

SYNTHESIS OF 12-HYDROXY AND 12-DIOXANE DERIVATIVES OF THE *closo*-1-CARBADODECABORATE(1-) ION. VARIATIONS ON THE PLEŠEK'S COBALT BIS(DICARBOLLIDE) PATTERN

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Dedicated to our always young and enthusiastic teacher and colleague, Professor Jaromír Plešek on the occasion of his 75th birthday in recognition of his outstanding contribution to boron cluster chemistry.

Synthesis of two new B(12) substituted derivatives of the *closo*-[1-CB₁₁H₁₂]⁻ anion (**1**) is reported. The zwitterionic derivative containing dioxane ring {12-[O(CH₂CH₂)₂O]⁺-1-CB₁₁H₁₁]⁻⁰ (**2**) was obtained in moderate yield using reaction of anion **1** with dioxane as solvent, induced by dimethyl sulfate. The anion [12-(HO)-1-CB₁₁H₁₁]⁻ (**3**) was obtained in high yield upon treatment of the parent anion with 80% H₂SO₄ at high temperature. Both compounds containing reactive functionalities were designed to serve as useful synthons for a variety of synthetic purposes. The compounds were characterized by ¹¹B and ¹H high-field NMR, IR spectroscopy, mass spectrometry, melting points and TLC. Molecular structure of compound **2** was determined by single crystal X-ray diffraction analysis.

Keywords: Boranes; Carboranes; Monocarboranes; *closo*-1-Carbadodecaborate(1-) ion; BNCT; X-Ray diffraction; Crystal structure.

A significant part of the synthetic effort in the field of chemistry of cluster boron compounds in the last decade has been addressed to the substitution chemistry of the singly charged [CB₁₁H₁₂]⁻ anion¹⁻³ (**1**) (Fig. 1). The high symmetry and charge delocalization over the whole cluster surface qualifies this anion and its substitution derivatives to govern among the least

nucleophilic anions known in the contemporary chemistry⁴. Hence, its recent chemistry has been directed to making it less nucleophilic using halogenation⁵⁻⁷ or alkylation⁸⁻¹¹ schemes or combinations of both methods^{11,12}. Possible applications⁴ in catalysis and electrochemistry promoted the search for improved¹³ or principally new preparative routes¹⁴ for **1**. Their future extensions and new developments may lead to a larger scale availability of these chemicals.

The high stability, low nucleophilicity, and presence of the two reactive sites in antipodal positions C(1) and B(12) predestine the anion **1** derivatives as perfect candidates for other important applications¹⁵, *e.g.* in boron neutron capture therapy (BNCT), synthesis of linear charged oligomers, surface chemistry, molecular recognition, and for use as selective extraction agents for radionuclide recovery from high-activity nuclear waste. For these purposes it seems desirable to block both reaction sites with introduction of at least one reactive functionality. This should allow for subsequent bonding of a variety of more sophisticated functional selective groups on the cage, attachment of the anion to larger molecules, to solid supports, *etc.* In this respect, the chemistry of $[\text{CB}_{11}\text{H}_{12}]^-$ anion remains still grossly underdeveloped; only few such derivatives almost exclusively substituted on the C(1) site, were reported⁵. A direct B(12) atom substitution has been studied to a even more limited extent. Only zwitterionic B(12)- SMe_2 ⁵ and B(12)- NH_3 derivative arising as the minority product from reaction with hydroxylamine-*O*-sulfonic acid¹⁶, ionic B(12)- SMe^5 , and B(12) mercurated species⁶ have been reported. Noteworthy is the recently published $[\text{CHB}_{11}(\text{OH})_{11}]^-$ polysubstituted anion¹⁷.

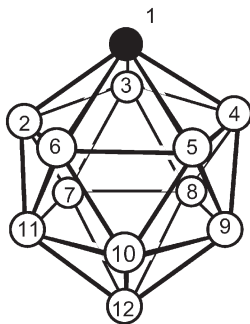


FIG. 1

Schematic drawing of the $[\text{CB}_{11}\text{H}_{12}]^-$ anion geometry showing the cage numbering scheme; ○ represent BH groups, ● correspond to CH moiety

In this article we present synthesis and characterization of new derivatives containing oxygen bonded group, the $\{12-[O(CH_2CH_2)O]^+-1-CB_{11}H_{11}\}^0$ zwitterion (**2**) and the $[12-(HO)-1-CB_{11}H_{11}]^-$ (**3**) anion. Both compounds can be obtained using simple preparative procedures. These compounds can serve as reactive synthons for easy attachment of a variety of functional groups on the cage.

RESULTS AND DISCUSSION

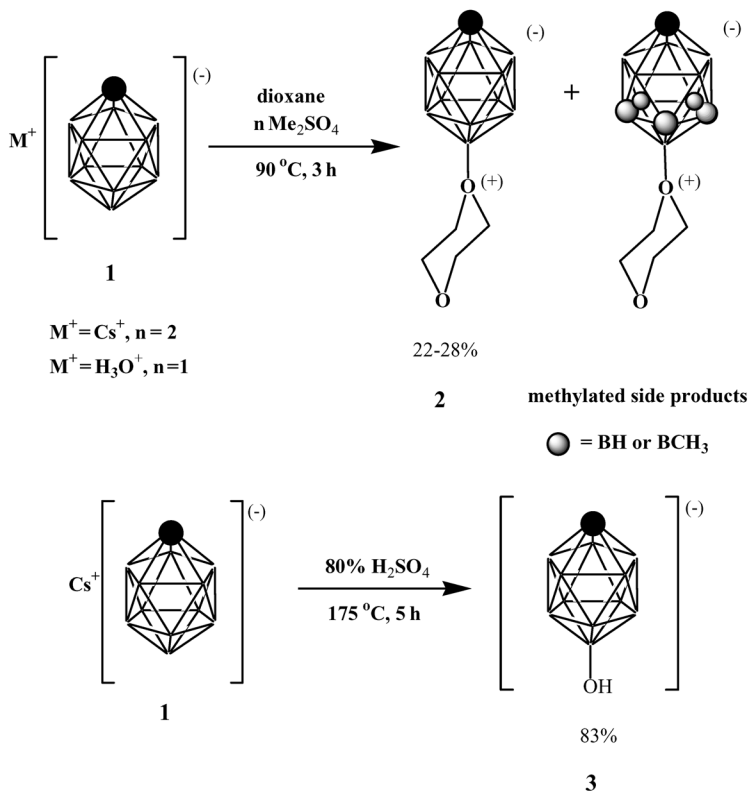
Our groups have been aimed in synthesis of borate extraction agents. In this field, a bulkier chlorinated cobalt bis(dicarbollide) anion has been designed years ago¹⁵ for nuclear waste treatment, and this compound is now used as the effective extractant on industrial scale¹⁸. On the other hand, limited stability of this anion in alkaline media prevents its use at high pH values. The $[CB_{11}H_{12}]^-$ ion and most of its derivatives are stable in the whole pH range, which can favour their use for extraction purposes. Preferably, as in the advanced cobalt bis(dicarbollide) series¹⁹⁻²¹, along with introduction of hydrophobic groups, a substitution with metal-selective group might be desirable on the opposite side of the anion **1**. Two compounds described below containing reactive functionalities represent first step forward toward derivatives of **1** modified with metal-selective groups for extraction.

*Synthesis of the Zwitterionic $\{12-[O(CH_2CH_2)O]-1-CB_{11}H_{12}\}^0$ Derivative (**2**)*

The zwitterionic compounds containing an organic ring attached *via* an oxonium oxygen to skeletal boron atom were described in metallaborate^{22,23}, dicarbaundecaborate²⁴ and dodecaborate²⁵ series. Such derivatives can be considered as particularly useful intermediates for introduction of a variety of groups due to an easy cleavage of the ring by a nucleophile. This reaction path was first described by Plešek *et al.*²⁶ and further studied and used in synthesis by his group^{19,20} and other authors^{25b,25c,27,28}. Synthesis of the above zwitterionic derivatives usually proceeds *via* acid-catalysed reactions of the respective anion with THF or dioxane^{25b}. The simplest described reaction scheme comprises a direct reaction of the free conjugate acid $(H_3O)_2[NH_3B_{12}H_{11}]$ with THF^{25c}.

In case of the $[CB_{11}H_{12}]^-$ ion this approach failed. The reaction of conjugate acid or triflic acid catalysed reaction of **1**-Cs led only to trace isolable amounts of the target compound **2**. Recently, an interesting reaction of dioxane with cobalt bis(dicarbollide)(1-) anion induced by dimethyl sulfate

was reported by Plešek *et al.*²³ Application of this method to the $[\text{CB}_{11}\text{H}_{12}]^-$ chemistry led finally to successful synthesis of compound **2** in moderate yields. The reaction of either carefully vacuum-dried free conjugate acid $(\text{H}_3\text{O})[\text{CB}_{12}\text{H}_{12}] \cdot n\text{H}_2\text{O}$ with dioxane in the presence of 1.1 equivalents of Me_2SO_4 , or by a more reliable procedure, the reaction of **1**-Cs with 2.05–2.2 equivalents of dimethyl sulfate, led to respective zwitterionic product (Scheme 1). On the other hand, we found, that the yield depends critically on the amount of Me_2SO_4 in the reaction mixture. No reaction was observed below *ca* 2.05 equivalents of this promotor; appreciable amounts of side products were formed with more than *ca* 2.2 equivalents of Me_2SO_4 . These side products were found always if only a slight excess of Me_2SO_4 was used. These species could not be completely characterized due to separation difficulties. MS and NMR evidence (see Experimental) indicate that their



SCHEME 1

Reactions leading to products **2** and **3**. Composition of the methylated side products from the first reaction corresponds to formula $\{12\text{-}[\text{O}(\text{CH}_2\text{CH}_2)\text{O}]^{-1}\text{-CB}_{11}\text{H}_{11-n}(\text{CH}_3)_n\}^0$ ($n = 1\text{-}5$)

composition corresponds to zwitterionic species of general formula $\{12-[(O(CH_2CH_2)_2O)^+-7,8,9,10,11-(CH_3)_n-CB_{11}H_{11-n}]^0$ (where $n = 1-5$), *i.e.* to compounds substituted by up to five methyl groups on the lower skeletal pentagon of the boron icosahedron. This facile methylation seems surprising and unexpected. In a blank experiment, the parent anion **1** was heated at 60 °C for 5 h in neat dimethyl sulfate and recovered intact. A possible explanation can be seen inspecting the molecular structure of the zwitterion **2** (see the discussion below). The structure showed a systematic lengthening, or activation of the B(7)–H bond and an increased electron density on this hydrogen. In solution, where this effect is probably averaged on the whole pentagonal belt due to free rotation, such activation may facilitate sequential substitution of all hydrogen atoms B(7-11).

In fact, the inevitable presence of methylated species leads to decreased yields, since their formation proceeds at the expense of Me_2SO_4 and the reaction stops when concentration of the promotor drops below a certain level. Moreover, these side products cause difficulties in isolation of pure **2**. Separation of the mixture of these species by chromatography on silica gel was found rather difficult. More effective was the crystallization of the crude product from a CH_2Cl_2 –hexane mixture. Substantially pure product in yields 22–28% can be obtained after single crystallization step (based on multiple experiments). The main product crystallizes exceptionally well whereas the side products accumulate in mother liquors.

The molecular structure of compound **2** was unambiguously determined by single-crystal X-ray diffraction analysis (see Fig. 2). The dioxane ring is attached in position B(12) of the cage opposite to the carbon atom. Selected interatomic distances and angles are summarized in Table I. The interatomic distances B(12)–O and O(1)–C2, O(1)–C3 fall within the range of equivalent distances for 14 crystal structures with the boron cage $O(CH_2)_2$ moiety found in the Cambridge Structural database²⁹. (B–O (1.506–1.543); O–C (1.447–1.496)) suggesting similarity of the reported structure with the compounds where the presence of oxonium oxygen is assumed^{22-25a}. The B–B and B–C interatomic distances fall within the usual limits, even those for B(12) do not differ significantly from the average value ($B-B_{average} = 1.778 \text{ \AA}$).

The most striking feature seems to be the influence of the dioxane ring on the carborane hydrogen position (H(7)). The orientation of the dioxane ring toward the $CB_{11}H_{11}$ moiety brings the hydrogen H(21) of the CH_2 moiety close to the regular position of H(7) (this distances would be 2.317 Å for idealized position of H(7) with all H–B–B angles equal 122° and B–H distances 1.1 Å). Therefore, the H(7) atom is moved out of its expected posi-

tion to increase the H(7)···H(21) distance up to 2.51(2) Å. This distortion is accompanied by a significant increase in the the B(7)–H(7) distance. Meanwhile the configuration of hydrogen of C(6) remains tetrahedral within five esd's. The position of the H(7) hydrogen can be clearly distinguished on a difference Fourier map since its maximum has the highest electron density of all hydrogen peaks. This effect suggests an unusual redistribution of electron density.

In agreement with the molecular structure are also the NMR results. ^{11}B NMR spectrum (see Experimental) exhibiting three peaks of intensities 1 : 5 : 5 corresponds to the C_{5v} symmetry of the molecule, which seems to indicate free rotation of the dioxane moiety around the B–O bond in solution. The large downfield shift 11.06 ppm (–6.74 for parent anion) of the first peak in the spectrum (singlet) correlates well with the B(12)–O $^{(+)}$ substitution. ^1H NMR spectra also agree with the structure showing two signals of intensity 4 corresponding to two symmetrically non-equivalent dioxane CH $_2$ O proton signals and one CH signal. Also the EI mass spectrum shows clearly the molecular peak.

Synthesis of the [12-HO-1-CB $_{11}$ H $_{12}$] $^-$ Anion **3**

Recently, Peymann and Hawthorne 30 proved that the basic member of the *closo*-borate series, anion B $_{12}$ H $_{12}^{2-}$ can react with a slightly dilute sulfuric acid

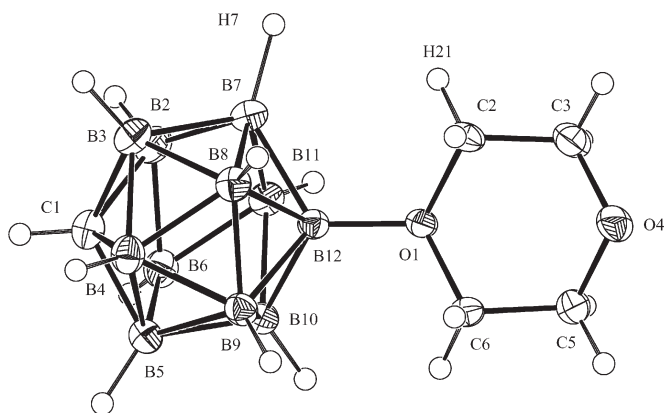


FIG. 2

Overall view on the molecules of {12-[O(CH $_2$ CH $_2$) $_2$ O] $^+$ -1-CB $_{11}$ H $_{11}$] 0 (**2**) with the atom labeling scheme. The thermal ellipsoids are drawn on 50% probability level by PLATON 35 . The dihedal angle between the least-square planes defined by atoms O1, C2, C3, O4, C5, C6 and C1, B5, B7, B12 is 5.26(8) $^\circ$

at high temperatures giving $B_{12}H_{12-n}(OH)_n$ derivatives, where $n = 1-3$. More recently, a direct hydroxylation of the cobalt bis(dicarbollide) anion producing mono dihydroxy derivatives was reported³¹. Encouraged by these results, we have attempted synthesis of hydroxy derivatives of the $[CB_{11}H_{12}]^-$ anion, even if this anion has been believed to be the most inert in the series towards attack with acids. Indeed, only mono substituted anion **3** $[12-HO-CB_{11}H_{11}]^-$ resulted upon treatment of **1**-Cs with 80% H_2SO_4 at elevated temperatures in almost quantitative yield. The hydroxy derivative could be easily isolated by extraction into diethyl ether, transfer of the re-

TABLE I
Selected bond lengths (in Å) and angles (in °) for dioxane- $CB_{11}H_{11}$ zwitterion

C1-B5	1.7023(16)	B9-B12	1.7686(15)
C1-B3	1.7026(17)	B10-B12	1.7613(15)
C1-B4	1.7070(17)	B11-B12	1.7722(16)
C1-B2	1.7082(17)	B12-O1	1.5200(13)
C1-B6	1.7096(16)	O1-C2	1.4885(12)
C1-H1	0.966(15)	O1-C6	1.4890(12)
B7-B12	1.7727(16)	C2-C3	1.5014(16)
B7-B11	1.7993(16)	C3-O4	1.4227(13)
B7-B8	1.8025(17)	O4-C5	1.4225(12)
B7-H7	1.326(11)	C5-C6	1.5040(14)
B8-B12	1.7709(15)		
B2-B7-H7	110.9(5)	C6-O1-B12	117.41(7)
B12-B7-H7	134.6(5)	O1-C2-C3	107.53(8)
B3-B7-H7	115.3(5)	O1-C2-H21	106.3(8)
B11-B7-H7	120.8(5)	C3-C2-H21	112.5(8)
B8-B7-H7	128.2(5)	O1-C2-H22	104.6(8)
O1-B12-B10	118.39(8)	C3-C2-H22	113.3(8)
O1-B12-B9	120.48(8)	H21-C2-H22	111.9(11)
O1-B12-B8	121.93(8)	O4-C3-C2	111.06(9)
O1-B12-B11	118.69(8)	C5-O4-C3	109.34(8)
O1-B12-B7	120.86(8)	O4-C5-C6	111.60(8)
C2-O1-C6	110.22(8)	O1-C6-C5	108.43(8)
C2-O1-B12	118.11(7)		

sulting conjugate acid into water and precipitation with bulky cations. The anion was characterized by ^{11}B NMR spectroscopy and high resolution mass spectrometry using electrospray ionisation. ^{11}B NMR spectrum consists of three peaks, one singlet and two doublets, of relative intensities 1 : 5 : 5. The similarity of the chemical shifts for both compounds **2** and **3** clearly evidences their close relationship. In agreement with the proposed composition is also the mass spectrum showing clearly the molecular peak and the isotopic pattern has been also found in full agreement with the calculated spectrum.

Derivatization chemistry of both new compounds closely resembles the synthetic potential reported for the members of the $[\text{B}_{12}\text{H}_{12}]^{2-}$ series^{25,27} and for compounds from the cobalt bis(dicarbollide) family^{19–21,26,28}. Hence, both novel compounds **2** and **3** may serve as a useful toolbox for construction of various $[\text{CB}_{11}\text{H}_{12}]^{-}$ derivatives bearing metal-selective groups and for other synthetic purposes and applications. First attempts at the dioxane ring cleavage of **2** with several bases, including sodium dibutyl phosphite; primary amines, and amides were successful producing species with the respective end groups attached on the cage *via* the diethylene glycol chain. Application of these reactions to the synthesis of selective extraction agents will be the subject of a subsequent article. Also, the OH group in **3** seems to be prone to substitution using synthetic procedures common in organic and boron chemistry. This study is currently in progress.

EXPERIMENTAL

General

Cesium *closo*-1-carbadodecaborate (**1**) was prepared using the known procedure¹³. Dioxane was dried over sodium metal and distilled prior to use. Sulfuric acid and all solvents were analytical grade reagents and were used without further treatment. All reactions were carried out under nitrogen atmosphere. Silica gel Aldrich 200–400 mesh was used for column chromatography. TLC was performed on Silufol (silica gel on Al foil, 5% of starch as binder); the spots were detected with iodine vapor. Melting points were measured in sealed capillaries and are uncorrected. Analyses were performed in the Institute of Inorganic Chemistry, Analytical Department using standard procedures. IR spectra (wavenumbers in cm^{-1}) were measured in KBr pellets using Pye Unicam PU 9512 Spectrometer. The NMR spectra were measured in deuterated solvents on a Varian Unity 500 spectrometer at 500 MHz (^1H NMR) and at 160.4 MHz (^{11}B NMR). The procedures for $[^{11}\text{B}-^{11}\text{B}]$ -COSY 2D NMR and for $^1\text{H}\{-^{11}\text{B}\}$ selective decoupling were performed essentially as described in the literature³². The positive chemical shifts (ppm, δ -scale) and coupling constants (J , Hz) are given downfield. Mass spectra of the uncharged species were measured on a Magnum GS-MS ion trap system (Finnigan MAT, U.S.A.) equipped with heated inlet option (Spectronex AG., Basel). High-resolution mass spectra of ionic species were measured on a Bruker Esquire-LC ion trap instrument

using electrospray ionisation. Negative ions were detected. Samples dissolved in acetonitrile (concentrations 1 ng/ μ l) were introduced to ion source by infusion at 3 μ l/min; drying temperature was 300 °C, drying gas flow 5 l/min, nebulizing gas pressure 10 psi. Single-crystal X-ray diffractions were measured on a Nonius Kappa CCD device (see below).

X-Ray Crystallography

Crystal data for 12-dioxane-closo-1-carbadecahydrododecaborate (2): $C_5H_{19}B_{11}O_2$, $M = 230.11$, monoclinic, $P2_1/c$ (No. 14), $a = 12.5900(3)$ Å, $b = 7.6630(2)$ Å, $c = 14.6240(3)$ Å, $\beta = 113.015(1)^\circ$, $V = 1298.58(5)$ Å³, $Z = 4$, $D_x = 1.177$ Mg m⁻³. A colorless crystal of dimensions 0.3 × 0.3 × 0.2 mm was mounted on a glass capillary with epoxy glue and measured at Nonius Kappa CCD diffractometer with monochromatized MoK α radiation ($\lambda = 0.71073$ Å) at 150(2) K. Absorption was neglected ($\mu = 0.064$ mm⁻¹). A total of 20 681 reflections were measured in the range $h = -16$ to 16, $k = -9$ to 9, $l = -18$ to 17 ($\theta_{\max} = 27.5^\circ$), of which 2 955 were unique ($R_{\text{int}} = 0.028$) and 2 595 observed according to the $I > 2\sigma(I)$ criterion. The structure was solved by direct methods (SIR92)³³ and refined by full-matrix least squares based on F^2 (SHELXL97)³⁴. The hydrogen atoms of three CH₂ moieties were fixed in idealized positions (riding model) and assigned temperature factors either $H_{\text{iso}}(H) = 1.2 U_{\text{eq}}$ (pivot atom). Hydrogen atoms of the carborane cage and C2 atom were refined isotropically. The refinement converged ($\Delta/\sigma_{\max} = 0.000$) to $R = 0.040$ for observed reflections and $wR = 0.109$, GOF = 1.037 for 215 parameters and all 2 955 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{\max} = 0.366$, $\Delta\rho_{\min} = -0.199$ e Å⁻³).

CCDC 182777 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

The results are shown in condensed form in Fig. 2 and Table I.

Synthesis of the 12-Dioxane-1-carbadodecaborane (2)

A typical experiment included: Carefully dried (8 h at 110 °C in vacuum) Cs[CB₁₁H₁₂] (2.8 g, 10.14 mmol) was dispersed in dioxane (25 ml) and dimethyl sulfate (2.2 ml, 23.8 mmol) was added in one portion. The slurry was placed on a bath and stirred at 90 °C for 3 h. Partial dissolution occurred and the color of the reaction mixture turned to brownish. At this moment, TLC in CH₂Cl₂ exhibited a round spot with R_f 0.65 along with anionic species moving only slightly from the start. After cooling down, the reaction mixture was poured into water (150 ml) and left to stand overnight in a refrigerator. The brownish precipitate was collected by filtration and dried in vacuum. The crude product (1.85 g) was then dissolved in benzene or toluene and prepurified by flash chromatography on a silica gel column using the same eluent. Fractions containing the zwitterionic products corresponding to the above spot on TLC were collected and combined. The crude product was dissolved in CH₂Cl₂ and layered with hexane and left to crystallize for 4 days. Crystals were collected by filtration and recrystallized once more. Colorless crystalline solid, yield 635 mg (27.2%); m.p. 216–218 °C. TLC: R_f 0.65 (CH₂Cl₂), 0.33 (benzene). MS, m/z (%): calculated for ¹²C₅¹¹B₁₁¹H₁₉O₂: 232; found: 232 (33), 229 (100). For B₁₁C₅H₁₉O₂ calculated: 51.67% B; found: 51.45% B. IR: 302 w, 478 w, 728 w, 800 w, 862 w, 912 s, 985 m, 1 020 s, 1 058 m, 1 130 s, 1 256 m, 1 284 w, 1 444 m, 2 544 sh, 2 576 vs, 2 916 m, 3 067 w, 3 424 w. ¹¹B NMR chemical shifts $\delta(^{11}\text{B})$, $J(^{11}\text{B}-^1\text{H})$ in parentheses, assignment by relative intensities, [¹¹B-¹¹B]-COSY (measured

in CDCl_3): 11.06 s (B(12)), -16.82 d (139) (B(7-11)), -19.1 d (158) (B(2-6)). The observed ^{11}B - ^{11}B COSY NMR crosspeaks: B(12)-B(7-11) strong, B(7-11)-B(2-6) very strong. ^1H NMR chemical shifts $\delta(^{11}\text{B})$, selectively decoupled, $\delta(^1\text{H})\{^{11}\text{B}_{\text{selective}}\}$ assignments in brackets (measured in CDCl_3): 4.483 m (4 H, CH_2O); 3.949 (4 H, CH_2O); 2.395 (1 H, CH); 1.862 [5 H, H(7-11)]; 1.775 [5 H, H(2-6)].

Side products: MS of the solids recovered from the mother liquors after crystallization exhibited peaks with m/z : 246, 260, 274, 288 and 302 corresponding to the methylated species. The ^{11}B and ^1H NMR spectra of the crude product comprised, in addition to the above three signals of **2**, also typically the following peaks in ^{11}B NMR: 6.8 s, 6.6 s, 1.04 s, 0.05 s, -5.8 s, -6.16 s, -15.15 d, -17.20 d, -18.90 d, -19.67 d, -20.56 d, -21.54 d. ^1H NMR: 4.65 m (CH_2O); 4.472 m (CH_2O); 3.93 m (CH_2O); 3.866 m (CH_2O) and overlapping singlets in the interval 0.33 to -0.1 (B- CH_3).

Synthesis of the Trimethylammonium (Tetramethylammonium) Salt of 12-Hydroxy-1-carbadodecaborate **3**

A suspension of $\text{Cs}[\text{CB}_{11}\text{H}_{12}]$ (2.0 g, 7.25 mmol) was made in 80% H_2SO_4 (25 ml) and the reaction mixture was heated to 175 °C while stirring. The solids gradually dissolved. The heating was continued for 5 h. After cooling down, the content of the flask was poured into water (150 ml) and the product was extracted with three portions of diethyl ether (20 ml). Water (30 ml) was added to the combined extracts, and the organic solvent was evaporated in vacuum together with about 10 ml of water. The aqueous solution was filtered using a paper filter. The product was precipitated by addition of excess of $\text{Me}_3\text{N}\cdot\text{HCl}$ in water (alternatively, in another similar run, Me_4NCl in water was used). The precipitate was filtered, washed with water and recrystallized from hot water by addition of ethanol until dissolution and cooling down. Colorless microcrystalline salts were filtered and dried in vacuum at 80 °C. Me_3NH^+ was found to be monohydrate, whereas Me_4N^+ salt was anhydrous. Data for $\text{Me}_3\text{NH}[12\text{-HO-CB}_{11}\text{H}_{11}]\cdot\text{H}_2\text{O}$: yield 1.43 g (82.8%); m.p. 343-348 °C. TLC: R_F 0.12 (CH_2Cl_3 : CH_3CN , 3 : 1). MS, m/z (%) calculated for $^{12}\text{C}^{11}\text{B}_{11}\text{H}_{12}\text{O}$: 162.2; found: 161.1, 158.9 (100). For $\text{B}_{11}\text{C}_4\text{H}_{24}\text{O}_2\text{N}$ calculated: 50.14% B; found: 49.76% B. (For Me_4N^+ salt: for $\text{B}_{11}\text{C}_5\text{H}_{24}\text{ON}$ calculated: 51.00% B; found: 51.30% B.) IR: 294 w, 392 w, 474 w, 584 w, 722 m, 810 w, 985 m, 1 004 m, 1 054 s, 1 158 m, 1 474 s, 2 564 vs, 2 712 sh, 3 036 m, 3 584 vs. ^{11}B NMR chemical shifts $\delta(^{11}\text{B})$, $J(^{11}\text{B}\text{-}^1\text{H})$ in parentheses, assignment by relative intensities [^{11}B - ^{11}B]-COSY, and ^1H - $\{^{11}\text{B}(\text{selective})\}$ experiments (for ^1H) (measured in acetone- d_6): 10.65 s (B(12)), -14.13 d (135) (B(7-11)), -18.67 d (150) (B(2-6)). ^{11}B - ^{11}B NMR crosspeaks: B(12)-B(7-11) strong, B(7-11)-B(2-6) very strong. ^1H NMR chemical shifts in $\delta(^1\text{H})$, selectively decoupled, $\delta(^1\text{H})\{^{11}\text{B}_{\text{selective}}\}$ assignments in brackets (measured in acetone- d_6): 10.63 (1 H, HNMe_3); 3.81 (1 H, OH); 3.05 (2 H, H_2O); 2.94 (12 H, Me_3N); 1.99 (1 H, CH); 1.670 [5 H, H(7-11)]; 1.48 [5 H, H(2-6)].

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