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N-Alkylation of Ammonioundecahydro-*closo*-dodecaborate(1–) for the Preparation of Anions for Ionic Liquids

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Different *N*-alkylated derivatives of ammonioundecahydro-*closo*-dodecaborate(1–), $[B_{12}H_{11}NH_3]^-$, were prepared. Strategies for the introduction of one alkyl chain or two equal alkyl chains and the trisubstitution by two different alkyl chains were developed. Several of the resulting salts have low melting points and are examples of a new class of ionic liquids.

Introduction

Dodecahydro-*closo*-dodecaborate(2–), $[B_{12}H_{12}]^{2-}$ (**1**), as well as other negatively charged clusters such as $[CB_{11}H_{12}]^{1-}$ and $[SnB_{11}H_{11}]^{2-}$, possess a number of interesting properties not found in other anionic structures. The monocarbon carborane and its derivatives have been used as a superacid [1] and a very weakly nucleophilic anion, which allows, for example, stabilization of the protonated fullerene cation.[2] *C*-alkylated derivatives of $[CB_{11}H_{12}]^{1-}$ are ionic liquids and promote catalytic dehalogenation reactions.[3] Sn-alkylated derivatives of the stannadodecaborate are also meltable salts.[4]

The introduction of heteroatoms into **1** occurs through nucleophilic attack of the cluster on a suitable heteroatom compound. Sulfur,[5] nitrogen,[6] and oxygen [5] can be introduced. Disubstitution of the cluster is possible at a much reduced rate and occurs mostly in the 7-position (i.e., *meta* to the first substituent). The cluster is stable towards strong bases and acids. Reactions with elemental halogens result in mono- and polyhalogenation (depending on the nature of the halogen and the reaction conditions).[7] Electrochemically, the dimer $[B_{24}H_{23}]^{3-}$ can be obtained at +1.5 V.[8]

After the introduction of boron-bound heteroatoms such as S, O, and N, the latter can be reacted more readily. The reactivity of these atoms is influenced by the great electron donating power of the cluster. This results, for example, in the formation of stable sulfonium[9] and oxonium salts[10] and in the formation of stable imino acids.[11]

Cluster **1** can be prepared readily from commercially available stable chemicals on a 100-g scale without specialized equipment.[6,12]

We recently found that *N*,*N*,*N*-trialkyl derivatives of $[B_{12}H_{11}NH_3]^{1-}$ (**2**) represent a new class of ionic liquids.[13] Depending on the cation, these compounds have a melting point below 100 °C and some are liquids at room temperature. By alkylation reactions of **2**, we obtained trisubstituted derivatives carrying three identical alkyl chains. With asymmetrical cations such as *N*-methyl-*N*′-alkylimidazolium or methyltrioctylammonium the salts had a much lower melting point than with symmetrical cations such as tetramethylammonium or tetrabutylammonium. *N*-Hexylpyridinium gave the lowest melting point of all cations investigated. Interestingly, potassium and lithium cations also gave ionic liquids, as did a (solvent-free) proton.

The introduction of *N*-alkyl groups into **2** was first achieved by Kuznetsov and coworkers,[14] who treated $H_3B{\cdot}N(CH_3)_3$ with diborane to afford $[B_{12}H_{11}N(CH_3)_3]^{1-}$ (**3a**), whereas the ethyldimethyl complex yielded $[B_{12}H_{11}NEtMe_2]^{1-}$ (**4**).[15] *N*,*N*,*N*-Triethyl derivative **3b** was obtained through reaction of decaborane(14) with triethylamine and triethylamine–borane complex.[14] All these procedures require the use of toxic and flammable compounds, which are not readily available.

Alkylation of the nitrogen atom in **2** is another more flexible possibility to obtain *N*-alkylated derivatives.[16] With unbranched alkyl halides, trisubstitution was observed in the presence of a base. Sterically more-demanding residues such as benzyl and isopropyl allowed disubstitution but not trisubstitution. *N*-Alkylation of **2** gives higher yields than the direct introduction of a substituted ammonio ligand, and there are no side reactions at the cluster atoms when reasonable care is taken.

It was therefore desirable to investigate in detail conditions under which *N*-alkylation of **2** occurs. Furthermore, it was expected that *N*-substitution with two or three different alkyl chains would yield compounds with still-lower melting points and reduced viscosity. Therefore, we developed synthetic strategies that allow the synthesis of trialkyl

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derivatives of **2** with two different substituents. We found two different routes to such derivatives. In the first route, a methyl substituent was introduced together with an ammonio group to afford **7** (Scheme 3). The second method involved the reduction of Schiff bases of **2** with benzaldehyde[17] to give monobenzyl derivative **10** (Scheme 4). In both of these routes, realkylation to a trisubstituted derivative was possible.

The yields of the obtained products were good (isolated yields 80–90% for one-step alkylations). The purities of the compounds were assessed by NMR spectroscopy and mass spectrometry and were found to be well above 95%. We previously found that elemental analysis of dodecaborate cluster compounds is not reliable.[13]

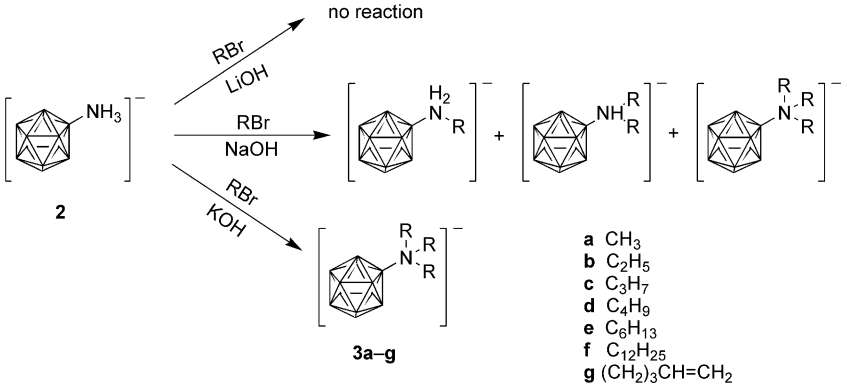
Results and Discussion

For direct alkylation of **2** we found that acetonitrile was the best solvent in the presence of a base. The choice of the base was critical. No reaction occurred when LiOH was used as the base, whereas with NaOH, a mixture of mono-, di-, and trialkyl derivatives of **2** were obtained, with a preponderance of dialkylated products. With the use of KOH, the main product was the trialkylated derivative, with trace amounts of dialkylated product (see Scheme 1). Products **3a**–**g** were isolated as potassium salts.

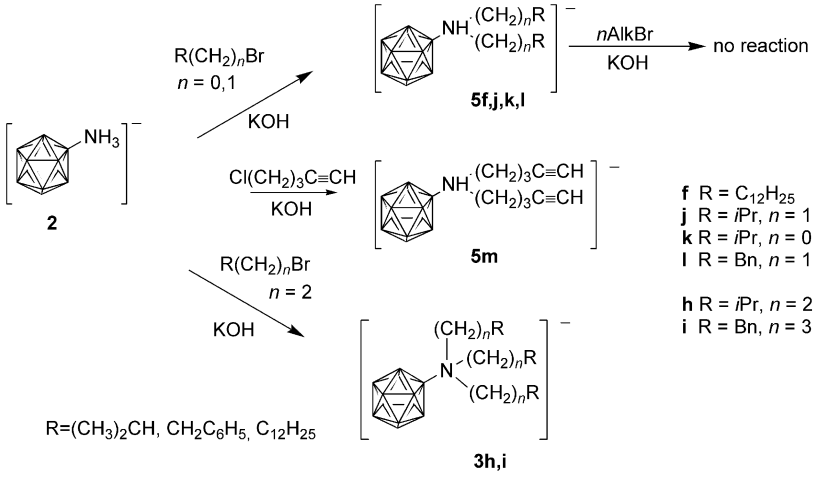
With branched alkyl halides, trialkylation was observed when two (and probably more) methylene groups were present between the halogen and the branching atom (Scheme 2); reactions with isopropyl bromide [16] and isobutyl bromide gave only disubstituted derivatives **5k** and **5j**, respectively, which could not be alkylated further even with unbranched alkyl halides. Compound **2** did not react with *tert*-butyl bromide. We suspect that elimination of HBr to isobutene is the reason. With less reactive 5-chloro-1-pentyne, only disubstitution to **5m** was observed.

Previously, it was observed for benzyl chloride that substitution also stops after the introduction of two benzyl groups.[16] Here we found that the same was true for 1-bromo-2-phenylethane (resulting in **5l**). Again, this ammonio derivative was unreactive to further alkylation.

The successful introduction of an unsubstituted ammonio group by reaction of **1** with hydroxylamine-*O*-sulfonic acid led us to try the reaction of *N*-methylhydroxylamine-*O*-sulfonic acid [18] with **1**. We obtained **7**; the yield was 49% when a 1:6 ratio of **1** and *N*-methylhydroxylamine-*O*-

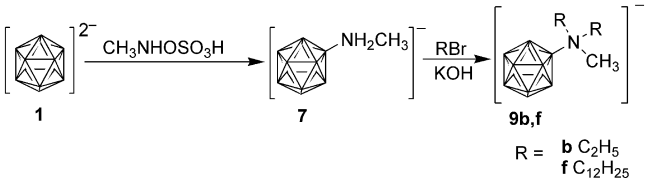


Scheme 1. Influence of base on alkylation.



Scheme 2. Influence of alkyl halide on alkylation.

sulfonic acid was used. Further alkylation proceeded in the same manner as that observed for **2**, which was expected because of the small steric demand of the methyl group (Scheme 3).



Scheme 3. Preparation of **7** and subsequent alkylation.

Monobenzyl derivative **10** was first obtained by Sivaev et al.[17] The nitrogen atom could be alkylated under standard conditions. In contrast to the alkylation with benzyl chloride, which stopped at dibenzyl derivative **5l**, alkylation proceeded to afford trisubstituted ammonio derivative **11** (Scheme 4). Interestingly, no reaction occurred with 2-bromo-1-(*N*,*N*,*N*-trimethylammonio)ethane, whereas *N*,*N*-dimethylaminoethyl derivative **11n** was obtained with the corresponding 1-dimethylamino-2-bromoethane. In aqueous solution, **11n** is positively charged at neutral pH, and it is only the second derivative of **1** described with a net positive charge (the first one was described by us recently).[11]

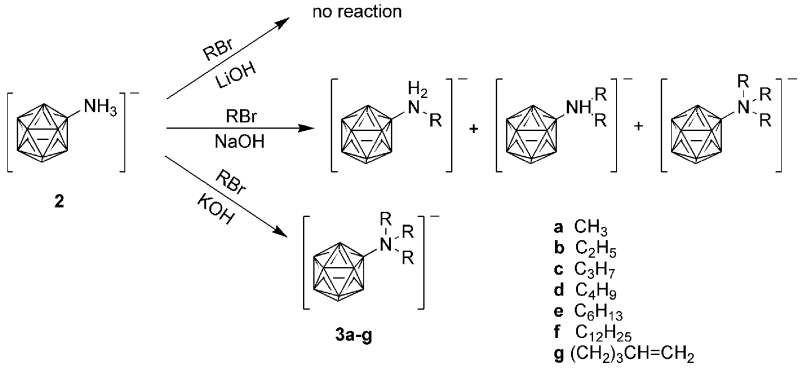
The compounds can be purified by recrystallization from diethyl ether or purified by silica-gel chromatography with ethyl ether/ethyl acetate (2:1).

Assessment of the purity of the compounds was slightly hampered by their usually UV-transparent nature, which prevented the use of HPLC with UV detection, and their obvious lack of volatility. From ^{1}H NMR spectroscopy, the purity of the compounds was to be better than 90%. Electrospray mass spectrometry showed very little, if any, impurities; these could be seen after, for example, carrying out the alkylation at too high temperatures, where bromination can occur; this can easily be detected by mass spectrometry, although the extent of bromination is too low to be seen by ^{11}B NMR spectroscopy. Elemental analysis for dodecaborate-containing compounds was previously found to be unreliable.[19] For the ionic liquids prepared by us, we found the same analytical problem.[13]

For most compounds prepared here, K^+ is the initial counterion, but this ion can be exchanged with other cations by a variety of methods. For short chains, compounds **3** could be exchanged by dissolving the K^+ salt in water and adding an equivalent amount of an organic cation halide. The organic cation salts precipitate and can be filtered off or extracted with ethyl acetate. For longer chains, when the K^+ salts are not soluble in water, the exchange can be performed by dissolving the K^+ salt in a mixture of ethyl acetate/methanol (adding enough methanol to dissolve the salt) and adding an equimolar amount of the desired cation chloride. KCl precipitates and can be filtered off. The solvent can then be evaporated, and the remaining solvent and water are removed under high vacuum and high temperature (150–200 °C) in a kugelrohr oven. Alternatively, K^+ can be exchanged by H^+ through cation exchange, and the resulting solution can be neutralized with the appropriate hydroxide. In this way, the Li^+ salts can be obtained. The H^+ salt can also be obtained from the K^+ salt by adding HCl gas and removing the KCl precipitate. Interestingly, the salts are obtained without solvent, and noteworthy is that the H^+ ion is obtained free of water. We found no ^{1}H NMR signal for H^+, which indicates that the proton exchanges rapidly with the protons of the cluster. This was previously observed for hexahydrohexaborate, $[B_6H_6]^{2-}$,[20] and is also borne out by the ease with which H–D exchange can be achieved with DCl.[21]

The melting points of the compounds (Table 1) are highest when tetramethylammonium serves as the counterion. It should be mentioned that the exact determination of the melting points by direct observation was sometimes not easy, as some of the melts are highly viscous liquids.

A few trends concerning the dependence of the melting points on the kind and structure of the *N*-alkyl chains can be deduced. The melting points of the K^+ salts decrease dramatically when going from the tributyl (**3d**) to the tris(2-methylbutyl) (**3h**) chain and even more so when going to the trihexyl (**3e**) chain. For the *N*-hexylpyridinium and the



Scheme 4. Alkylation of benzyl derivative.

Table 1. Melting points [°C] of $[B_{12}H_{11}NR_2R']^{1-}$ anions with different cations.

Anion	R = (R′ =)	Tetramethyl-ammonium	Tetrabutyl-ammonium	Methyltrioctyl-ammonium	*N*-Hexyl-pyridinium	*N*-Methyl-*N*′-butyl-imidazolium	K^+	Li^+
2	H	>250[a]	188–190[a]				>250[a]	222 (decomp.)[a]
3a	methyl				128–129[a]			
3b	ethyl	314[b]	194[c]		130–132[a]	128–130[a]	370[a]	
3c	propyl	256–258[a]	172–174[a]		126–128[a]	143–145[a]	>250[a]	
3d	butyl	222–225[a]	175–176[a]		40–50[a]	115–116[a]	190[a]	
3e	hexyl	183–186[a]	75–78[a]	<25	47–50[a]	95–97 [c]	≈65[a]	≈65[a]
3f	dodecyl	60[a]	40–45[a]		<25[a]	25[a]	≈40[a]	
3g	pent-4-enyl	191 (decomp.)	50–60[a]			<25		
3h	3-methylbutyl	>250	112–114[a]		<25[a]	87–90[a]	117–120	
3i	3-phenylpropyl	191–193						
5f	dodecyl (H)	135–140	72–74			58–62		
5j	2-methylpropyl (H)	>250						
5k	isopropyl (H)		226[c]					
5l	benzyl (H)	236[c]						
5m	pent-4-ynyl	163–173						
7	H (methyl)	>250						
9b	ethyl (methyl)	>250						
9f	dodecyl (methyl)	65–70						
11b	ethyl (benzyl)		122					

[a] Ref.[13] [b] Ref.[14] [c] Ref.[16]

tetrabutylammonium salts, this decrease is observed when changing from the tributyl (**3d**) to the trihexyl (**3e**) chain. For short chains, this trend is not observed with the *N*-methyl-*N*′-butylimidazolium cation. For this cation, trihexyl derivative **3e** has a higher melting point than the K^+ salt. Interestingly, for many compounds, *N*-methyl-*N*′-butylimidazolium salts have higher melting points than the *N*-hexylpyridinium salts.

For methyldidodecylammonio derivative **9f**, the tetramethylammonium salt melts at only a few degrees higher than the tridodecyl derivative. Similarly, benzyldiethyl derivative **11b** as the tetrabutylammonium salt shows a melting point that is lower than that of tributyl compound **3d** and about the same as that of tris(2-methylbutyl) compound **3h**. With two hexynyl groups as alkyl chains, the melting point for the tetramethylammonium salt is lower than that with three hexyl chains.

Conclusions

We found conditions under which alkyl halides can produce *N*,*N*,*N*-trialkyammonio derivatives of dodecaborate from ammonio derivative **2**, and we could exchange the cation through metathesis or ion exchange. Many of the salts prepared have melting points below 100 °C and can be considered as ionic liquids. Even liquid K^+ and Li^+ salts can be obtained. Trisubstitution with two different side chains is possible for special cases (methyl and benzyl). Initial trends for the correlation between structure and melting points have been found; these will be explored further when compounds are to be optimized for specific uses.

Experimental Section

General: The disodium salt of **1** was prepared through oxidation of $NaBH_4$ with I_2 according to Komura et al.[12] or purchased (as the cesium salt) from BASF (Ludwigshafen, Germany). The triethylammonium salt of **2** was prepared from **1** according to Hertler and Raasch.[6] NMR spectra were recorded with a Bruker DPX 200 spectrometer (200, 50, and 64 MHz for ^1H, ^{13}C, and ^{11}B, respectively). IR spectra (KBr pellet) were collected with a BioRad FTS 155 spectrometer. Electrospray mass spectra were measured with a Bruker Esquire spectrometer. The charge was determined through isotope satellite peaks. For boron-containing compounds, the peak with the highest intensity is given. Melting points were measured with a Büchi 512 apparatus. *N*-Methylhydroxylamine-*O*-sulfonic acid was prepared according to Schmitz et al.[18] Substances were characterized and their purity assessed by electrospray mass spectrometry and ^1H, ^{13}C, and ^{11}B NMR spectroscopy. As previously found for this class of substances, and for other substances containing the dodecaborate cage, elemental analysis was erratic and unreliable.[13,19] *N*-Benzylammonioundecahydrododecaborate(1–) tetrabutylammonium salt (**10**) was prepared according to Sivaev et al.[17] Melting points of the compounds are found in Table 1.

Preparation of $KB_{12}H_{11}NH_3$ (2): The triethylammonium salt of **2** (25.96 g, 0.1 mol) was suspended in distilled water (100 mL). KOH (5.6 g, 0.1 mol) in water (50 mL) was added at room temperature and then heated to boiling to evaporate triethylamine. The water was removed by rotary evaporation, and the residue was dried under vacuum. Yield: 19.66 g (100%).

General Method for the Preparation of *N*,*N*,*N*-Trialkylammonioundecahydrododecaborate(1–) K^+ Salts (3a–i): The K^+ salt of **2** (0.1966 g, 1.0 mmol) was dissolved in dry acetonitrile (15–20 mL) at room temperature. Finely powdered KOH (0.84 g, 15.0 mmol) was added. Then, alkyl bromide (3.2 mmol; in case of methyl, CH_3I was used), diluted in acetonitrile, was added through a dropping funnel. The mixture was stirred for 24 h at room temperature, and the solids (KBr and excess KOH) were removed by filtration. The solvent was removed, and the residue was recrystallized from diethyl ether (chain lengths up to 5 carbon atoms) or chromatographed on silica gel (diethyl ether/ethyl acetate, 2:1). The yields were 80–94%.

3a: ^1H NMR (CD_3CN): δ = 2.84 [s, 9 H, $N(CH_3)_3$], 0.12–2.42 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): *m*/*z* = 200 $[A]^-$.

3b: ^{1}H NMR (CD_3CN): δ = 3.24 (q, J = 5.4 Hz, 6 H, CH_2CH_3), 1.32 (t, J = 3.7 Hz, 9 H, CH_2CH_3), 0.1–2.7 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 241 $[A]^-$.

3c: ^{1}H NMR (CD_3CN): δ = 2.97–3.06 (m, 6 H, N-CH_2-), 1.71–1.89 (m, 6 H, CH_3-CH_2-), 0.84 (t, J = 3.7 Hz, 9 H, CH_3-CH_2-), 0.1–2.6 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 284 $[A]^-$, 606 $[2A + K]^-$. MS (ESI+, CH_3CN): m/z = 362 $[A + 2K]^+$.

3d: ^{1}H NMR (CD_3CN): δ = 3.06 (m, 6 H, N-CH_2-), 1.79 (m, 6 H, N-CH_2-CH_2-), 1.29 (m, 6 H, CH_3-CH_2-), 0.92 (t, J = 3.4 Hz, 9 H, CH_3-CH_2-), –0.1–2.4 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 326 $[A]^-$. MS (ESI+, CH_3CN): m/z = 404 $[A + 2K]^+$.

3e: ^{1}H NMR (CD_3CN): δ = 3.07 (m, 6 H, N-CH_2-), 1.77 (m, 6 H, N-CH_2-CH_2-), 1.29 [s, 18 H, CH_3-$(CH_2)_3$-], 0.89 (t, J = 3.2 Hz, 9 H, CH_3-CH_2-), 0.1–2.5 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 410 $[A]^-$.

3f: ^{1}H NMR ($CDCl_3$): δ = 3.06 (m, 6 H, N-CH_2-), 1.82 [m, 6 H, CH_3-CH_2-$(CH_2)_{10}$-], 1.26 [s, 54 H, CH_3-CH_2-$(CH_2)_9$-CH_2-], 0.89 [t, J = 3.3 Hz, 9 H, CH_3-$(CH_2)_{11}$-], 0.2–2.3 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 662 $[A]^-$. MS (ESI+, CH_3CN): m/z = 740 $[A + 2K]^+$.

3g: ^{1}H NMR ($CDCl_3$): δ = 5.81 (m, 3 H, CH_2=C*H*-), 4.99 (m, 6 H, CH_2=CH-), 3.02 (m, 6 H, N-CH_2-), 1.95 (m, 6 H, N-CH_2-CH_2-), 1.82 (m, 6 H, H_2C=CH-CH_2-), –0.3–2.7 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 362 $[A]^-$.

3h: ^{1}H NMR (CD_3CN): δ = 3.09–3.18 (m, 6H N-CH_2-), 3.07 [s, 12 H, N(CH_3)$_4$], 1.61–1.76 (m, 6 H, N-CH_2-CH_2-), 1.49–1.59 [m, 3 H, $(CH_3)_2CH$-], 0.92 (s, 6 H,CH_3-CH-CH_3), 0.89 (s, 6 H, CH_3-CH-CH_3) 0.11–2.56 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 368 $[A]^-$.

3i: ^{1}H NMR (CD_3CN): δ = 7.15–7.32 (m, 15 H, CH_{Ar}), 3.10–3.15 (m, 6 H, N-CH_2-), 3.06 [s, 12 H, (CH_3)$_4$N], 2.48–2.55 (m, 6 H, Ph-CH_2-), 1.98–2.12 (m, 6 H, N-CH_2-CH_2-) ppm. MS (ESI–, CH_3CN): m/z = 512 $[A]^-$. MS (ESI+, CH_3CN): m/z = 74 $[cat]^+$, 660 $[A + 2cat]^+$.

General Method for the Preparation of *N*,*N*-Dialkylammonioundecahydrododecaborate(1–) Tetramethylammonium Salts 5j–m: The procedure for the preparation of **3** was followed. Compounds **5k** and **5l** are known in the literature.[16]

5j: ^{1}H NMR (CD_3CN): δ = 3.51–3.87 (m, 1 H, N*H*), 3.23–3.36 (m, 4 H, N-CH_2-), 3.07 [s, 12 H, (CH_3)$_4$N], 2.11–2.31 [m, 2 H, $(CH_3)_2$-C*H*-], 0.91 [t, J = 1.4 Hz, 12 H, $(CH_3)_2$CH-], 0.07–2.45 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 270 $[A]^-$, 614 $[2A + cat]^-$. MS (ESI+): m/z = 74 $[cat]^+$, 418 $[A + 2cat]^+$.

5m: 5-Chloropent-1-yne was used. Yield: 0.284 g (78%). ^{1}H NMR ([D$_6$]DMSO): δ = 3.07 [s, 12 H, (CH_3)$_4$N], 2.68–2.87 (m, 4 H, N-CH_2-), 2.09–2.22 (m, 4 H, N-CH_2-CH_2-), 1.62–1.98 (m, 6 H, *H*C≡C-CH_2-), –0.12–2.32 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 290 $[A]^-$, 654 $[cat + 2A]^-$. MS (ESI+, CH_3CN): m/z = 74 $[cat]^+$, 438 $[A + 2cat]^+$.

Preparation of *N*,*N*-Didodecylammonioundecahydrododecaborate(1–) Tetramethylammonium Salt (5f): The procedure for the preparation of **3** was followed, but NaOH was used instead of KOH. The residue was chromatographed on silica gel. The main fraction was **5f**, which was converted into the tetramethylammonium salt. ^{1}H NMR (CD_3CN): δ = 3.58–3.89 (m, 1 H, N*H*-CH_2-), 3.08 (m, 4 H, N-CH_2-), 1.81 [m, 4 H, CH_3-CH_2-$(CH_2)_{10}$-], 1.27 [s, 36 H, CH_3-CH_2-$(CH_2)_9$-CH_2-], 0.88 [t, J = 3.2 Hz, 9 H, CH_3-$(CH_2)_{11}$-] ppm. MS (ESI–, CH_3CN): m/z = 494 $[A]^-$. MS (ESI+, CH_3CN): m/z = 572 $[A + 2cat]^+$.

***N*-Methylammonioundecahydrododecaborate(1–) Tetramethylammonium Salt (7):** A mixture of the Na^+ salt of **1** (8.9 g, 40 mmol), *N*-methylhydroxylamine-*O*-sulfonic acid (30.5 g, 240 mmol), and water (100 mL) was heated at reflux overnight. The mixture was cooled and tetramethylammonium chloride (8.76 g, 80 mmol) in water was added. The precipitate was filtered, dried in air, suspended in hot acetonitrile (200 mL), and then filtered hot. The solid was unreacted **1** (tetramethylammonium salt). The solvent was removed, and the white residue was dried in air. Yield: 4.81 g (49%). ^{1}H NMR (CD_3CN): δ = 4.62–5.18 (m, 2 H, NH_2-CH_3), 3.07 [s, 12 H, (CH_3)$_4$N], 2.44 (t, J = 3.01 Hz, 3 H, CH_3-NH_2), –0.18–2.42 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 172 $[A]^-$, 417 $[2A + cat]^-$. MS (ESI+, CH_3CN): m/z = 74 $[cat]^+$, 320 $[A + 2cat]^+$, 566 $[2A + 3cat]^+$.

General Method for the Alkylation of 7 To Afford *N*,*N*-Dialkyl-*N*-methylammonioundecahydrododecaborates(1–) 9b and 9f: At room temperature, the tetramethylammonium salt of **7** (0.246 g, 1.0 mmol) was dissolved in dry acetonitrile (15 mL) and powdered KOH (0.84 g, 15.0 mmol) was added, followed by the dropwise addition of alkyl bromide (3.0 mmol). The mixture was stirred for 24 h at room temperature and worked up as described above for **3**.

9b: Yield: 96%. ^{1}H NMR ([D$_6$]DMSO): δ = 3.03–3.16 (m, 4 H, CH_3-CH_2-), 3.06 [s, 12 H, (CH_3)$_4$N], 2.95 (s, 3 H, CH_3-N), 1.16 (t, J = 3.5 Hz, 6 H), 0.1–2.38 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 228 $[A]^-$, 529 $[2A + cat]^-$. MS (ESI+, CH_3CN): m/z = 74 $[cat]^+$, 376 $[2cat + A]^+$.

9f: Yield: 88%. ^{1}H NMR ($CDCl_3$): δ = 3.31 [s, 12 H, (CH_3)$_4$N], 2.95–3.15 (m, 4 H, N-CH_2-), 2.85 (s, 3 H, N-CH_3), 1.48–1.70 [m, 4 H, CH_3-CH_2-$(CH_2)_{10}$-], 1.25 [s, 36 H, CH_3-CH_2-$(CH_2)_9$-CH_2-], 0.88 [t, J = 3.3 Hz, 9 H, CH_3-$(CH_2)_{11}$-], 0.1–2.38 (m, 11 H, B*H*) ppm. MS (ESI–, CH_3CN): m/z = 508 $[A]^-$. MS (ESI+, CH_3CN): m/z = 74 $[cat]^+$.

***N*-Benzyl-*N*,*N*-diethylammonioundecahydrododecaborate(1–) K^+ Salt (11b):** A mixture of **10** (0.20 g, 0.41 mmol), powdered KOH (0.23 g, 4.10 mmol), and ethyl bromide (0.27 g, 2.46 mmol) in dry acetonitrile (5 mL) was stirred overnight at room temperature. Work up as for **3b**. Yield: 0.21 g (94%). IR (KBr): $\tilde{\nu}$ = 2965, 2937, 2876 (C–H) 2491 (B–H) 1472 (arene) cm^{-1}. ^{1}H NMR (CD_3CN): δ = 7.37–7.51 (m, 5H CH_{Ar}), 4.66 (s, 2 H, N-CH_2-Ph), 3.37 (q, J = 5.5 Hz, 4 H, N-CH_2-CH_3), 3.03–3.12 (m, 8 H, N-CH_2-CH_2), 1.52–1.67 (m, 8 H, N-CH_2-CH_2-CH_2-), 1.25–1.44 (m, 8H CH_3-CH_2-CH_2-), 1.14 (t, J = 4.0 Hz, 6 H, CH_3-CH_2-), 0.97 (t, J = 3.5 Hz, 9 H, CH_3-CH_2-CH_2-), 0.0–2.8 (m, 11 H, B*H*) ppm. ^{13}C NMR (CD_3CN): δ = 11.28, 13.22, 19.73, 23.72, 54.52, 58.76, 67.97, 128.89, 129.17, 129.37, 133.22 ppm. ^{11}B NMR (CD_3CN): δ = –7.52, –11.02 ppm. MS (ESI–, CH_3CN): m/z = 304 $[A]^-$. MS (ESI+, CH_3CN): m/z = 242 $[cat]^+$.

***N*-Benzyl-*N*,*N*-bis(2-dimethylaminoethylammonio)undecahydrododecaborate(1–) K^+ Salt (11n):** The same procedure as that used for the preparation of **11b** was followed. The product was identified by mass spectrometry, but was not purified further.

General Method for the Exchange of K^+ to Other Cations (Tetramethylammonium, Tetrabutylammonium, *N*-Methyl-*N*′-butylimidazolium, *N*-Hexylpyridinium)

By Precipitation from Water: For short side chains (up to hexyl), the K^+ salt was dissolved in water and a solution of of the appropriate organic cation as bromide or chloride (1 equiv.) in water was added, whereupon the cluster with the organic cation was precipitated and recovered by filtration.

By Metathesis in Organic Solvents: For longer chains, the K^+ salt was dissolved in acetonitrile to which enough methanol was added

to dissolve the salt. A solution of the appropriate cation as chloride (1 equiv.) in acetonitrile was added, and the precipitated KCl was removed by filtration. The solvent was evaporated to obtain the desired salt.

Method for the Exchange of K^+ to Li^+: The K^+ salt was dissolved in water and passed over ion exchange resin (Dowex 50) in H^+ form. The eluate was titrated to neutrality with LiOH, and the solvent was evaporated.

Method for the Exchange of K^+ to H^+: The K^+ salt was dissolved in dry acetonitrile, and dry HCl gas was bubbled through the solution. The KCl precipitate was filtered off, the solvent was removed, and the residue was thoroughly dried at 200 °C under vacuum. Alternatively, the exchange was made as for the exchange to Li^+.

Supporting Information (see footnote on the first page of this article): ESI mass spectra, ^1H and ^{13}C NMR spectra of the compounds.

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