **4**. Because of the quadrupole of the adjacent boron nucleus, the three methyl peaks of **3** and the two methyl peaks of **4** are broad and unresolved in $^{13}C\{^1H\}$ spectra, and distinct methyl groups in such carborane structures are hard to record separately. Using $\{^{13}C\}\{^{11}B\}^1H$-gHMQC (C—H) spectroscopy (gradient selected heteronuclear multiple quantum coherence spectroscopy with continuous broadband decoupling of ^{11}B throughout the pulse sequence and broadband ^{13}C and ^{11}B decoupling during the acquisition time), we were able to observe and assign them unambiguously.

Substituent Effects

It is known from calculations of atomic charges in the parent (protiated) and in methylated CB_{11} cluster anions [12] and neutral C_2B_{10} clusters [31] that the methyl group withdraws more electron density from the vertex atom than a hydrogen atom does. Relative to the hydrogen standard, methyl on boron or carbon is thus calculated to be an electron-withdrawing substituent, and this agrees with the order of Pauling electronegativites (2.1 for hydrogen and 2.5 for carbon). The electron density acquired by the methyl carbon is stored primarily in its sigma-symmetry orbital, and the electron-withdrawing effect thus is of the inductive type (+I; some authors use the opposite sign convention). It is expected

to fall off rapidly with distance from the methyl substituent.

Other than He, H is the only substituent attached through an atom that does not have p orbitals in its valence shell, and all other substituents have a pi (conjugative or hyperconjugative) effect as well. It is net electron donating (−E) or withdrawing (+E), depending on the relative strength of the interaction of the pi-symmetry donating occupied and withdrawing unoccupied orbitals of the atom through which the substituent is attached with the unoccupied and occupied orbitals of the substrate, respectively. In organic aromatic systems and apparently also in carborane cages, E effects are able to propagate over quite long distances, selectively to different atoms in the substrate.

On nearly all substrates, methyl is a −E substituent. Depending on the property examined, its −E effect may dominate its +I effect, as reflected for instance in the much lower oxidation potential of $CB_{11}Me_{12}^-$ [10] and other methylated derivatives [25] relative to **1**, and in the reduction of the acidity of the CH vertex in **1** upon methylation.

A +I,−E effect combination in the same substituent has long been recognized for halogens in electrophilic aromatic substitution. The +I effect deactivates all positions in **2**, the closer 2–6 more than the more distant 7–11. Their reactivity difference in methylation diminishes from **2a** to **2d** as the +I effect drops from F to I. Surprisingly, the absolute rate of substitution in positions 2–6 of **4b–4d** is reduced in the same order, presumably due to a combination of differences of the steric and activating −E effect of the halogens. A detailed analysis is hampered by poor mechanistic understanding of the methylation reaction on carboranes and the scarcity of quantitative data on reactivity. Values of NMR chemical shifts for the vertex atoms are more generally available but are not simply related to reactivity or total atomic charges.

CONCLUSION

The polymethylated 1-halo anions **3** and **4** are now readily available. Although most of the time we ran the syntheses on small scale, unchanged yields were obtained in runs with up to 2 g of the starting material. Exchange of the halogen for lithium and subsequent reactions with electrophiles promise enhanced access to compounds carrying permethylated and hexamethylated carborate anions as substituents. Elsewhere [7], we report that such reaction sequences have been successfully carried out with **3c** and **3d**.

EXPERIMENTAL

General

All experimental manipulations were carried out using standard vacuum and inert atmosphere techniques. Chemicals were reagent grade (Aldrich); some **1** was synthesized [32] and some purchased from Katchem, Ltd., Elišky Krásnohorské 6, 11000 Prague 1, Czech Republic. THF was dried over sodium and distilled before use. ^{1}H NMR spectra were measured with a Varian Inova-500 spectrometer, ^{11}B NMR spectra with a Varian VXR-300 instrument, and ^{13}C NMR with a Varian Inova-400 instrument. Proton shifts of BH protons were measured with boron decoupling using a Varian Inova-500 instrument. Chemical shifts are given in ppm (δ scale) with positive shifts downfield: all ^{1}H chemical shifts were referenced relative to internal residual protons from a lock solvent and ^{11}B shifts to $BF_3{\cdot}Et_2O$ [$B(OMe)_3$ at 18.1 ppm]. The external reference was contained in a capillary within the same tube. The NMR solvent was $(CD_3)_2CO$ unless noted otherwise. Unambiguous ^{11}B assignments were achieved using the gradient-selected 2-D ^{11}B–^{11}B COSY experiment on a Varian Inova-500 NMR spectrometer. Electrospray negative and positive ion mass spectra were measured in methanol solution using a Hewlett-Packard 5989 API/ES/MS instrument. IR spectra were measured with a Termo Nicolet Avatar 360 FTIR. All chromatographic separations were performed on Sorbent Technologies C 18 (60 Å, 40 μm) reverse phase columns. TLC was performed on C 18 silica TLC Plates w/UV254 aluminum backed (150 μm), with detection by rhodamine 6G (ethanolic solution) in methanol/water (1:1).

General Procedures

Preparation of Tetraphenylphosphonium Salts, Procedure P1. A Cs^+ salt (1 eq.) was dissolved in 4 M HCl (25 mL) and extracted with diethyl ether (3 × 15 mL). Water (15 mL) was added to the combined ether layers, and the diethyl ether was evaporated. The aqueous solution was filtered and treated with excess Ph_4PCl to yield a white solid precipitate.

Conversion to Cesium Salts, Procedure P2. A Me_3NH^+ salt was dissolved in excess 20% aqueous NaOH. The aqueous layer was extracted with diethyl ether (3 × 10 mL) and the ethereal layer was extracted twice with 20% aqueous CsCl and the CsCl solutions twice with ether. The solvent of the combined organic layers was removed under reduced pressure to give a solid that was dried under reduced pressure.

Cesium 1-Chloro-1-carba-closo-dodecaborate [Cs^+]-[1-Cl-$CB_{11}H_{11}^-$] **2b** [28]. At −20 °C under argon, **1** (500 mg, 1.81 mmol) in 50 mL THF was treated with 3.0 mL of 1.6 M *n*-BuLi (4.5 mmol) and stirred for 30 min. The resulting solution was brought to RT and then added over a period of 30 min to a solution of $ClCH_2CH_2Cl$ (446 mg, 4.5 mmol) in THF (20 mL). Two days later, the reaction was quenched by the addition of methanol. The solvent was evaporated, and **2b** was extracted into diethyl ether (3 × 20 mL) followed by the extraction with 20% aqueous CsCl. After evaporation of the organic layers, the resulting solid was purified by reverse phase column chromatography using buffered water/methanol eluent (55% methanol, 45% water, each containing 0.7% of Et_3N and 1% AcOH) to give the cesium salt of **2b** (470 mg, 84%).

Cesium 1-Bromo-1-carba-closo-dodecaborate [Cs^+]-[1-Br-$CB_{11}H_{11}^-$] **2c** [28]. At −20 °C under argon, **1** (1.0 g, 3.62 mmol) in 50 mL THF was treated with 5.7 mL of 1.6 M *n*-BuLi (9.05 mmol) and stirred for 30 min. The resulting solution was brought to RT and then added over a period of 30 min to a solution of $BrCH_2CH_2Br$ (1.7 g, 9.05 mmol) in THF (20 mL). Two days later, the reaction was quenched by the addition of MeOH. The solvent was evaporated, and **2c** was extracted into diethyl ether (3 × 20 mL) followed by the extraction with 20% aqueous CsCl. After evaporation of the organic layers, the resulting solid was purified by reverse phase column chromatography using buffered water/methanol eluent (55% methanol, 45% water, each containing 0.7% of Et_3N and 1% AcOH) to give the cesium salt of **2c** (1.15 g, 89%).

Cesium 1-Iodo-1-carba-closo-dodecaborate [Cs^+]-[1-I-$CB_{11}H_{11}^-$] **2d** [28]. At 0 °C under argon, **1** (200 mg, 0.72 mmol) in 10 mL 1,2-dimethoxyethane (DME) was treated with 0.54 mL of 1.6 M *n*-BuLi (2.96 mmol) and stirred for 30 min. The resulting solution was then added over a period of 30 min to a solution of freshly sublimed iodine (237 mg, 0.94 mmol) in DME at −10 °C. Two hours later, reaction was quenched by the addition of 5% $Na_2S_2O_3$(aq), until the solution became colorless. DME was evaporated, and **2d** was extracted into diethyl ether (3 × 20 mL). After evaporation of the solvent, the resulting solid was recrystallized from MeOH/water. Higher yield is obtained by reverse phase column chromatography using buffered water/methanol eluent (60% methanol, 40% water, each containing 0.7% of Et_3N and 1% AcOH) to give the cesium salt of **2d** (247 mg, 81%).

In an alternative procedure, at −20 °C under argon, **1** (1.0 g, 3.62 mmol) in 30 mL THF was treated with 6.0 mL of 1.6 M *n*-BuLi (9.60 mmol) and stirred for 30 min. The resulting solution was brought to RT and then added over a period of 30 min to a solution of $I(CH_2)_2I$ (2.0 g, 9.05 mmol). Two days later, the reaction was quenched by the addition of MeOH. The solvent was evaporated, and **2d** was extracted into diethyl ether (3 × 20 mL) followed by extraction with 20% aqueous CsCl. After evaporation of the organic layers, the resulting solid was purified by recrystallization with water/methanol (9:1) to give **2d** (1.39 g, 96%).

Preparation of Permethylated 1-Halocarborate Anions **3**, *Procedure P3.* The 1-halocarborate anion **2** was dissolved in tetramethylene sulfone (20 mL). CaH_2 (40 equiv.) was added, and the first portion of methyl triflate (1 mL) was added via syringe pump over a period of 20 h. After stirring for 36 h, a second portion (1 mL) of MeOTf was added. The reaction course was monitored by ESI. If neccessary, a next equivalent of MeOTf was added. After the ESI showed the absence of partially methylated alkylated anions and only the presence of the permethylated one, the slurry was diluted with methylene chloride and filtered through a coarse frit. The filtrate was carefully washed with 27% aqueous ammonium hydroxide (15 mL), and the solvent was removed under reduced pressure. The aqueous layer was extracted three times with diethyl ether (3 × 25 mL). The ethereal layer was extracted twice with 20% aqueous CsCl (3 × 15 mL) and the CsCl solutions twice with ether (3 × 25 mL). The solvent was removed from the combined organic layers under reduced pressure to give a brown solid. To remove the sulfolane the resulting oil was heated under reduced pressure at 100 °C for 12 h. The crude product was purified by recrystallization from methanol/water (1:9).

Cesium 1-Chloroundecamethylcarba-closo-dodecaborate [Cs^+][1-Cl-$CB_{11}(CH_3)_{11}^-$] **3b**. According to procedure P3, **2b** (0.50 g, 1.61 mmol) was methylated using MeOTf and CaH_2 in sulfolane at RT for 18 days to give a crude brown solid which was recrystallized from MeOH/water (1:9) to give the cesium salt of **3b** (0.62 g, 83%), whose spectra were identical with those reported earlier [17]. Chemical shifts of the methyl carbon atoms have now also been obtained: {^{13}C}{^{11}B} ^{1}H-gHMQC (C—H) δ−2.25 [CH_3 (2–6)], −3.95 [CH_3 (7–11)], −3.73 [CH_3 (12)].

Cesium 1-Bromoundecamethylcarba-closo-dodecaborate [Cs^+][1-Br-$CB_{11}(CH_3)_{11}^-$] **3c**. According to procedure P3, **2c** (1.50 g, 4.21 mmol) was methylated using MeOTf and CaH_2 in sulfolane at RT for 3.5 weeks to give a crude brown solid which was recrystallized from MeOH/water (1:9) to give the cesium salt of **3c** (1.72 g, 81%). ^{1}H NMR (300 MHz, DMSO-d_6) δ −0.14 [s, 15H, CH_3(2–6)], −0.33 [s,

15H, CH_3(7–11)], −0.460 [s, 3H, CH_3(12)]; {^{1}H} ^{11}B NMR δ −0.931 [s, 1B, B(12)], −9.291 [s, 5B, (7–11)], −10.28 [s, 5B, (2–6)]; {H}^{13}C δ −3.66 [vb, CH_3(2–12)]. Methyl carbons: {^{13}C}{^{11}B} ^{1}H-gHMQC (C—H) δ −2.12 [CH_3(2–6)], −3.89 [CH_3(7–11)], −3.69 [CH_3(12)]. For Cs^+ salt: IR (KBr pellet) 905, 1288, 1370, 1407, 2840, 2892, 2950 cm^{-1}. MS (ESI-) *m/z* 374, expected isotopic distribution. For PPh_4^+, Anal. Calcd for $C_{36}B_{11}H_{53}BrP$: C, 60.42; H, 7.47. Found: C, 60.45; H, 7.51.

Cesium 1-Iodoundecamethylcarba-closo-dodecaborate [Cs^+][1-I-$CB_{11}(CH_3)_{11}^-$] **3d**. According to procedure P3, **2d** (1.00 g, 2.49 mmol) was methylated using MeOTf and CaH_2 in sulfolane at RT for 6 weeks to give a crude brown solid which was recrystallized from MeOH/water (1:9) to give the cesium salt of **3d** (1.22 g, 87%). ^{1}H NMR (300 MHz, DMSO-d_6) δ −0.13 [s, 15H, CH_3(2–6)], −0.31 [s, 15H, CH_3(7–11)], −0.46 [s, 3H, CH_3(12)]; {^{1}H} ^{11}B NMR δ 0.325 [s, 1B, B(12)], −8.92 [s, 5B, (7–11)], −9.93 [s, 5B, (2–6)]; {H}^{13}C δ −4.22 [vb, CH_3(2–12)]. Methyl carbons: {^{13}C}{^{11}B} ^{1}H-gHMQC (C—H) δ −0.97 [CH_3 (2–6)], −3.32 [CH_3(7–11)], −3.53 [CH_3(12)]. For Cs^+ salt: IR (KBr pellet) 922, 1222, 1366, 1484, 2802, 2839, 2970 cm^{-1}. MS (ESI-) *m/z* 423, expected isotopic distribution. For PPh_4^+, Anal. Calcd for $C_{36}B_{11}H_{53}IP$: C, 56.69; H, 7.01. Found: C, 56.72; H, 6.99.

Cesium 1-Fluoro-7,8,9,10, 11, 12-hexamethyl-carbacloso-dodecaborate [Cs^+][1-F-7,8,9,10,11,12-Me_6-$CB_{11}H_5^-$] **4a**. A solution of **2a** [28] (0.22 g, 1 mmol) in 3.6 mL of sulfolane (4.8 g, 40 mmol, freshly distilled from CaH_2) was stirred at room temperature under argon with methyl triflate (2.3 mL, 3.3 g, 20 mmol) in the presence of CaH_2 (1.7 g, 40 mL). The reaction was monitored by ESI/MS. After 6 h, the mixture contained mainly **4a** with *m/z* 247, with traces of **1** and a heptamethylated product. The reaction mixture was diluted with 60 mL of dry CH_2Cl_2, and CaH_2 was removed by vacuum filtration. The filtrate was quenched slowly with 20 mL of 27% aqueous ammonium hydroxide to remove excess methyl triflate, and extracted three times with 10 mL of Et_2O. The combined organic layers were washed with 15% aqueous CsCl. The solvent was evaporated. The residual sulfolane was removed by washing with chloroform. The white solid collected was the cesium salt of **4a** (0.34 g, 89%). The crude solid which contained traces of the heptamethyl compound was further purified by reverse phase chromatography using buffered water/methanol as the eluent (50% methanol, 50% water, each containing 0.7% of Et_3N and 1% AcOH). {^{11}B}^{1}H NMR δ 1.33[s, 5H, 2–6] −0.144 [s, 15H, CH_3(7–11)], −0.660 [s, 3H, CH_3(12)]; ^{1}H NMR δ 1.33 [d(J_{BH} = 148.6 Hz), 5H, 2–6], −0.144 [s, 15H, CH_3(7–11)], −0.660 [s, 3H, CH_3(12)]; ^{19}F NMR δ −169.2 [vb]; {^{1}H} ^{11}B NMR δ−6.48 [s, B(12)], −8.01 [s, 5B, B(7–11)], −18.88 [s, 5B, B(2–6)]; {^{1}H}^{13}C NMR δ 50.05 [vb, C(cluster)], [CH_3(7–12)]. Methyl carbons: {^{13}C}{^{11}B} ^{1}H-gHMQC (C—H) δ− 2.21 [CH_3 (7–11)], −3.01 [CH_3(12)]. For Cs salt: IR (KBr) 703, 788, 920, 1180, 1262, 1475, 2483, 2741, 2970 cm^{-1}; ESI MS(-) *m/z* 247, expected isotopic distribution. For PPh_4^+, Anal. Calcd for $C_{31}B_{11}H_{43}FP$: C, 63.69; H, 7.41. Found: C, 63.65; H, 7.45.

Cesium 1-Chloro-7,8,9,10,11,12-hexamethylcarba closo-dodecaborate [Cs^+][1-Cl-7,8,9,10,11,12-$(CH_3)_6$-$CB_{11}H_5^-$] **4b**. Cs^+**2b**$^-$ (0.5 g, 1.61 mmol) was combined with CaH_2 (5.0 g, 120 mmol) and sulfolane (25 mL) in a round bottom flask (100 mL) equipped with a PTFE clad stir bar at 10 °C using a cryocool apparatus. MeOTf (4.0 mL, 38 mmol) was added using a syringe pump over 18 h at 10 °C. After 6 days, the mixture was diluted with CH_2Cl_2 (200 mL) and filtered through a coarse frit. The filtrate was quenched with 20 mL 27% aqueous NH_4OH and then evaporated to dryness using a rotary evaporator. The residue was dissolved in Et_2O (100 mL), and countercurrent extracted (2 × 20 mL) with 20% aqueous CsCl. The ethereal phases were combined and rotary evaporated to dryness. The residue was triturated with Et_2O and the filtered solvent evaporated to afford the crude product, which was recrystallized from MeOH/water. Yield: 405 mg (63%). {^{11}B}^{1}H NMR δ 1.42 [s, 5H, 2–6] −0.152 [s, 15H, CH_3(7–11)], −0.515 [s, 3H, CH_3(12)]; ^{1}H NMR δ 1.42 [d(J_{BH} = 148.3), 5H, 2–6], −0.152 [s, 15H, CH_3(7–11)], −0.515 [s, 3H, CH_3(12)]; {^{1}H} ^{11}B NMR δ−6.70 [s, B(12)], −8.21 [s, 5B, B(7–11)], −18.05 [s, 5B, B(2–6)]; {^{1}H} ^{13}C NMR δ 47.77 [s, C(cluster)], −2.30 [vb, B-CH_3(7–12)]. Methyl carbons: {^{13}C}{^{11}B} ^{1}H-gHMQC (C—H) δ −2.05 [CH_3 (7–11)], −2.92 [CH_3(12)]. For Cs salt: IR (KBr) 690, 732, 966, 1125, 1284, 1455, 2490, 2803, 2995 cm^{-1}; ESI MS(-) *m/z* 263, expected isotopic distribution. For PPh_4^+, Anal. Calcd for $C_{31}B_{11}H_{43}ClP$: C, 61.95; H, 7.21. Found: C, 62.02; H, 7.18.

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