Undecahydro-*closo*-dodecaborates as good leaving groups in organic synthesis: generation of substituted styrenes *via* elimination of arylethyl dodecaborates

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New functionalized arylethyl undecahydro-*closo*-dodecaborates (*S*,*S*-disubstituted $B_{12}H_{11}SH^{2-}$, *N*,*N*-disubstituted $B_{12}H_{11}NH_3^-$ and *O*-substituted $B_{12}H_{11}OH^{2-}$) are prepared by a simple one-step reaction. Moderate to good yields are obtained in the presence of various functional aryl groups. The synthesis of functionalized styrene derivatives can be readily achieved by treating arylethyl undecahydro-*closo*-dodecaborates with various bases. The scope and limitations of this procedure are demonstrated by investigating an array of alkylated dodecaborates. Based on an E2 elimination reaction, we identify the mechanistic pathway for dealkylation of arylethyl dodecaborates. Mechanistic studies indicate the following essential requirements to promote the elimination reaction: (i) the presence of α-CH acidity of the phenethyl group; (ii) steric hindrance; (iii) a substituted heteroatom on the *closo*-$B_{12}H_{11}^{2-}$ cage and (iv) the presence of an electron-withdrawing group on the aromatic ring.

Introduction

Functionalized derivatives of the undecahydro-*closo*-dodecaborate anion $[B_{12}H_{12}]^{2-}$ are promising candidates for boron neutron capture therapy (BNCT).[1,2] For example, the thiol-substituted derivative, mercaptoundecahydro-*closo*-dodecaborate(2–) [HS–$B_{12}H_{11}]^{2-}$ **1a**, is utilized in the treatment of gliomas.[3,4] To link the boron cluster $[B_{12}H_{12}]^{2-}$ to organic moieties known to be tumor-seeking,[5–10] the icosahedron itself is not suitable. There are two approaches to functionalize the $[B_{12}H_{12}]^{2-}$ anion: (i) the introduction of a reactive centre such as an amino, mercapto or hydroxy group into the boron cage, followed by the attachment of a side chain containing a functional group;[11–14] (ii) direct synthesis of $[B_{12}H_{12}]^{2-}$ oxonium and its use in the syntheses of various functional derivatives of the $[B_{12}H_{12}]^{2-}$ anion for BNCT.[15]

Alkylation of **1a** with excess halide generally results in the formation of *S*,*S*-disubstituted sulfonium derivatives.[12] Moreover, stable thioesters were obtained from the acylation of **1a** with acid halides.[12] The alkylation of amino-undecahydro-*closo*-dodecaborate(1–) [H_3N–$B_{12}H_{11}]^-$ **1c**, which was first described by Hertler and Raasch,[16] leads to mixtures of mono-, di- and trialkylated products.[11] The degree of alkylation is governed by the steric demand of the alkyl chain. The formation of a Schiff base and its subsequent reduction to a primary amine has been reported for **1c** using aromatic and α,β-unsaturated aldehydes.[17] Alkylation of hydroxyundecahydro-*closo*-dodecaborate(2–) [HO–$B_{12}H_{11}]^{2-}$ **1d**[18] was also studied.[13] It was demonstrated that **1d** is a very weak nucleophile, and that its alkylation under strong basic conditions results in monoalkylated derivatives. Furthermore, monoalkylated derivatives of **1d** were prepared *via* the ring-opening reaction of the tetramethylene oxonium derivative with different nucleophiles.[14] Recently, there was a demonstration of the possibility of alkylation of undecahydro-*closo*-dodecaborates with alkyne halides to provide dodecaborate terminal alkyne groups for click chemistry.[19,20]

In contrast, under basic conditions in certain cases, a boron cluster acts as a good leaving group. For example, *ortho*-carboranyl carbinols undergo a retroaddition reaction in the presence of NaOH, revealing that *ortho*-carborane can be used as a protective group for carbonyl groups.[21] Furthermore, a similar retroaddition can also be observed in [3 + 2] annulations between *o*-carboranyltrimethylsilane and conjugated carbonyl compounds.[22] In this example, in the protection of the sulfur atom, both *ortho*-carborane and thioether derivatives of **1a** behaved as good leaving groups.[12] In this reaction, a cyanoethyl group was dealkylated from unsymmetric *S*,*S*-dialkylated sulfoniums $[B_{12}H_{11}SR^1R^2]^-$ in the presence of tetramethylammonium hydroxide (TMAOH) at room temperature.

In this paper, we report that under basic conditions, mercapto-, amino- and hydroxyl-undecahydro-*closo*-dodecaborane anions act as good leaving groups in the formation of substituted styrenes from the corresponding arylethyl-substituted dodecaborate derivatives. In this transformation, dianion formation is more favorable as compared to the formation of monoanion molecules.

Results and discussion

Alkylation reactions

The preparation of symmetrical *S*,*S*-di-alkylated sulfonium salts $[B_{12}H_{11}SR_2]^-$ (**2–13**) is illustrated in Scheme 1. Alkylation of **1a** with phenethyl bromide proceeded in acetonitrile–water (4 : 1) for 24 h at room temperature to provide *S*,*S*-bisphenethyl sulfonium **2** in 81% yield. Similarly, *S*,*S*-disubstituted derivatives **3** and **7–12** were obtained from **1a** in 72–90% yields. However, alkylation of **1a** with methoxyphenethyl bromides and 2-bromo-1-phenylpropane required 48 h to provide the desired products **4–6** and **13** in 45–53% yields. The longer reaction times and lower product yields were the result of either the electron-donating effect of the methoxy group

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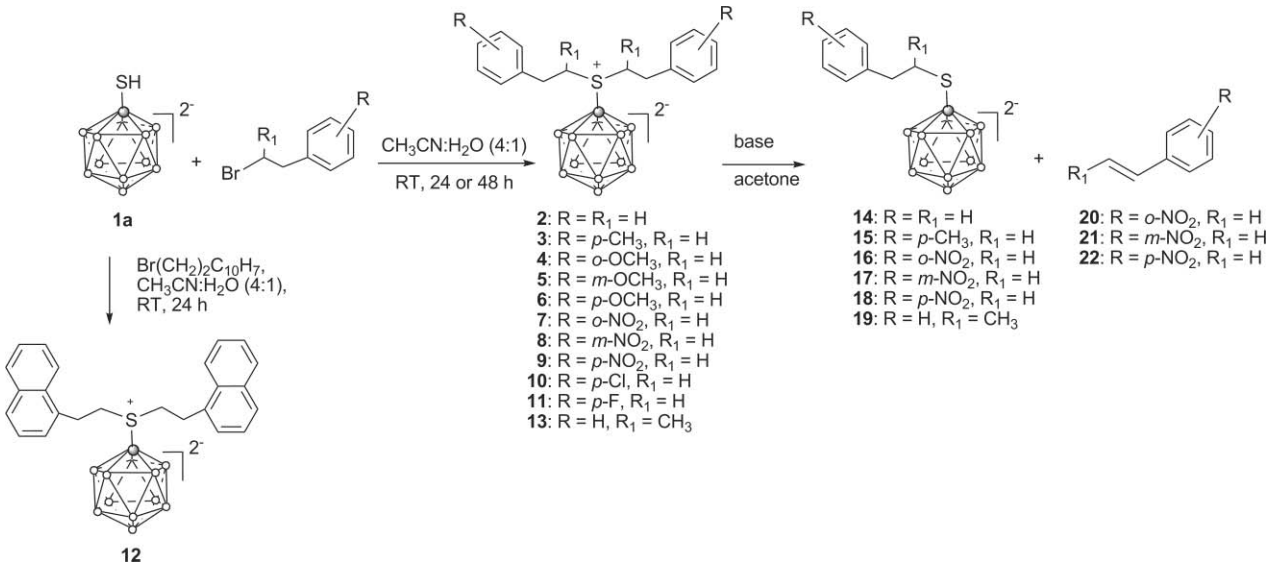
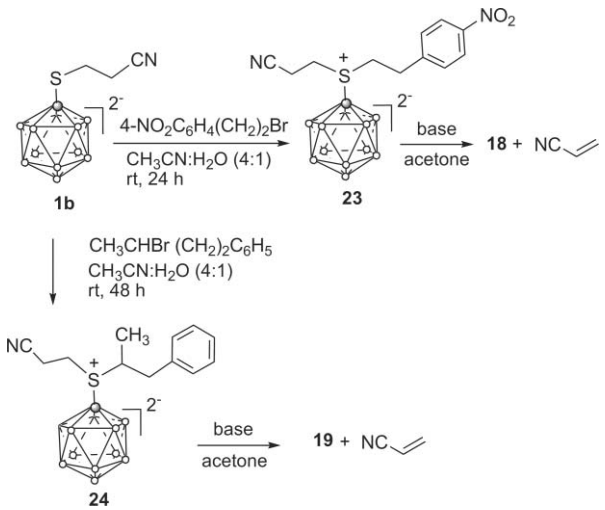


Scheme 1

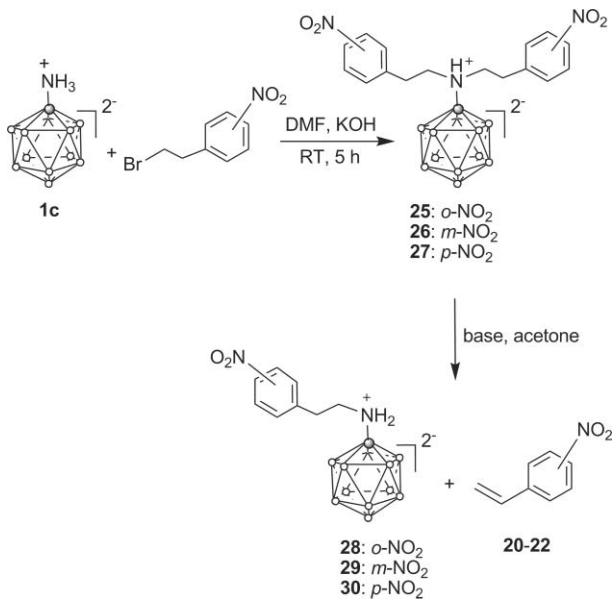
of the methoxyphenethyl bromides or the steric effect of the methyl group of 2-bromo-1-phenylpropane.

Unsymmetrical sulfonium salts (**23** and **24**) were prepared from the reaction of **1b** with *p*-nitrophenethyl bromide and 2-bromo-1-phenylpropane in 87% and 53% yields, respectively, (Scheme 2).



Scheme 2

Gabel *et al.* have reported a method for preparing mono-, di- and tri-alkylated amino-undecahydro-*closo*-dodecaborates $[B_{12}H_{11}NH_2R]^-$, $[B_{12}H_{11}NHR_2]^-$ and $[B_{12}H_{11}NR_3]^-$, by the reaction of **1c** with various alkyl halides in dimethylsulfoxide (DMSO), under strong basic conditions at room temperature.[11] We applied this protocol for preparing *N*,*N*-dialkylated derivatives (**25–27**). Using *N*,*N*-dimethylformamide (DMF) instead of DMSO as a solvent was effective for the dialkylation of **1c** with *o*-nitro-, *m*-nitro- and *p*-nitrophenethyl bromides to produce **25–27** in 20–30% yields (Scheme 3). Low yields of **25–27** can be explained by the initial attack of a base (hydroxyl anion) on nitrophenethyl bromide to produce nitrostyrene. We were able to separate nitrostyrene



Scheme 3

from the reaction medium as a byproduct in 28–79% yield, with a structure in accord with that described in the literature.[23]

An extension of a similar alkylation strategy to $[HO–B_{12}H_{11}]^{2-}$ was also examined. In this case, *O*-alkylated derivatives **31–33** were obtained by the reaction of **1d** with *o*-nitro-, *m*-nitro- and *p*-nitrophenethyl bromides in 22%, 27% and 18% yields, respectively, as shown in Scheme 4.

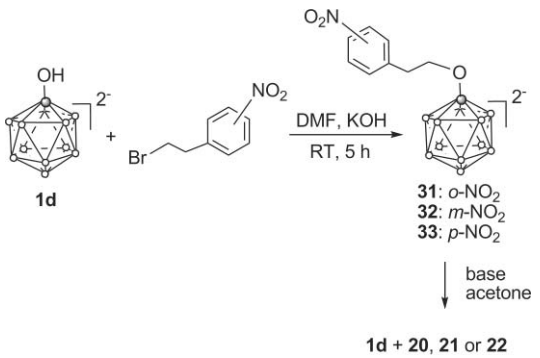
Elimination of aryl dodecaborates to form styrenes

We investigated the reactivity of the resulting compounds (**2–13**, **23–27** and **31–33**) in elimination reactions. The results are shown in Schemes 1 and 2, and Table 1. Conversion of symmetrical (**2–13**) and unsymmetrical (**23** and **24**) sulfonium salts into the desired thioethers **14–19** was carried out in acetone at room temperature,

Table 1 Dealkylation of *S*,*S*-disubstituted derivatives **2–13**, **23** and **24** with different bases

Substrate	Thioether (nitrostyrene)	Yield (%) KOH	TMAOH	DMAP	TEA
2[a]	**14**	15	77	67	52
3[a]	**15**	5	72	58	43
4[a]	—	—	—	—	—
5	—	—	—	—	—
6[b]	—	—	—	—	—
7[c]	**16** (**20**)	62 (39)	93 (74)	80 (61)	71 (52)
8[c]	**17** (**21**)	45 (28)	82 (66)	69 (47)	57 (35)
9[d]	**18** (**22**)	63 (42)	97 (79)	80 (63)	69 (56)
10[b]	—	—	—	—	—
11[b]	—	—	—	—	—
12[b]	—	—	—	—	—
13[e]	**19**	40	90	69	55
23[e]	**18**	67	98	90	82
24[e]	**19**	70	97	88	80

[a] Reaction time: 24 h in KOH, 10 min in TMAOH, 6 h in DMAP and 6 h in TEA. [b] Reaction time: 24 h in KOH, 20 min in TMAOH, 24 h in DMAP and 24 h in TEA. [c] Reaction time: 1 h in KOH, 10 min in TMAOH, 1 h in DMAP and 1 h in TEA. [d] Reaction time: 30 min. in KOH, 10 min in TMAOH, 30 min in DMAP and 30 min in TEA. [e] Reaction time: 2 h in KOH, 10 min in TMAOH, 30 min in DMAP and 30 min in TEA.



Scheme 4

using KOH, TMAOH, *N*,*N*-dimethylaminopyridine (DMAP) or triethylamine (TEA) as the base (Schemes 1 and 2, and Table 1).

This method was also applied to the dealkylation of the *N*,*N*-disubstituted derivatives **25–27** and *O*-alkylated derivatives **31–33** (Schemes 3 and 4, and Table 2). Unlike the volatile styrenes, which are derived by base treatment of compounds **2**, **3**, **10**, **11** and **13** *in situ*, nitrostyrenes (**20–22**) are sufficiently stable to be bottled and stored.

Gabel *et al.* reported that bis-cyanoethylmercaptoundecahydro-*closo*-dodecaborate loses one substituent upon treatment with TMAOH to yield the corresponding thioether.[12] However, studies on the mechanistic pathways of dealkylation reactions of the aryl dodecaborates have not yet been conducted. Therefore, in this study, we have attempted the dealkylation of aryl dodecaborates using different bases. As predicted, the products formed in the reaction were the elimination products, monoalkylated derivatives and styrenes.

To understand the effect of the base strength on the present elimination reaction, the reaction of **2** with different bases was carried out in acetone. TMAOH showed the highest activity, giving **14** in 77% yield. DMAP and TEA were also effective for the reaction but **14** was obtained in lower yields of 67 and 52%, respectively (Table 1). When KOH was used, the reaction rates and yields were low. This can be explained by the incomplete solubility of KOH in acetone. Equimolar reactions of base and aryl dodecaborates (**2–13** and **23–27**) led to the loss of one aryl group. However, the excessive amount of base led to the formation of **1a** or **1c**.

Table 2 Dealkylation of *N*,*N*-disubstituted derivatives of **1c** and *O*-substituted derivatives of **1d** with different bases

Substrate	Product	Yield (%) KOH	TMAOH	DMAP	TEA
25[a]	**28**	51	82	70	65
26[a]	**29**	33	70	65	49
27[a]	**30**	64	87	72	50
31[b]	**1d**	39	62	55	39
32[b]	**1d**	21	56	48	34
33[b]	**1d**	52	70	60	47

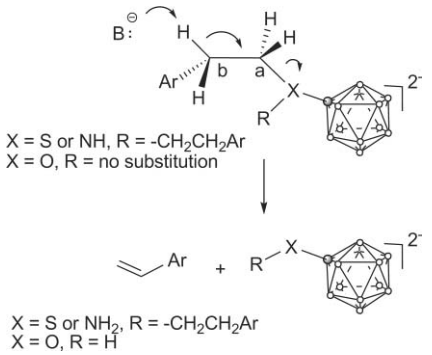
[a] Reaction time: 3 h in KOH, 30 min in TMAOH, 1 h in DMAP and 1 h in TEA. [b] Reaction time: 24 h in KOH, 120 min in TMAOH, 8 h in DMAP and 8 h in TEA.

The reaction of dodecaborates containing a cyanobenzyl group with base was unsuccessful under similar reaction conditions. For this reason the presence of β-hydrogen on the boron-cluster-substituted ethylene group is an important factor in the elimination reaction.

On the other hand the elimination of these aryl dodecaborates is strongly affected by the aryl moiety attached at the β-position of the ethyl group. Aryl groups constituting electron-withdrawing substituents will increase the acidity of the β-hydrogen. In this case, the overall reaction rate was greater, with satisfactory yields occurring even in the presence of a weak base. Better results were obtained when **7–9** or **23–27** were used as substrates. However, aryl groups with an electron-donating substituent will increase electron density at the β-CH_2 on the boron-cluster-substituted ethylene group, thus presumably decreasing the acidity of the β-hydrogen atom. Although **10** and **11** have electron-withdrawing substituents on the aromatic group, the resonance effect of the halogen groups may affect the β-hydrogen absorption by bases. Therefore, we were unable to convert *S*,*S*-disubstituted derivatives (**4–6** and **10–12**) into the desired thioethers. Based on these results, we note the following trend of aryl group influence on the reaction rate: *p*-$NO_2C_6H_5$ > *o*-$NO_2C_6H_5$ > *m*-$NO_2C_6H_5$ > C_6H_5 > *p*-$CH_3C_6H_5$.

Furthermore, the effect of steric hindrance on the elimination reaction was also studied using compound **13** as a substrate. The observed reactivity of the branched derivative **13** towards elimination, as compared to that of compound **2**, can be attributed to the steric effect of the methyl group and the higher stability of the resulting (1*E*)-1-propenylbenzene as compared to styrene.

Based on these data, a plausible reaction pathway is depicted in Scheme 5. This implies that there is an interaction between the base used and the aryl dodecaborate. This pathway is a concerted process with the following characteristics: (i) simultaneous removal of the proton by the base; (ii) loss of X–dodecaborate (where X = S, N or O) as a leaving group and (iii) formation of the π-bond. Therefore, highly substituted systems undergo E2 elimination more rapidly due to the stability of the resulting products. The C–$XB_{12}H_{11}^{2-}$ bond (where X = S, N or O) is broken



Scheme 5

during the rate-determining step. Therefore, the rate does depend on the nature of the leaving group. Since the base is involved in the rate-determining step, the nature of the base is a very important factor in an E2 reaction. More reactive bases will favour an E2 reaction, as indicated from the results in Tables 1 and 2.

Conclusions

We succeeded in preparing a series of structurally interesting arylethyl undecahydrododecaborates in good yields. The *S*,*S*-dialkylated sulfonium salts $[B_{12}H_{11}SR_2]^-$, *N*,*N*-dialkyalted derivatives $[B_{12}H_{11}NHR_2]^-$ and *O*-alkylated derivatives $[B_{12}H_{11}OR]^{2-}$ underwent elimination reactions in the presence of various bases such as KOH, TMAOH, DMAP and TEA. The presence of electron-withdrawing groups substituted at the aromatic ring as well as a substituent (R^1) at the α-position of the symmetric and unsymmetric *S*,*S*-dialkylated sulfonium salts of the undecahydrododecaborate accelerated the rate of elimination. Although undecahydrododecaborate cluster derivatives have attracted attention as potential water-soluble boron carriers in neutron capture therapy, the behaviour of undecahydrododecaborate derivatives has not been thoroughly studied earlier. In this regard, the current investigation is important for the development of undecahydrododecaborate-conjugated molecules in organic synthesis.

Experimental section

Materials and instruments

^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL JNM-AL 300 (300 MHz) and VARIAN UNITY-INOVA 400 (400 MHz) spectrometers. Chemical shifts of ^{1}H NMR and ^{13}C NMR were expressed in parts per million (ppm, δ units), and coupling constant (J) values were expressed in units of hertz (Hz). ^{11}B NMR spectra were recorded on a JEOL JNM-AL 300 spectrometer (96.3 MHz) and the chemical shifts were reported in δ units relative to external $BF_3{\cdot}Et_2O$ in $CDCl_3$. IR (cm^{-1}) spectra were determined as KBr discs on a Shimadzu FTIR-8600PC spectrometer. Electron spray ionization (ESI) mass spectra were recorded on a Shimadzu LCMS-2010 eV spectrometer. Elemental analyses were performed by a Perkin-Elmer 2400 automatic elemental analyzer. All compounds gave elemental analysis within ± 0.4% of the theoretical values. Analytical thin layer chromatography (TLC) was performed on glass plates of silica gel 60 GF_{254} (Merck). Visualization was accompanied by UV light (254 nm), I_2, $KMnO_4$, or $PdCl_2$. Melting points (mp) were determined on an Asone ATM-01 melting point apparatus. Preparative TLC was carried out using 0.75 mm layers of silica gel 60 GF_{254} (Merck) made from water slurries on glass plates of dimensions 20 × 20 cm^2, followed by drying in air at 100 °C. Column chromatography was conducted on silica gel (Merck Kieselgel 70–230 mesh). Analytical grade aryl bromides were purchased from Aldrich Chemical Co. and were not generally purified prior to use. Starting materials (**1a–1d**) were prepared as described in the literature.[11,12,16,18]

S,*S*-Bis(phenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (2)

A solution of phenethyl bromide (1.57 g, 8.5 mmol) in 10 ml CH_3CN was added dropwise over 20 min to a stirring solution of **1a** (500 mg, 1.55 mmol) in acetonitrile–water (4 : 1, 125 ml). The stirring continued for 24 h (48 h for compounds **4–6** and **13**) at room temperature. The solvent was removed on a rotary evaporator and the obtained solid was redissolved in acetonitrile (10 ml). The insoluble material was removed by filtration and the product was precipitated with ether (300 ml). A white precipitate was collected by filtration and recrystallized from water to yield (576 mg, 81%) white needle crystals of the desired product: mp 278–280 °C; IR (KBr, cm^{-1}) 3024, 2954 (ν_{CH}), 2495 (ν_{BH}), 1481, 1415 (ν_{CH}), 1049 (ν_{B-B}), 948, 837, 718 (ν_{CH}). ^{1}H NMR (300 MHz, CD_3CN) δ = 7.17–7.3 (m, 10H, CH-phenyl), 3.27 (t, 4H, J_{CH} = 14.4 Hz, S-CH_2), 3.09 (s, 12H, $N(CH_3)_4$), 3.05 (t, 4H, J_{CH} = 14.4 Hz, phenyl-CH_2), 1.85–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (75 MHz, CD_3CN) δ = 129.9, 129.3, 128.9 (12C, CH and C-phenyl), 56.2 (4C, $N(CH_3)_4$), 42.2 (2C, phenyl-CH_2), 37.4 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ −15.59 (bs, 1B, B1), −18.98 (d, J_{BH} = 163.9 Hz, 11B, B2-12). MS (ESI) *m*/*z* 382.4 [100, M^-]. Anal. Calc. for $C_{20}H_{41}B_{12}NS$: C, 52.52; H, 9.04; N, 3.06%. found: C, 52.37; H, 8.76; N, 2.89%.

S,*S*-Bis(4-methylphenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (3)

This compound was prepared from **1a** (500 mg, 1.55 mmol) and *p*-methylphenethyl bromide (1.69 g, 8.5 mmol) using the procedure described for **2** to give **3** (544 mg, 72%) as a white solid. mp 276–278 °C. IR (KBr, cm^{-1}) 3024, 2954 (ν_{CH}), 2496 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 948, 837, 721 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.12 (d, J_{CH} = 8.4 Hz, 4H, CH-phenyl), 7.05 (d, J_{CH} = 8.0 Hz, 4H, CH-phenyl), 3.25 (m, 4H, S-CH_2), 3.09 (s, 12H, $N(CH_3)_4$), 3.06 (m, 4H, phenyl-CH_2), 1.82–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 130.2, 128.7, 125.9 (12C, CH and C-phenyl), 56.2 (4C, $N(CH_3)_4$), 41.8 (2C, phenyl-CH_2), 37.3 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ −15.52 (bs, 1B, B1), −18.79 (d, J_{BH} = 161.87 Hz, 11B, B2-12). MS (ESI) *m*/*z* 411.4 [100, M^-]. Anal. Calc. for $C_{22}H_{45}B_{12}NS$: C, 54.44; H, 9.34; N, 2.89%. found: C, 54.37; H, 8.99; N, 2.73%.

S,*S*-Bis(2-methoxyphenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (4)

This compound was prepared from **1a** (500 mg, 1.55 mmol) and *o*-methoxyphenethyl bromide (1.83 g, 8.5 mmol) using the procedure described for **2** to give **4** (379 mg, 47%) as a white solid: mp > 300 °C. IR (KBr, cm^{-1}) 3026, 2955 (ν_{CH}), 2487 (ν_{BH}), 1485,

1415 (ν_{CH}), 1049 (ν_{B-B}), 949, 839, 725 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.19–6.87 (m, 8H, CH-phenyl), 3.81 (s, 6H, -OMe), 3.24 (m, 4H, S-CH_2), 3.09 (s, 12H, N(CH_3)$_4$), 3.05 (m, 4H, phenyl-CH_2), 1.75–0.51 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 158.3 (2C, O-Cphenyl), 129.8, 119.8, 113.8, 113.3 (10C, CH and C-phenyl), 56.2 (4C, N(CH_3)$_4$), 55.1 (2C, O-CH_3), 42.1 (2C, phenyl-CH_2), 36.8 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ –15.56 (bs, 1B, B1), –19.02 (d, J_{BH} = 161.88 Hz, 11B, B2-12). MS (ESI) m/z 444.4 [100, M$^-$]. Anal. Calc. for $C_{22}H_{45}B_{12}NO_2S$: C, 51.07; H, 8.77; N, 2.71%. found: C, 50.88; H, 8.51; N, 2.59%.

S,*S*-Bis(3-methoxyphenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (5)

This compound was prepared analogously to **4**, using *m*-methoxyphenethyl bromide as the halide source to give **5** (411 mg, 51%) as a white solid: mp 265–267 °C; IR (KBr, cm^{-1}) 3025, 2954 (ν_{CH}), 2489 (ν_{BH}), 1481, 1415 (ν_{CH}), 1045 (ν_{B-B}), 948, 838, 721 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.2–6.75 (m, 8H, CH-phenyl), 3.77 (s, 6H, -OMe), 3.25 (m, 4H, S-CH_2), 3.09 (s, 12H, N(CH_3)$_4$), 3.05 (m, 4H, phenyl-CH_2), 1.81–0.54 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 159.5 (2C, O-Cphenyl), 130.1, 119.4, 113.6, 113.5 (10C, CH and C-phenyl), 56.2 (4C, N(CH_3)$_4$), 55.1 (2C, O-CH_3), 42.1 (2C, phenyl-CH_2), 37.0 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ –15.49 (bs, 1B, B1), –19.06 (d, J_{BH} = 162.52 Hz, 11B, B2-12). MS (ESI) m/z 444.4 [100, M$^-$]. Anal. Calc. for $C_{22}H_{45}B_{12}NO_2S$: C, 51.07; H, 8.77; N, 2.71%. found: C, 50.75; H, 8.49; N, 2.51%.

S,*S*-Bis(4-methoxyphenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (6)

This compound was prepared analogously to **4**, using *p*-methoxyphenethyl bromide as the halide source to give **6** (363 mg, 45%) as a white solid: mp 235–237 °C; IR (KBr, cm^{-1}) 3025, 2954 (ν_{CH}), 2489 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 945, 837, 722 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.22 (d, J_{CH} = 7.85 Hz, 4H, CH-phenyl), 6.77 (d, J_{CH} = 7.85 Hz, 4H, CH-phenyl), 3.75 (s, 6H, -OMe), 3.25 (m, 4H, S-CH_2), 3.09 (s, 12H, N(CH_3)$_4$), 3.03 (m, 4H, phenyl-CH_2), 1.82–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 159.7 (2C, O-Cphenyl), 131.0, 122.7, 113.5 (10C, CH and C-phenyl), 56.3 (4C, N(CH_3)$_4$), 55.4 (2C, O-CH_3), 42.2 (2C, phenyl-CH_2), 37.4 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ –15.62 (bs, 1B, B1), –19.02 (d, J_{BH} = 161.26 Hz, 11B, B2-12). MS (ESI) m/z 444.4 [100, M$^-$]. Anal. Calc. for $C_{22}H_{45}B_{12}NO_2S$: C, 51.07; H, 8.77; N, 2.71%. found: C, 50.92; H, 8.63; N, 2.55%.

S,*S*-Bis(2-nitrophenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (7)

This compound was prepared from **1a** (500 mg, 1.55 mmol) and *o*-nitrophenethyl bromide (1.83 g, 8.5 mmol) using the procedure described for **2** to give **7** (724 mg, 85%) as a white solid: mp 285–287 °C; IR (KBr, cm^{-1}) 3028, 2956 (ν_{CH}), 2480 (ν_{BH}), 1527, 1353 (ν_{NO_2}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 949, 837, 725 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.99, 7.63–6.47 (m, 8H, CH-phenyl), 3.34 (m, 4H, S-CH_2), 3.07 (s, 12H, N(CH_3)$_4$), 3.02 (m, 4H, phenyl-CH_2), 1.69–0.32 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 149.2 (2C, NO_2-Cphenyl), 130.1, 126.2, 122.5, 113.2 (10C, CH and C-phenyl), 56.3 (4C, N(CH_3)$_4$), 41.8 (2C, phenyl-CH_2), 37.0 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ –15.57 (bs, 1B, B1), –18.93 (d, J_{BH} = 162.41 Hz, 11B, B2-12). MS (ESI) m/z 473.4 [100, M$^-$]. Anal. Calc. for $C_{20}H_{39}B_{12}N_3O_4S$: C, 43.89; H, 7.18; N, 7.68%. found: C, 43.66; H, 6.91; N, 7.42%.

S,*S*-Bis(3-nitrophenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (8)

This compound was prepared analogously to **7**, using *m*-nitrophenethyl bromide as the halide source to give **8** (673 mg, 79%) as a white solid: mp > 300 °C; IR (KBr, cm^{-1}) 3025, 2955 (ν_{CH}), 2495 (ν_{BH}), 1523, 1350 (ν_{NO_2}), 1485, 1415 (ν_{CH}), 1045 (ν_{B-B}), 945, 837, 721 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 8.06, 7.67–7.52 (m, 8H, CH-phenyl), 3.35 (m, 4H, S-CH_2), 3.07 (s, 12H, N(CH_3)$_4$), 3.02 (m, 4H, phenyl-CH_2), 1.75–0.52 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 148.2 (2C, NO_2-Cphenyl), 130.1, 128.4, 119.6, 114.4 (10C, CH and C-phenyl), 56.2 (4C, N(CH_3)$_4$), 42.1 (2C, phenyl-CH_2), 37.1 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ –15.55 (bs, 1B, B1), –18.96 (d, J_{BH} = 163.73 Hz, 11B, B2-12). MS (ESI) m/z 473.3 [100, M$^-$]. Anal. Calc. for $C_{20}H_{39}B_{12}N_3O_4S$: C, 43.89; H, 7.18; N, 7.68%. found: C, 43.52; H, 6.85; N, 7.39%.

S,*S*-Bis(4-nitrophenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (9)

This compound was prepared analogously to **7**, using *p*-nitrophenethyl bromide as the halide source to give **9** (766 mg, 90%) as a white solid: mp 293–295 °C; IR (KBr, cm^{-1}) 3022, 2955 (ν_{CH}), 2491 (ν_{BH}), 1525, 1352 (ν_{NO_2}), 1489, 1416 (ν_{CH}), 1049 (ν_{B-B}), 947, 838, 725 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 8.08 (d, J_{CH} = 8.4 Hz, 4H, CH-phenyl), 7.45 (d, J_{CH} = 9.2 Hz, 4H, CH-phenyl), 3.41 (m, 4H, S-CH_2), 3.09 (s, 12H, N(CH_3)$_4$), 3.01 (m, 4H, phenyl-CH_2), 1.81–0.54 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 149.1 (2C, NO_2-Cphenyl), 131.7, 130.9, 123.5 (10C, CH and C-phenyl), 56.2 (4C, N(CH_3)$_4$), 42.0 (2C, phenyl-CH_2), 37.2 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ –15.57 (bs, 1B, B1), –18.87 (d, J_{BH} = 163.59 Hz, 11B, B2-12). MS (ESI) m/z 473.5 [100, M$^-$]. Anal. Calc. for $C_{20}H_{39}B_{12}N_3O_4S$: C, 43.89; H, 7.18; N, 7.68%. found: C, 43.71; H, 7.02; N, 7.48%.

S,*S*-Bis(4-chlorophenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (10)

This compound was prepared from **1a** (500 mg, 1.55 mmol) and *p*-chlorophenethyl bromide (1.87 g, 8.5 mmol) using the procedure described for **2** to give **10** (622 mg, 76%) as a white solid: mp > 300 °C; IR (KBr, cm^{-1}) 3025, 2956 (ν_{CH}), 2495 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 948, 837, 721 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.3 (d, J_{CH} = 18.0 Hz, 4H, CH-phenyl), 7.17 (d, J_{CH} = 17.2 Hz, 4H, CH-phenyl), 3.28 (m, 4H, S-CH_2), 3.11 (s, 12H, N(CH_3)$_4$), 3.02 (m, 4H, phenyl-CH_2), 1.68–0.33 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 132.8 (2C, Cl-Cphenyl), 130.9, 129.6, 122.7 (10C, CH and C-phenyl), 56.2 (4C, N(CH_3)$_4$), 42.0 (2C, phenyl-CH_2), 37.3 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ –15.53 (bs, 1B, B1), –18.99 (d, J_{BH} = 162.66 Hz, 11B, B2-12). MS (ESI) m/z 450.4 [100, M$^-$]. Anal. Calc. for $C_{20}H_{39}B_{12}Cl_2NS$: C, 45.65; H, 7.47; N, 2.66%. found: C, 45.29; H, 7.19; N, 2.34%.

S,*S*-Bis(4-fluorophenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (11)

This compound was prepared from **1a** (500 mg, 1.55 mmol) and *p*-fluorophenethyl bromide (1.73 g, 8.5 mmol) using the procedure described for **2** to give **11** (614 mg, 80%) as a white solid: mp > 300 °C; IR (KBr, cm^{-1}) 3020, 2952 (ν_{CH}), 2480 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 949, 837, 721 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.2 (d, J_{CH} = 8.8 Hz, 4H, CH-phenyl), 7.05 (d, J_{CH} = 8.8 Hz, 4H, CH-phenyl), 3.32 (m, 4H, S-CH_2), 3.07 (s, 12H, N(CH_3)$_4$), 3.01 (m, 4H, phenyl-CH_2), 1.75–0.5 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 162.1 (2C, Cl-Cphenyl), 131.3, 130.3, 123.7 (10C, CH and C-phenyl), 56.3 (4C, N(CH_3)$_4$), 41.9 (2C, phenyl-CH_2), 37.3 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ −15.55 (bs, 1B, B1), −18.98 (d, J_{BH} = 163.52 Hz, 11B, B2-12). MS (ESI) *m*/*z* 419.3 [100, M^-]. Anal. Calc. for $C_{20}H_{39}B_{12}F_2NS$: C, 48.69; H, 7.97; N, 2.84%. found: C, 48.46; H, 7.68; N, 2.73%.

S,*S*-Bis(naphthethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (12)

This compound was prepared from **1a** (500 mg, 1.55 mmol) and 1-(2-bromoethyl)naphthalene (2.0 g, 8.5 mmol) using the procedure described for **2** to give **12** (649 mg, 75%) as a white solid: mp 295–297 °C; IR (KBr, cm^{-1}) 3020, 2954 (ν_{CH}), 2491 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 948, 837, 718 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.46–7.07 (m, 14H, CH-naphthalene), 3.39 (m, 4H, S-CH_2), 3.11 (s, 12H, N(CH_3)$_4$), 3.07 (m, 4H, naphthalene-CH_2), 1.75–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 134.3, 133.1 132.2, 129.9, 129.2, 128.2, 127.3, 126.3, 125.6, 124.4 (20C, CH and C-naphthalene), 56.2 (4C, N(CH_3)$_4$), 42.0 (2C, phenyl-CH_2), 37.2 (2C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ −15.57 (bs, 1B, B1), −18.97 (d, J_{BH} = 161.92 Hz, 11B, B2-12). MS (ESI) *m*/*z* 482.4 [100, M^-]. Anal. Calc. for $C_{28}H_{45}B_{12}NS$: C, 60.33; H, 8.14; N, 2.51%. found: C, 59.98; H, 7.82; N, 2.28%.

S,*S*-Bis(1-phenypropan-2-yl)sulfonioundecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (13)

This compound was prepared from **1a** (500 mg, 1.55 mmol) and 2-bromo-1-phenylpropane (1.69 g, 8.5 mmol) using the procedure described for **2** to give **12** (576 mg, 53%) as a white solid: mp 255–257 °C; IR (KBr, cm^{-1}) 3028, 2958 (ν_{CH}), 2487 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 948, 840, 721 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.35–7.07 (m, 10H, CH-phenyl), 3.89 (m, 4H, S-CH), 3.08 (s, 12H, N(CH_3)$_4$), 3.02 (m, 4H, phenyl-CH_2), 1.35 (d, 6H, J_{CH} = 8.0 Hz, CH_3), 1.85–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 129.5, 129.1, 127.8 (12C, CH and C-phenyl), 56.2 (4C, N(CH_3)$_4$), 42.4 (2C, phenyl-CH_2), 40.8 (2C, S-CH), 22.7 (2C, CH_3). ^{11}B NMR (96.3 MHz; CD_3CN): δ −15.54 (bs, 1B, B1), −18.96 (d, J_{BH} = 163.21 Hz, 11B, B2-12). MS (ESI) *m*/*z* 411.4 [100, M^-]. Anal. Calc. for $C_{22}H_{45}B_{12}NS$: C, 54.44; H, 9.34; N, 2.89%. found: C, 54.19; H, 9.07; N, 2.74%.

S-Phenethyl-thioundecahydro-*closo*-dodecaborate (2–) ditetramethylammonium salt (14)

To a solution of **2** (228 mg, 0.5 mmol) in acetone (15 ml), 1 equiv. of a 25% solution of TMAOH in methanol was added dropwise. A white precipitate of the product formed immediately. The precipitate was filtered off and dried to give **14** (163 mg, 77%) as a white solid: mp > 300 °C;. IR (KBr, cm^{-1}) 3025, 2955 (ν_{CH}), 2492 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 947, 838, 722 (ν_{CH}). ^{1}H NMR (300 MHz, CD_3CN) δ = 7.15–7.29 (m, 5H, CH-phenyl), 3.25 (m, 2H, S-CH_2), 3.11 (s, 24H, N(CH_3)$_4$), 3.02 (m, 2H, phenyl-CH_2), 1.79–0.52 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (75 MHz, CD_3CN) δ = 129.1, 128.6, 128.0 (6C, CH and C-phenyl), 54.5 (8C, N(CH_3)$_4$), 41.0 (1C, phenyl-CH_2), 37.2 (1C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ −9.87 (bs, 1B, B1), −19.98 (d, J_{BH} = 161.7 Hz, 11B, B2-11), −21.59 (bs, 1B, B12). MS (ESI) *m*/*z* 138.8 [100, M^-/2]. Anal. Calc. for $C_{16}H_{44}B_{12}N_2S$: C, 45.08; H, 10.4; N, 6.57%. found: C, 44.87; H, 10.11; N, 6.22%.

S-4-Methylphenethyl-thioundecahydro-*closo*-dodecaborate (2–) ditetramethylammonium salt (15)

This compound was prepared from **3** (242 mg, 0.5 mmol) using the procedure described for **14** to give **15** (158 mg, 72%) as a white solid: mp > 300 °C; IR (KBr, cm^{-1}) 3020, 2951 (ν_{CH}), 2495 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 947, 838, 725 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.15 (d, J_{CH} = 7.52 Hz, 2H, CH-phenyl), 7.07 (d, J_{CH} = 7.52 Hz, 2H, CH-phenyl), 3.29 (m, 2H, S-CH_2), 3.12 (s, 24H, N(CH_3)$_4$), 3.02 (m, 2H, phenyl-CH_2), 1.82–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 130.3, 129.1, 126.1 (6C, CH and C-phenyl), 54.3 (6C, N(CH_3)$_4$), 42.5 (1C, phenyl-CH_2), 36.9 (1C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ −9.85 (bs, 1B, B1), −19.97 (d, J_{BH} = 161.97 Hz, 11B, B2-11), −21.56 (bs, 1B, B12). MS (ESI) *m*/*z* 145.8 [100, M^-/2]. Anal. Calc. for $C_{17}H_{47}B_{12}N_2S$: C, 46.26; H, 10.73; N, 6.35%. found: C, 46.01; H, 10.69; N, 6.17%.

S-2-Nitrophenethylthio-undecahydro-*closo*-dodecaborate (2–) ditetramethylammonium salt (16)

This compound was prepared from **7** (236 mg, 0.5 mmol) using the procedure described for **14** to give **16** (189 mg, 93%) as a white solid: mp > 300 °C; IR (KBr, cm^{-1}) 3025, 2955 (ν_{CH}), 2487 (ν_{BH}), 1525, 1355 (ν_{NO_2}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 949, 837, 725 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.95, 7.61–6.43 (m, 4H, CH-phenyl), 3.35 (m, 2H, S-CH_2), 3.12 (s, 24H, N(CH_3)$_4$), 2.99 (m, 2H, phenyl-CH_2), 1.79–0.51 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 150.0 (1C, NO_2-Cphenyl), 130.3, 127.5, 123.1, 114.7 (5C, CH and C-phenyl), 54.3 (8C, N(CH_3)$_4$), 41.5 (1C, phenyl-CH_2), 37.2 (1C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ −9.86 (bs, 1B, B1), −19.98 (d, J_{BH} = 162.19 Hz, 11B, B2-11), −21.55 (bs, 1B, B12). MS (ESI) *m*/*z* 161.5 [100, M^-/2]. Anal. Calc. for $C_{16}H_{43}B_{12}N_3O_2S$: C, 40.77; H, 9.20; N, 8.92%. found: C, 40.55; H, 9.08; N, 8.68%.

S-3-Nitrophenethylthio-undecahydro-*closo*-dodecaborate (2–) ditetramethylammonium salt (17)

This compound was prepared from **8** (236 mg, 0.5 mmol) using the procedure described for **14** to give **17** (166 mg, 82%) as a white solid: mp > 300 °C; IR (KBr, cm^{-1}) 30204, 2956 (ν_{CH}), 2494 (ν_{BH}), 1526, 1351 (ν_{NO_2}), 1485, 1415 (ν_{CH}), 1045 (ν_{B-B}), 947, 838, 725 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 8.02, 7.63–7.5 (m, 4H, CH-phenyl), 3.37 (m, 2H, S-CH_2), 3.11 (s, 24H, N(CH_3)$_4$), 3.05 (m, 2H, phenyl-CH_2), 1.8–0.54 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz,

CD_3CN) δ = 149.4 (1C, NO_2-Cphenyl), 13.8, 128.6, 120.3, 115.1 (5C, CH and C-phenyl), 56.2 (8C, $N(CH_3)_4$), 42.1 (1C, phenyl-CH_2), 37.1 (1C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ –9.85 (bs, 1B, B1), –19.95 (d, J_{BH} = 162.24 Hz, 11B, B2-11), –21.61 (bs, 1B, B12). MS (ESI) m/z 161.5 [100, $M^-/2$]. Anal. Calc. for $C_{16}H_{43}B_{12}N_3O_2S$: C, 40.77; H, 9.20; N, 8.92%. found: C, 40.49; H, 9.11; N, 8.73%.

S-4-Nitrophenethylthio-undecahydro-*closo*-dodecaborate (2–) ditetramethylammonium salt (18)

This compound was prepared from **9** (236 mg, 0.5 mmol) using the procedure described for **14** to give **18** (197 mg, 97%) as a white solid: mp 275–277 °C; IR (KBr, cm^{-1}) 3024, 2954 (ν_{CH}), 2493 (ν_{BH}), 1522, 1355 (ν_{NO_2}), 1489, 1416 (ν_{CH}), 1049 (ν_{B-B}), 948, 837, 722 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 8.05 (d, J_{CH} = 6.75 Hz, 2H, CH-phenyl), 7.41 (d, J_{CH} = 6.75 Hz, 2H, CH-phenyl), 3.49 (m, 2H, S-CH_2), 3.11 (s, 24H, $N(CH_3)_4$), 3.03 (m, 2H, phenyl-CH_2), 1.79–0.52 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 149. 9 (1C, NO_2-Cphenyl), 130.5, 130.0, 125.5 (5C, CH and C-phenyl), 54.2 (8C, $N(CH_3)_4$), 42.0 (1C, phenyl-CH_2), 37.6 (1C, S-CH_2). ^{11}B NMR (96.3 MHz; CD_3CN): δ –9.88 (bs, 1B, B1), –19.98 (d, J_{BH} = 162.34 Hz, 11B, B2-11), –21.59 (bs, 1B, B12). MS (ESI) m/z 161.5 [100, $M^-/2$]. Anal. Calc. for $C_{16}H_{43}B_{12}N_3O_2S$: C, 40.77; H, 9.20; N, 8.92%. found: C, 40.59; H, 9.15; N, 8.74%.

S-(1-Phenylpropan-2-yl)thioundecahydro-*closo*-dodecaborate (2–) ditetramethylammonium salt (19)

This compound was prepared from **13** (220 mg, 0.5 mmol) using the procedure described for **14** to give **19** (179 mg, 90%) as a white solid: mp 284–286 °C; IR (KBr, cm^{-1}) 3026, 2954 (ν_{CH}), 2489 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 947, 838, 722 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.33–7.04 (m, 5H, CH-phenyl), 3.77 (m, 2H, S-CH), 3.10 (s, 24H, $N(CH_3)_4$), 3.03 (m, 2H, phenyl-CH_2), 1.38 (d, 3H, J_{CH} = 9.1 Hz, CH_3), 1.82–0.53 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 130.0, 129.9, 127.0 (6C, CH and C-phenyl), 54.2 (8C, $N(CH_3)_4$), 42.6 (1C, phenyl-CH_2), 42.0 (1C, S-CH), 23.1 (1C, CH_3). ^{11}B NMR (96.3 MHz; CD_3CN): δ –9.87 (bs, 1B, B1), –19.98 (d, J_{BH} = 161.83 Hz, 11B, B2-11), –21.59 (bs, 1B, B12). MS (ESI) m/z 145.8 [100, $M^-/2$]. Anal. Calc. for $C_{17}H_{46}B_{12}N_2S$: C, 46.37; H, 10.53; N, 6.36%. found: C, 46.02; H, 10.23; N, 6.21%.

S-(2-Cyanoethyl)-*S*-(4-nitrophenethyl)sulfonio-undecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (23)

This compound was prepared from **1b** (187 mg, 0.5 mmol) and 4-nitrophenethyl bromide (630 mg, 8.5 mmol), using the procedure described for **2** to give **23** (195 mg, 87%) as a white solid: mp 239–241 °C; IR (KBr, cm^{-1}) 3024, 2952 (ν_{CH}), 2491 (ν_{BH}), 1523, 1355 (ν_{NO_2}), 1489, 1416 (ν_{CH}), 1049 (ν_{B-B}), 946, 837, 722 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 8.06 (d, J_{CH} = 7.3 Hz, 2H, CH-phenyl), 7.42 (d, J_{CH} = 7.3 Hz, 2H, CH-phenyl), 3.56 (m, 2H, S-CH_2), 3.29 (m, 2H, S-CH_2), 3.12 (s, 12H, $N(CH_3)_4$), 3.03 (m, 2H, phenyl-CH_2), 2.98 (m, 2H, CH_2-CN), 1.82–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 148.8 (1C, NO_2-Cphenyl), 131.2, 130.7, 123.5 (5C, CH and C-phenyl), 119.3 (C, CN), 56.3 (4C, $N(CH_3)_4$), 42.0 (1C, phenyl-CH_2), 37.2 (1C, S-CH_2), 31.2 (C, S-CH_2), 16.3 (C, CH_2-CN). ^{11}B NMR (96.3 MHz; CD_3CN): δ –9.82 (bs, 1B, B1), –19.96 (d, J_{BH} = 161.51 Hz, 11B, B2-11), –21.51 (bs, 1B, B12). MS (ESI) m/z 376.6 [100, M^-]. Anal. Calc. for $C_{15}H_{35}B_{12}N_3O_2S$: C, 39.92; H, 7.82; N, 9.31%. found: C, 39.59; H, 7.61; N, 8.99%.

S-(2-Cyanoethyl)-*S*-(1-phenypropan-2-yl)sulfonioundecahydro-*closo*-dodecaborate (1–) tetramethylammonium salt (24)

This compound was prepared from **1b** (187 mg, 0.5 mmol) and 2-bromo-1-phenylpropane (545 mg, 8.5 mmol), using the procedure described for **2** to give **24** (576 mg, 53%) as a white solid: mp 271–273 °C; IR (KBr, cm^{-1}) 3024, 2955 (ν_{CH}), 2487 (ν_{BH}), 1485, 1415 (ν_{CH}), 1049 (ν_{B-B}), 946, 840, 722 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.33–7.05 (m, 5H, CH-phenyl), 3.82 (m, 2H, S-CH), 3.25 (m, 2H, S-CH_2), 3.11 (s, 12H, $N(CH_3)_4$), 3.01 (m, 2H, phenyl-CH_2), 2.95 (m, 2H, CH_2-CN), 1.39 (d, 3H, J_{CH} = 5.9 Hz, CH_3), 1.78–0.52 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 130.0, 129.4, 127.0 (6C, CH and C-phenyl), 119.8 (C, CN), 56.2 (4C, $N(CH_3)_4$), 42.6 (2C, phenyl-CH_2), 40.9 (2C, S-CH), 32.1 (C, S-CH_2), 22.4 (2C, CH_3), 16.6 (C, CH_2-CN). ^{11}B NMR (96.3 MHz; CD_3CN): δ –9.86 (bs, 1B, B1), –19.93 (d, J_{BH} = 161.42 Hz, 11B, B2-11), –21.52 (bs, 1B, B12). MS (ESI) m/z 345.6 [100, M^-]. Anal. Calc. for $C_{16}H_{38}B_{12}N_2S$: C, 45.72; H, 9.11; N, 6.67%. found: C, 45.53; H, 8.87; N, 6.43%.

General synthesis for compounds 25–27

A solution of **1c** (125 mg, 0.54 mmol) and KOH (152 mg, 2.72 mmol) in dry DMF (15 ml) was stirred at room temperature under argon atmosphere. Nitrophenethyl bromide (2.59 g, 11.27 mmol) was added. After stirring for 5 h, the solvent was evaporated *in vacuo* and the orange residue dissolved in 10 ml of acetonitrile. The insoluble material was filtered off to give the *N*,*N*-bisalkylated derivative. This was recrystallized from water and dissolved in water–acetonitrile. A solid was precipitated by addition of 175 mg of tetrabutylammonium bromide (0.54 mmol) and chromatographed on TLC using MeOH–CH_2Cl_2 (1 : 4) as a mobile phase to give the *N*,*N*-bisalkylated derivative as white needle crystals.

***N*,*N*-Bis(2-nitrophenethyl)amino-undecahydro-*closo*-dodecaborate (1–) tetrabutylammonium salt (25).** (141 mg, 25%, R_f 0.29), mp 177–179 °C. IR (KBr, cm^{-1}) 3500 (ν_{NH}), 3030, 2939 (ν_{CH}), 2500 (ν_{BH}), 1525, 1351 (ν_{NO_2}), 1510 (ν_{BN}), 1485, 1407, 1350 (ν_{CH}), 1145 (ν_{CN}), 1055 (ν_{B-B}), 998, 952, 856, 725, 675 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 5.45 (bs, 1H, NH), 7.79, 7.59–7.23 (m, 8H, CH-phenyl), 3.43 (m, 4H, NH-CH_2), 3.05 (m, 8H, $N(CH_2\text{-})_4$), 3.02 (m, 4H, phenyl-CH_2), 1.55 (m, 8H, $N(CH_2\mathbf{CH_2}\text{-})_4$), 1.35 (m, 8H, $N(CH_2CH_2\mathbf{CH_2}\text{-})_4$), 0.95 (t, J = 7.56 Hz, 12H, $N(CH_2CH_2CH_2\mathbf{CH_3})_4$), 1.79–0.51 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 148.5 (2C, NO_2-Cphenyl), 130.2, 127.2, 123.6, 114.2 (10C, CH and C-phenyl), 59.3 (4C, $N(CH_2\text{-})_4$), 52.4 (2C, NH-CH_2), 41.5 (2C, CH_2-phenyl), 24.3 (4C, $N(CH_2\mathbf{CH_2}\text{-})_4$), 20.3 (4C, $N(CH_2CH_2\mathbf{CH_2}\text{-})_4$), 13.8 (4C, $N(CH_2CH_2CH_2\mathbf{CH_3})_4$). ^{11}B NMR (96.3 MHz; CD_3CN): δ –3.12 (s, 1B, B1), –20.89 (bs, 11B, B2-12). MS (ESI) m/z 454.4 [100, M^-]. Anal. Calc. for $C_{32}H_{64}B_{12}N_4O_4$: C, 55.02; H, 9.23; N, 8.02%. found: C, 54.83; H, 8.92; N, 7.79%.

***N*,*N*-Bis(3-nitrophenethyl)amino-undecahydro-*closo*-dodecaborate (1–) tetrabutylammonium salt (26).** (170 mg, 30%, R_f 0.26),

mp 199–201 °C. IR (KBr, cm^{-1}) 3489 (ν_{NH}), 3035, 2951 (ν_{CH}), 2494 (ν_{BH}), 1523, 1352 (ν_{NO_2}), 1489 (ν_{BN}), 1485, 1405, 1350 (ν_{CH}), 1149 (ν_{CN}), 1057 (ν_{B-B}), 995, 955, 857, 722, 677 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 5.52 (bs, 1H, NH), 7.73, 7.53–7.37 (m, 8H, CH-phenyl), 3.45 (m, 4H, NH-CH_2), 3.12 (m, 8H, N(CH_2-)$_4$), 3.01 (m, 4H, phenyl-CH_2), 1.56 (m, 8H, N(CH_2**CH_2**-)$_4$), 1.35 (m, 8H, N(CH_2CH_2**CH_2**-)$_4$), 0.96 (t, J = 6.75 Hz, 12H, N($CH_2CH_2CH_2$**CH_3**)$_4$), 1.82–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 149.6 (2C, NO_2-Cphenyl), 130.1, 129.0, 126.0, 114.8 (10C, CH and C-phenyl), 59.3 (4C, N(CH_2-)$_4$), 52.5 (2C, NH-CH_2), 41.7 (2C, CH_2-phenyl), 24.4 (4C, N(CH_2**CH_2**-)$_4$), 20.3 (4C, N(CH_2CH_2**CH_2**-)$_4$), 13.8 (4C, N($CH_2CH_2CH_2$**CH_3**)$_4$). ^{11}B NMR (96.3 MHz; CD_3CN): δ –3.07 (s, 1B, B1), –20.85 (bs, 11B, B2-12). MS (ESI) m/z 455.4 [100, M^-]. Anal. Calc. for $C_{32}H_{64}B_{12}N_4O_4$: C, 55.02; H, 9.23; N, 8.02%. found: C, 54.91; H, 8.95; N, 7.86%.

***N*,*N*-Bis(4-nitrophenethyl)amino-undecahydro-*closo*-dodecaborate (1–) tetrabutylammonium salt (27).** (113 mg, 20%, R_f 0.32), mp 169–171 °C. IR (KBr, cm^{-1}) 3505 (ν_{NH}), 3032, 2950 (ν_{CH}), 2499 (ν_{BH}), 1522, 1352 (ν_{NO_2}), 1499 (ν_{BN}), 1485, 1407, 1350 (ν_{CH}), 1145 (ν_{CN}), 1055 (ν_{B-B}), 998, 952, 856, 725, 675 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 5.49 (bs, 1H, NH), 8.1 (d, J_{CH} = 8.4 Hz, 4H, CH-phenyl), 7.45 (d, J_{CH} = 9.2 Hz, 4H, CH-phenyl), 3.45 (m, 4H, NH-CH_2), 3.15 (m, 8H, N(CH_2-)$_4$), 3.06 (m, 4H, phenyl-CH_2), 1.57 (m, 8H, N(CH_2**CH_2**-)$_4$), 1.36 (m, 8H, N(CH_2CH_2**CH_2**-)$_4$), 0.98 (t, J = 7.25 Hz, 12H, N($CH_2CH_2CH_2$**CH_3**)$_4$), 1.83–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 148.9 (2C, NO_2-Cphenyl), 130.2, 127.2, 125.9, 114.3 (10C, CH and C-phenyl), 59.3 (4C, N(CH_2-)$_4$), 52.5 (2C, NH-CH_2), 41.6 (2C, CH_2-phenyl), 24.4 (4C, N(CH_2**CH_2**-)$_4$), 20.24 (4C, N(CH_2CH_2**CH_2**-)$_4$), 13.8 (4C, N($CH_2CH_2CH_2$**CH_3**)$_4$). ^{11}B NMR (96.3 MHz; CD_3CN): δ –3.11 (s, 1B, B1), –20.91 (bs, 11B, B2-12). MS (ESI) m/z 455.4 [100, M^-]. Anal. Calc. for $C_{32}H_{64}B_{12}N_4O_4$: C, 55.02; H, 9.23; N, 8.02%. found: C, 54.77; H, 8.81; N, 7.69%.

N-(2-Nitrophenethyl)amino-undecahydro-*closo*-dodecaborate (1–) tetrabutylammonium salt (28)

This compound was prepared from **25** (175 mg, 0.25 mmol), using the procedure described for **14** to give **28** (112 mg, 82%) as a white solid: mp 225–227 °C; IR (KBr, cm^{-1}) 3520 (ν_{NH}), 3035, 2945 (ν_{CH}), 2493 (ν_{BH}), 1525, 1352 (ν_{NO_2}), 1510 (ν_{BN}), 1485, 1405, 1350 (ν_{CH}), 1145 (ν_{CN}), 1056 (ν_{B-B}), 998, 955, 857, 721, 677 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 6.87 (bs, 2H, NH_2), 7.71, 7.55–7.31 (m, 4H, CH-phenyl), 3.42 (m, 2H, NH-CH_2), 3.14 (m, 4H, N(CH_2-)$_4$), 3.02 (m, 2H, phenyl-CH_2), 1.59 (m, 8H, N(CH_2**CH_2**-)$_4$), 1.36 (m, 8H, N(CH_2CH_2**CH_2**-)$_4$), 0.95 (t, J = 6.85 Hz, 12H, N($CH_2CH_2CH_2$**CH_3**)$_4$), 1.73–0.46 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 149.0 (1C, NO_2-Cphenyl), 130.3, 128.5, 124.5, 113.9 (5C, CH and C-phenyl), 59.2 (4C, N(CH_2-)$_4$), 52.0 (1C, NH_2-CH_2), 41.2 (1C, CH_2-phenyl), 24.2 (4C, N(CH_2**CH_2**-)$_4$), 20.3 (4C, N(CH_2CH_2**CH_2**-)$_4$), 13.9 (4C, N($CH_2CH_2CH_2$**CH_3**)$_4$). ^{11}B NMR (96.3 MHz; CD_3CN): δ –3.15 (s, 1B, B1), –20.05 (s, 10B, J = 86.27 Hz, B2-11), –16.18 (s, 1B, B12). MS (ESI) m/z 306.5 [100, M^-]. Anal. Calc. for $C_{24}H_{57}B_{12}N_3O_2$: C, 52.46; H, 10.46; N, 7.65%. found: C, 52.12; H, 10.24; N, 7.38%.

N-(3-Nitrophenethyl)amino-undecahydro-*closo*-dodecaborate (1–) tetrabutylammonium salt (29)

This compound was prepared from **26** (175 mg, 0.25 mmol), using the procedure described for **14** to give **29** (96 mg, 70%) as a white solid: mp 188–190 °C; IR (KBr, cm^{-1}) 3515 (ν_{NH}), 3030, 2955 (ν_{CH}), 2494 (ν_{BH}), 1524, 1350 (ν_{NO_2}), 1495 (ν_{BN}), 1485, 1405, 1350 (ν_{CH}), 1149 (ν_{CN}), 1057 (ν_{B-B}), 995, 955, 857, 725, 676 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 6.95 (bs, 2H, NH_2), 7.68, 7.55–7.35 (m, 4H, CH-phenyl), 3.42 (m, 2H, NH-CH_2), 3.11 (m, 8H, N(CH_2-)$_4$), 3.02 (m, 2H, phenyl-CH_2), 1.55 (m, 8H, N(CH_2**CH_2**-)$_4$), 1.38 (m, 8H, N(CH_2CH_2**CH_2**-)$_4$), 0.97 (t, J = 7.5 Hz, 12H, N($CH_2CH_2CH_2$**CH_3**)$_4$), 1.82–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 149.8 (1C, NO_2-Cphenyl), 130.2, 129.4, 125. 7, 114.1 (5C, CH and C-phenyl), 59.3 (4C, N(CH_2-)$_4$), 52.5 (1C, NH_2-CH_2), 41.7 (1C, CH_2-phenyl), 24.3 (4C, N(CH_2**CH_2**-)$_4$), 20.3 (4C, N(CH_2CH_2**CH_2**-)$_4$), 13.8 (4C, N($CH_2CH_2CH_2$**CH_3**)$_4$). ^{11}B NMR (96.3 MHz; CD_3CN): δ –3.08 (s, 1B, B1), –19.97 (s, 10B, J = 85.79 Hz, B2-11), –16.34 (s, 1B, B12). MS (ESI) m/z 306.6 [100, M^-]. Anal. Calc. for $C_{24}H_{57}B_{12}N_3O_2$: C, 52.46; H, 10.46; N, 7.65%. found: C, 52.19; H, 10.23; N, 7.41%.

N-(4-Nitrophenethyl)amino-undecahydro-*closo*-dodecaborate (1–) tetrabutylammonium salt (30)

This compound was prepared from **27** (175 mg, 0.25 mmol), using the procedure described for **14** to give **30** (119 mg, 87%) as a white solid: mp 214–216 °C; IR (KBr, cm^{-1}) 3515 (ν_{NH}), 3035, 2952 (ν_{CH}), 2487 (ν_{BH}), 1523, 1351 (ν_{NO_2}), 1497 (ν_{BN}), 1485, 1407, 1350 (ν_{CH}), 1145 (ν_{CN}), 1055 (ν_{B-B}), 998, 952, 856, 725, 675 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 6.79 (bs, 2H, NH_2), 8.05 (d, J_{CH} = 7.55 Hz, 2H, CH-phenyl), 7.42 (d, J_{CH} = 7.55 Hz, 2H, CH-phenyl), 3.42 (m, 2H, NH-CH_2), 3.15 (m, 8H, N(CH_2-)$_4$), 3.05 (m, 4H, phenyl-CH_2), 1.55 (m, 8H, N(CH_2**CH_2**-)$_4$), 1.35 (m, 8H, N(CH_2CH_2**CH_2**-)$_4$), 0.96 (t, J = 7.2 Hz, 12H, N($CH_2CH_2CH_2$**CH_3**)$_4$), 1.83–0.55 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 149.2 (1C, NO_2-Cphenyl), 130.2, 129.0, 125.7, 114.5 (5C, CH and C-phenyl), 59.3 (4C, N(CH_2-)$_4$), 52.5 (1C, NH-CH_2), 41.5 (1C, CH_2-phenyl), 24.4 (4C, N(CH_2**CH_2**-)$_4$), 20.2 (4C, N(CH_2CH_2**CH_2**-)$_4$), 13.8 (4C, N($CH_2CH_2CH_2$**CH_3**)$_4$). ^{11}B NMR (96.3 MHz; CD_3CN): δ –3.12 (s, 1B, B1), –20.06 (s, 10B, J = 87.01 Hz, B2-11), –16.23 (s, 1B, B12). MS (ESI) m/z 306.5 [100, M^-]. Anal. Calc. for $C_{24}H_{57}B_{12}N_3O_2$: C, 52.46; H, 10.46; N, 7.65%. found: C, 52.22; H, 10.19; N, 7.42%.

General synthesis for compounds 31–33

Nitrophenethyl bromide (1.61 g, 7 mmol) was added to a stirred solution of **1d** (0.5 g, 0.7 mmol) and KOH (198 mg, 3.55 mmol) in 20 ml dry DMF under argon atmosphere. The solution was stirred for 5 h at room temperature. The solvent was evaporated *in vacuo* and the residue was washed with diethyl ether and dissolved in 20 ml of water. Addition of 2.25 g (7 mmol) of tetrabutylammonium bromide gave a white precipitate of *O*-alkylated derivative. Crystallization from dichloromethane–ethanol yielded colorless needles.

***O*-(2-Nitrophenethyl)hydroxo-undecahydro-*closo*-dodecaborate (2–) ditetrabutylammonium salt (31).** (174 mg, 22%), mp 179–181 °C. IR (KBr, cm^{-1}) 3024, 2953 (ν_{CH}), 2492 (ν_{BH}), 1526, 1350 (ν_{NO_2}), 1705 (ν_{BO}), 1485, 1405, 1285 (ν_{CH}), 1045 (ν_{B-B}), 995, 948,

825, 722, 675 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.66, 7.52–7.33 (m, 2H, CH-phenyl), 3.89 (m, 2H, O-CH_2), 3.11 (m, 16H, N(CH_2-)$_4$), 3.06 (m, 2H, CH_2-phenyl), 1.57 (m, 16H, N(CH_2**CH_2**-)$_4$), 1.38 (m, 16H, N(CH_2CH_2**CH_2**-)$_4$), 0.95 (t, J = 14.41 Hz, 24H, N($CH_2CH_2CH_2$**CH_3**)$_4$), 1.87–0.35 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 148.2 (1C, NO_2-Cphenyl), 131.1, 129.3, 125.7, 114.8 (5C, CH and C-phenyl), 59.3 (8C, N(CH_2-)$_4$), 56.8 (C, O-CH_2), 41.3 (1C, CH_2-phenyl), 24.3 (8C, N(CH_2**CH_2**-)$_4$), 20.3 (8C, N(CH_2CH_2**CH_2**-)$_4$), 13.8 (8C, N($CH_2CH_2CH_2$**CH_3**)$_4$). ^{11}B NMR (96.3 MHz; CD_3CN): δ 8.51 (s, 1B, B1), –12.05 (d, J = 166.21 Hz, 10B, B2-11), –21.06 (s, 1B, B12). MS (ESI): m/z 153.5 [100, $M^-/2$]. Anal. Calcd. for $C_{35}H_{86}B_{12}N_2O$: C, 60.67; H, 11.58; N, 5.31%. found: C, 60.33; H, 11.29; N, 5.06%.

***O*-(3-Nitrophenethyl)hydroxo-undecahydro-*closo*-dodecaborate (2–) ditetrabutylammonium salt (32).** (187 mg, 27%), mp 168–170 °C. IR (KBr, cm^{-1}) 3025, 2955 (ν_{CH}), 2489 (ν_{BH}), 1525, 1352 (ν_{NO_2}), 1706 (ν_{BO}), 1485, 1405, 1285 (ν_{CH}), 1045 (ν_{B-B}), 995, 948, 825, 722, 675 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 7.72, 7.59–7.39 (m, 2H, CH-phenyl), 3.92 (m, 2H, O-CH_2), 3.11 (m, 16H, N(CH_2-)$_4$), 3.02 (m, 2H, CH_2-phenyl), 1.55 (m, 16H, N(CH_2**CH_2**-)$_4$), 1.35 (m, 16H, N(CH_2CH_2**CH_2**-)$_4$), 0.95 (t, J = 14.41 Hz, 24H, N($CH_2CH_2CH_2$**CH_3**)$_4$), 1.87–0.35 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 148.7 (1C, NO_2-Cphenyl), 131.4, 129.4, 125.5, 114.9 (5C, CH and C-phenyl), 59.4 (8C, N(CH_2-)$_4$), 56.8 (C, O-CH_2), 41.4 (1C, CH_2-phenyl), 24.4 (8C, N(CH_2**CH_2**-)$_4$), 20.3 (8C, N(CH_2CH_2**CH_2**-)$_4$), 13.8 (8C, N($CH_2CH_2CH_2$**CH_3**)$_4$). ^{11}B NMR (96.3 MHz; CD_3CN): δ 8.52 (s, 1B, B1), –12.11 (d, J = 165.96 Hz, 10B, B2-11), –20.99 (s, 1B, B12). MS (ESI): m/z 153.5 [100, $M^-/2$]. Anal. Calcd. for $C_{35}H_{86}B_{12}N_2O$: C, 60.67; H, 11.58; N, 5.31%. found: C, 60.30; H, 11.36; N, 5.12%.

***O*-(4-Nitrophenethyl)hydroxo-undecahydro-*closo*-dodecaborate (2–) ditetrabutylammonium salt (33).** (124 mg, 18%), mp 192–194 °C. IR (KBr, cm^{-1}) 3022, 2956 (ν_{CH}), 2492 (ν_{BH}), 1525, 1350 (ν_{NO_2}), 1705 (ν_{BO}), 1485, 1405, 1285 (ν_{CH}), 1152 (ν_{CN}), 1045 (ν_{B-B}), 995, 948, 825, 722, 675 (ν_{CH}). ^{1}H NMR (400 MHz, CD_3CN) δ = 6.79 (bs, 2H, NH_2), 8.06 (d, J_{CH} = 7.2 Hz, 2H, CH-phenyl), 7.42 (d, J_{CH} = 7.2 Hz, 2H, CH-phenyl), 3.95 (m, 2H, O-CH_2), 3.11 (m, 16H, N(CH_2-)$_4$), 3.05 (m, 2H, CH_2-phenyl), 1.55 (m, 16H, N(CH_2**CH_2**-)$_4$), 1.36 (m, 16H, N(CH_2CH_2**CH_2**-)$_4$), 0.95 (t, J = 14.41 Hz, 24H, N($CH_2CH_2CH_2$**CH_3**)$_4$), 1.82–0.42 (m, 11H, $B_{12}H_{11}$). ^{13}C NMR (100 MHz, CD_3CN) δ = 149.3 (1C, NO_2-Cphenyl), 131.6, 129.8, 125.9, 114.8 (5C, CH and C-phenyl), 59.3 (8C, N(CH_2-)$_4$), 56.6 (C, O-CH_2), 41.4 (1C, CH_2-phenyl), 24.4 (8C, N(CH_2**CH_2**-)$_4$), 20.3 (8C, N(CH_2CH_2**CH_2**-)$_4$), 13.8 (8C, N($CH_2CH_2CH_2$**CH_3**)$_4$). ^{11}B NMR (96.3 MHz; CD_3CN): δ 8.49 (s, 1B, B1), –12.07 (d, J = 165.76 Hz, 10B, B2-11), –21.02 (s, 1B, B12). MS (ESI): m/z 153.3 [100, $M^-/2$]. Anal. Calcd. for $C_{35}H_{86}B_{12}N_2O$: C, 60.67; H, 11.58; N, 5.31%. Found: C, 60.47; H, 11.33; N, 5.19%.

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