Inorganic Chemistry
Article

Inorg. Chem. **2010**, *49*, 10255–10263 **10255**
DOI: 10.1021/ic101235e

Lithium Salts of [1,12-Dialkyl-$CB_{11}Me_{10}$]$^-$ Anions

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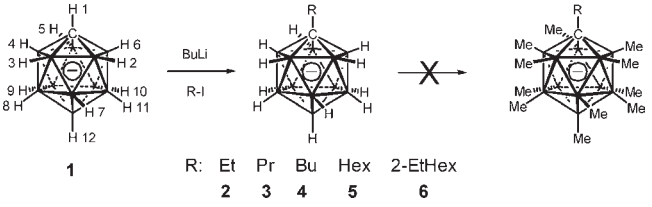
Received June 21, 2010

We report the syntheses of several [1-R-CB_{11}-Me_{11}]$^-$ and [1-R-12-R′-CB_{11}-Me_{10}]$^-$ anions (R, R′ = alkyl) and the solubilities of their lithium salts in cyclohexane. These solutions are of interest as Lewis acid catalysts. The new anions are not directly accessible by methylation with methyl triflate because of intervening triflyloxy substitution on one or more boron vertices. The difficulty has been circumvented in two ways. Either (i) an iodo substituent is first introduced into position 12, permitting a clean decamethylation, and then replaced with a methyl by reaction with trimethylaluminum or (ii) the offending triflyloxy substituents are replaced with methyls by reaction with trimethylaluminum.

Introduction

Lithium salts of polymethylated carborane anions[1−3] are soluble in solvents of low polarity, such as benzene and 1,2-dichloroethane. In these solutions, the lithium cation acts as a strong Lewis acid and catalyzes pericyclic reactions[4] and radical-induced polymerization of terminal alkenes.[5,6]

The catalytic activity might be higher in solvents with even lower ability to solvate the Li^+ cation, such as cyclohexane. However, extremely nonpolar solvents fail to dissolve salts such as Li[$CB_{11}Me_{12}$] and Li[$HCB_{11}Me_{11}$] to a sufficient extent. A remedy is now being sought in the replacement of one or more of the methyl groups with a longer alkyl. Positions 1 and 12 are obvious candidates because substitution at these sites preserves 5-fold symmetry and is least likely to be plagued by the formation of mixtures. The introduction of a longer alkyl group on the carbon vertex 1 by deprotonation followed by alkylation is facile.[7] Ordinarily, the boron vertices are subsequently methylated with strong electrophiles such as methyl triflate,[1,2] methyl bromide,[8] or a trimethylaluminum/methyl iodide mixture.[9] The ease of these reactions depends strongly on the substituents that are already present, and it is unfortunate that 1-alkyl groups other than methyl greatly promote a side reaction in which one or more of the substituents carried by the boron vertices are replaced with triflyloxy groups. This is especially likely to occur at the higher temperatures that often need to be employed for exhaustive alkylation. Therefore, such direct methylation does not represent a viable route to the desired anions.



Presently, we describe two routes to the previously unknown peralkylated anions [1-R-$CB_{11}Me_{11}$]$^-$ and [1-R-12-R′-$CB_{11}Me_{10}$]$^-$. We have converted some of the most promising candidates to their lithium salts and find that they are indeed several times more soluble in cyclohexane than that of [$CB_{11}Me_{12}$]$^-$.

Results

Synthesis. Alkylation of the lithiated cesium salt of [$CB_{11}H_{12}$]$^-$ (**1**) with alkyl iodides to yield the 1-alkylcar-

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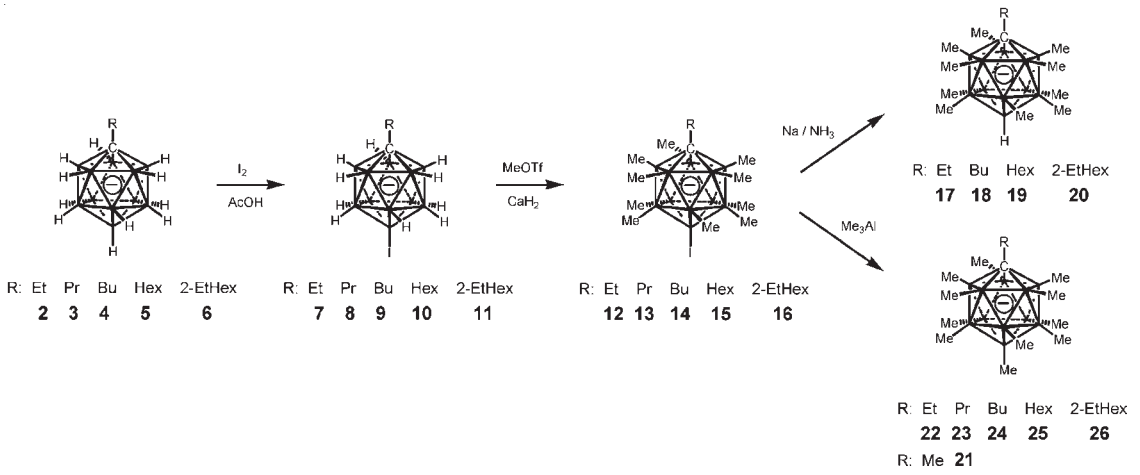
Published on Web 10/08/2010

Scheme 1



borane anions **2**−**6** was performed according to an improved standard procedure.[2,7]

Permethylation of 1-alkylcarborane anions under a variety of conditions produces complex mixtures of partly methylated anions, with anions substituted with both methyl and triflyloxy groups. This is true both at room temperature and with microwave heating.[10] The same results were observed in the case of perethylation. Our attempts to separate the desired permethylated 1-alkylated carborane anions from the mixture of partially methylated and partially triflyloxy-substituted derivates failed, but we have found two routes that circumvent the problem (Scheme 1).

(i) Triflyloxy substitution is suppressed[2] when an iodine substituent is present in position 12, as in the anions **7**−**11**. In that case, permethylation with methyl triflate in sulfolane in the presence of CaH_2 yields decamethylated 1-alkyl-12-iodocarborane anions **12**−**16** easily, especially with microwave assistance.[10]

Iodine in position 12 of the anions **12**−**16** can be removed by Birch reduction[2] to obtain the salts of the pure anions $[1\text{-R-12-H-CB}_{11}\text{Me}_{10}]^-$, **17**−**20**. The reduction is best performed by the addition of a solution of the iodinated carborane anion to a solution of excess sodium metal in liquid ammonia. For reasons that we do not understand, the reduction of **13** was special in that it reproducibly generated a byproduct that we were unable to separate.

More important for our purposes, we find that the iodine atom of the $[1\text{-R-12-I-CB}_{11}\text{Me}_{10}]^-$ anions can be readily substituted with a methyl group upon heating with trimethylaluminum. This procedure was inspired by a previous report of permethylation of $[B_{12}H_{12}]^{2-}$.[9,11] The properties of the previously available permethylated anion $[CB_{11}Me_{12}]^-$ (**21**) can now be compared with those of the five new $[1\text{-R-CB}_{11}\text{Me}_{11}]^-$ anions, **22**−**26**, that have been prepared in this fashion. Other trialkylaluminum reagents have been used (triethylaluminum, triisobutylaluminum, and trioctylaluminum)

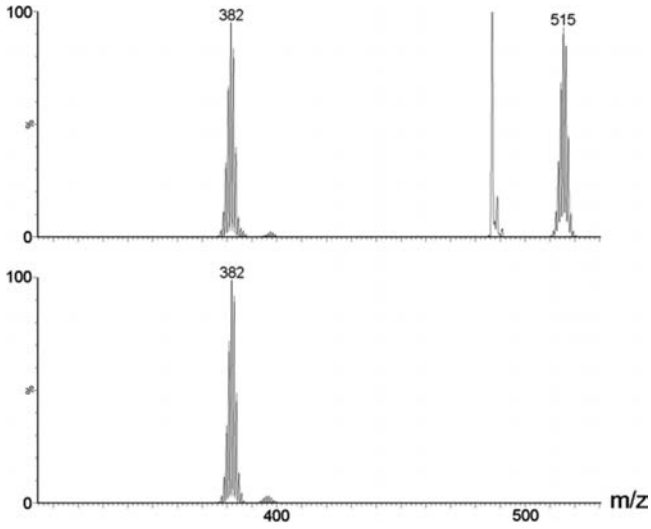
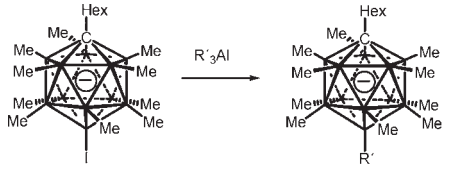


Figure 1. ESI(−)-MS of a mixture of $[1\text{-Hex-CB}_{11}\text{Me}_{11}]^-$ and $[1\text{-Hex-CB}_{11}\text{Me}_{10}(\text{OTf})]^-$ before (top) and after (bottom) reaction with Me_3Al.

and provided access to the anions $[1\text{-R-12-R}'\text{-CB}_{11}\text{Me}_{10}]^-$, **27**−**29**.



(ii) We also find that the triflyloxy groups of B-OTf vertices can be substituted with methyl groups by heating with trimethylaluminum. This is valuable in those $[1\text{-alkyl-CB}_{11}H_{11}]^-$ anions, **2**−**6**, whose peralkylation yields a mixture of $[1\text{-alkyl-CB}_{11}\text{Me}_{(11-m)}(\text{OTf})_m]^-$ anions with no residual B−H bonds on the carborane cage. Figure 1 illustrates the clean nature of this process. Two pure $[1\text{-R-CB}_{11}\text{Me}_{11}]^-$ anions (**21** and **25**) were prepared in this way

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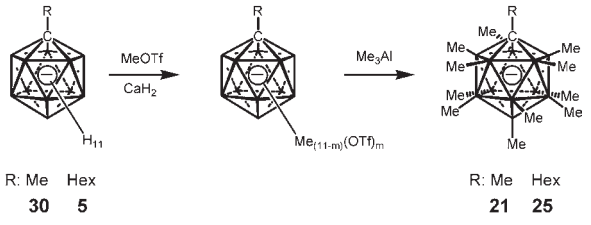
Table 1. Solubility of the Lithium Salts of $[1\text{-R-12-R}'\text{-CB}_{11}\text{Me}_{10}]^-$ in Cyclohexane at 21 ± 0.5 °C

$[1\text{-R-12-R}'\text{-CB}_{11}\text{Me}_{10}]^-$			solubility[a]	
no.	R	R′	g/L	Li^+ (10^{-3} M)
21	Me	Me	1.04 ± 0.19	3.27 ± 0.60
22	Et	Me	2.89 ± 0.22	8.70 ± 0.66
23	Pr	Me	2.91 ± 0.20	8.40 ± 0.58
24	Bu	Me	3.09 ± 0.23	8.57 ± 0.64
25	Hex	Me	3.55 ± 0.24	9.14 ± 0.62
26	2-EtHex	Me	4.57 ± 0.27	10.97 ± 0.65
27	Hex	Et	3.63 ± 0.25	9.02 ± 0.62
28	Hex	*i*-Bu	4.32 ± 0.24	10.03 ± 0.56
29	Hex	Octyl	4.77 ± 0.21	9.80 ± 0.43

[a] The standard deviation from 10 determinations is given.

from $[1\text{-R-CB}_{11}\text{Me}_{11}]^-$ starting materials (**30** and **5**, respectively).



Solubility of Lithium Salts in Cyclohexane. The solubility of the lithium salts of $[1\text{-R-12-R}'\text{-CB}_{11}\text{Me}_{10}]^-$ (**21**−**29**) in dry cyclohexane has been determined at 21 ± 0.5 °C (Table 1). It increases from ∼3 to ∼11 mM as the alkyl chain length and branching increase from $[\text{CB}_{11}\text{Me}_{12}]^-$ to $[1\text{-(2-EtHex)-CB}_{11}\text{Me}_{11}]^-$.

Discussion

This paper describes three significant results. The first two have to do with the manipulation of substituents on the CB_{11}^- skeleton and may well be generalizable to other cage boranes. The third may have significance beyond boron chemistry.

Iodo-to-Alkyl Conversion. Because iodination of the BH vertices on the CB_{11} cage is particularly easy, the ability to convert the iodo substituent to a methyl substituent is a generally valuable synthetic tool. It has been accomplished before by Kumada coupling with MeMgI,[2] but we have never been able to extend this and similar palladium-catalyzed couplings to sterically hindered cases in which five methyl groups surround the iodine atom. The present success with trimethylaluminum significantly expands the range of alkylated CB_{11} anions that are easily accessible in pure form, and the generalization to other trialkylaluminum reagents adds further value.

Triflyloxy-to-Methyl Conversion. The significance of the presently described conversion of a triflyloxy substituent on the CB_{11} skeleton to a methyl substituent is quite different. The triflyloxy group is hardly ever introduced intentionally. Rather, its presence is usually an unintended consequence of a side reaction that competes with the desired methylation of one or more BH vertices with methyl triflate. The ability to replace it with a methyl group now permits the synthesis of clean products from many methylation reactions that previously led to inseparable mixtures, at least in our hands. It is quite possible that conversion of the triflyloxy substituent to alkyls other than methyl with other trialkylaluminums could also be achieved.

Achieving Higher Li^+ Concentrations in Nonligating Solvents. As anticipated, the lithium salts of permethylated CB_{11} anions carrying one or two longer alkyl chains are more soluble in cyclohexane than $\text{Li}[\text{CB}_{11}\text{Me}_{12}]$ (Table 1). What we did not anticipate is the fact that most of the effect on the Li^+ molarity, a factor of ∼2.5, already results from changing the 1-methyl to the 1-ethyl substituent. Making the alkyl longer has basically no additional effect, and branching it to 2-ethylhexyl increases the factor only up to ∼3.3. The introduction of a longer or a branched alkyl in position 12 of the 1-hexyl carrying anion makes little, if any, difference. It appears that, for the purposes of testing Li^+ catalysis in cyclohexane, the easily prepared undecamethylated 1-ethyl anion will be quite adequate, although the presently unknown decamethylated 1-(2-ethylhexyl)-12-isobutyl anion could possibly be marginally better.

We plan to report elsewhere the results of our efforts to find out whether the resulting ∼10 mM concentrations of Li^+ in cyclohexane are high enough for efficient Lewis acid catalysis in an otherwise nonligating medium. In the catalytic complex, the Li^+ cation will undoubtedly not be free but will be associated with a tight ion pair or higher aggregate and presumably located near vertex 12 of the carborane anion.[3] The differently substituted anions may then hinder access to the Li^+ ion to different degrees. It will be interesting to determine whether the catalytic ability of saturated solutions of the new salts parallels their solubility and, if not, to prepare salts of anions carrying chiral substitution near vertex 12 and examine their catalytic behavior.

Experimental Part

Materials. All experimental manipulations were carried out using standard inert-atmosphere techniques. Sulfolane (reagent grade from Aldrich) was vacuum distilled from CaH_2 or dried with 4 Å molecular sieves. Cyclohexane was dried over sodium/benzophenone and distilled. THF was dried and distilled from LiAlH_4. CaH_2, methyl triflate, Me_3Al (2 M solution in toluene), Et_3Al (2 M solution in toluene), *i*-Bu_3Al (2 M solution in toluene), and Octyl_3Al (25% solution in hexane) were of reagent grade and were used as purchased (Aldrich). The Me_3NH^+ salt of $[\text{CB}_{11}\text{H}_{12}]^-$ (**1**) was purchased from Katchem Ltd. (Elišky Krásnohorské 6, Prague 110 00, Czech Republic). The salts $\text{Cs}[\text{CB}_{11}\text{Me}_{12}]$ (**21**)[1,2,10,12] and **12**−**16**[10] were prepared according to published procedures.

Equipment and Measurements. NMR spectra were measured in acetone-d_6, and the following referencing was used: ^{1}H, residual signal of acetone-d_6 (δ = 2.05 ppm); ^{13}C, signal of a acetone-d_6 deuteriomethyl group (δ =29.80 ppm); ^{11}B, signal of $\text{BF}_3\cdot\text{Et}_2\text{O}$ as an external standard in a coaxial capillary (δ = 0.00 ppm). ^{1}H 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 ^{1}H NMR and 125.7 and 150.9 MHz for ^{13}C NMR, respectively. $^1\text{H}\{^{11}\text{B}\}$, ^{11}B, and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were recorded with a Bruker Avance 500 spectrometer working at 499.8 MHz for ^{1}H NMR and 160.4 MHz for ^{11}B NMR, respectively. Assignments of boron signals were done using $^{11}\text{B},^{11}\text{B}$ COSY NMR. Carbon signals of C-1 and methyl groups on carborane are not detectable directly because of $^{11}\text{B}-^{13}\text{C}$ coupling, and therefore H,C-HSQC and H,C-HMBC techniques were used for the assignment of ^{13}C NMR resonances. The methyls in positions 2−6 were distinguished by a H,C-HMBC

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experiment that showed cross-peaks between their protons and 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 as 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 using the CEM Discover S-class or Biotage AB Initiator EXP Microwave synthesis system in a septum-capped 10, 20, or 35 mL microwave tube with magnetic stirring. The temperature was measured by an IR camera, and the power was usually set up in the range of 1 W/10 °C. Open-vessel experiments were performed in the CEM system. Because of hydrogen evolution, the sealed vessels are pressurized during the reaction. The CEM system permits the use of the open-vessel mode, which was used in some cases and is recommended.

Solubility of the Lithium Salts of [1-R-12-R′-$CB_{11}Me_{10}$]$^-$. A dry Li[1-R-12-R′-$CB_{11}Me_{10}$] salt (**21**−**29**) (40−60 mg) was stirred for 24 h under argon in dry cyclohexane (10−15 mL) at 21 ± 0.5 °C. The saturated cyclohexane solution was filtered using a 0.20 μm Teflon filter, and two different volumes (0.5 and 1 mL) were pipetted off to dry preweighed glass vials, which were immediately placed in the CentriVap Centrifugal Vacuum Concentrator (Labconco) and evaporated under reduced pressure (10^{-2} mbar) to dryness at 30 °C for 1 h and then at 90 °C for 12 h. The vials were capped and cooled to room temperature in a desiccator over P_2O_5, and the residue was weighed using automatic Mettler Toledo MX5/A microbalances. The measurements of the solubility were repeated five times for each lithium salt in two different volumes (0.5 and 1 mL).

General Procedure for Cation Exchange from $NHMe_3^+$ to Cs^+. A Me_3NH^+ salt (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 approximately 15 mL volume. This suspension was then extracted with diethyl ether (3 × 150 mL). The combined organic phases were dried over Cs_2CO_3. Diethyl ether was evaporated, and the desired solid of a cesium salt was dried under reduced pressure (10^{-2} mbar/120−140 °C).

General Procedure for Cation Exchange from Cs^+, R_4N^+, and Ph_4P^+ to Li^+. A 1-cm-diameter column was filled with Dowex X-50 cation exchange resin (acid form, 20 g, Fluka), previously washed with a solution of HCl (100 mL, 10%), water (2 × 100 mL), and then acetonitrile (3 × 100 mL). Through this column was eluted a solution of Cs^+, R_4N^+, or Ph_4P^+ salt of [1-R-12-R′-$CB_{11}Me_{10}$]$^-$ (**21**−**29**) (100 mg) in acetonitrile (10 × 20 mL). The column was washed with acetonitrile (~300 mL) until the eluate contains no boron by $^{11}B\{^1H\}$ NMR. The combined acetonitrile fractions were concentrated to ~10 mL using a rotary evaporator. A 10% aqueous solution of LiOH (30 mL) was added, and the solution was evaporated to dryness under reduced pressure. The resulting solid was extracted with ether (3 × 60 mL). The combined ether fractions were subsequently washed with an aqueous solution of LiOH (30 mL, 10%), LiCl (30 mL, 20%), and water (2 × 30 mL), and dried with activated molecular sieves (powder, 4 Å). The sieves were filtered off and washed with dry ether (3 × 20 mL). The combined ether extracts were stirred with LiH (1 g) for 24 h under an argon atmosphere at room temperature to remove any residual LiOH, filtered, and evaporated under reduced pressure to afford a brown oil. To obtain a white product, the oil was dissolved in acetonitrile (~50 mL, HPLC) and the solution was stirred overnight with activated charcoal (5−10% by weight). The charcoal was filtered off using a paper filter and then a 0.45 μm Teflon filter and washed with acetonitrile (3 × 10 mL). Combined filtrates were evaporated, and the product was dried under reduced pressure (10^{-4} mbar) at room temperature (4−8 h), then at 80 °C (6−12 h), and then at 140 °C (overnight). The hygroscopic Li salts of [1-R-12-R′-$CB_{11}Me_{10}$]$^-$ (**21**−**29**) are best stored under argon.

General Procedure for Cation Exchange from $NHMe_3^+$ to Li^+. For exchange of the $NHMe_3^+$ salts of [1-R-12-R′-$CB_{11}Me_{10}$]$^-$ for lithium, instead of cation-exchange chromatography, the following procedure was used. The $NHMe_3^+$ salt of [1-R-12-R′-$CB_{11}Me_{10}$]$^-$ (**21**−**29**, 100 mg) was treated with water (30 mL, HPLC), and an excess of $LiOH \cdot H_2O$ (~100 mg) was added. This solution was stirred for 30 min and then was evaporated to dryness. The solid was again treated with water (30 mL) and concentrated to ~10 mL volume. This suspension was then extracted with diethyl ether (3 × 50 mL). The combined ether fractions were washed with an aqueous solution of LiOH (30 mL, 10%), LiCl (30 mL, 20%), and water (2 × 30 mL) and dried with activated molecular sieves (powdered, 4 Å). The following filtration and workup were the same as those described above.

General Procedure A for Alkylation of 1 in Position 1. **1** (276 mg, 1 mmol) was placed in a Schlenk flask and dried under reduced pressure at 100 °C for 1 h. The flask was charged with argon, and THF (8 mL, freshly distilled from $LiAlH_4$) was added. The solution was cooled to −78 °C and degassed. A solution of *n*-BuLi (1.6 M in hexane, 2.1 mmol) was added at once, and the mixture was stirred for an additional 10 min. The flask was then stirred for 1 h in an ice bath. A white precipitate of Li[1-Li-$CB_{11}H_{11}$] formed during this period. Alkyl iodide (2.5 mmol) was added at 0 °C, and the reaction mixture was allowed to warm to room temperature. Stirring was continued for another 2−4 h, and completion of the reaction was checked by ESI-MS. After the reaction was complete, water was added slowly and the reaction mixture was evaporated to dryness. The residue was extracted with diethyl ether (3 × 10 mL), and the solution was then washed with a 20% solution of CsCl (2 × 10 mL). The combined CsCl wash was extracted with diethyl ether (3 × 10 mL). The combined organic phase was dried over Cs_2CO_3 and evaporated to dryness. The residue was recrystallized from hot water, and hot filtration provided the product as a solid, which was filtered off, washed with water and pentane, and dried at 10^{-2} mbar/120−140 °C to obtain pure Cs[1-R-$CB_{11}H_{11}$] (**2**−**6**).

Cesium 1-Ethyl-1-carba-*closo*-dodecaborate, Cs[1-Et-$CB_{11}H_{11}$] (2). The product was prepared according to the general procedure A, starting from **1** (1 g, 3.62 mmol) in dry THF (30 mL), *n*-BuLi (1.6 M in hexane, 4.8 mL, 7.68 mmol), and ethyl iodide (1.41 g, 9.05 mmol). **2** was isolated as a white solid (884 mg in 80% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.82 (t, 3H, J_{vic} = 7.7 Hz, CH_3CH_2), 1.55 (bs, 6H, H-7,8,9,10,11,12), 1.74 (bs, 5H, H-2,3,4,5,6), 1.82 (q, 2H, J_{vic} = 7.7 Hz, CH_2CH_3). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 14.88 (CH_3CH_2), 33.08 (CH_2CH_3), 71.66 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −12.84 (bs, 5B, B-2,3,4,5,6), −12.53 (bs, 5B, B-7,8,9,10,11), −9.13 (bs, 1B, B-12). IR (KBr pellet): ν 2971 (w, $\nu_{as}(CH_3)$, Et), 2935 (w, $\nu_{as}(CH_2)$, Et), 2876 (w, $\nu_s(CH_3)$, Et), 2535 (vs, ν(B−H)), 1459 and 1451 (w, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, Et), 1378 (w, $\delta_s(CH_3)$, Et), 1337 (w, $\gamma_s(CH_2)$, Et), 1183 (w), 1048 (m), 907 (w) and 728 (m, δ(B−H), CB; ν(C−C), r(CH_3), Et) cm^{-1}. ESI(−)-MS: *m*/*z* 179, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{27}H_{36}B_{11}P$: C, 63.53; H, 7.11. Found: C, 63.66; H, 7.19.

Cesium 1-Propyl-1-carba-*closo*-dodecaborate, Cs[1-Pr-$CB_{11}H_{11}$] (3). The product was prepared according to the general procedure A, starting from **1** (1 g, 3.62 mmol) in dry THF (30 mL), *n*-BuLi (1.6 M in hexane, 4.8 mL, 7.68 mmol), and propyl iodide (1.54 g, 9.05 mmol). **3** was isolated as a white solid (831 mg in 72% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.73 (t, 3H, J_{vic}=7.3 Hz, $CH_3CH_2CH_2$), 1.29 (m, 2H, $CH_3CH_2CH_2$), 1.54 (bs, 6H, H-7,8,9,10,11,12), 1.74 (bm, 7H, H-2,3,4,5,6 and $CH_3CH_2CH_2$). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 14.37 ($CH_3CH_2CH_2$), 24.05 ($CH_3CH_2CH_2$), 42.69 ($CH_3CH_2CH_2$), 70.65 (C-1). $^{11}B\{^1H\}$ NMR

(160.4 MHz, acetone-d_6): δ −12.64 (bs, 10B, B-2,3,4,5,6,7, 8,9,10,11), −9.06 (bs, 1B, B-12). IR (KBr pellet): ν 2958 (w, $\nu_{as}(CH_3)$, Pr), 2933 (w, $\nu_{as}(CH_2)$, Pr), 2871 (w, $\nu_s(CH_3)$, Pr), 2560 (vs), 2542 (vs), 2530 (vs) and 2490 (s, ν(B−H)), 1466, 1457, and 1439 (vw, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, Pr), 1379 (vw, $\delta_s(CH_3)$, Pr), 1180 (w), 1054 (m), 1033 (w) and 726 (w, δ(B−H), CB, ν(C−C), r(CH_3)) cm^{-1}. ESI(−)-MS: m/z 185, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{28}H_{38}B_{11}P$: C, 64.12; H, 7.30. Found: C, 64.26; H, 7.27.

Cesium 1-Butyl-1-carba-*closo*-dodecaborate, Cs[1-Bu-$CB_{11}H_{11}$] (4). The product was prepared according to the general procedure A, starting from **1** (1 g, 3.62 mmol) in dry THF (30 mL), *n*-BuLi (1.6 M in hexane, 4.8 mL, 7.68 mmol), and butyl iodide (1.67 g, 9.05 mmol). **4** was isolated as a white solid (1.02 g in 85% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.81 (t, 3H, J_{vic} = 7.3 Hz, $CH_3CH_2CH_2CH_2$), 1.13 (h, 2H, J_{vic} = 7.3 Hz, $CH_3CH_2CH_2CH_2$), 1.27 (b, 2H, $CH_3CH_2CH_2CH_2$), 1.55 (bs, 5H, H-7,8,9,10,11), 1.75 (bs, 5H, H-2,3,4,5,6), 1.76 (bm, 2H, $CH_3CH_2CH_2CH_2$). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 14.17 ($CH_3CH_2CH_2CH_2$), 23.36 ($CH_3CH_2CH_2CH_2$), 33.19 ($CH_3CH_2CH_2CH_2$), 40.11 (CH_3CH_2-CH_2CH_2), 70.72 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −12.63 (bs, 10B, B-2,3,4,5,6,7,8,9,10,11), −9.07 (bs, 1B, B-12). IR (KBr pellet): ν 2968 (w, $\nu_{as}(CH_3)$, Bu), 2950 and 2928 (w, $\nu_{as}(CH_2)$, Bu), 2866 (w, $\nu_s(CH_3)$, $\nu_s(CH_2)$, Bu), 2600 (w), 2543 (vs), 2521 (vs) and 2490 (s, ν(B−H)), 1467, 1458, 1450, and 1437 (w, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, Bu), 1374 (vw, $\delta_s(CH_3)$, Bu), 1180 (w), 1051 (m) and 726 (w, δ(B−H), CB, ν(C−C), r(CH_3)) cm^{-1}. ESI(−)-MS: m/z 199, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{29}H_{40}B_{11}P$: C, 64.68; H, 7.49. Found: C, 64.56; H, 7.53.

Cesium 1-Hexyl-1-carba-*closo*-dodecaborate, Cs[1-Hex-$CB_{11}H_{11}$] (5). The product was prepared according to the general procedure A, starting from **1** (4 g, 14.50 mmol) in dry THF (100 mL), *n*-BuLi (1.6 M in hexane, 19 mL, 30.40 mmol), and hexyl iodide (7.69 g, 36.26 mmol). **5** was isolated as a white solid (4.47 g in 86% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.85 (t, 3H, J_{vic} = 7.1 Hz, $CH_3(CH_2)_4CH_2$), 1.13 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.20 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.25 (m, 2H, $CH_3CH_2CH_2CH_2$-$CH_2CH_2CH_2$), 1.29 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.55 (bs, 6H, H-7,8,9,10,11,12), 1.76 (bm, 5H, H-2,3,4,5,6), 1.77 (m, 2H, $CH_3(CH_2)_4CH_2$). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 14.25 ($CH_3(CH_2)_4CH_2$), 23.19 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 30.04 (CH_3-$CH_2CH_2CH_2CH_2CH_2$), 30.92 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 32.39 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 40.39 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 70.75 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −12.62 (bs, 10B, B-2,3,4,5,6,7,8,9,10,11), −9.06 (bs, 1B, B-12). IR (KBr pellet): ν 2957 (m, $\nu_{as}(CH_3)$, Hex), 2944 and 2927 (m, $\nu_{as}(CH_2)$, Hex), 2858 (w, $\nu_s(CH_2)$, Hex), 2590 (m), 2560 (s), 2547 (vs), 2533 (vs), 2502 (s) and 2480 (s, ν(B−H)), 1467, 1460, and 1440 (w, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, Hex), 1378 (vw, $\delta_s(CH_3)$, Hex), 1182 (w), 1056 (w), 735 (w) and 723 (w, δ(B−H), CB, ν(C−C), r(CH_3)) cm^{-1}. ESI(−)-MS m/z 227, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{31}H_{44}B_{11}P$: C, 65.72; H, 7.83. Found: C, 65.88; H, 7.74.

Cesium 1-(2-Ethylhexyl)-1-carba-*closo*-dodecaborate, Cs[1-(2-EtHex)-$CB_{11}H_{11}$] (6). The product was prepared according to the general procedure A, starting from **1** (1 g, 3.62 mmol) in dry THF (30 mL), *n*-BuLi (1.6 M in hexane, 4.8 mL, 7.68 mmol), and 2-ethylhexyl iodide (2.17 g, 9.04 mmol). **6** was isolated as a white solid (761 mg in 54% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.77 (t, 3H, J_{vic} = 7.3 Hz, CH_3CH_2CH), 0.87 (t, 3H, J_{vic} = 7.1 Hz, $CH_3CH_2CH_2CH_2CH$), 1.09−1.36 (m, 9H, CH_3CH_2-$CHCH_2CH_2CH_2CH_3$), 1.56 (bs, 6H, H-7,8,9,10,11,12), 1.71 (dd, 1H, J_{gem} = 14.6 Hz, J_{vic} = 5.3 Hz, CCH_aH_bCH), 1.75 (dd, 1H, J_{gem} = 14.6 Hz, J_{vic} = 4.8 Hz, CCH_aH_bCH), 1.78 (bs, 5H, H-2,3,4,5,6). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 11.18 (CH_3CH_2CH), 14.38 ($CH_3CH_2CH_2CH_2CH$), 23.70 (CH_3CH_2-CH_2CH_2CH), 27.25 (CH_3CH_2CH), 29.65 ($CH_3CH_2CH_2CH_2$-CH), 34.18 ($CH_3CH_2CH_2CH_2CH$), 40.52 ($CHCH_2C$), 44.31 ($CHCH_2C$), 70.90 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −12.45 (bs, 10B, B-2,3,4,5,6,7,8,9,10,11), −8.79 (bs, 1B, B-12). IR (KBr pellet): ν 2960 (m, $\nu_{as}(CH_3)$, EtHex), 2928 (m, $\nu_{as}(CH_2)$, EtHex), 2872 (w, $\nu_s(CH_3)$, EtHex), 2858 (w, $\nu_s(CH_2)$, EtHex), 2533 (vs) and 2490 (s, ν(B−H)), 1460 and 1440 (w, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, EtHex), 1379 (w, $\delta_s(CH_3)$, EtHex), 1174 (w), 1054 (w) and 727 (w, δ(B−H), CB, ν(C−C), r(CH_3)) cm^{-1}. ESI(−)-MS: m/z 255, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{33}H_{48}B_{11}P$: C, 66.66; H, 8.14. Found: C, 66.91; H, 8.30.

General Procedure B (Iodination of [1-R-12-H-$CB_{11}H_{10}$]$^-$ at Position 12). A salt of the [1-R-12-H-$CB_{11}H_{10}$]$^-$ anion (**2**−**6**, 1 mmol) was dissolved in glacial acetic acid (20 mL), and iodine was added (2.1 mmol). The reaction mixture was heated overnight at 40 °C. Completion of the reaction was checked by ESI-MS, and if the starting material was still present, another portion of iodine (0.2 mmol) was added and heating was continued. After completion of the reaction, a 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 was dried under reduced pressure. Water was added to the residue and extracted with diethyl ether (3 × 5 mL). The solution was then washed with a 20% solution of CsCl (2 × 5 mL), and the combined CsCl wash was extracted with diethyl ether (3 × 5 mL). The combined organic phase was dried over Cs_2CO_3 and evaporated to dryness, and the residue was recrystallized from water. The crystals were filtered, washed with water and pentane, and dried at 10^{-2} mbar/120−140 °C to obtain a pure salt of [1-R-12-I-$CB_{11}H_{10}$]$^-$ (**7**−**11**) as a white solid.

Cesium 1-Ethyl-12-iodo-1-carba-*closo*-dodecaborate, Cs[1-Et-12-I-$CB_{11}H_{10}$] (7). The product was prepared according to the general procedure B, starting from **2** (400 mg, 1.32 mmol) and iodine (703 mg, 2.77 mmol) in AcOH (13 mL). **7** was isolated as a white solid (418 mg in 74% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.79 (t, 3H, J_{vic} = 7.6 Hz, CH_3CH_2), 1.71 (q, 2H, J_{vic} = 7.6 Hz, CH_3CH_2), 1.76 (bs, 5H, H-2,3,4,5,6), 2.01 (bs, 5H, H-7,8,9,10,11). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 14.72 (CH_3CH_2), 32.66 (CH_3CH_2), 68.80 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −18.16 (bs, 1B, B-12), −12.67 (bs, 5B, B-2,3,4,5,6), −10.87 (bs, 5B, B-7,8,9,10,11). IR (KBr pellet): ν 3598 (m, ν(B−H)), 2965 (w, $\nu_{as}(CH_3)$, Et), 2929 (w, $\nu_{as}(CH_2)$, Et), 2873 (w, $\nu_s(CH_3)$, Et), 2855 (vw, $\nu_s(CH_2)$, Et), 2568 (vs), 2551 (vs), 2523 (s), and 2490 (s, ν(B−H)), 1460, 1452, and 1436 (w, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, Et), 1378 (vw, $\delta_s(CH_3)$, Et), 1337 (vw, $\gamma_s(CH_2)$, Et), 1285 (vw, $\gamma_{as}(CH_2)$, Et), 1182 (w), 1030 (w), 910 (m), 826 (w), 811 (w, ν(B−I)), 736 (w), 725 (w, δ(B−H), β_{as}-(CH_2)), 675 (w, ν(B−I)) cm^{-1}. ESI(−)-MS: m/z 297, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{27}H_{35}$-$B_{11}IP$: C, 50.96; H, 5.54. Found: C, 51.08; H, 5.60.

Cesium 1-Propyl-12-iodo-1-carba-*closo*-dodecaborate, Cs[1-Pr-12-I-$CB_{11}H_{10}$] (8). The product was prepared according to the general procedure B, starting from **3** (400 mg, 1.26 mmol) and iodine (668 mg, 2.63 mmol) in AcOH (13 mL). **8** was isolated as a white solid (445 mg, 80% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.73 (t, 3H, J_{vic} = 7.3 Hz, $CH_3CH_2CH_2$), 1.24 (m, 2H, $CH_3CH_2CH_2$), 1.63 (m, 2H, $CH_3CH_2CH_2$), 1.77 (bs, 5H, H-2,3,4,5,6), 2.00 (bs, 5H, H-7,8,9,10,11). ^{13}C NMR (125.7 MHz, acetone-d_6): 14.25 ($CH_3CH_2CH_2$), 23.96 ($CH_3CH_2CH_2$), 42.03 ($CH_3CH_2CH_2$), 68.00 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −18.10 (bs, 1B, B-12), −12.53 (bs, 5B, B-2,3,4,5,6), −10.88 (bs, 5B, B-7,8,9,10,11). IR (KBr pellet): ν 2963 (m, $\nu_{as}(CH_3)$, Pr), 2933 (w, $\nu_{as}(CH_2)$, Pr), 2871 (w, $\nu_s(CH_3)$, Pr), 2856 (w, $\nu_s(CH_2)$, Pr), 2568 (vs), 2546 (vs), and 2514 (s, ν(B−H)), 1464 and 1457 (w, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, Pr), 1373 (vw, $\delta_s(CH_3)$, Pr), 1293 (vw, $\gamma_{as}(CH_2)$, Pr), 1182 (w), 1113 (vw), 1048 (w), 1033 (w), 945 (w), 898 (w), 829 (w), 812 (m, ν(B−I)), 737 (w), 729 (w, δ(B−H), $\beta_{as}(CH_2)$, $\gamma_{as}(CH_2)$), 683 (w, ν(B−I)) cm^{-1}. ESI(−)-MS: m/z 311, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{28}H_{37}B_{11}IP$: C, 51.71; H, 5.73. Found: C, 51.84; H, 5.80.

Cesium 1-Butyl-12-iodo-1-carba-*closo*-dodecaborate, Cs[1-Bu-12-I-$CB_{11}H_{10}$] (9). The product was prepared according to the general procedure B, starting from **4** (400 mg, 1.20 mmol) and iodine (640 mg, 2.52 mmol) in AcOH (13 mL). **9** was isolated as a white solid (450 mg in 82% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.80 (t, 3H, J_{vic} = 7.3 Hz, CH_3CH$_2$CH$_2$-CH$_2$), 1.13 (m, 2H, CH$_3$CH_2CH$_2$CH$_2$), 1.22 (bm, 2H, CH$_3$CH$_2$-CH_2CH$_2$), 1.66 (bm, 2H, CH$_3$CH$_2$CH$_2$CH_2), 1.78 (bs, 5H, H-2,3,4,5,6), 2.01 (bs, 5H, H-7,8,9,10,11). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 14.10 (*C*H$_3$CH$_2$CH$_2$CH$_2$), 23.25 (CH$_3$*C*H$_2$-CH$_2$CH$_2$), 33.08 (CH$_3$CH$_2$*C*H$_2$CH$_2$), 39.52 (CH$_3$CH$_2$CH$_2$*C*H$_2$), 67.91 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −18.14 (bs, 1B, B-12), −12.50 (bs, 5B, B-2,3,4,5,6), −10.87 (bs, 5B, B-7,8,9, 10,11). IR (KBr pellet): ν 2956 (m, ν_{as}(CH$_3$), Bu), 2945 and 2929 (w, ν_{as}(CH$_2$), Bu), 2863 (w, ν_s(CH$_3$), ν_s(CH$_2$), Bu), 2562 and 2536 (vs, ν(B−H)), 1466, 1457, and 1440 (w, δ_{as}(CH$_3$), β_s(CH$_2$), Bu), 1374 (w, δ_s(CH$_3$), Bu), 1182 (w), 1036 (m), 942 (w), 829 (w), 812 (m, ν(B−I)), 737 (w), 729 (w, δ(B−H), β_{as}(CH$_2$), γ_{as}(CH$_2$)), 684 (w, ν(B−I)) cm^{-1}. For PPh_4^+ salt. Anal. Calcd for $C_{29}H_{39}B_{11}IP$: C, 52.42; H, 5.92. Found: C, 52.61; H, 6.09.

Cesium 1-Hexyl-12-iodo-1-carba-*closo*-dodecaborate, Cs[1-Hex-12-I-$CB_{11}H_{10}$] (10). The product was prepared according to the general procedure B, starting from **5** (2 g, 5.55 mmol) and iodine (3.40 g, 13.40 mmol) in AcOH (100 mL). **10** was isolated as a white solid (2.21 g in 82% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.84 (t, 3H, J_{vic} = 7.0 Hz, CH_3(CH$_2$)$_4$CH$_2$), 1.12 (m, 2H, CH$_3$CH$_2$CH$_2$CH_2CH$_2$CH$_2$), 1.21 (m, 2H, CH$_3$-CH$_2$CH_2CH$_2$CH$_2$CH$_2$), 1.24 (m, 4H, CH$_3$CH_2CH$_2$CH$_2$CH_2-CH$_2$), 1.66 (m, 2H, CH$_3$(CH$_2$)$_4$CH_2), 1.78 (bs, 5H, H-2,3,4,5,6), 2.01 (bs, 5H, H-7,8,9,10,11). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 14.22 (*C*H$_3$(CH$_2$)$_4$CH$_2$), 23.14 (CH$_3$*C*H$_2$CH$_2$CH$_2$CH$_2$-CH$_2$), 29.89 (CH$_3$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$), 30.83 (CH$_3$CH$_2$-CH$_2$CH$_2$*C*H$_2$CH$_2$), 32.30 (CH$_3$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$), 39.77 (CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 67.95 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −18.14 (bs, 1B, B-12), −12.53 (bs, 5B, B-2,3,4,5,6), −10.87 (bs, 5B, B-7,8,9,10,11). IR (KBr pellet): ν 2953 (w, ν_{as}(CH$_3$), Hex), 2944 (w) and 2926 (m, ν_{as}(CH$_2$), Hex), 2857 (w, ν_s(CH$_2$), Hex), 2592 (m), 2549 (s), 2518 (m) and 2493 (m, ν(B−H)), 1466 (w), 1455 and 1440 (vw, δ_{as}(CH$_3$), β_s(CH$_2$), Hex), 1373 (vw, δ_s(CH$_3$), Hex), 1182 (vw), 1049 (vw), 1035 (vw), 939 (w), 829 (w), 813 (w, ν(B−I)), 735 (w), 729 (w, δ(B−H), β_{as}(CH$_2$), γ_{as}(CH$_2$)), 684 (w, ν(B−I)) cm^{-1}. ESI(−)-MS: *m*/*z* 353, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{31}H_{43}B_{11}IP$: C, 53.77; H, 6.26. Found: C, 53.91; H, 6.12.

Cesium 1-(2-Ethylhexyl)-12-iodo-1-carba-*closo*-dodecaborate, Cs[1-(2-EtHex)-12-I-$CB_{11}H_{10}$] (11). The product was prepared according to the general procedure B, starting from **6** (400 mg, 1.03 mmol) and iodine (548 mg, 2.16 mmol) in AcOH (15 mL). **11** was isolated as a white solid (343 mg in 65% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ 0.76 (t, 3H, J_{vic} = 7.1 Hz, CH_3CH$_2$CH), 0.87 (t, 3H, J_{vic} = 7.2 Hz, CH_3CH$_2$CH$_2$-CH$_2$CH), 1.08−1.32 (m, 9H, CH$_3$CH_2CHCH_2CH$_2$CH$_2$CH$_3$), 1.57 (dd, 1H, J_{gem} = 14.6 Hz, J_{vic} = 5.3 Hz, CCH$_a$*H*$_b$CH), 1.63 (dd, 1H, J_{gem} = 14.6 Hz, J_{vic} = 4.8, CC*H*$_a$H$_b$CH), 1.81 (bs, 5H, H-2,3,4,5,6), 2.02 (bs, 5H, H-7,8,9,10,11). ^{13}C NMR (125.7 MHz, acetone-d_6): δ 11.13 (*C*H$_3$CH$_2$CH), 14.35 (*C*H$_3$CH$_2$-CH$_2$CH$_2$CH), 23.64 (CH$_3$*C*H$_2$CH$_2$CH$_2$CH), 27.14 (CH$_3$*C*H$_2$CH), 29.57 (CH$_3$CH$_2$*C*H$_2$CH$_2$CH), 34.05 (CH$_3$CH$_2$CH$_2$*C*H$_2$CH), 40.56 (*C*HCH$_2$C), 43.62 (CH*C*H$_2$C), 68.00 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −17.88 (bs, 1B, B-12), −12.24 (bs, 5B, B-2,3, 4,5,6), −10.83 (bs, 5B, B-7,8,9,10,11). IR (KBr pellet): ν 2959 (m, ν_{as}(CH$_3$), EtHex), 2926 (m, ν_{as}(CH$_2$), EtHex), 2872 (w, ν_s(CH$_3$), EtHex), 2857 (m, ν_s(CH$_2$), EtHex), 2570 (s) and 2537 (vs, ν(B−H)), 1462 and 1444 (w, δ_{as}(CH$_3$), β_s(CH$_2$), EtHex), 1379 (w, δ_s(CH$_3$), EtHex), 1171 (vw), 1037 (w), 943 (w), 829 (w), 813 (m, ν(B−I)), 734 (w, δ(B−H), β_{as}(CH$_2$), γ_{as}(CH$_2$)), 683 (w, ν(B−I)) cm^{-1}. ESI(−)-MS: *m*/*z* 381, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{33}H_{47}B_{11}IP$: C, 55.01; H, 6.57. Found: C, 55.28; H, 6.70.

General Procedure C (Reduction of Iodine in [1-R-12-I-$CB_{11}Me_{10}]^-$ under Birch Conditions). Sodium (1−4 mmol) was dissolved in liquid ammonia (10 mL) in a dry Schlenk flask at −78 °C. A salt of [1-R-12-I-$CB_{11}Me_{10}]^-$ (**12**, **14**−**16**, 0.1 mmol) was dissolved in the minimum amount of dry THF and added dropwise to the solution under vigorous stirring, which was continued for an additional 20 min. A small aliquot was removed and checked by ESI-MS to ensure that the reaction was complete prior to workup. When the reduction was complete, the flask was removed from 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 (5 mL). The solution was acidified with 10% HCl and extracted with diethyl ether (3 × 10 mL). The solution was then washed with a 20% solution of CsCl (2 × 10 mL), and combined CsCl washes were extracted with diethyl ether (3 × 5 mL). The combined organic phases were dried over Cs_2CO_3 or molecular sieves (4 Å), evaporated to dryness, and recrystallized from water. The white crystals were filtered, washed with water and pentane, and vacuum-dried to provide the cesium salt of the pure product [1-R-12-H-$CB_{11}Me_{10}]^-$ (**17**−**20**).

Cesium 1-Ethyl-(2−11)-decamethyl-1-carba-*closo*-dodecaborate, Cs[1-Et-12-H-$CB_{11}Me_{10}$] (17). The product was prepared according to the general procedure C, starting from Cs[1-Et-12-I-$CB_{11}Me_{10}$][10] (**12**; 120 mg, 0.21 mmol) and sodium metal (86 mg, 3.74 mmol) in liquid ammonia (10 mL). **17** was isolated as a white solid (73 mg in 78% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ −0.26 (s, 15H, CH$_3$-7,8,9,10,11), −0.19 (s, 15H, CH$_3$-2,3,4,5,6), 0.81 (t, 3H, J_{vic} = 7.9 Hz, CH_3CH$_2$), 1.31 (s, 1H, H-12), 1.61 (q, 2H, J_{vic} = 7.9 Hz, CH$_3$CH_2). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −2.40 (CH$_3$-2,3,4,5,6), −1.70 (CH$_3$-7,8,9,10,11), 13.37 (*C*H$_3$CH$_2$), 25.34 (CH$_3$*C*H$_2$), 61.40 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −9.21 (bs, 5B, B-2,3,4,5,6), −7.59 (bs, 5B, B-7,8,9,10,11), −1.03 (bs, 1B, B-12). IR (KBr pellet): ν 2925 (s) and 2893 (vs, ν_{as}(CH$_3$), CB), 2970 (m, ν_{as}(CH$_3$), Et), 2944 (s, ν_{as}(CH$_2$), Et), 2827 (s, ν_s(CH$_3$), CB, Et), 2456 (m, ν(B−H)), 1458 (w, δ_{as}(CH$_3$), β_s(CH$_2$), Et), 1436 (w, δ_{as}(CH$_3$), CB), 1375 (w, δ_s(CH$_3$), Et), 1307 (s), 1299 (s), and 1263 (w, δ_s(CH$_3$), CB), 1162 (m), 1148 (m, B-CH$_3$), 1106 (w, B-CH$_3$), 1071 (w), 971 (w), 907 (m; ν(B-CH$_3$), r(CH$_3$)), 864 (w), 803 (vw), 570 and 441 (vw, B-CH$_3$) cm^{-1}. ESI(−)-MS: *m*/*z* 311, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{37}H_{56}B_{11}P$: C, 68.29; H, 8.67. Found: C, 68.51; H, 8.53.

Cesium 1-Butyl-(2−11)-decamethyl-1-carba-*closo*-dodecaborate, Cs[1-Bu-12-H-$CB_{11}Me_{10}$] (18). The product was prepared according to the general procedure C, starting from Cs[1-Bu-12-I-$CB_{11}Me_{10}$][10] (**14**; 207 mg, 0.35 mmol) and sodium metal (170 mg, 7.39 mmol) in liquid ammonia (15 mL). **18** was isolated as a white solid (139 mg in 85% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ −0.26 (bs, 15H, CH$_3$-7,8,9,10,11), −0.20 (bs, 15H, CH$_3$-2,3,4,5,6), 0.81 (t, 3H, J_{vic} = 7.3 Hz, CH_3CH$_2$CH$_2$-CH$_2$), 1.09 (m, 2H, CH$_3$CH_2CH$_2$CH$_2$), 1.29 (bm, 2H, CH$_3$CH$_2$-CH_2CH$_2$), 1.31 (s, 1H, H-12), 1.51 (bm, 2H, CH$_3$CH$_2$CH$_2$CH_2). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −2.20 (CH$_3$-2,3,4,5,6), −1.40 (CH$_3$-7,8,9,10,11), 14.22 (*C*H$_3$CH$_2$CH$_2$CH$_2$), 24.53 (CH$_3$*C*H$_2$CH$_2$CH$_2$), 30.34 (CH$_3$CH$_2$*C*H$_2$CH$_2$), 32.56 (CH$_3$-CH$_2$CH$_2$*C*H$_2$), 61.10 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −9.20 (bs, 5B, B-2,3,4,5,6), −7.59 (bs, 5B, B-7,8,9, 10,11), −1.00 (bs, 1B, B-12). IR (KBr pellet): ν 2928 and 2897 (s, ν_{as}(CH$_3$), CB), 2958 (m, ν_{as}(CH$_3$), Bu), 2870 (m, ν_s(CH$_3$), Bu), 2830 (s, ν_s(CH$_3$), CB), 2439 (m, ν(B−H)), 1465 and 1456 (w, δ_{as}(CH$_3$), β_s(CH$_2$), Bu), 1450, 1437, and 1412 (w, δ_{as}(CH$_3$), CB), 1378 (w, δ_s(CH$_3$), Bu), 1305 (vs), 1278 (w), and 1258 (w, δ_s(CH$_3$), CB), 1162 (m), 1149 (m, B-CH$_3$), 1112 (m, B-CH$_3$), 1062 (w), 993 (w), 928 and 914 (m, ν(B-CH$_3$), r(CH$_3$)), 869 (w), 734 (vw), 569 and 439 (w, B-CH$_3$) cm^{-1}. ESI(−)-MS: *m*/*z* 339, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{39}H_{60}B_{11}P$: C, 69.01; H, 8.91. Found: C, 69.23; H, 9.02.

Cesium 1-Hexyl-(2−11)-decamethyl-1-carba-*closo*-dodecaborate, Cs[1-Hex-12-H-$CB_{11}Me_{10}$] (19). The product was prepared according to the general procedure C, starting from Cs[1-Hex-12-I-$CB_{11}Me_{10}$][10] (**15**; 700 mg, 1.12 mmol) and sodium metal (360 mg, 15.66 mmol) in liquid ammonia (25 mL). **19** was isolated as a white solid (443 mg in 79% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ −0.26 (bs, 15H, CH_3-7,8,9,10,11), −0.20 (bs, 15H, CH_3-2,3,4,5,6), 0.85 (t, 3H, J_{vic} = 7.1 Hz, $CH_3(CH_2)_4CH_2$), 1.08 (m, 2H, $CH_3CH_2CH_2CH_2$-CH_2CH_2), 1.21 (m, 2H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.25 (m, 4H, $CH_3CH_2CH_2CH_2CH_2CH_2$), 1.30 (m, 4H, $CH_3CH_2CH_2$-$CH_2CH_2CH_2$), 1.31 (s, 1H, H-12), 1.51 (m, 2H, $CH_3(CH_2)_4CH_2$). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −2.30 (CH_3-2,3,4,5,6), −1.60 (CH_3-7,8,9,10,11), 14.27 ($CH_3(CH_2)_4CH_2$), 23.25 (CH_3-$CH_2CH_2CH_2CH_2CH_2$), 28.03 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 31.28 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 32.36 ($CH_3CH_2CH_2CH_2$-CH_2CH_2), 32.90 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 61.24 (C-1). ^{11}B-$\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −9.20 (bs, 5B, B-2,3,4,5,6), −7.59 (bs, 5B, B-7,8,9,10,11), −1.00 (bs, 1B, B-12). IR (KBr): ν 2927 and 2898 (vs, $\nu_{as}(CH_3)$, CB), 2958 (s, $\nu_{as}(CH_3)$, Hex), 2853 (s, $\nu_s(CH_2)$, Hex), 2830 (m, $\nu_s(CH_3)$, CB), 2451 (m, ν(B−H)), 1465 and 1455 (w, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, Hex), 1436 (w, $\delta_{as}(CH_3)$, CB), 1374 (vw, $\delta_s(CH_3)$, Hex), 1307 (vs) and 1292 (m, $\delta_s(CH_3)$, CB), 1154 (m, B-CH_3), 1119 (w, B-CH_3), 1064 (vw), 970 (w), 930 and 913 (m, ν(B-CH_3), r(CH_3)), 868 (w), 728 (vw), 669 (vw), 565 (vw), 473 (vw) cm^{-1}. ESI(−)-MS *m*/*z* 367, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{41}H_{64}B_{11}P$: C, 69.67; H, 9.13. Found: C, 69.81; H, 9.21.

Cesium 1-(2-Ethylhexyl)-(2−11)-decamethylcarba-*closo*-dodecaborate, Cs[1-(2-EtHex)-12-H-$CB_{11}Me_{10}$] (20). The product was prepared according to the general procedure C, starting from Cs[1-(2-EtHex)-12-I-$CB_{11}Me_{10}$][10] (**16**; 194 mg, 0.30 mmol) and sodium metal (250 mg, 10.87 mmol) in liquid ammonia (15 mL). **20** was isolated as a white solid (139 mg in 88% yield). $^1H\{^{11}B\}$ NMR (499.8 MHz, acetone-d_6): δ −0.26 (bs, 15H, CH_3-7,8,9,10,11), −0.18 (bs, 15H, CH_3-2,3,4,5,6), 0.74 (t, 3H, J_{vic} = 7.5 Hz, CH_3CH_2CH), 0.88 (t, 3H, J_{vic} = 7.3 Hz, CH_3CH_2-CH_2CH_2CH), 1.10−1.35 (m, 8H, $CH_3CH_2CHCH_2CH_2$-CH_2CH_3), 1.33 (s, 1H, H-12), 1.41 and 1.45 (2 × dd, 2 × 1H, J_{gem} = 15.5 Hz, J_{vic} = 4.4 Hz, CCH_2CH), 1.65 (m, 1H, CCH_2-CH). ^{13}C NMR (150.9 MHz, acetone-d_6): δ −2.45 (CH_3-2,3,4,5,6), −1.65 (CH_3-7,8,9,10,11), 10.33 (CH_3CH_2CH), 14.45 ($CH_3CH_2CH_2CH_2CH$), 23.96 ($CH_3CH_2CH_2CH_2CH$), 27.43 (CH_3CH_2CH), 29.03 ($CH_3CH_2CH_2CH_2CH$), 34.57 (CH_3-$CH_2CH_2CH_2CH$), 34.60 ($CHCH_2C$), 37.11 ($CHCH_2C$), 62.39 (C-1). $^{11}B\{^1H\}$ NMR (160.4 MHz, acetone-d_6): δ −9.09 (bs, 5B, B-2,3,4,5,6), −7.50 (bs, 5B, B-7,8,9,10,11), −0.76 (bs, 1B, B-12). IR (KBr): ν 2929 and 2899 (vs, $\nu_{as}(CH_3)$, CB), 2956 (s, $\nu_{as}(CH_3)$, 2-EtHex), 2861 (s, $\nu_s(CH_2)$, 2-EtHex), 2829 (s, $\nu_s(CH_3)$, CB), 2447 (m, ν(B−H)), 1460 (m, $\delta_{as}(CH_3)$, $\beta_s(CH_2)$, 2-EtHex), 1439 (m, $\delta_{as}(CH_3)$, CB), 1379 (w, $\delta_s(CH_3)$, 2-EtHex), 1308 and 1297 (s, $\delta_s(CH_3)$, CB), 1146 (m, B-CH_3), 1111 (m, B-CH_3), 1064 (w), 1041 (w), 972 (w), 938 and 914 (m, ν(B-CH_3), r(CH_3)), 868 (w), 730 (vw), 569 and 439 (vw, B-CH_3) cm^{-1}. ESI(−)-MS: *m*/*z* 396, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{43}H_{68}B_{11}P$: C, 70.28; H, 9.33. Found: C, 70.51; H, 9.20.

General Procedure D (Substitution of Iodine in [1-R-12-I-$CB_{11}Me_{10}$]$^-$ with Alkyl Using R_3Al). A dry thick-walled Pyrex MW tube was charged with a salt of [1-R-12-I-$CB_{11}Me_{10}$]$^-$ (**12**−**16**; 0.5 mmol) under an argon atmosphere and capped with a rubber septum. The tube was evacuated and refilled with argon three times. A trimethylaluminum solution (20 mmol, 2 M in toluene) was added, and the rubber septum was quickly replaced with a crimp cap. [***Caution!*** *Me_3Al is moisture-sensitive and pyrophoric and should be handled with extreme caution!*] The reaction mixture was heated at 120−130 °C until the substitution was complete. A small aliquot was removed from the tube and checked by ESI(−)-MS to ensure that the reaction was complete prior to workup. After cooling to room temperature, the reaction mixture was slowly poured onto a mixture of crushed ice (ca. 200 mL), CsOH (30 mmol), and disodium ethylenediaminetetraacetic acid (20 mmol). The mixture was then extracted with dichloromethane (3 × 80 mL). The collected organic layers were washed with a 20% solution of CsCl (2 × 10 mL), and combined CsCl washes were extracted with diethyl ether (3 × 5 mL). The combined organic phases were dried over Cs_2CO_3, evaporated to dryness, and recrystallized from water. The white crystals were filtered, washed with water and pentane, and vacuum-dried to provide the pure product [1-R-CB_{11}-Me_{11}]$^-$ (**22**−**26**) as a cesium salt. Alternatively, the product was precipitated as a $NHMe_3^+$ or Ph_4P^+ salt by adding $NHMe_3Cl$ or Ph_4PCl to the solution of [1-R-$CB_{11}Me_{11}$]$^-$ in MeOH/water (1:1−10). The same procedure was applied for the substitution of iodine using triethylaluminum, trioctylaluminum, and triisobutylaluminum to provide a pure salt of [1-R-12-R′-$CB_{11}Me_{10}$]$^-$ (**27**−**29**).

In the case of volatile trimethylaluminum and triethylaluminum, an alternative workup can be used. The excess of trialkylaluminum is removed under reduced pressure, and the oily product mixture is carefully hydrolyzed with crushed ice under argon. The resulting mixture is diluted with diethyl ether, and the workup is continued with extraction as described above.

Tetraphenylphosphonium 1-Ethylundecamethyl-1-carba-*closo*-dodecaborate, Ph_4P[1-Et-$CB_{11}Me_{11}$] (22). The product was prepared according to the general procedure D, starting from Cs[1-Et-12-I-$CB_{11}Me_{10}$][10] (**12**; 400 mg, 0.70 mmol) and a Me_3Al solution (10 mL, 20 mmol, 2 M in toluene) in a dry thick-walled Pyrex MW tube (25 mL) at 130 °C for 40 h. **22** was isolated as a white solid (320 mg, 69% yield). ^1H NMR (500.0 MHz, acetone-d_6): δ −0.52 (bs, 3H, CH_3-12), −0.42 (bs, 15H, CH_3-7,8,9,10,11), −0.19 (bs, 15H, CH_3-2,3,4,5,6), 0.82 (t, 3H, J_{vic} = 7.9 Hz, CH_3CH_2), 1.63 (bq, 2H, J_{vic} = 7.9 Hz, CH_3CH_2), 7.81−7.93 (m, 16H, H-*o*,*m*-Ph), 8.02 (m, 4H, H-*p*-Ph). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −3.10 (CH_3-7,8,9,10,11), −2.76 (CH_3-12), −2.64 (CH_3-2,3,4,5,6), 13.44 (CH_3CH_2), 25.32 (CH_3CH_2), 59.40 (C-1), 118.90 (d, $J_{C,P}$ = 89.6 Hz, C-*i*-Ph), 131.31 (d, $J_{C,P}$ = 12.9 Hz, CH-*m*-Ph), 135.64 (d, $J_{C,P}$ = 10.4 Hz, CH-*o*-Ph), 136.32 (d, $J_{C,P}$ = 3.0 Hz, CH-*p*-Ph). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −9.56 (bs, 5B, B-2,3,4,5,6), −7.50 (bs, 5B, B-7,8,9,10,11), 0.70 (bs, 1B, B-12). IR (KBr pellet): ν 3062 (w, ν(=CH), Ph_4P^+, 20b), 2929 (s) and 2892 (vs, $\nu_{as}(CH_3)$, CB, Et), 2827 (s, $\nu_s(CH_3)$, CB, Et), 1588 (w, ν(CC), Ph_4P^+, 8a), 1485 (m, ν(CC), Ph_4P^+, 19a), 1455 (w, $\delta_{as}(CH_3)$, Et), 1441 (s, ν(CC), Ph_4P^+, 19b), 1436 (s, $\delta_{as}(CH_3)$, CB, ν(CC), Ph_4P^+), 1377 (w, $\delta_s(CH_3)$, Et), 1302 (s, $\delta_s(CH_3)$, CB), 1162 (m), 1188 (w, ν(CC), Ph_4P^+, 9a), 1109 (s, ν(CC), Ph_4P^+, 1, B-CH_3), 1072 (w, ν(CC), Ph_4P^+, 18b), 1029 (w, ν(CC), Ph_4P^+, 18a), 999 (m, ν(CC), Ph_4P^+, 12), 912 (m, ν(B-CH_3)), 751 (w, $\nu_{as}(P^+C_4)$), 723 (s, ν(CC), Ph_4P^+, 11), 689 (s, ν(CC), Ph_4P^+, 4), 616 (vw, ν(CC), Ph_4P^+, 6b), 527 (vs, ν_s-(P^+C_4)), 433 (vw, ν(CC), Ph_4P^+, 7a) cm^{-1}. ESI(−)-MS: *m*/*z* 325, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{38}H_{58}B_{11}P$: C, 68.66; H, 8.79. Found: C, 68.82; H, 8.89.

Cesium 1-Propylundecamethyl-1-carba-*closo*-dodecaborate, Cs[1-Pr-$CB_{11}Me_{11}$] (23). The product was prepared according to the general procedure D, starting from Cs[1-Pr-12-I-$CB_{11}Me_{10}$][10] (**13**; 200 mg, 0.34 mmol) and a Me_3Al solution (7 mL, 14 mmol, 2 M in toluene) in a dry thick-walled Pyrex MW tube (25 mL) at 120−130 °C for 48 h. **23** was isolated as a white solid (104 mg in 65% yield). ^1H NMR (500.0 MHz, acetone-d_6): δ −0.51 (bs, 3H, CH_3-12), −0.41 (bs, 15H, CH_3-7,8,9,10,11), −0.20 (bs, 15H, CH_3-2,3,4,5,6), 0.70 (t, 3H, J_{vic} = 7.3 Hz, CH_3-CH_2CH_2), 1.33 (m, 2H, $CH_3CH_2CH_2$), 1.50 (bm, 2H, $CH_3CH_2CH_2$). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −2.97 (CH_3-7,8,9,10,11), −2.33 (CH_3-12), −2.07 (CH_3-2,3,4,5,6), 15.48 ($CH_3CH_2CH_2$), 21.51 ($CH_3CH_2CH_2$), 35.49 (CH_3CH_2-CH_2), 59.45 (C-1). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −9.57 (bs, 5B, B-2,3,4,5,6), −7.51 (bs, 5B, B-7,8,9,10,11), 0.80 (bs, 1B, B-12). IR (KBr pellet): ν 2934 and 2897 (m, $\nu_{as}(CH_3)$, CB), 2830

(m, $\nu_s(CH_3)$, CB), 1450 (w, $\delta_{as}(CH_3)$, Pr, CB), 1413 (m, $\delta_{as}(CH_3)$, CB), 1375 (w, $\delta_s(CH_3)$, Pr), 1301 (vs) and 1276 (s, $\delta_s(CH_3)$, CB), 908 (m, ν(B-CH_3)), 735 (w), 671 (vw), 570 (m), 441 (m) cm^{-1}. ESI(−)-MS: *m*/*z* 339, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{39}H_{60}B_{11}P$: C, 69.01; H, 8.91. Found: C, 69.27; H, 9.10.

Trimethylammonium 1-Butylundecamethyl-1-carba-*closo*-dodecaborate, NHMe$_3$[1-Bu-CB$_{11}$Me$_{11}$] (24). The product was prepared according to the general procedure D, starting from Cs[1-Bu-12-I-$CB_{11}Me_{10}$][10] (**14**; 150 mg, 0.25 mmol) and a Me_3Al solution (5 mL, 10 mmol, 2 M in toluene) in a dry thick-walled Pyrex MW tube (25 mL) at 120−130 °C for 36 h. **24** was isolated as a white solid (73 mg in 71% yield). ^{1}H NMR (499.8.0 MHz, acetone-d_6): δ −0.51 (bs, 3H, CH_3-12), −0.41 (bs, 15H, CH_3-7,8,9,10,11), −0.19 (bs, 15H, CH_3-2,3,4,5,6), 0.82 (t, 3H, J_{vic} = 7.3 Hz, C*H*$_3$CH$_2$CH$_2$CH$_2$), 1.10 (m, 2H, CH$_3$C*H*$_2$CH$_2$CH$_2$), 1.32 (bm, 2H, CH$_3$CH$_2$C*H*$_2$CH$_2$), 1.55 (bm, 2H, CH$_3$CH$_2$CH$_2$C*H*$_2$), 3.21 (s, 9H, CH_3N). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −3.30 (CH_3-7,8,9,10,11), −2.60 (CH_3-12), −2.20 (CH_3-2,3,4,5,6), 14.26 (*C*H$_3$CH$_2$CH$_2$CH$_2$), 24.59 (CH$_3$*C*H$_2$CH$_2$CH$_2$), 30.43 (CH$_3$CH$_2$*C*H$_2$CH$_2$), 32.63 (CH$_3$CH$_2$CH$_2$*C*H$_2$), 59.20 (C-1), 46.11 (CH_3N). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −9.54 (bs, 5B, B-2,3,4,5,6), −7.51 (bs, 5B, B-7,8,9,10,11), 0.75 (bs, 1B, B-12). IR (KBr pellet): ν 3193 (m, ν(NH), TMA), 2954 (s, $\nu_s(CH_3)$, TMA), 2928 (s) and 2895 (vs, $\nu_{as}(CH_3)$, CB), 2829 (s, $\nu_s(CH_3)$, CB), 2750 (w) and 2524 (vw, ν(NH), TMA), 1478 and 1469 (m, $\beta_s(CH_2)$, Bu), 1455 (m, $\delta_{as}(CH_3)$, Bu), 1435 (w, $\delta_{as}(CH_3)$, CB), 1417 (w, $\delta_s(CH_3)$, TMA), 1378 (w, $\delta_s(CH_3)$, Bu), 1303 (s, $\delta_s(CH_3)$, CB), 1257 (vw), 1250 (vw) and 1047 (w, r(CH_3), TMA), 1151 (m, B-CH_3), 1118 (w, B-CH_3), 970 (m, $\delta_{as}(N^+C_3)$), 913 (m, δ(B-CH_3)), 805 (vw, $\nu_s(N^+C_3)$), 749 (vw) cm^{-1}. ESI(−)-MS: *m*/*z* 353, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{40}H_{60}B_{11}P$: C, 69.34; H, 9.02. Found: C, 69.58; H, 9.19.

Cesium 1-Hexylundecamethyl-1-carba-*closo*-dodecaborate, Cs[1-Hex-CB$_{11}$Me$_{11}$] (25). The product was prepared according to the general procedure D, starting from Cs[1-Hex-12-I-$CB_{11}Me_{10}$][10] (**15**; 140 mg, 0.22 mmol) and a Me_3Al solution (4 mL, 8 mmol, 2 M in toluene) in a dry thick-walled Pyrex MW tube (25 mL) at 120−130 °C for 22 h. **25** was isolated as a white solid (87 mg in 77% yield). ^{1}H NMR (500.0 MHz, acetone-d_6): δ −0.51 (bs, 3H, CH_3-12), −0.41 (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} = 7.1 Hz, C*H*$_3$(CH$_2$)$_4$CH$_2$), 1.09 (m, 2H, CH$_3$CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$), 1.23 (m, 2H, CH$_3$CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$), 1.26 (m, 2H, CH$_3$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 1.33 (m, 2H, CH$_3$CH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$), 1.54 (m, 2H, CH$_3$(CH$_2$)$_4$C*H*$_2$). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −2.70 (CH_3-7,8,9,10,11), −2.20 (CH_3-12), −1.80 (CH_3-2,3,4,5,6), 14.31 (*C*H$_3$(CH$_2$)$_4$CH$_2$), 23.30 (CH$_3$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 28.12 (CH$_3$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$), 31.36 (CH$_3$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$), 32.43 (CH$_3$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$), 32.97 (CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 59.40 (C-1). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −9.55 (bs, 5B, B-2,3,4,5,6), −7.50 (bs, 5B, B-7,8,9,10,11), 0.75 (bs, 1B, B-12). IR (KBr pellet): ν 3193 (m, ν(NH), TMA), 2956 (s, $\nu_s(CH_3)$, TMA), 2928 and 2895 (vs, $\nu_{as}(CH_3)$, CB), 2828 (s, $\nu_s(CH_3)$, CB), 2742 (m) and 2529 (m, ν(NH), TMA), 1480 and 1469 (s, $\beta_s(CH_2)$, Hex), 1455 (m, $\delta_{as}(CH_3)$, Hex), 1438 (m, $\delta_{as}(CH_3)$, CB), 1418 (m, $\delta_s(CH_3)$, TMA), 1379 (m, $\delta_s(CH_3)$, Hex), 1303 (vs, $\delta_s(CH_3)$, CB), 1247 (w), 1056 (w) and 1047 (w, r(CH_3), TMA), 1149 (m, B-CH_3), 1118 (m, B-CH_3), 980 and 971 (m, $\nu_{as}(N^+C_3)$), 913 (s, ν(B-CH_3)), 807 (w, $\nu_s(N^+C_3)$) cm^{-1}. ESI(−)-MS: *m*/*z* 381, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{42}H_{66}B_{11}P$: C, 69.98; H, 9.23. Found: C,70.21; H, 9.34.

Tetramethylammonium 1-(2-Ethylhexyl)undecamethyl-1-carba-*closo*-dodecaborate, Me$_4$N[1-(2-EtHex)-CB$_{11}$Me$_{11}$] (26). The product was prepared according to the general procedure D, starting from Cs[1-(2-EtHex)-12-I-$CB_{11}Me_{10}$][10] (**16**; 200 mg, 0.31 mmol) and a Me_3Al solution (8 mL, 16 mmol, 2 M in toluene) in a dry thick-walled Pyrex MW tube (25 mL) at 120−130 °C for 16 h. **26** was isolated as a white solid (108 mg in 72% yield). ^{1}H NMR (499.8.0 MHz, acetone-d_6): δ −0.51 (bs, 3H, CH_3-12), −0.41 (bs, 15H, CH_3-7,8,9,10,11), −0.18 (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} = 7.1 Hz, C*H*$_3$CH$_2$CH$_2$CH$_2$CH), 1.09−1.39 (m, 8H, CH$_3$C*H*$_2$CHC*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.44 and 1.49 (2× dd, 2 × 1H, J_{gem} = 15.7 Hz, J_{vic} = 4.5 Hz, CCH$_2$CH), 1.68 (m, 1H, CCH$_2$C*H*), 3.46 (s, 12H, CH_3N). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −3.20 (CH_3-7,8,9,10,11), −2.60 (CH_3-12), −2.10 (CH_3-2,3,4,5,6), 10.37 (*C*H$_3$CH$_2$CH), 14.47 (*C*H$_3$CH$_2$CH$_2$CH$_2$CH), 24.00 (CH$_3$*C*H$_2$CH$_2$CH$_2$CH), 27.48 (CH$_3$*C*H$_2$CH), 29.08 (CH$_3$CH$_2$*C*H$_2$CH$_2$CH), 34.63 (CH$_3$CH$_2$CH$_2$*C*H$_2$CH), 34.67 (*C*HCH$_2$C), 37.16 (CH*C*H$_2$C), 56.00 (CH_3N), 60.40 (C-1). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −9.49 (bs, 5B, B-2,3,4,5,6), −7.45 (bs, 5B, B-7,8,9,10,11), 1.05 (bs, 1B, B-12). IR (CCl_4, Li salt): ν 2957 (s, $\nu_{as}(CH_3)$, EtHex), 2931 and 2903 (vs, $\nu_{as}(CH_3)$, CB), 2874 (m, $\nu_s(CH_3)$, EtHex), 2858 (s, $\nu_{as}(CH_2)$), 2834 (m, $\nu_s(CH_3)$, CB), 1459 (m, $\delta_{as}(CH_3)$, EtHex), 1440 (m, $\delta_{as}(CH_3)$, CB), 1379 (w, $\delta_s(CH_3)$, EtHex), 1365 (w, $\gamma_s(CH_2)$), 1312 (s, $\delta_s(CH_3)$, CB), 916 (m, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: *m*/*z* 410, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{44}H_{70}B_{11}P$: C, 70.56; H, 9.42. Found: C, 70.85; H, 9.58.

Cesium 1-Hexyl-12-ethyl-(2−11)-decamethyl-1-carba-*closo*-dodecaborate, Cs[1-Hex-12-Et-CB$_{11}$Me$_{10}$] (27). The product was prepared according to the general procedure D, starting from Cs[1-Hex-12-I-$CB_{11}Me_{10}$][10] (**15**; 200 mg, 0.32 mmol) and Et_3Al (3 mL, 6 mmol, 2 M solution in toluene) in a dry thick-walled Pyrex MW tube (25 mL) at 120−130 °C for 3 days. **27** was isolated as a white solid (110 mg in 65% yield). ^{1}H NMR (499.8 MHz, acetone-d_6): δ −0.32 (bs, 15H, CH_3-7,8,9,10,11), −0.20 (bs, 15H, CH_3-2,3,4,5,6), 0.37 (bm, 2H, CH$_3$C*H*$_2$), 0.76 (bt, 3H, J_{vic} = 7.8 Hz, C*H*$_3$CH$_2$), 0.85 (t, 3H, J_{vic} = 7.1 Hz, C*H*$_3$(CH$_2$)$_4$CH$_2$CH$_2$), 1.08 (m, 2H, CH$_3$CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$), 1.22 (m, 2H, CH$_3$CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$), 1.26 (m, 2H, CH$_3$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 1.32 (m, 2H, CH$_3$CH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$), 1.52 (m, 2H, CH$_3$(CH$_2$)$_4$C*H*$_2$). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −2.80 (CH_3-7,8,9,10,11), −2.20 (CH_3-2,3,4,5,6), 9.90 (CH$_3$*C*H$_2$), 13.15 (*C*H$_3$CH$_2$), 14.30 (*C*H$_3$(CH$_2$)$_4$CH$_2$), 23.30 (CH$_3$*C*H$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 28.04 (CH$_3$CH$_2$CH$_2$CH$_2$*C*H$_2$CH$_2$), 31.35 (CH$_3$CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$), 32.42 (CH$_3$CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_2$), 32.95 (CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$), 59.65 (C-1). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −9.39 (bs, 5B, B-2,3,4,5,6), −7.56 (bs, 5B, B-7,8,9,10,11), 0.87 (bs, 1B, B-12). IR (KBr pellet): ν 2927 and 2894 (vs, $\nu_{as}(CH_3, CH_2)$, CB, alkyl), 2858 (s, $\nu_s(CH_2)$, alkyl), 2827 (s, $\nu_s(CH_3)$, CB), 1456 (w, $\delta_{as}(CH_3)$, alkyl), 1435 (w, $\delta_{as}(CH_3)$, CB), 1377 and 1369 (w, $\delta_s(CH_3)$, alkyl), 1306 (s) and 1295 (m, $\delta_s(CH_3)$, CB), 1147 (m, B-CH_3), 1117 (m, B-CH_3), 911 (m, ν(B-CH_3)), 894 (m) cm^{-1}. ESI(−)-MS: *m*/*z* 396, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{43}H_{68}B_{11}P$: C, 70.28; H, 9.33. Found: C, 70.50; H, 9.47.

Cesium 1-Hexyl-12-isobutyl-(2,11)-decamethyl-1-carba-*closo*-dodecaborate, Cs[1-Hex-12-(*i*-Bu)-CB$_{11}$Me$_{10}$] (28). The product was prepared according to the general procedure D, starting from Cs[1-Hex-12-I-$CB_{11}Me_{10}$][10] (**15**; 200 mg, 0.32 mmol) and *i*-Bu_3Al (8 mL, 2 M solution in toluene) in a dry thick-walled Pyrex MW tube (25 mL) at 120−130 °C for 20 h. The reaction produced a mixture of the desired product and reduced Cs[1-Hex-12-H-$CB_{11}Me_{10}$] (about 20%). The product was purified by repeated recrystallization from water. **28** was isolated as white crystals (97 mg in 54% yield). ^{1}H NMR (499.8 MHz, acetone-d_6): δ −0.33 (bs, 15H, CH_3-7,8,9,10,11), −0.20 (bs, 15H, CH_3-2,3,4,5,6), 0.27 (bm, 2H, (CH$_3$)$_2$CHC*H*$_2$), 0.76 (d, 6H, J_{vic} = 6.5 Hz, (C*H*$_3$)$_2$CHCH$_2$), 0.85 (t, 3H, J_{vic} = 7.1 Hz, C*H*$_3$(CH$_2$)$_4$CH$_2$), 1.07 (m, 2H, CH$_3$CH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$), 1.22 (m, 2H, CH$_3$CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_2$), 1.25 (m, 2H, CH$_3$C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 1.32 (m, 2H, CH$_3$CH$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$), 1.51 (m, 2H, CH$_3$(CH$_2$)$_4$C*H*$_2$), 1.71 (bm, 2H, (CH$_3$)$_2$C*H*CH$_2$). ^{13}C NMR (125.7 MHz, acetone-d_6): δ

−2.60 (CH_3-7,8,9,10,11), −2.10 (CH_3-2,3,4,5,6), 14.30 (CH_3-$(CH_2)_4CH_2$), 23.30 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 26.15 $(CH_3)_2$-$CHCH_2$), 28.00 $(CH_3)_2CHCH_2$), 28.04 ($CH_3CH_2CH_2CH_2CH_2$-CH_2), 28.60 $(CH_3)_2CHCH_2$), 31.35 ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2$), 32.42 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 32.97 ($CH_3CH_2CH_2CH_2$-$CH_2CH_2$), 59.90 (C-1). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −9.34 (bs, 5B, B-2,3,4,5,6), −7.69 (bs, 5B, B-7,8,9,10,11), 0.67 (bs, 1B, B-12). IR (KBr pellet): ν 2927 and 2897 (vs, $\nu_{as}(CH_3, CH_2)$, CB, alkyl), 2856 (s, $\nu_s(CH_2)$), 2829 (s, $\nu_s(CH_3)$, CB), 1465 (w, $\beta_s(CH_2)$), 1455 (w, $\delta_{as}(CH_3)$, alkyl), 1439 (w, $\delta_{as}(CH_3)$, CB), 1375 and 1359 (w, $\delta_s(CH_3)$, alkyl), 1306 (s) and 1297 (m, $\delta_s(CH_3)$, CB), 1148 (m, B-CH_3), 1116 (m, B-CH_3), 908 (m, ν(B-CH_3)) cm^{-1}. ESI(−)-MS: m/z 424, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{45}H_{72}B_{11}P$: C, 70.84; H, 9.51. Found: C, 71.01; H, 9.59.

Cesium 1-Hexyl-12-octyl-(2,11)-decamethyl-1-carba-*closo*-dodecaborate, Cs[1-Hex-12-Octyl-$CB_{11}Me_{10}$] (29). The product was prepared according to the general procedure D, starting from Cs[1-Hex-12-I-$CB_{11}Me_{10}$][10] (**15**; 200 mg, 0.32 mmol) in dry toluene (2 mL) and $Octyl_3Al$ (10 mL, 25% solution in hexane) in a dry thick-walled Pyrex MW tube (25 mL) at 120−130 °C for 4 days. **29** was isolated as a clear oil (142 mg in 72% yield). ^{1}H NMR (500.0 MHz, acetone-d_6): δ −0.32 (bs, 15H, CH_3-7,8,9,10,11), −0.20 (bs, 15H, CH_3-2,3,4,5,6), 0.33 (bm, 2H, $CH_3(CH_2)_6CH_2$), 0.855 (t, 3H, J_{vic} = 7.2 Hz, $CH_3(CH_2)_4CH_2$), 0.87 (t, 3H, J_{vic} = 7.0 Hz, $CH_3(CH_2)_6CH_2$), 1.08 (m, 2H, CH_3-$(CH_2)_2CH_2CH_2CH_2$), 1.12 (m, 2H, $CH_3(CH_2)_4CH_2CH_2CH_2$), 1.17−1.37 (m, 16H, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2$, $CH_3CH_2CH_2$-$CH_2CH_2CH_2CH_2CH_2CH_2$), 1.52 (m, 2H, $CH_3(CH_2)_4CH_2$). ^{13}C NMR (125.7 MHz, acetone-d_6): δ −2.65 (CH_3-7,8,9,10,11), −2.15 (CH_3-2,3,4,5,6), 14.30 ($CH_3(CH_2)_4CH_2$), 14.35 (CH_3-$(CH_2)_6CH_2$), 23.30 ($CH_3CH_2(CH_2)_3CH_2$), 23.36 (CH_3CH_2-$(CH_2)_5CH_2$), 18.60 ($CH_3(CH_2)_6CH_2$), 28.04 ($CH_3(CH_2)_3CH_2$-CH_2), 28.85 ($CH_3(CH_2)_5CH_2CH_2$), 30.26, 30.48 ($CH_3(CH_2)_2$-$CH_2CH_2(CH_2)_2CH_2$), 31.35 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 32.42 ($CH_3CH_2CH_2(CH_2)_2CH_2$), 32.76 ($CH_3CH_2CH_2(CH_2)_4$-CH_2), 32.96 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 35.59 ($CH_3(CH_2)_4$-$CH_2CH_2CH_2$), 59.70 (C-1). ^{11}B NMR (160.4 MHz, acetone-d_6): δ −9.39 (bs, 5B, B-2,3,4,5,6), −7.55 (bs, 5B, B-7,8,9,10,11), 0.76 (bs, 1B, B-12). IR (KBr pellet): ν 2954 (s, $\nu_{as}(CH_3)$, C−CH_3), 2926 and 2904 (vs, $\nu_{as}(CH_3, CH_2)$, CB, alkyl), 2855 (s, $\nu_s(CH_2)$), 2831 (s, $\nu_s(CH_3)$, CB), 1466 (m, $\beta_s(CH_2)$), 1458 (w, $\delta_{as}(CH_3)$, alkyl), 1438 (w, $\delta_{as}(CH_3)$, CB), 1378 (w, $\delta_s(CH_3)$, alkyl), 1306 (s, $\delta_s(CH_3)$, CB), 1147 (m, B-CH_3), 1116 (m, B-CH_3), 915 (m, ν(B-CH_3)), 724 (w) cm^{-1}. ESI(−)-MS: m/z 480, expected isotopic distribution. For PPh_4^+ salt. Anal. Calcd for $C_{49}H_{80}B_{11}P$: C, 71.85; H, 9.84. Found: C, 72.10; H, 9.97.

General Procedure E (Substitution of a Triflyloxy Group in [1-R-$CB_{11}Me_{(11-m)}(OTf)_m$]$^-$ with a Methyl Group Using Me_3Al). A dry thick-walled Pyrex MW tube was charged with a crude mixture of [1-R-$CB_{11}Me_{(11-m)}(OTf)_m$]$^-$ (200 mg, ∼0.3 mmol) under an argon atmosphere and capped with a rubber septum. The tube was evacuated and refilled with argon three times. A trimethylaluminum solution (12 mmol, 2 M in toluene) was added, and the rubber septum was quickly replaced with a crimp cap. [***Caution!*** *Me_3Al is moisture sensitive and pyrophoric and should be handled with extreme caution!*] The reaction mixture was heated to 120−130 °C. A small aliquot was removed from the tube at periodic intervals and checked by ESI(−)-MS to ensure that the reaction was complete prior to cooling to room temperature and workup, which followed the general procedure D.

For example, the general procedure E was used for the preparation of **25**, starting from **5** (0.2 g, 0.56 mmol), CaH_2 (1.18 g, 28 mmol), and MeOTf (2.30 g, 14 mmol) in sulfolane (10 mL) in a 35 mL microwave tube capped with a rubber septum under an argon atmosphere. The reaction mixture was placed into the MW system and heated at 60 °C for 60 min, then at 80 °C for 60 min, and finally at 100 °C for 4 h. A microwave-accelerated reaction provided a mixture of **25** and Cs-[1-Hex-$CB_{11}Me_{10}$(OTf)],[10] which was isolated as a brown oil (∼350 mg) and used without further purification. The pure product was prepared according to the general procedure E, starting from the mixture of [1-Hex-$CB_{11}Me_{11}$]$^-$ and [1-Hex-$CB_{11}Me_{10}$(OTf)]$^-$ salts (∼350 mg; see Figure 1) with a Me_3Al solution (10 mL, 20 mmol, 2 M solution in toluene) in a dry thick-walled Pyrex MW tube (25 mL) at 130 °C for 18 h. **25** was isolated as a white solid (132 mg in 46% overall yield). The course of the reaction is shown in Figure 1.

The two-step conversion of **30**[2] to **21** was performed in a similar fashion in an overall yield of 41%.

Acknowledgment. This work was supported by the Grant Agency of the Czech Republic (Grant 203/09/J058), the Grant Agency of the Academy of Sciences of the Czech Republic (Grant IAA 400550708), and the Academy of Sciences of the Czech Republic (Grant M 200550906).