SYNTHESIS OF *N*- AND *B*-SUBSTITUTED DERIVATIVES OF *closo*-AMINO-UNDECAHYDRO-DODECABORATE(1–) ANION

Bohumir GRUNER[a], Bernard BONNETOT[b1] and Henri MONGEOT[b2]

[a] *Institute of Inorganic Chemistry Academy of Sciences of the Czech Republic, 250 68 Rez near Prague, Czech Republic; e-mail: gruner@iic.cas.cz*

[b] *Laboratoire des Multimatériaux et Interfaces UMR no 5615, Université Claude Bernard Lyon I, 43Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France; e-mail: [1] bonnetot@cismsun.univ-lyon1.fr, [2] mongeot@cismsun.univ-lyon1.fr*

Received November 14, 1996
Accepted June 9, 1997

We have pleasure to dedicate this article to Jaromir Plesek on the occasion of his 70th birthday, in recognition of his outstanding contribution to cage-boron chemistry.

The synthesis of nitrogen and boron substituted derivatives of the 1-amino- *closo*-dodecaborate anion(1–) **1** is reported. Reasonable yields of the $[R_2NH\text{-}B_{12}H_{11}]^-$ derivatives (R = $C_6H_5CH_2$, 2-$C_{10}H_7CH_2$, n-$C_{16}H_{33}$, n-$C_{12}H_{25}$) were obtained *via* conventional alkylation of **1** in aqueous propan-2-ol, starting from bulky primary alkylhalides. These $[R_2NH\text{-}B_{12}H_{11}]^-$ derivatives were subsequently methylated by dimethyl sulfate under similar conditions. Reaction of **1** with palmitoyl chloride gave under anhydrous conditions the corresponding *N*-acyl derivative. Reaction of **1** with hydroxymethyl-18-crown-6 tosylate in THF in the presence of NaH led to the novel $[(18\text{-crown-6-}CH_2)_2NH\text{-}B_{12}H_{11}]^-$ anion, the Cs^+ salt of which exhibits unusual solubility properties. A direct cyclization reaction of pentaethylene glycol ditosylate with **1** gave under similar conditions $[(15\text{-azacrown})\text{-}5\text{-}B_{12}H_{11}]^-$, the first known *closo*-borate anion with an attached aza-crown ring. These species exhibit potentially interesting complexation efficiency and solubility properties. Selective substitution of the boron cage by a bulky naphthyl substituent was achieved by palladium-mediated cross-coupling reaction between **1** and 1-$BrMgC_{10}H_7$. All derivatives were characterized by high-field ^{11}B, ^1H NMR and negative FAB mass spectrometry methods.

Key words: Boranes; *closo*-Hydroborate anions; Dodecahydro-*closo*-dodecaborate(2–) anion; 1-Amino-undecahydro-*closo*-dodecaborate(1–).

Because of a very high stability and weak nucleophilicity, all $[B_{12}H_{12}]^{2-}$ anion derivatives are suitable for many special purposes, such as optimization of solid ionic electrolytes[1], boron neutron capture therapy[2,3] (BNCT), liquid crystals[4], *etc*.

A relatively extensive literature[1–8] on the synthesis of the $[B_{12}H_{12}]^{2-}$ derivatives has been available. Nevertheless, except the recent studies on the BNCT-active[2,3] $[B_{12}H_{11}SH]^{2-}$ anion, the recently reported *S*- and *O*- alkyl and aryl derivatives[3,4], halogen derivatives[6–9] and a few others (see *e.g.* ref.[10]), all other articles, patent and

monographs deal with the earlier work of the Muetterties group[11–16]. This work originated in the sixties when the high-field NMR spectroscopy and efficient separation methods were not available.

We have been interested in the synthesis of dodecaborate anions with bulky organic groups or a metal complexing group attached either to the amino nitrogen or to the boron cage. Such species facilitate transfer of mono- and divalent cations, *via* formation of tight ion pairs with the hydrophobic anions under discussion, into an organic phase. These properties can be used for advanced extraction methods, particularly those used for the Cs^+ and Sr^{2+} extraction from high-level nuclear waste. The skeleton of the parent anion is known to belong to the class of so-called "solvophobic" anions that expel water molecules. Nevertheless, its two negative charges inevitably promote hydration. For a successful transfer into organic layer, the charge should be reduced to (1–). The most convenient way of charge reduction is apparently the substitution by amino group, which leaves the molecule stability comparable with the starting compound. Additional modification of either the amino functionality or the skeleton by bulky organic substituents is necessary in order to achieve sufficient selectivity and hydrophobic properties. Both the synthesis and study of properties of such compounds have already been the subject of several EC Project reports[12] but the results have not been published yet. Here, we report on the synthesis of several species discussed above along with the preparation of two crown-ether derivatives. The study on their extraction properties will be the subject of a separate communication. When the study had been initiated two years ago, only the trimethylamine derivative, obtained by dimethyl sulfate alkylation of **1**, was reported in the literature[13,14]. Recently, synthesis of some alkylamino derivatives under anhydrous conditions has been reported[17].

EXPERIMENTAL

General

All manipulations were carried out under argon or nitrogen using standard inert atmosphere techniques. Analytical grade THF dried over sodium wire was freshly distilled from sodium diphenylketyl prior to use. Dry DMF (Aldrich) was used through the study. The 1 M solution of 1-$BrMgC_{10}H_7$ in THF was prepared from 1-bromonaphthalene and magnesium turnings in dry THF under ultrasonic activation.

Et_3NH-$B_{12}H_{12}$ was provided by Katchem Ltd, Prague. Diethyl ether (analytical grade), acetonitrile (HPLC grade) were purchased from Aldrich (France); other chemicals were a reagent grade and used as received. All solvent evaporations were performed in vacuum using a standard rotary evaporator, unless otherwise stated.

Exchange of Cations in Salts of Borate Anions *via* Conjugate Acids

The tetramethylammonium or cesium salts of **1**, **11** and **12** were converted with the strong acid ion-exchange resin Amberlyte IRN 77 in the H^+ cycle to the aqueous solution of the corresponding free acids. $Me_4N[H_3NB_{12}H_{11}]$ and [aza-15-crown-5-$B_{12}H_{11}$]NMe_4 were passed through an ion exchanger

as aqueous solutions, [(18-crown-6-CH_2)$_2$-$NHB_{12}H_{11}$]Cs in 30% aqueous acetonitrile. The solutions were concentrated and then neutralized with an aqueous base (usually by KOH).

The tetramethylammonium salts of all other anions were transformed into the corresponding conjugate acids by the following procedure: The well-ground tetramethylammonium salt was overlayed in a separation funnel by ether (50 ml) and then treated with 3 M HCl (5 × 30 ml). The undissolved powder that remained during three first extractions on the interface of the aqueous and organic layer was kept always with the organic layer. In the last extraction, the ether layer was separated together with an organic phase at the bottom. The combined aqueous solutions were extracted once by additional diethyl ether (30 ml) and ether extracts were combined, poured into water and the ether was evaporated in vacuum. When the ether was removed completely, a base was added (usually CsOH) to pH 7.0.

NMR Spectra

^{11}B NMR spectra were measured at 96.29 and 160.364 MHz on Bruker WP-300 and Varian XL-500 spectrometers. All ^{11}B chemical shifts are referenced to $BF_3 . OEt_2$. ^{1}H NMR spectra were measured on Bruker WP-300 at 300.135 MHz, selectively decoupled $^1H\{^{11}B\}$ spectra on Varian XL-500 spectrometer at 499.843 MHz. Proton chemical shifts were measured relative to internal residual protons from the lock deuteriosolvent and referenced to tetramethylsilane (0.0 ppm).

Chromatographic Methods

TLC was performed on DEAE cellulose[6,18] with 2 M solution of NH_4NO_3 as eluent. The spots were detected by 0.5% solution of $PdCl_2$ in 5% HCl.

A Merck–Hitachi HPLC system consisting of L-6200A intelligent pump, Rheodyne 7125 injector, D 6000 interface, and LaChrom-L7450 diode array detector with HSM 2.0 software was used through the study. Two HPLC methods were used through the study.

A. A simple ion-pair reverse phase (IP RP) HPLC method[19] was used for the separation and detection of all hydrophobic aryl-containing anions and most of their impurities even under isocratic conditions. For capacity factors (k') values, see Table I. Chromatographic parameters: steel HPLC column Separon SGX (C8, 7 μm) 250 × 4 mm (Tessek Ltd., Prague); mobile phase: 6 mM solution of hexylamine hydrochloride in 50% aqueous acetonitrile; flow rate 1ml/min; detection: 260 nm, sensitivity 0.2 A.U.F.S.; injection: 20 μl of samples (1 mg/ml) in 50% aqueous acetonitrile.

B. HPLC for the analysis of the starting $[H_3NB_{12}H_{11}]^-$ anion and 15-azacrown-5-*N*-dodecaborate(1–) anion (for k' values see Table I) was based on the HIC HPLC methods[6–8] for the separation of the $[B_{12}H_{12}]^{2-}$ derivatives. Chromatographic parameters: cartridge glass column (CGC) Separon HEMA (hydroxyethyl methacrylate) BIO 300, 12 μm, 150 × 3 mm (Tessek Ltd., Prague); mobile phase: 0.1 M $NaClO_4$ in water–acetonitrile A, 10% CH_3CN; B, 25% CH_3CN; C, 30% CH_3CN; flow rate 0.5 ml/min; detection at 192–200 nm, sensitivity range 0.2 A.U.F.S.; injection: 20 μl aqueous solutions of samples (2–5 mg/ml).

Mass Spectrometry

All analyses were performed in the Mass Spectrometry Laboratory, Central Analytical Service of CNRS, Solaize, France, on a hybrid Mass Spectrometer ZAB 2-SEQ (Micromass) by SIMS technique with cesium beam. The samples were dissolved in acetone and mixed with a matrix of thioglycerol or nitrobenzyl alcohol. The mass was measured with the accuracy of 0.1 mass unit.

closo-[1-$H_3NB_{12}H_{11}$]NMe_4 (**1**)

The reaction of $Na_2B_{12}H_{12}$ (33.6 g, 0.179 mol) solution in water (300 ml) at pH 7 and *O*-hydroxylaminesulfonic acid (45.0 g, 0.398 mol) was carried out under reflux according to the described procedure[13]. Most of the starting anion (90%) had been spent after 3 h of reaction (HPLC monitoring). The following isolation procedure allowed isolation of pure product **1** and disubstituted species **1b–1d**: After cooling down, the crude product was precipitated by the addition of Me_4NCl (20 g, 0.182 mol) in water (50 ml). The product was recrystallized from hot water (500 ml). The crystalline material was filtered off and air-dried (26.5 g). The combined mother liquors were evaporated to 100 ml, acidified by 3 M HCl (20 ml), extracted with ethyl acetate (4 × 25 ml) and left to crystallize. Crude product (6.5 g) was recrystallized from water. Combined product crops were treated with hot acetonitrile (300 ml) on a steam bath, the insoluble material filtered off, the volume was adjusted to 100 ml and the product was left to crystallize. Repeated recrystallization gave pure [$H_3NB_{12}H_{11}$]NMe_4, as white crystals (25.2 g, 61%).

Combined ethyl acetate extracts from the above procedure were evaporated to dryness and the solid residue recrystallized from hot water (25 ml) to give white crystals (1.5 g, 5%) of a pure 1,7-$(H_3N)_2B_{12}H_{10}$ (**1b**), R_F 0.55 (DEAE cellulose, 2 M NH_4NO_3. *m/z* for $B_{12}H_{16}N_2$ calculated 176.2; found 176.2.

TABLE I
Some characteristic properties of the anions **1–15**

Compound	FAB-MS[a] *m/z*	HPLC *k′*	TLC R_F
1a	160.3	2.98[b]	0.35[c]
2	340.3	3.96[d]	0.38[e]
3	440.3	9.33[d]	–
4	328.4	–	0.25[f]
5	496.6	–	0.12[f]
6	384.5	–	0.20[f]
7	609.0	–	0.10[f]
8	354.3	4.66[d]	0.34[e]
9	454.4	11.08[d]	–
10	398.4	–	0.02[c]
11	710.4	–	0.15[c]
12	362.3	4.67[b]	0.29[c]
13	286.2[g]	8.67[h]	0.29[c]
14	466.2	6.55[d]	0.17[e]
15	454.4	13.08[d]	–

[a] Negative FAB-MS. [b] HIC HPLC method, conditions *A* (see Experimental). [c] 2 M aqueous NH_4NO_3. [d] IP HPLC (see Experimental). [e] 1 M $NaClO_4$ in 12.5% aqueous acetonitrile. [f] 2 M $NaClO_4$ in 20% aqueous acetonitrile. [g] [M–H]. [h] 0.1 M $NaClO_4$ in 30% AcCN.

Recrystallization from water of the solids filtered off from hot acetonitrile solutions gave 5.5 g (18%) of a mixture of the two isomers (**1c** and **1d**), giving one spot on TLC of R_F 0.23. 1,12-**1c** to 1,2-**1d** isomer ratio 5 : 2, *m/z* 176.2.

closo-[1-$(C_6H_5CH_2)_2HNB_{12}H_{11}$]Cs (**2**)

The Me_4N^+ salt of **1** (3.0 g, 12.3 mmol) was converted into the conjugate acid by ion-exchange technique (see above). The volume of the resulting aqueous solution was reduced to 190 ml and aqueous solution of KOH (12.0 g, 0.21 mol in 20 ml of H_2O) was then added, followed by propan-2-ol (100 ml). This solution was heated under stirring to reflux temperature and benzyl bromide (5.0 ml, 42 mmol) in propan-2-ol (25 ml) was then added dropwise over a period of 4 h. The reaction slurry was heated under reflux for additional 12 h. At that time less than 20% of the unreacted starting material persisted (TLC and HPLC monitoring). Additional amount of KOH was added (2.0 g, 36 mmol) in water (10 ml), followed by benzyl bromide (2.0 ml, 16.8 mmol) in propan-2-ol (10 ml). The reaction mixture was heated under reflux for additional 20 h and then cooled down to room temperature; pH was adjusted to 7 with 3 M HCl and the volume of the slurry was then reduced to 75 ml. This slurry was extracted with a toluene–hexane mixture (2 : 1; 4 × 25 ml), the bottom fluffy layer was kept with the aqueous one and the upper clear layer was discarded. The extraction was continued with ether (3 × 25 ml), the aqueous layer was acidified with 6 M HCl (50 ml) and then re-extracted with ether (3 × 20 ml). The ether exctracts were always separated with the bottom organic layer. Combined ether extracts were poured into water (75 ml) and the ether was evaporated. The crude product was then precipitated with an excess of 1 M Me_4NCl, filtered off, washed with water (4 × 30 ml) and vacuum dried. The product was purified by chromatography on silica gel column (25 × 2 cm) using $CHCl_3$–CH_3CN mixture (4 : 1 to 3 : 1) as mobile phase. Fractions containing pure product (HPLC monitoring) were combined, evaporated to dryness, dissolved in a minimum amount of EtOH, followed by the addition of 1 M Me_4NCl (5 ml) and water (20 ml). The product was then filtered off, washed with water and recrystallized from aqueous acetone to give a white microcrystalline material, yield 4.4 g (83%).

closo-[1-$(C_{10}H_7CH_2)_2HNB_{12}H_{11}$]Cs (**3**)

The synthesis was performed as described for compound **2**. The Me_4N^+ salt of **1** (3.0 g, 13 mmol), converted into a solution of the potassium salt, was alkylated in 50% propan-2-ol (200 ml) in the presence of KOH (12.0 g, 0.21 mol). Solid 2-(bromomethyl)naphthalene (8.5 g, 38.4 mmol) was added in nine portions during 12 h under reflux. The reaction mixture was stirred under reflux overnight and additional KOH (2.0 g, 36.5 mmol) and 2-(bromomethyl)naphthalene (2.5 g, 11.3 mmol) were then added in three portions during 3 h, and the reflux was continued for additional 20 h. Separation and purification of the product (by LC and recrystallization) was accomplished as for **2**, except that the cesium salt of the product was precipitated by the addition of CsF (3.0 g) in water (20 ml). Pale yellow-green crystals, yield 6.3 g (84%).

closo-[1-$(C_{12}H_{25})H_2NB_{12}H_{11}$]Cs (**4**) and *closo*-[1-$(C_{12}H_{25})_2HNB_{12}H_{11}$]Cs (**5**)

A solution of the Me_4N^+ salt of **1** (2.0 g, 8.6 mmol) in 70% aqueous propan-2-ol, to which NaOH was added (1.6 g, 40 mmol, in 25 ml of H_2O), was heated to reflux. A solution of 1-bromododecane (6.45 g, 25.8 mmol) in 25 ml of propan-2-ol was then added dropwise over a period of 3 h and the reaction slurry was refluxed for 24 h. Solid NaOH (0.6 g, 15 mmol) was then added, followed by additional portion of 1-bromododecane (3.2 g, 12.8 mmol) and the reflux was continued for 48 h. After cooling down, the solvents were evaporated and the residue was treated with water (50 ml) and 6 M HCl (50 ml). The resulting slurry was extracted with hexane (4 × 25 ml) and then with toluene

and ether (4 × 30 ml each). The hexane extracts were discarded, combined toluene and ether extracts containing a similar product mixture were evaporated with water (75 ml) until the organic solvents were removed. An excess of Me_4NCl in water was added to the aqueous solution and the precipitate filtered off and vacuum dried. The dry powder was treated with toluene (4 × 25 ml), the residue dissolved in a $CHCl_3$–CH_3CN mixture (4 : 1), placed onto the top of a silica gel column and eluted with the same mobile phase, increasing gradually the acetonitrile content to 2 : 1. In this manner, both mono- and dialkyl derivatives were obtained as white powders. Yields: 0.45 g (13%) of **4** and 1.6 g (32%) of **5**.

closo-[1-($C_{16}H_{33}$)$H_2NB_{12}H_{11}$]Cs (**6**) and *closo*-[1-($C_{16}H_{33}$)$_2$$HNB_{12}H_{11}$]Cs (**7**)

The synthesis was carried out similarly to the previous syntheses of compounds **2** and **3**. The potassium salt of **1** (1.99 g, 10 mmol) was alkylated by addition of dropwise 1-iodohexadecane (10.6 g, 30.2 mmol in 25 ml of propan-2-ol) during the first 4 h into a solution of 5% KOH in 60% aqueous propan-2-ol (250 ml), while the mixture was heated at reflux for 24 h. Additional KOH (2.0 g, 37 mmol) and hexadecyl iodide (3.7 g, 10.4 mmol) were then added and the reaction mixture was refluxed for 16 h. The isolation of crude products was performed as for compounds **2** and **3**, but a toluene–hexane mixture (1 : 3) was used for the first four extractions. The main product (disubstituted) was obtained as a Me_4N^+ salt from the combined ether extracts of the neutral reaction slurry and purified by column chromatography (similarly to compounds **2** and **5**). Pure monoalkyl derivative was obtained by chromatography of combined ether extracts obtained upon acidification of the aqueous layer (see procedure for **2**). White solids, yields: 0.25 g (5%) of **6** and 2.9 g (42%) of **7**.

closo-[1-($C_6H_5CH_2$)$_2$$CH_3NB_{12}H_{11}$]Cs (**8**)

The Me_4N^+ salt of **3** (1.8 g, 4.3 mmol) was converted into the corresponding conjugate acid by the procedure described above and then sodium hydroxide (2.5 g, 62 mmol) was added to the aqueous solution, followed by propan-2-ol (30 ml). The solution was stirred and heated at reflux and then dimethyl sulfate (1.0 ml) was added. Over a period of 3 days, 50 portions of 0.5 ml of dimethyl sulfate were repeatedly added followed by additions of NaOH to keep the pH alkaline. The reaction course was followed by HPLC (see Table I and the text above) and the reaction was stopped when only approximately 5% of the starting material remained. The mixture was cooled down and the excess of dimethyl sulfate decomposed by aqueous ammonia (20 ml). pH was adjusted to 7.0 with diluted HCl and the propan-2-ol was evaporated with a part of water. The aqueous slurry was then extracted with toluene (4 × 25 ml), the toluene extracts were discarded, and the aqueous layer was acidified with 6 M HCl (30 ml) and extracted four times with ether. The ether extracts were separated together with the bottom organic layer and poured into 50 ml of water. The ether was evaporated and the crude product precipitated with cesium fluoride, filtered off, and vacuum dried. The product was purified by chromatography on a silica gel column (30 × 2 cm), using a chloroform–acetonitrile mixture (from 10 to 40% CH_3CN) as the eluent (HPLC monitoring). Yield of the pure methyl derivative **8** (white semicrystalline solid) was 0.53 g (25%).

closo-[1-(2-$C_{10}H_7CH_2$)$_2$$CH_3N$-$B_{12}H_{11}$]$NMe_4$ (**9**)

The Me_4N^+ salt of **3** (2.0 g, 3.9 mmol) was converted to conjugate acid as described above for the Me_4N^+ salt of **2**. The methylation and product isolation were accomplished similarly to the procedure for **2**. The solution was neutralized, extracted with toluene (2 × 20 ml), then acidified with 6 M HCl (50 ml) and extracted with ether (4 × 30 ml). The combined ether extracts containing the crude product were evaporated with water (50 ml). The product was precipitated with an excess of Me_4NCl

and, after drying, purified by column chromatography on a silica gel using $CHCl_3$–CH_3CN mixtures (from 9 : 1 to 2 : 1) as eluents (HPLC monitoring). Yield was 0.73 g (35%, yellowish solid). The product was converted into the Cs^+ salt by standard procedure *via* conjugate acid and precipitation with CsF.

closo-[1-($C_{15}H_{31}C(O)NH_2B_{12}H_{11}$]Cs (**10**)

The Me_3NH^+ salt of **1** (1.15 g, 5.27 mmol) was dried (3 h at 90 °C and 10 Pa) and dissolved in THF (70 ml). NaH (60% suspension in paraffin oil; 0.45 g, 11.5 mmol was added) under stirring for 1 h, followed by the dropwise addition of palmitoyl chloride (2.2 ml, 6.8 mmol) in THF (20 ml) during 30 min to the solution stirred at 60 °C. This temperature was maintained for additional 1.5 h. Most of the starting material disappeared at this time (TLC). The reaction mixture was decomposed by the addition of methanol (3 ml) and the solvents were evaporated. The residual semi-solid was washed with hexane (3 × 10 ml), treated carefully with water (30 ml), and then acidified with 1 M HCl (30 ml) and extracted with Et_2O (3 × 30 ml). The combined organic extracts were coevaporated with water (50 ml) until the ether distilled off. The remaining aqueous solution was treated with a trimethylamine hydrochloride solution to precipitate the product as the insoluble Me_3NH^+ salt. The precipitate was filtered off, washed with water and air-dried at room temperature to obtain 1.52 g of the crude product as a white powder. However, according to ^{11}B NMR spectra, this product was contaminated with *ca* 30% of unknown impurity that could not be detected by both TLC and NMR spectra of the crude reaction mixture. The pure compound was obtained after repeated chromatography on a silica gel column (30 × 2.5 cm) with $CHCl_3$–CH_3CN (2 : 1) as the mobile phase; yield 0.98 g, 47%.

closo-[*N*,*N*-1-(18-crown-6-CH_2)$_2$$NHB_{12}H_{11}$]Cs (**11**)

The synthesis of $TosOCH_2$-18-crown-6 was performed analogously to described[20] procedure from $HOCH_2$-18-crown-6 (10.0 g, 34 mmol) and *p*-toluenesulfonyl chloride (7.78 g, 40.6 mmol) in a CH_2Cl_2–H_2O slurry with NaOH as a base. Yellowish oil, yield 14.5 g. ^1H NMR spectrum (500 MHz, $CDCl_3$): 2.435 s, 3 H (CH_3Ar); 3.45–3.75 m, 23 H (CH_2O, CHO); 4.04–4.15 m, 2 H (CH_2OTos); 7.26, 7.34, 7.78, 7.80 m, 4 H (arom H).

To a slurry of dried $Me_3NH[H_3NB_{12}H_{11}]$ (2.0 g, 9.2 mmol) in THF (50 ml), NaH (1.1 g, 80% suspension in paraffin oil, 37 mmol) was added. The mixture was then heated under reflux for 30 min to remove Me_3N. After cooling down to room temperature, $TosOCH_2$-18-crown-6 (10.0 g, 22.3 mmol) was added dropwise during 1 h, the reaction mixture was then stirred 13 h at ambient temperature, and then refluxed for 45 min. After cooling down to room temperature, THF was evaporated, the oily brown residue dissolved in 50% ethanol (100 ml), and CsF was added (2.0 g in 20 ml of water). The solvents were then evaporated and the brown oily residue was extracted with toluene (3 × 25 ml) and ether (4 × 24 ml) in an ultrasonic bath. The resulting yellow powder was treated with a hot water–ethanol–acetone mixture (1 : 2 : 2, 250 ml). The small insoluble fraction was removed by filtration and the solution left to crystallize in a refrigerator overnight. The first impure fraction (1.5 g) was then filtered off and purified by chromatography on a silica gel column in AcCN–$CHCl_3$ mixture (30–40% CH_3CN). After stepwise evaporation of the filtrate to volumes 175 and 75 ml, two additional product crops were obtained (3.5 g and 3.1 g), leaving the respective solutions stand for 12h at –4 °C. Combined product crops were dissolved in hot aqueous acetone and left to crystallize at –4 °C to isolate a white, crystalline powder; yield 6.1 g (79%).

[1-(Aza-15-crown-5)-$B_{12}H_{11}$]NMe_4 (**12**)

The Me_4N^+ salt of **1** (2.0 g, 8.6 mmol) was converted into the potassium salt *via* standard ion exchange technique, followed by neutralization of the resulting aqueous solution with 2 M KOH. The solution of the potassium salt was evaporated to dryness and then vacuum dried for 5 h at 80 °C. After cooling down, dry DMF (100 ml) and anhydrous $SrCl_2$ (0.75 g) were added, followed by NaH (1.2 g, 30 mmol, 60% suspension in paraffin oil). The reaction slurry was stirred for 3 h and pentaethylene glycol di-*p*-toluenesulfonate (5.0 g, 9.1 mmol in 100 ml of dry DMF) was then added dropwise over a 5 h period. The reaction mixture was stirred at ambient temperature for 12 h, and then at 60 °C for 5 h. After cooling down, the reaction mixture was filtered under argon, the filtrate was decomposed by dropwise addition of EtOH (5 ml) and the resulting mixture was vacuum-evaporated at 0.1 Pa at 50 °C. The viscous residue was diluted with EtOH (50 ml) and Me_4NCl (1.5 g) in water (20 ml) was added. The brown solution was evaporated and the oily residue treated with toluene and diethyl ether (4 × 20 ml each). Remaining pale-brown powder (6.5 g) was purified by chromatography on a silica gel column with a $CHCl_3$–CH_3CN mixture (10 to 50% acetonitrile) as eluent (TLC and HPLC monitoring). The product containing fractions were recrystallized from hot ethanol, to which water was added dropwise until dissolution; the solutions were then left to crystallize one week at 0 °C to give pure, white crystalline **12**; yield 31%.

closo-[1-H_3N-$B_{12}H_{10}I$]NMe_4 (**13**)

The Me_4N^+ salt of 1 (3.0 g, 13 mmol) was dissolved in water (500 ml), the solution was acidified with glacial acetic acid (10 ml) and a solution of I_2 (3.3 g, 12.9 mmol) in CH_2Cl_2 (200 ml) was then added dropwise during 3 h. The mixture was stirred at ambient temperature. The reaction course was monitored by HPLC (HIC method *B*, see above) and TLC (R_F values for the [H_3N-$B_{12}H_{10}I$]NMe_4 and [H_3N-$B_{12}H_9I_2$]NMe_4 species were 0.19 and 0.10, respectively). The reaction was stopped after first 24 h, when almost only the monosubstituted product was present in the reaction mixture. (If the reaction was carried out for additional 24 h, the content of a disubstituted species in the reaction mixture increased appreciably.) The aqueous layer was separated, the remaining traces of iodine were removed with sodium thiosulfate (0.5 g), the mixture was reduced in volume to *ca* 200 ml, and the solution left to crystallize overnight. The first crop (0.35 g) contained almost pure diiodo derivative. The solution was then evaporated gradually to volumes of 150 and 50 ml to afford two crystal crops in 0.5 g and 2.5 g quantities; the former contained approximately 50% of the diiodinated species and the later was almost pure product. The monoiodo derivative was twice recrystallized from hot water; the yield of [1-H_3N-$B_{12}H_{10}I$]NMe_4 was 2.0 g (43%). For the ^{11}B, MS-FAB and HPLC results see Tables I, III and IV.

closo-[1-$(C_6H_5CH_2)_2HN$-$B_{12}H_{10}I$]$HNMe_3$ (**14**)

The Me_4N^+ salt of **2** (2.0 g, 4.8 mmol) was converted into the sodium salt using the procedure described above. The volume of the sodium salt aqueous solution was adjusted to 75 ml, and the solution was acidified with glacial acetic acid (5 ml). Iodine (1.23 g, 4.8 mmol) in CH_3Cl (200 ml) was then added dropwise under vigorous stirring during 16 h at room temperature and the reaction course was monitored by HPLC (see Experimental, method C). In the end, less than 10% of the starting material persisted, and three small peaks with higher k' values, belonging apparently to several isomers of the diiodo derivative, could be seen. Chloroform was evaporated, 6 M HCl (50 ml) was added to resulting aqueous solution, and the product was extracted into diethyl ether (4 × 30 ml). The combined ether extracts were co-evaporated with water (50 ml). The product was precipitated by excess

of aqueous trimethylamine and twice recrystallized from hot water to yield 2.0 g (77%) of a white, crystalline solid. For ^{11}B, ^{1}H NMR, MS and other results see Tables I, III and IV.

closo-[1-$(C_6H_5CH_2)_2$HN-$B_{12}H_{10}C_{10}H_7$]NMe_4 (**15**)

The Me_3NH^+ salt of **14** (2.0 g, 3.80 mmol), carefully dried under vacuum (80 °C and 10 Pa for 5 h), was dissolved under stirring in dry THF (50 ml). 1-Naphthylmagnesium bromide (1 M solution in THF, (25 ml), see general procedures) was introduced with a syringe through a rubber septum to form a white, fluffy precipitate. The slurry was refluxed for 1 h and a vacuum-dried catalyst, consisting of $(PPh)_3PdCl_3$ (150 mg) and CuI (50 mg), was then added to the reaction mixture. The slurry was heated under reflux for 1 h in an ultrasonic bath and for 16 h using a conventional oil-bath heating. The colour of the reaction mixture turned slowly to brown-black, the second portion of the naphthylmagnesium bromide solution (13 ml) was then introduced, followed by the second addition of the catalyst (100 and 50 mg). The reflux was continued for additional 22 h and, after cooling to ambient temperature, the reaction mixture was decomposed with water (100 ml). Tetrahydrofuran was evaporated and the volume of the aqueous slurry was adjusted to 70 ml, acidified by 6 M HCl (50 ml), and extracted with hexane (3 × 25 ml), followed by diethyl ether (4 × 30 ml). Hexane extracts were discarded and the combined dark ether extracts coevaporated with water (70 ml) until the volume was adjusted to 50 ml. The crude product was precipitated with excess of 10% aqueous Me_4NCl solution. The brown precipitate was filtered off, dissolved in acetone (50 ml) and the solution was filtered twice with charcoal (2 g) which was each time washed twice with additional 15 ml of acetone. The pale yellow acetone solution was evaporated to dryness and the crude product was purified by repeated chromatography on a silica gel column (30 × 2 cm) using a CH_2Cl_2–CH_3CN mixture (10–30% CH_3CN) as the eluent. The product was dissolved in acetone (30 ml), water (50 ml) was poured into this solution and the acetone was evaporated at 20 °C. The slurry was left overnight at –4 °C and the precipitate was then filtered off and vacuum-dried at room temperature to yield 0.85 g (43%) of a white solid. A part of this product (0.5 g) was converted into cesium salt *via* extraction between ether and 3 M HCl and then precipitation by CsF. For the ^{11}B, ^{1}H NMR and MS data see Tables I, III and IV.

RESULTS AND DISCUSSION

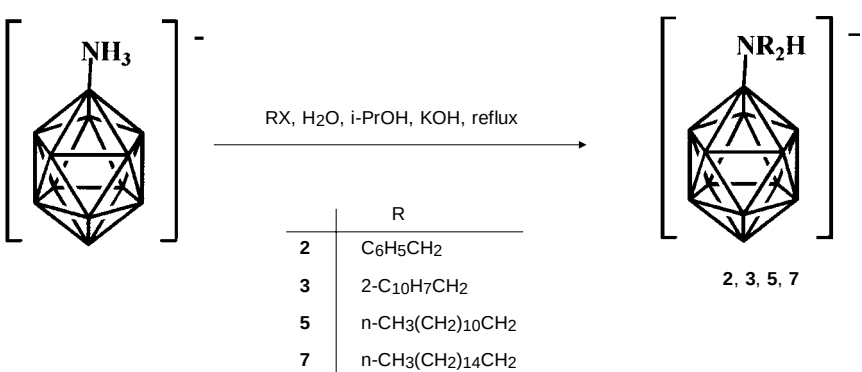
As described by Hertler[14], the reaction of $Na_2[B_{12}H_{12}]$ with *O*-hydroxylaminesulfonic acid in a neutral aqueous solution proceeds smoothly, producing the anion **1** as the main product. Indeed, HPLC monitoring of the reaction proved that about 90% of the starting compound disappeared during first three hours of the reaction. Nevertheless, as determined by high-field ^{11}B spectroscopy, resonances of impurities (corresponding to two spots in TLC differing in R_F values from the product) could be always observed. These impurities were characterized as three possible positional isomers of the $(H_3N)_2B_{12}H_{10}$ neutral zwitterion. The first spot of higher R_F value belonged to the pure isomer **1b**, while the second of R_F lower than the main product was found to be a mixture of the two remaining isomers **1c** and **1d**. The first compound (more soluble in water than the monosubstituted anion) was obtained in a pure form from mother liquors upon acidification and extraction by ethyl acetate. According to ^{11}B-^{11}B COSY NMR, showing crosspeaks between substituted and antipodal borons, the isomer should be 1,7-$H_3NB_{12}H_{10}$. A mixture of the two remaining species, apparently the 1,2- and 1,12-

isomers, which is less soluble in acetonitrile, separated on recrystallization of the crude product from the hot solvent. Separation of these two isomers was found very difficult, but their ratio could be estimated by ^{11}B NMR spectroscopy. Also the assignment of the peaks in the spectrum of the mixture could be made, taking into account that 1,12-isomer should have only two signals in the spectrum with the relative intensities ratio 2 : 10.

*Synthesis of N-Monoalkyl and N,N-Dialkyl Derivatives (***2–7***)*

As we have found, the amino group in $[H_3NB_{12}H_{11}]^-$ is only very weakly nucleophilic, not resembling those in ordinary organic molecules. Therefore, reactive alkyl halides and forced reaction conditions must be employed to accomplish the alkylation (for details see Experimental). On the other hand, the substitution was affected under conventional conditions when higher boiling water–propan-2-ol mixture and sodium or preferably potassium hydroxide as a base were used . The use of the potassium salt of **1** instead of the tetramethylammonium salt was found more convenient, apparently due to a higher solubility of both the starting compound and by-products in the reaction mixture. With an excess of organic halide, the reactions with benzyl bromide and 2-(bromomethyl)naphthalene led mostly to disubstituted species **2** and **3**. As expected, reaction with aliphatic halides, dodecyl iodide and hexadecyl iodide, provided a mixture of a smaller amounts of monosubstituted species **4** and **6** along with disubstituted amino derivatives **5** and **7** as major products. Both the monosubstituted and disubstituted products could be successfully isolated from the reaction mixture and fully characterized (Scheme 1). The NMR, MS and other data are summarized in Tables I–IV.

Anhydrous reaction conditions (THF, NaH) led to similar results for benzyl bromide and 2-(bromomethyl)naphthalene, only a small amount of the trisubstituted derivative could be detected in the ^{11}B NMR spectrum and by HPLC. These results correspond to those presented just recently by another group[17].



	R
2	$C_6H_5CH_2$
3	2-$C_{10}H_7CH_2$
5	n-$CH_3(CH_2)_{10}CH_2$
7	n-$CH_3(CH_2)_{14}CH_2$

SCHEME 1

Synthesis of closo-[1-MeR$_2$N-B$_{12}$H$_{11}$]$^-$ Anions

Methylation of the amino group in the Na[R$_2$NH-B$_{12}$H$_{11}$] compounds **2** and **3** (R = C$_6$H$_5$CH$_2$, 2-C$_{10}$H$_7$CH$_2$) were found to proceed sparingly even with dimethyl sulfate. Under the conditions employed for the synthesis of the (until recently) single known compound of this type[13,14], [Me$_3$NB$_{12}$H$_{11}$]$^-$, *i.e.* using dimethyl sulfate in alkaline aqueous THF, the reaction did not go to completion. The methylated products **8**, **9** were obtained after prolonged treatment with large excess of dimethyl sulfate in an alkaline

TABLE II
^{11}B NMR data of the *N*-substituted 1-amino-*closo*-dodecahydroborate(1–) anions **1–12**

Compound	Formula	δ, ppm (*J*(B-H), Hz)			
		B(1)	B(2-11)		B(12)
1a[a]	[H$_3$NB$_{12}$H$_{12}$]$^-$	–7.23	–15.76 (128)		–18.91 (131)
2[b]	[(C$_6$H$_5$CH$_2$)$_2$HNB$_{12}$H$_{11}$]$^-$	–0.32 s	–15.53 B(7-11) (128)	–16.29 B(2-6) (128)	–17.59 d
3[b]	[(C$_{10}$H$_7$CH$_2$)$_2$HNB$_{12}$H$_{11}$]$^-$	–0.25 s	–15.43 B(7-11) (125)	–16.16 B(2-6) (125)	–17.39 (171)
4[c]	[C$_{12}$H$_{25}$H$_2$NB$_{12}$H$_{11}$]$^-$	–4.31 s	–15.39 (121)		–17.39 d
5[c]	[(C$_{12}$H$_{25}$)$_2$HNB$_{12}$H$_{11}$]$^-$	–1.50 s	–14.87 d	–15.62 d	–17.04 d
6[c]	[C$_{16}$H$_{33}$H$_2$NB$_{12}$H$_{11}$]$^-$	–4.22 s	–15.27 (105)		–17.31 d
7[c]	[(C$_{16}$H$_{33}$)$_2$HNB$_{12}$H$_{11}$]$^-$	–0.68 s	–15.38 (105)		–17.16 d
8[b]	[(C$_6$H$_5$CH$_2$)$_2$CH$_3$NB$_{12}$H$_{11}$]$^-$	4.21 s	–15.68 (107)	–16.10 (109)	–16.90 d
9[b]	[(C$_{10}$H$_7$CH$_2$)$_2$CH$_3$NB$_{12}$H$_{11}$]$^-$	4.30 s	–15.67 (101)	–16.10 (101)	–16.97 d
10[d]	[C$_{15}$H$_{31}$C(O)H$_2$NB$_{12}$H$_{11}$]$^-$	–4.18 s	–15.45 (105)		–17.59 d
11[a]	[(18-crown-6-CH$_2$)HNB$_{12}$H$_{11}$]$^-$	–2.24 s	–16.72 (113)	–17.23 (116)	–18.09 d
12[a]	[aza-15-crown-5-B$_{12}$H$_{11}$]$^-$	–2.08 s	16.16 (98)	–16.65 (116)	–17.57 (153)

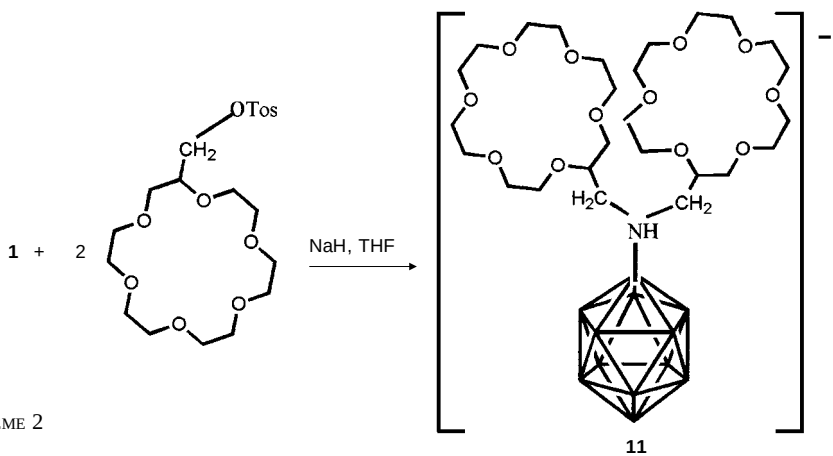
[a] 160 MHz, deuterioacetonitrile. [b] 160 MHz, deuterioacetone. [c] 100 MHz, acetone. [d] 100 MHz, acetonitrile.

aqueous propan-2-ol solution under reflux. The formation of the product was monitored by ion pair reverse phase HPLC (for details see Table I and the Experimental). To accomplish the reaction and to ensure the purity of the products would be almost impossible without this rapid screening. According to NMR and HPLC, a side transmethylation reaction proceeded to a relatively large extent, leading apparently to $Na[RMe_2NHB_{12}H_{11}]$ and other *closo*-borate products. The presence of these side products decreased the yield appreciably, and complicated the isolation of products. In spite of these difficulties, the synthesis of pure species **8** and **9** with a trisubstituted amino group was successfully achieved.

Synthesis of Acyl and Crown-Ether Derivatives of the Anion **1**

The use of anhydrous reaction conditions through the study was restricted to special cases, when the reaction did not work sufficiently under the conditions outlined above. An *N*-acylated product was obtained from the reaction of palmitoyl chloride in THF or DMF. A reaction carried out in dry pyridine was very slow, and only small conversions of the starting compound were observed with potassium *tert*-butoxide (30%) or NaH (40%) at room temperature. However, with NaH at 60 °C, the starting material almost disappeared in 2 h and the corresponding acyl derivative was formed in 50% yield; the crude product **10** was contaminated with about 30% of an impurity removable by chromatography on silica gel.

The synthesis of the first known bis-crown derivative of a borate anion, the $[(18\text{-crown-6-}CH_2)_2NH\text{-}B_{12}H_{11}]^-$ **11**, based on the reaction of **1** with the functionalized crown-ether synthon, was carried out under similar conditions (see Scheme 2).



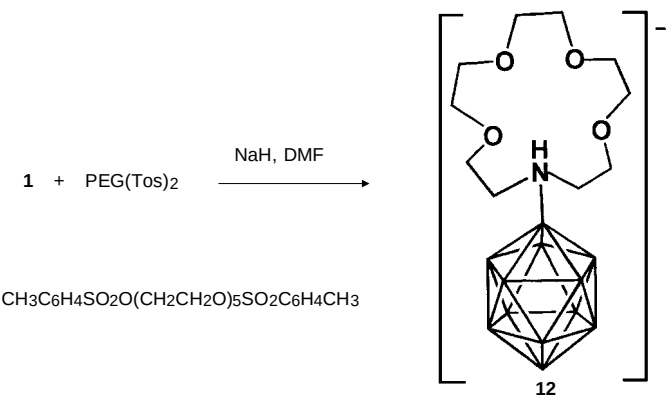
SCHEME 2

The reaction of the starting tosylate, which was synthesized from the hydroxymethyl-18-crown-6, gave almost exclusively the anionic compound **11**, which was obtained in

a high yield by a simple isolation procedure. The amine functionality was substituted by two crown-ether moieties, as identified by FAB mass spectrometry and NMR spectroscopy (see Tables II–IV).

Although no hydrophobic group is present, the cesium salt of the anion **11** exhibits a very interesting solubility characteristics, derived apparently from strong Cs^+ complexation properties, *e.g.*, insolubility in water and ethanol along with a low solubility in acetone. The properties mentioned above are very different from the behaviour of the salts of the first crown-substituted anion **12** to be reported (see the text below). This is characterized by a single five-membered aza-crown-ether ring and is very soluble in any polar solvent. An explanation is that the Cs^+ cation is probably tightly bound between two crown-ether rings of **11** in a sandwich-like manner to form a hydrophobic neutral complex prone to an easy extraction into an organic layer.

Analogously to the reaction known from organic chemistry[21,22], cyclization reaction of the pentaethylene glycol ditosylate with the amino derivative **1**, carried out with NaH in DMF (see Scheme 3), led to the first known direct synthesis of an aza-crown ether derivative of a hydroborate anion.



SCHEME 3

The product was characterized by ^{11}B and ^{1}H NMR spectra, FAB mass spectra, and HPLC that brought an unambiguous evidence on the purity and cyclic structure of this species. Using template effect of Sr^{2+} and optimization of the reaction conditions, especially isolation and purification methods, led to reasonable yields of **12**.

On the other hand, the substitution by single crown-ether ring containing polar oxygen and nitrogen atoms renders the resulting anion hydrophilic. The solubility properties are uncommon to ordinary *closo*-borate species, *e.g.*, salts of **12** with bulky cations, such as Cs^+ or Bu_4N^+ are soluble in water.

Skeletal Substitution

Until recently, the most suitable approach to an alkyl substitution at cage boron atoms has seemed the autocatalyzed addition[13] of olefins to the free conjugate acid $[H_3O]_2^+[B_{12}H_{12}]^{2-}$. *n* H_2O. We have thoroughly revised the reaction, using anion **1** as the starting boron synthon. As has been found, the reaction of the far less reactive $[H_3O]^+[H_3NB_{12}H_{11}]^-$ with styrene, carried out in propan-2-ol or propan-1-ol, gave products substituted at boron sites with two ethylbenzene substituents per cage on average. On the other hand, an undesirable substitution with 2-propoxy or 1-propoxy groups has always occurred. An average composition of the product was found $Me_4N[H_3NB_{12}H_7(C_8H_9)_2(C_3H_7O)_2]^-$. Furthermore, the product was a mixture of several derivatives and positional isomers of unknown structures. Attempts at finding other suitable solvents or at carrying out the reaction without solvent have also failed. The following reaction scheme has been applied in order to avoid side reactions and to achieve a selective substitution (Scheme 4).

TABLE III
^{11}B NMR chemical shifts of disubstituted species **1b–1d** and **13–15**

Compound	Formula	δ, ppm
1b[a]	1,7-$(H_3N)_2B_{12}H_{10}$	–7.948 s (B1, B7); –16.59 d, *J*(B,H) = 131 (B2, B3, B4, B6, B8, B9, B10, B11); –19.309 d, *J*(B,H) = 134 (B5, B12)
1c, **1d**[a]	1,12- (**1c**) and 1,2- (**1d**) $(H_3N)_2B_{12}H_{10}$ mixture	–7.35 s, 2 B (**1c**); –7.95 s, 2 B (**1d**); –16.04 d, 8 B (**1d**); –16.59 d, 10 B (**1c**); –19.23 d, 2 B, *J*(B,H) = 127 (**1d**)
13[b]	$[1\text{-}H_3N\text{-}B_{12}H_{10}\text{-}7\text{-}I]^-$	–7.00 s (B1); –14.14 d (B2, B3, B8, B11); –15.51 d (B4, B6, B9, B10); –17.24 d (B5, B12); –23.27 s (B7)
14[b,c]	$[1\text{-}(C_6H_5CH_2)_2HN\text{-}B_{12}H_{10}\text{-}7\text{-}I]^-$	–0.28 s (B1); –13.95 d, –14.67 d (B2, B3, B8, B11); –15.74 d (B4, B6, B9, B10, B12); –17.83 d (B5); –23.52 s, 1 B (B7)
15[b,d]	$[1\text{-}(C_6H_5CH_2)_2HN\text{-}B_{12}H_{10}\text{-}7\text{-}C_{10}H_7]^-$	–0.07 s (B1); –5.745 s (B7); –14.25 d, –15.470 d, –16.12 d (B2, B3, B4, B6, B8, B9, B10, B11); –16.95 d, 1 B (B12); –18.00 d (B5)

[a] 100 MHz, deuterioacetonitrile. [b] 160 MHz, deuterioacetone. [c] Peaks corresponding to main 1,7-isomer in the spectrum of a mixture with 1,2-isomer (singlets at 0.65 (B1) and –21.4 (B2). [d] Peaks corresponding to main 1,7-isomer in the spectrum of a mixture with 1,2-isomer (singlet at –6.46 (B2)).

TABLE IV
^{1}H NMR shifts of the 1-amino-*closo*-dodecahydroborate(1–) derivatives **1–15**

Compound	Formula	δ, ppm
1a[a]	$[H_3NB_{12}H_{11}]NMe_4$	1.12 s, 1 H {BH, B(12)}; 1.27 s, 5 H {BH}; 1.38 s, 5 H {BH}; 3.44 s, 12 H (Me_4N^+); 5.45 br s, 3 H (NH_3)
1b[a]	1,7-$(H_3N)_2B_{12}H_{10}$	1.09 s, 2 H (BH); 1.31 s, 2 H (BH); 1.51 s, 2 H (BH); 1.161 s, 2 H {BH, B(5), B(12)}; 4.84 br s, 6 H (H_3N)
1c + **1d**[a]	1,2- and 1,12-$(H_3N)_2B_{12}H_{10}$	0.875 s (BH); 1.039 s (BH); 1.044 s (BH); 1.087 s (BH); 1.154 s (BH); 1.247 s (BH); 1.251 s (BH); 1.301 s (BH); 1.508 s (BH); 4.7 br s (H_3N, **1c**); 4.9 br s (H_3N, **1d**)
2[b]	$[(C_6H_5CH_2)_2HNB_{12}H_{11}]NMe_4$	1.29 s, 1 H {BH, B(12)}; 1.33 s, 5 H {BH, B(7-11)}; 1.61 s, 5 H {BH, B(2-6)}; 3.38 s, 12 H (Me_4N^+); 4.18 m, 2 H (CH_2N); 4.99 m, 2 H (CH_2N); 5.04 br s, 1 H (NH); 7.15–7.22 m, 10 H (H arom)
3[b]	$[(C_{10}H_7CH_2)_2HNB_{12}H_{11}]NMe_4$	1.31 s, 1 H {BH, B(12)}; 1.41 s, 5 H {BH, B(7-11)}; 1.70 s, 5 H {BH, B(2-6)}; 3.42 s, 12 H (Me_4N^+); 4.28 m, 2 H (CH_2N); 5.18 m, 2 H (CH_2N); 5.38 br s, 1 H (NH); 7.29–7.72 m, 14 H (H arom)
4[c]	$[C_{12}H_{25}H_2NB_{12}H_{11}]NMe_4$	0.868 t, 3 H (CH_3); 1.1–1.6 br m, 11 H (BH); 1.28 br m, 18 H (CH_2); 1.91 m, 2 H (CH_2CH_2N); 2.96 m, 2 H (CHN); 3.40 s, 12 H (Me_4N^+); 5.3 br s, 2 H (NH)
5[c]	$[(C_{12}H_{25})_2HNB_{12}H_{11}]NMe_4$	0.89 t, 6 H (CH_3); 1.1–1.6 br m, 11 H (BH); 1.28 br m, 36 H (CH_2); 1.73 br m, 4 H (CH_2CH_2N); 2.85 m, 4 H (CH_2N); 3.09 s (Me_4N^+); 4.7 br s, 1 H (NH)
6[c]	$[(C_{16}H_{33}H_2NB_{12}H_{11}]NMe_4$	0.88 t, 3 H (CH_3); 1.1–1.6 br m, 11H (BH); 1.28 m, 26 H (CH_2); 1.77 m, 2 H (CH_2CH_2N); 2.97 m, 2 H (CH_2N); 3.42 s, 12 H (Me_4N^+); 5.5 br s, 2 H (NH)
7[c]	$[(C_{16}H_{33})_2HNB_{12}H_{11}]Cs$	0.88 t, 6 H (CH_3); 1.1–1.6 br m, 11 H (BH); 1.29 br m, 52 H (CH_2); 1.50 m, 4 H (CH_2CH_2N); 3.41 m, 4 H (CH_2N); 4.5 br s, 1 H (NH)

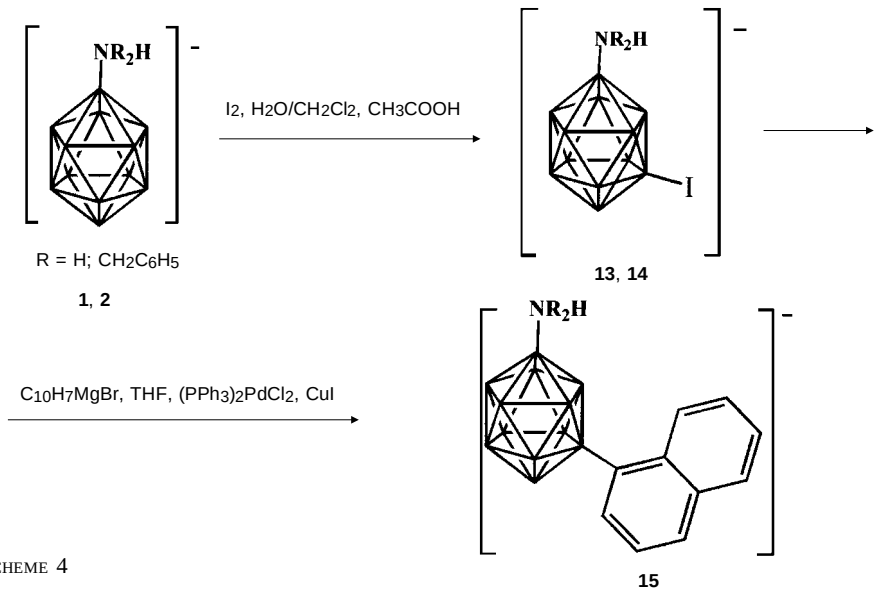
TABLE IV
(*Continued*)

Compound	Formula	δ, ppm
8[b]	$[(C_6H_5CH_2)_2CH_3NB_{12}H_{11}]NMe_4$	1.29 s, 1 H (BH); 1.36 s, 5 H (BH); 1.69 s, 5 H (BH); 2.58 s, 3 H (CH_3N); 4.54 m, 2 H (CH_2N); 5.02 m, 2 H (CH_2N); 7.26–7.37 m, 10 H (H arom)
9[b]	$[(C_{10}H_7CH_2)_2CH_3NB_{12}H_{11}]NMe_4$	1.37 s, 1 H (BH); 1.42 s, 5 H (BH); 1.78 s, 5 H (BH); 2.90 s, 3 H (CH_3N); 3.42 s, 12 H (Me_4N^+); 4.86 m, 2 H (CH_2N); 5.23 m, 2 H (CH_2N); 7.30–7.90 m, 14 H (H arom)
10[d]	$[C_{15}H_{31}C(O)H_2NB_{12}H_{11}]NMe_4$	0.88 t, 3 H (CH_3); 1.0–1.7 br m, 11 H (BH); 1.26 m, 24 H (CH_2); 1.48 m, 2 H (CH_2CH_2CO); 2.55 m, 2 H (CH_2CON); 3.11 s, 12 H (Me_4N^+); 5.31 br s, 2 H (NH)
11[b]	$[(18\text{-crown-6-}CH_2)_2HNB_{12}H_{11}]NMe_4$	1.07 s, 5 H (BH); 1.26 s, 5 H (BH); 1.31 s, 1 H (BH); 2.8–3.6 m, 46 H (CH_2O, CHO); 3.77 m, 4 H (CH_2NH); 5.3 br s, 1 H (NH)
12[a]	$[\text{aza-15-crown-5-}B_{12}H_{11}]NMe_4$	1.48 s, 1 H {BH, B(12)}; 1.07 s, 5 H (BH); 1.29 s, 5 H {BH, B(2-11)}; 2.95 m, 4 H (NCH_2CH_2O); 3.09 s, 12 H (Me_4N^+); 3.63 m, 12 H (CH_2O); 3.91 m, 4 H (CH_2N); 5.08 br s, 1 H (NH)
13[b]	$[1\text{-}(H_3N)\text{-}7\text{-I-}B_{12}H_{10}]NMe_4$	1.73 s, 2 H, 1.86 s, 2 H {BH, B2, B3, B8, B11}; 1.29 s, 2 H, 1.42 s, 2 H {BH, B4, B6, B9, B10}; 1.633 s, 1 H, 1.57 s, 1 H {BH, B5, B12}; 2.42 s, 12 H (Me_4N^+); 5.641 br s, 3 H (NH)
14[b]	$[(C_6H_5CH_2)_2HNB_{12}H_{10}I]NHMe_3$	1.18 s, 1.65 s, 1.85 s, 10 H (BH); 3.09 m, 9 H ($(CH_3)_3NH^+$); 4.05 m, 2 H (CH_2N); 4.95 m, 2 H (CH_2N); 5.38 br s, 1 H (NH); 7.15–7.35 m, 10 H (H arom)
15[a]	$[(C_6H_5CH_2)_2HNB_{12}H_{10}C_{10}H_7]NMe_4$	1.45 s, 1.48 s, 1.60 s, 1.75 s, 1.94 s, 10 H (BH); 2.86 s, 12 H (Me_4N^+); 4.07 m, 2 H (CH_2N); 5.02 m, 2 H (CH_2N); 5.20 br s, 1 H (NH); 7.19–7.27 m, 10 H (H arom, C_6H_5); 7.45–8.25 m, 7 H (H arom, $C_{10}H_7$)

[a] 500 MHz, deuterioacetonitrile (BH, broad band ^{11}B decoupling) or {^1H selective ^{11}B decoupling}. [b] 500 MHz, deuterioacetone (BH, broad band ^{11}B decoupling) or {^1H selective ^{11}B decoupling}. [c] 300 MHz in deuterioacetone, ^{11}B coupled. [d] 300 MHz, deuterioacetonitrile, ^{11}B coupled.

The reaction outlined in Scheme 4 was already employed on the neutral *o*-carborane as early as in the middle of seventies[23], and the reaction conditions have been since then several times improved[24,25]. This procedure is known to give good yields of neutral aryl and alkyl derivatives, especially if CuI is used as a co-catalyst[25]. This reaction type has also been recently applied successfully to the monoanionic *closo*-$[CB_{11}H_{12}]^-$ system[26,27]. However, there is a lot of experimental evidence in cluster boron chemistry that reactions proceeding easily with one type of a skeleton may fail with a different cage of different heteroatoms and external charge. The presence of heteroatoms affects the reactivity appreciably. The charge differences are responsible for different solubility of both the starting compounds and reaction intermediates. This fact alone is sufficient enough to avert a successful course of a reaction. Furthermore, a paper appeared last year in which similar reaction conditions, without employing Grignard reagents, led to high yields of the $B_{12}H_{11}L_2$ species[28]. Therefore, the possibility to accomplish such reactions on the anion **1** remains uncertain until positive experimental evidence is obtained.

The iodination (Scheme 4) can provide generally several positional isomers along with diiodo derivatives. Under properly selected conditions monoiodinated products **13** and **14** were successfully obtained. However, the products were found to be mixtures of two or all three possible isomers. The directive effect of the amino group under the conditions of electrophilic substitution afforded only one positional isomer. In the case of the iodination of **1**, the product was the 1,7-monoiodo derivative **13** (80% purity), contaminated by a small quantity of the 1,2-isomer. The assignment of all ^{11}B NMR



SCHEME 4

signals of the most abundant isomer was possible based on the ^{11}B-^{11}B COSY NMR experiment. The ^{11}B NMR spectrum of the crude reaction mixture from the direct iodination of **2** exhibited a more complex pattern, pointing to about a 70 : 25 ratio of the 1,7- and 1,2-isomers; also a small quantity of the $[1,12\text{-}R_2HN\text{-}B_{12}H_{10}I]^-$ species was present. The separation of these isomeric mixtures was not possible, either by chromatographic methods developed for the *closo*-borate species (the ion-pair HPLC method, the hydrophobic interaction method on hydroxyethyl methacrylate gels that had been found more powerful in the resolution of positional isomers[6–8], or by LC on DEAE cellulose[5–7].

Reaction Scheme 4 was examined using $[(C_6H_5CH_2)_2HNB_{12}H_{10}I]HNMe_3$ derivative **14**, synthesized by iodination of the respective $[(C_6H_5CH_2)_2HNB_{12}H_{11}]^-$ anion **3**, and $1\text{-}BrMgC_{10}H_7$ as starting materials. As stated above, the iodo derivative was in fact a mixture of three unseparable positional isomers. In spite the complex ^{11}B NMR spectra, the iodine–aryl replacement on the boron atoms could be clearly seen due to distinctly different patterns from the corresponding iodo derivative. Although the chemical shifts of the BH cluster are basically the same in both derivatives, the aryl substituted boron atoms are deshielded giving the lowest downfield resonances, whereas the signals of the iodo substituted borons appear at the upfield area of the spectrum. The successful catalytic exchange of iodine by bulky naphthyl substituent was confirmed by ^{11}B and ^1H NMR spectra and high resolution FAB mass spectroscopy methods. The reaction went on the end almost completely within 38 h if an excess of the Grignard reagent was used. This reaction is first known example of a controlled, reproducible monoarylation on a single boron vertex of the $[B_{12}H_{12}]^{2-}$ skeleton. This scheme can undoubtedly lead to the generation of derivatives of **1** with several different substituents. Ultimately, many new anions of structurally tailored properties are expected to be available.

The systematic evaluation of the chemical stability and extraction properties of the anions **2–15** will be the subject of a separate communication[29].

NMR Results

The ^{11}B NMR spectra of all *closo*-borate anions of the $[R^1_2R_2N\text{-}B_{12}H_{11}]^-$ type consist of one singlet and three doublets of expected intensity patterns 1 : 5 : 5 : 1. For species with unsubstituted and monoalkylated amino groups, the two doublets of intensity 5 are incidentally overlapped. The low-field singlet is shifted downfield with increasing substitution, about 3 ppm per substituted hydrogen (see the data in Table II for illustration).

The assignment of ^{11}B chemical shifts in NMR spectra of disubstituted derivatives is often complicated by incidental overlaps. A particular examples are the spectra of the diamino isomers with eight or ten overlapping peaks for the 1,7- or 1,2- and 1,12-isomers, respectively. Based on the ^{11}B-^{11}B COSY NMR spectroscopy, the ^{11}B NMR shifts of the $1,7\text{-}(H_3N)B_{12}H_{10}$ **1b** could be assigned due to the presence of the cross-

peaks between substituted and antipodal borons. Also the assignment of the peaks to individual species in the spectrum of the isomeric 1,2-**1c** and 1,12-**1d** mixture was possible, taking into account, that the 1,12-isomer should display only one singlet and one doublet of relative intensities 2 : 10. The spectrum of the prevailing iodinated isomer, $[1\text{-}H_3N\text{-}7\text{-}I\text{-}B_{12}H_{10}]^-$, exhibits 1 : 4 : 4 : 2 : 1 patterns with two singlets in the lowest (B-NH_3) and highest (B-I) field. Despite coincidence overlaps, complete signal assignment could be made from ^{11}B-^{11}B COSY experiments. The spectra of the $[R_2NB_{12}H_{10}I]^-$ and $[R_2NB_{12}H_{10}C_{10}H_7]^-$ derivatives are more complex, partly due to higher content of the 1,2-isomer. Nevertheless, their patterns are very similar to those observed for $[1\text{-}H_3N\text{-}7\text{-}I\text{-}B_{12}H_{10}I]^-$.

The ^1H NMR spectra of all compounds correspond well to expected patterns for particular organic substitution. On the other hand, in the spectra of compounds **2**, **3**, **8** and **9** with two or three bulky substituents on the amino group, an unexpected splitting of the four (CH_2N) protons into two sets of multiplets with coupling constants of about 500 Hz was observed. A structure perturbation around the nitrogen atom due to steric requirements of the substituents or a restricted rotation around the B–N bonding vector might be a probable explanation.

Partial support of this work by the European Community in the framework of the Project CIPA-CT93-0133 of the PECO program is highly appreciated. The authors would like to express their thanks to Dr J. Fusek from the Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, Prague for an appreciable part of the NMR spectra measurements, Dr M. Belohradsky from the the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague, who kindly provided us with hydroxymethyl-18-crown-6. The authors acknowledge with gratitude Dr B. Stibr, Prof. J. Plesek and S. Hermanek from the Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, for helpful discussions.

REFERENCES

1. Schlaikjer C.: U.S. 484 9310, 1989; Chem. Abstr. *111*, 217217 (1989).
2. Hatanaka H.: *Boron Neutron Capture Therapy for Tumors*. Nishimura, Nigata City 1986; and references therein.
3. Gabel D., Moller D., Harfst S., Rosler J., Ketz H.: Inorg. Chem. *32*, 2276 (1993).
4. Kaszynski P., Laska J., Patel M. K.: *International Meeting on Boron Chemistry – IMEBORON IX*. Book of Abstracts, p. 149. Ruprecht Karls Universität Heidelberg, Heidelberg 1996.
5. Preetz W., Srebny M. G., Marsmann H. C.: Z. Naturforsch. B *39*, 189 (1984).
6. Gruner B.: *Ph.D. Thesis*. Czechoslovak Academy of Sciences, Prague 1990.
7. Gruner B., Hermanek S., Plzak Z.: *Proceedings of the 7th International Meeting on Boron Chemistry – IMEBORON VII*, Poster 5. Nicolaus Copernicus University Toruñ, Toruñ 1990.
8. Gruner B., Plzak Z., Vins I.: J. Chromatogr. *588*, 201 (1991).
9. Peymann T., Lork E., Gabel D.: Inorg. Chem. *35*, 1355 (1993).
10. Jasper S. A., Jr., Jones R. B., Mattern J., Huffman J. C., Todd L. J.: Inorg. Chem. *33*, 5621 (1994).
11. Muetterties E. L., Knoth W. H.: *Polyhedral Boranes*, Chap. 6, p. 103. Dekker, New York 1968; and references therein.

12. *CIPA-CT93-133 PROJECT*. Six Monthly Internal Reports, Institut de Ciencia de Materials, Barcelona (coordinator). September 1994, March 1995, September 1995, April 1996 and October 1996.
13. Miller H. C., Muetterties E. L.: U.S. 3,551,120; Chem. Abstr. *74*, P55815 (1971).
14. Hertler W. R., Raash M. S.: J. Am. Chem. Soc. *86*, 3661 (1964).
15. Knoth W. H., Sauer J. C., England D. C., Hertler W. R., Muetterties E. L.: J. Am. Chem. Soc. *86*, 3973 (1964).
16. Miller H. C., Hertler W. R., Muetterties E. L.: Inorg. Chem. *4*, 28 (1964).
17. Gabel D., Peymann T., Kuck K.: Ref.[4], p. 79.
18. Wellum G. R., Tolpin E. I., Andersen L. P., Sneath R.: J. Chromatogr. *103*, 153 (1975).
19. Plzak Z., Plesek J., Stibr B.: J. Chromatogr. *212*, 283 (1981).
20. Stibor I., Kocian O., Holy P., Zavada J.: Collect. Czech. Chem. Commun. *52*, 2057 (1986).
21. Gokel G. W., Korzeniowski S. H., Garcia B. J.: Tetrahedron Lett. *4*, 317 (1977).
22. Gokel G. W., Korzeniowski S. H.: *Macrocyclic Polyether Syntheses*, Chap. 3; and references therein. Springer, Berlin 1982.
23. Zakharkin L. I., Kovredov A. I., Oshevskaya V. A., Shaugumbekova Zh. S.: J. Organometall. Chem. *226*, 217 (1982)
24. Li J., Logan C. F., Jones M., Jr.: Inorg. Chem. *30*, 4866 (1991).
25. Zheng Z., Jiang W., Zinn A. A., Knobler C. B., Hawthorne M. F.: Inorg. Chem. *34*, 2095 (1995).
26. Janousek Z., Gruner B., Trammel M., Michl J.: *209th ACS National Meeting*, Book of Abstracts, Abstr. No. ORGN 315. American Chemical Society, CA, U.S.A. 1995.
27. Gruner B., Janousek Z., Michl J.: Ref.[4], p. 149.
28. Jasper S. A., Jr., Jones R. B., Mattern J., Huffman J. C., Todd L. J.: Inorg. Chem. *33*, 5621 (1994).
29. Rais J., Selucky P., Gruner B., Mongeot H.: Unpublished results.