Inorg. Chem. **1996,** *35,* 1355−1360 **1355**

Hydroxoundecahydro-*closo*-dodecaborate(2−) as a Nucleophile. Preparation and Structural Characterization of *O*-Alkyl and *O*-Acyl Derivatives of Hydroxoundecahydro-*closo*-dodecaborate(2−)

Toralf Peymann, Enno Lork, and Detlef Gabel*

Department of Chemistry, University of Bremen, P.O. Box 330 440, D-28334 Bremen, Germany

Received August 24, 1995[⊗]

The syntheses, solid state structures, and spectral properties of *O*-alkyl and *O*-acyl derivatives of hydroxoundecahydro-*closo*-dodecaborate(2−), **1**, are described. Alkylation of **1** with ethyl iodide was achieved in dimethyl sulfoxide using potassium hydroxide as a base, leading to $[N(n\text{-}C_4H_9)_4]_2[CH_3CH_2O-B_{12}H_{11}(2-)]$, **2**, bis(tetrabutylammonium) ethoxyundecahydro-*closo*-dodecaborate(2−) [monoclinic $P2_1/n$, $a = 1192.4(9)$ pm, $b = 1253.9(4)$ pm, $c = 3049.1(10)$ pm, $\beta = 92.69(4)°$, $Z = 4$, R1 = 0.0693, wR$_2$ = 0.1517]. Alkylation with 1,5-dibromopentane afforded the cyclic oxonium salt $[PPN][C_5H_{10}O-B_{12}H_{11}(1-)]$, **3**, ($\mu$-nitrido)bis(triphenylphosphorus)(1+) tetrahydropyrane−undecahydro-*closo*-dodecaborate(1−) [monoclinic $P2_1/c$, $a = 1938.1(2)$ pm, $b = 1329.7(10)$ pm, $c = 1944.0(2)$ pm, $\beta = 108.82(10)°$, $Z = 4$, R1 = 0.0484, wR$_2$ = 0.0833]. Acylation of **1** in acetonitrile with acyl chlorides in the presence of pyridine yielded $[N(n\text{-}C_4H_9)_4]_2[C_6H_5CO_2\text{-}B_{12}H_{11}(2-)]$, **4**, bis(tetrabutylammonium) undecahydrobenzoyl-*closo*-dodecaborate(2−) [monoclinic $P2_1/c$, $a = 1812.0(4)$ pm, $b = 1711.9(3)$ pm, $c = 1685.0(3)$ pm, $\beta = 114.03(3)°$, $Z = 4$, R1 = 0.0915, wR$_2$ = 0.2093], and $[N(n\text{-}C_4H_9)_4]_2[CH_3CO_2\text{-}B_{12}H_{11}(2-)]$, **5**, bis(tetrabutylammonium) acetoxyundecahydro-*closo*-dodecaborate(2−) [monoclinic $P2_1/n$, $a = 1190.5(2)$ pm, $b = 1243.0(10)$ pm, $c = 3078.4(4)$ pm, $\beta = 92.76(10)°$, $Z = 4$, R1 = 0.0642, wR$_2$ = 0.1462]. All crystal structures showed distortion of the pseudoicosahedral geometry of the boron cluster. The boron−oxygen distances varied from 144.2(5) pm for **2**, 148.5(3) pm for **5**, 149.4(12) pm for **4**, to 152.8(4) pm for **3**. The 3-fold coordinated oxygen of oxonium salt **3** is nearly planar.

Introduction

Boron neutron capture therapy (BNCT) provides an alternative way of treating cancer.[1] The basic idea is to destroy tumor cells by combining two methods: enrichment of boron-10 in cancer cells and subsequent irradiation of the tissue with neutrons. After capturing thermal neutrons the boron nucleus disintegrates in ionizing particles, destroying the cell. To realize this therapeutic model, boron compounds are needed which accumulate in cancer cells. They should be nontoxic and water-soluble. Since the icosahedron $[B_{12}H_{12}]^{2-}$ is hydrophilic and known to be harmless to man, it is an interesting compound for BNCT. Its thiol-substituted derivative mercaptoundecahydro-*closo*-dodecaborate(2−) $[HS-B_{12}H_{11}]^{2-}$, **6** (BSH), accumulates in tumor tissue and is therefore utilized in the therapy of gliomas in Japan[2] and Europe.[3]

To link the boron cluster $[B_{12}H_{12}]^{2-}$ to organic moieties known to be tumor-seeking, e. g. porphyrins or carbohydrates, the icosahedron itself is not suitable. Substitution of $[B_{12}H_{12}]^{2-}$ is usually achieved by acid-mediated hydride displacement.[4] We were interested in other ways of derivative chemistry because reactions of this type often lead to the formation of byproducts. Strongly acidic conditions are also often not compatible with the presence of other functional groups. Utilizing the sulfur-substituted icosahedron **6** as a nucleophile, it was found[5] that alkylation by primary alkyl halides leads to surprisingly stable sulfonium salts $[R_2S-B_{12}H_{11}]^{-}$. The reaction with acid halides gave stable *S*-acyl derivatives $[RCOS-B_{12}H_{11}]^{2-}$.

In our course of synthesizing new $[B_{12}H_{12}]^{2-}$ derivatives we have investigated the chemistry of the oxygen analogue of BSH, hydroxoundecahydro-*closo*-dodecaborate(2−) $[HO-B_{12}H_{11}]^{2-}$ **1**. The preparation of *O*-benzyl and *O*-acyl derivatives of **1** has been described before. $[C_6H_5CH_2O-B_{12}H_{11}]^{2-}$ was obtained by the reaction of $[B_{12}H_{12}]^{2-}$ with benzoyl *p*-toluenesulfonate.[6] Reaction of $[B_{12}H_{12}]^{2-}$ with carboxylic acids gave the corresponding carboxylatododecaborates.[7] We report here the reaction of **1** with primary alkyl halides and acid chlorides leading to *O*-alkyl and *O*-acyl derivatives of hydroxoundecahydro-*closo*-dodecaborate(2−). The new compounds were characterized by their crystal structures, infrared and NMR spectroscopy, and elemental analysis.

Experimental Section

General Information. The ^{1}H and ^{13}C NMR spectra were recorded at 360.1 MHz and 90.1 MHz on a Bruker WH 360; the ^{11}B NMR spectra were recorded at 200 MHz on a Bruker AM 200. All NMR spectra were measured in CD_3CN at room temperature; chemical shifts are given relative to TMS or $BF_3\cdot OEt_2$. The NMR data of the cations are omitted. The hydrogens of the boron cluster of all new compounds gave a broad multiplet at 2.0−0.2 ppm. This multiplet is not listed in the individual NMR data. Infrared spectra were determined as KBr pellets on a Biorad FTS-7 spectrometer. Microanalyses were performed by Analytische Laboratorien, Prof. Dr. H. Malissa und G. Reuter GmbH, Gummersbach, Germany. Melting points are uncorrected. $Cs_2[HO-B_{12}H_{11}]$ was prepared according to the literature.[6]

Preparation of $[N(n\text{-}C_4H_9)_4]_2[CH_3CH_2O\text{-}closo\text{-}B_{12}H_{11}(2-)]$ (2). A 200 mg (0.48 mmol) sample of **1** as the cesium salt, 136 mg (2.42

---

* To whom correspondence should be addressed. Telephone: +49 421 218 2200. Fax: +49 421 218 2871. E-mail: detlef.gabel@chemie.uni-bremen.de.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

(1) Hawthorne, M. F. *Angew. Chem.* **1993**, *105*, 997; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 950.

(2) Hatanaka, H. *Neutron Capture Therapy*; Nishimura: Niigata, Japan, 1986.

(3) Haritz, D.; Gabel, D.; Klein, H.; Piscol, K. *Adv. Neurosurg.* **1992**, *20*, 247.

(4) *Gmelin Handbuch, Borverbindungen,* Springer Verlag: New York, 1979; Vol. 20, Chapter 6.2.

(5) Gabel, D.; Moller, D.; Harfst, S.; Rösler, J.; Ketz, H. *Inorg. Chem.* **1993**, *32*, 2276.

(6) Knoth, W. H.; Sauer, J. C.; England, D. C.; Hertler, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 3973.

(7) Krause, U.; Preetz, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 516.

Table 1. Crystallographic Data for Compounds **2**−**5**

	2	**3**	**4**	**5**
formula	$C_{34}H_{88}B_{12}N_2O$	$C_{41}H_{51}B_{12}NOP_2 \cdot CHCl_3$	$C_{39}H_{88}B_{12}N_2O_2$	$C_{34}H_{86}B_{12}N_2O_2$
fw	670.8	884.9	746.8	684.8
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, pm	1192.4(9)	1938.1(2)	1812.0(4)	1190.5(2)
b, pm	1253.9(4)	1329.70(10)	1711.9(3)	1243.00(10)
c, pm	3049.10(10)	1944.0(2)	1685.0(3)	3078.3(4)
β, deg	92.69(4)	108.820(10)	114.03(3)	92.760(10)
V, nm^3	4.554(4)	4.7420(8)	4.774(2)	4.5500(10)
ρ(calcd), g cm^{-3}	0.978	1.239	1.039	1.000
Z	4	4	4	4
μ, mm^{-1}	0.052	0.295	0.058	0.055
λ, pm	71.073	71.073	71.073	71.073
T, K	173	173	173	173
$R1^a$	0.0693	0.0484	0.0915	0.0642
wR_2^b	0.1517	0.0833	0.2093	0.11462

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2$.

mmol) of potassium hydroxide, and 390 μL (4.8 mmol) of ethyl iodide were dissolved in 20 mL of dimethyl sulfoxide. The solution was stirred for 2 days at room temperature. The solvent was removed at reduced pressure at 60 °C. The residue was washed with methanol and dissolved in water. Addition of 1.42 g (4.8 mmol) of tetrabutylammonium chloride gave a precipitate which was filtered off. Crystals for X-ray analysis were prepared by dissolving in ethanol and allowing diethyl ether to diffuse into the solution. After a few days 100 mg (0.15 mmol, 31%) of colorless crystals of **2** (mp 208−210 °C) were isolated.

^{1}H-NMR: 3.5 (q, CH$_2$); 1.1 (t, CH$_3$). ^{13}C-NMR{^{1}H}: 65.0 (CH$_2$); 16.7 (CH$_3$). IR: 2963, 2875, 2481ν(B−H), 1470, 1379, 1154, 1114, 1045 ν(B−B), 1017, 916, 890, 803, 740, 717 cm^{-1}. Anal. Calcd for $C_{34}H_{88}B_{12}N_2O$: C, 60.88; H, 13.22; N, 4.18; B, 19.34. Found: C, 60.71; H, 13.16; N, 4.13; B, 19.10.

Preparation of [N(CH$_3$)$_4$]$_2$[C$_6$H$_5$CH$_2$O-*closo*-B$_{12}$H$_{11}$(2−)] (7). A 200 mg (0.48 mmol) sample of **1** as the cesium salt, 136 mg (2.42 mmol) of potassium hydroxide, and 544 μL (4.73 mmol) of benzyl chloride were dissolved in 20 mL of dimethyl sulfoxide. The solution was stirred for 2 days at room temperature. The solvent was removed at reduced pressure at 60 °C. The residue was washed with methanol and dissolved in water. Addition of 515 mg (4.7 mmol) of tetramethylammonium chloride and cooling over night gave a precipitate which was filtered off. The precipitate was washed with small amounts of water to afford 150 mg (0.39 mmol, 83%) of colorless crystals of **7** (mp > 250 °C).

^{1}H-NMR: 7.4−7.1 (m, C$_6$H$_5$); 4.4 (s, CH$_2$). ^{13}C-NMR{^{1}H}: 144.5 (C-1); 127.5, 126.0 (C-2, C-3); 125.5 (C-4); 70.0 (CH$_2$). IR: 3029, 2477 ν(B−H), 1487, 1198, 1152, 1052 ν(B−B), 1010, 950, 897, 755 cm^{-1}.

Preparation of [N(*n*-C$_4$H$_9$)$_4$][C$_5$H$_{10}$O-*closo*-B$_{12}$H$_{11}$(1−)] (3). A 200 mg (0.48 mmol) sample of **1** as the cesium salt, 136 mg (2.42 mmol) of potassium hydroxide, and 650 μL (4.73 mmol) of 1,5-dibromopentane were dissolved in 20 mL of dimethyl sulfoxide. The solution was stirred for 2 days at room temperature. The solvent was removed at reduced pressure at 60 °C. The residue was washed with diethyl ether, dissolved in hot water, and filtered. Addition of 1.42 g (4.7 mmol) of tetrabutylammonium chloride gave a precipitate which was recrystallized from ethanol to give 200 mg (0.41 mmol, 87%) of colorless crystals of **3** (mp 159 °C). Crystals of the (μ-nitrido)bis(triphenylphosphorus)(1+) salt of **3** for X-ray analysis were obtained by dissolving in chloroform/ethanol and cooling to −18 °C.

^{1}H-NMR: 4.4 (t, α-CH$_2$); 1.8 (m, β-CH$_2$); 1.6 (m, γ-CH$_2$). ^{13}C-NMR{^{1}H}: 82.1 (α-CH$_2$); 24.8 (β-CH$_2$); 21.1 (γ-CH$_2$). IR: 2964, 2933, 2874, 2491 ν(B−H), 1471, 1166, 1046 ν(B−B), 968, 946, 884, 738, 720 cm^{-1}. Anal. Calcd for $C_{21}H_{57}B_{12}NO$: C, 53.73; H, 12.24; N, 2.98; B, 27.63. Found: C, 53.97; H, 12.03; N, 2.86; B, 27.50.

Preparation of [N(*n*-C$_4$H$_9$)$_4$]$_2$[C$_6$H$_5$CO$_2$-*closo*-B$_{12}$H$_{11}$(2−)] (4). A 200 mg (0.48 mmol) sample of **1** as the cesium salt, 800 μL (9.90 mmol) of pyridine, and 800 μL (6.9 mmol) of benzoyl chloride were suspended in 20 mL of acetonitrile. The suspension was stirred for 2 h at room temperature. The solvent was removed at reduced pressure. The residue was washed with diethyl ether, dissolved in a small amount of acetonitrile, and filtered. The filtrate was evaporated to give a residue which was dissolved in boiling water. Addition of 1.42 mg (4.7 mmol) of tetrabutylammonium chloride gave a precipitate which was recrystallized from ethanol to give 240 mg (0.32 mmol, 68%) of colorless crystals of **4** (mp 174 °C).

^{1}H-NMR: 7.9 (m, H$_{\rm ortho}$); 7.5−7.4 (m, H$_{\rm meta}$, H$_{\rm para}$). ^{13}C-NMR-{^{1}H}: 165.2 (C═O); 135.2 (C-1); 130.6 (C-4); 128.9, 127.6 (C-2, C-3). IR: 2963, 2934, 2875, 2480 ν(B−H), 1683, 1473, 1327, 1152, 1045 ν(B−B), 1005, 891, 878, 800, 741, 714 cm^{-1}. Anal. Calcd for $C_{39}H_{88}B_{12}N_2O_2$: C, 62.72; H, 11.88; N, 3.75; B, 17.37. Found: C, 62.81; H, 11.77; N, 3.61; B, 17.45.

Preparation of [N(*n*-C$_4$H$_9$)$_4$]$_2$[CH$_3$CO$_2$-*closo*-B$_{12}$H$_{11}$(2−)] (5). A 200 mg (0.48 mmol) sample of **1** as the cesium salt, 800 μL (9.90 mmol) of pyridine, and 400 μL (5.6 mmol) of acetyl chloride were suspended in 20 mL of acetonitrile. The suspension was stirred for 1 h at room temperature. The solvent was removed at reduced pressure. The residue was washed with diethyl ether, dissolved in a small amount of acetonitrile, and filtered. The filtrate was evaporated to give a residue which was dissolved in warm water. Addition of 1.42 g (4.7 mmol) of tetrabutylammonium chloride gave a precipitate which was filtered and suspended in hot ethyl acetate. Ethanol was added until solution. Slow evaporation at room temperature afforded 120 mg (0.18 mmol, 38 %) slightly yellow crystals of **5** (mp 174 °C). Crystals for X-ray analysis were obtained from ethanol/diethyl ether as described for **2**.

^{1}H-NMR: 1.95 (s, CH$_3$). ^{13}C-NMR{^{1}H}: 171.5 (C═O); 12.7 (CH$_3$). IR: 2961, 2934, 2875, 2487 ν(B−H), 1697, 1477, 1377, 1364, 1291, 1046 ν(B−B), 1030, 883, 741 cm^{-1}. Anal. Calcd for $C_{34}H_{86}B_{12}N_2O_2$: C, 59.64; H, 12.66; N, 4.09; B, 18.94. Found: C, 59.46; H, 12.72; N, 4.04; B, 18.92.

X-ray Crystal Structure Determination

Crystallographic Data Collection and Refinement of the Structure of [N(*n*-C$_4$H$_9$)$_4$]$_2$[CH$_3$CH$_2$O-*closo*-B$_{12}$H$_{11}$(2−)] (2). The diffraction intensities of an approximately 1.2 × 0.4 × 0.1 mm colorless crystal of **2** were collected with graphite-monochromatized Mo Kα radiation using a Siemens P4 diffractometer at 173(2) K and the $\omega-2\theta$ scan technique to a $\theta_{\max}$ value of 22.49°. A total of 7825 reflections were measured, of which 5932 ($R_{\rm int} = 0.0591$) were unique. The data were corrected for Lorentz and polarization effects. The cell parameters were obtained from least-square refinement of the setting angles of 30 centered reflections with θ in the range 5.3−11.0°.

The structure was solved by direct methods.[8] All atoms except hydrogens were refined anisotropically.[9] Hydrogen atoms were included in calculated positions with the common isotropic thermal parameters for the methyl-, the methylene- and the boron-bonded hydrogen atoms. The full-matrix least-squares refinement based on F^2 converged with agreement factors R1 = 0.0693 and wR$_2$ = 0.1517 for 5932 reflections and 455 parameters. Crystallographic data are summarized in Table 1. Atomic positional parameters of **2** are listed in Table 2.

---

(8) Sheldrick, G. M. SHELXS-86. Universität Göttingen, 1986.
(9) Sheldrick, G. M. SHELXL-93. Universität Göttingen, 1993.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **2**[a]

	x	*y*	*z*	*U*(eq)
C(1)	4730(4)	2219(3)	1168(2)	58(1)
C(2)	5800(4)	1677(4)	1068(2)	72(2)
O(1)	4775(2)	3324(2)	1078(1)	42(1)
B(1)	3781(4)	3926(4)	1168(2)	34(1)
B(2)	3435(4)	4344(4)	1705(1)	34(1)
B(3)	3921(5)	5311(4)	1327(1)	35(1)
B(4)	3323(4)	4978(4)	798(1)	33(1)
B(5)	2474(4)	3829(4)	851(1)	39(1)
B(6)	2559(4)	3440(4)	1412(1)	38(1)
B(7)	2810(4)	5620(4)	1668(1)	32(1)
B(8)	2737(4)	6008(4)	1107(1)	39(1)
B(9)	1847(4)	5116(4)	817(2)	39(1)
B(10)	1367(4)	4149(4)	1193(1)	40(1)
B(11)	1966(4)	4480(4)	1721(1)	37(1)
B(12)	1516(4)	5523(4)	1357(1)	36(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Lengths (pm) and Angles (deg) for **2**

C(1)−O(1)	141.3(5)	C(1)−C(2)	148.9(6)
O(1)−B(1)	144.2(5)	B(1)−B(6)	177.4(7)
B(1)−B(2)	178.4(6)	B(1)−B(5)	180.0(7)
B(1)−B(4)	180.5(7)	B(1)−B(3)	180.9(6)
B(2)−B(6)	175.7(7)	B(2)−B(11)	176.3(7)
B(2)−B(7)	176.7(6)	B(2)−B(3)	178.7(6)
B(3)−B(7)	176.4(7)	B(3)−B(8)	176.6(7)
B(3)−B(4)	178.4(6)	B(4)−B(8)	176.3(7)
B(4)−B(5)	177.2(7)	B(4)−B(9)	177.2(7)
B(5)−B(10)	176.8(7)	B(5)−B(6)	177.7(6)
B(5)−B(9)	177.9(7)	B(6)−B(11)	177.5(7)
B(6)−B(10)	177.9(7)	B(7)−B(11)	175.9(7)
B(7)−B(12)	177.7(7)	B(7)−B(8)	177.7(6)
B(8)−B(9)	175.2(7)	B(8)−B(12)	178.2(7)
B(9)−B(10)	178.1(7)	B(9)−B(12)	178.4(6)
B(10)−B(11)	177.8(6)	B(10)−B(12)	180.0(7)
B(11)−B(12)	178.2(6)		
O(1)−C(1)−C(2)	111.5(4)	C(1)−O(1)−B(1)	115.9(3)
O(1)−B(1)−B(6)	126.8(4)	O(1)−B(1)−B(2)	123.8(4)
O(1)−B(1)−B(5)	124.1(3)	O(1)−B(1)−B(4)	119.4(3)
O(1)−B(1)−B(3)	119.2(4)		

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **3**[a]

	x	*y*	*z*	*U*(eq)
O(1)	1399(1)	8422(2)	2505(1)	46(1)
C(1)	920(2)	9266(3)	2194(2)	61(1)
C(2)	197(2)	8902(3)	1701(2)	59(1)
C(3)	288(2)	8231(3)	1107(2)	56(1)
C(4)	818(2)	7388(3)	1450(2)	62(1)
C(5)	1522(2)	7777(4)	1939(2)	66(1)
B(1)	1512(2)	8036(3)	3274(2)	30(1)
B(2)	1564(2)	6737(3)	3459(2)	34(1)
B(3)	2373(2)	7512(3)	3746(2)	35(1)
B(4)	2109(2)	8692(3)	3997(2)	30(1)
B(5)	1153(2)	8664(3)	3872(2)	31(1)
B(6)	823(2)	7446(3)	3539(2)	30(1)
B(7)	2209(2)	6600(3)	4335(2)	35(1)
B(8)	2543(2)	7816(3)	4674(2)	31(1)
B(9)	1796(2)	8516(3)	4752(2)	31(1)
B(10)	1009(2)	7746(3)	4472(2)	34(1)
B(11)	1263(2)	6561(3)	4215(2)	36(1)
B(12)	1865(2)	7217(3)	4960(2)	32(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Lengths (pm) and Angles (deg) for **3**

O(1)−C(1)	145.6(4)	O(1)−C(5)	147.3(4)
O(1)−B(1)	152.8(4)	C(1)−C(2)	150.0(5)
C(2)−C(3)	151.4(5)	C(3)−C(4)	152.2(5)
C(4)−C(5)	148.1(5)	B(1)−B(4)	174.0(5)
B(1)−B(5)	174.8(5)	B(1)−B(2)	176.1(6)
B(1)−B(6)	176.2(5)	B(1)−B(3)	176.8(5)
B(2)−B(11)	176.3(6)	B(2)−B(7)	176.7(5)
B(2)−B(6)	176.7(5)	B(2)−B(3)	180.6(5)
B(3)−B(7)	176.6(6)	B(3)−B(4)	176.8(5)
B(3)−B(8)	177.4(5)	B(4)−B(8)	175.6(5)
B(4)−B(9)	177.5(5)	B(4)−B(5)	179.0(5)
B(5)−B(10)	177.2(5)	B(5)−B(9)	177.2(5)
B(5)−B(6)	178.5(5)	B(6)−B(11)	176.5(5)
B(6)−B(10)	177.8(5)	B(7)−B(12)	176.6(6)
B(7)−B(11)	177.2(6)	B(7)−B(8)	178.7(5)
B(8)−B(9)	176.7(5)	B(8)−B(12)	177.2(6)
B(9)−B(12)	176.9(5)	B(9)−B(10)	177.1(5)
B(10)−B(12)	177.0(5)	B(10)−B(11)	177.0(6)
B(11)−B(12)	176.9(5)		
C(1)−O(1)−C(5)	111.9(3)	C(1)−O(1)−B(1)	122.4(3)
C(5)−O(1)−B(1)	121.8(3)	O(1)−C(1)−C(2)	110.9(3)
C(1)−C(2)−C(3)	111.2(3)	C(2)−C(3)−C(4)	109.2(3)
C(5)−C(4)−C(3)	112.1(3)	O(1)−C(5)−C(4)	110.2(3)
O(1)−B(1)−B(4)	118.0(3)	O(1)−B(1)−B(5)	121.9(3)
O(1)−B(1)−B(2)	120.7(3)	O(1)−B(1)−B(6)	123.5(3)
O(1)−B(1)−B(3)	117.0(3)		

Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **4**[a]

	x	*y*	*z*	*U*(eq)
B(1)	2599(5)	4547(7)	−2626(7)	43(3)
B(2)	1613(6)	4234(6)	−3215(7)	43(3)
B(3)	2351(6)	4071(6)	−3615(7)	45(3)
B(4)	3286(6)	3852(7)	−2709(7)	50(3)
B(5)	3113(5)	3900(6)	−1761(7)	38(3)
B(6)	2067(6)	4131(6)	−2061(7)	42(3)
B(7)	1653(6)	3309(6)	−3675(8)	56(4)
B(8)	2706(6)	3083(7)	−3380(7)	53(3)
B(9)	3155(6)	2996(6)	−2228(7)	51(3)
B(10)	2420(5)	3141(6)	−1832(7)	40(3)
B(11)	1493(6)	3357(6)	−2725(7)	48(3)
B(12)	2164(6)	2658(7)	−2822(7)	50(3)
O(1)	2715(3)	5411(4)	−2627(4)	50(2)
C(1)	3016(5)	5866(6)	−1950(8)	46(3)
O(2)	3401(4)	5674(4)	−1211(5)	70(2)
C(2)	2845(5)	6721(6)	−2192(7)	45(3)
C(3)	2510(5)	6952(6)	−3049(7)	54(3)
C(4)	2368(5)	7759(7)	−3256(8)	68(3)
C(5)	2569(6)	8300(7)	−2601(9)	73(4)
C(6)	2884(6)	8058(6)	−1741(9)	71(3)
C(7)	3047(5)	7273(6)	−1526(7)	59(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Crystallographic Data Collection and Refinement of the Structure of [PPN][$C_5H_{10}O$-*closo*-$B_{12}H_{11}$(1−)] (3). The diffraction intensities of a colorless crystal of approximate 0.5 × 0.3 × 0.1 mm were collected on a Siemens P4 diffractometer in a fashion similar to that used for **2**. A total of 10134 reflections were collected to a θ_{max} value of 26.85°. A total of 8329 intensities (R_{int} = 0.0385) were unique. The cell parameters were obtained from 28 carefully centered reflections with θ in the range 7.2−10.3°. The refinement similar to **2** converged with agreement factors of R1 = 0.0484 and wR$_2$ = 0.0833 for 8329 reflections and 566 parameters. The compound crystallizes with one solvent molecule of $CHCl_3$. Crystallographic data are summarized in Table 1. Atomic positional parameters of **3** are listed in Table 4.

Crystallographic Data Collection and Refinement of the Structure of [N(n-C_4H_9)$_4$]$_2$[$C_6H_5CO_2$-*closo*-$B_{12}H_{11}$(2−)] (4). The intensities of a colorless needle shaped crystal of approximate 1.2 × 0.1 × 0.1 mm were collected on a Siemens P4 diffractometer in a fashion similar to that used for **2**. A total of 5442 reflections were measured, of which 4335 (R_{int} = 0.1270) were unique. A total of 29 centered reflections with θ in the range 3.7−7.5° were used for determining the cell parameters. The refinement similar to **2** converged with R1 = 0.0915 and wR$_2$ = 0.2093 for 4335 reflections and 508 parameters. Crystallographic data are summarized in Table 1. Atomic positional parameters of **4** are listed in Table 6.

Table 7. Selected Bond Lengths (pm) and Angles (deg) for **4**

B(1)−O(1)	149.4(12)	B(1)−B(2)	173.9(13)
B(1)−B(3)	174.3(14)	B(1)−B(6)	175.8(14)
B(1)−B(5)	176.3(14)	B(1)−B(4)	176.9(14)
B(2)−B(3)	174.9(13)	B(2)−B(11)	176.9(14)
B(2)−B(7)	177.8(14)	B(2)−B(6)	178.6(14)
B(3)−B(7)	179.1(14)	B(3)−B(8)	179.0(2)
B(3)−B(4)	179.9(14)	B(4)−B(9)	174.0(2)
B(4)−B(5)	175.1(14)	B(4)−B(8)	177.3(14)
B(5)−B(9)	175.2(14)	B(5)−B(10)	177.7(13)
B(5)−B(6)	179.4(13)	B(6)−B(11)	177.2(14)
B(6)−B(10)	179.6(13)	B(7)−B(11)	174.0(2)
B(7)−B(12)	176.0(2)	B(7)−B(8)	180.6(14)
B(8)−B(12)	177.0(14)	B(8)−B(9)	178.0(2)
B(9)−B(10)	173.3(14)	B(9)−B(12)	176.1(13)
B(10)−B(12)	174.6(14)	B(10)−B(11)	177.9(13)
B(11)−B(12)	176.1(14)	O(1)−C(1)	130.2(10)
C(1)−O(2)	119.9(10)	C(1)−C(2)	151.7(13)
C(2)−C(3)	137.9(12)	C(2)−C(7)	139.7(12)
C(3)−C(4)	142.1(12)	C(4)−C(5)	137.2(13)
C(5)−C(6)	138.8(13)	C(6)−C(7)	139.3(12)
O(1)−B(1)−B(2)	114.6(7)	O(1)−B(1)−B(3)	116.3(8)
O(1)−B(1)−B(6)	120.7(8)	O(1)−B(1)−B(5)	126.6(7)
O(1)−B(1)−B(4)	124.2(8)	C(1)−O(1)−B(1)	126.8(8)
O(2)−C(1)−O(1)	127.3(9)	O(2)−C(1)−C(2)	120.7(10)
O(1)−C(1)−C(2)	112.0(10)		

Table 8. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($pm^2 \times 10^{-1}$) for **5**[a]

	x	*y*	*z*	*U*(eq)
O(1)	9558(1)	1914(1)	1019(1)	35(1)
O(2)	9462(2)	3184(1)	1539(1)	43(1)
C(1)	9847(2)	2825(2)	1219(1)	33(1)
C(2)	10771(2)	3397(2)	997(1)	60(1)
B(1)	8626(2)	1206(2)	1147(1)	27(1)
B(2)	8366(2)	785(2)	1680(1)	27(1)
B(3)	7372(2)	1625(2)	1387(1)	29(1)
B(4)	7334(2)	1208(2)	832(1)	32(1)
B(5)	8300(2)	121(2)	789(1)	31(1)
B(6)	8920(2)	−143(2)	1311(1)	29(1)
B(7)	6902(2)	527(2)	1699(1)	29(1)
B(8)	6266(2)	787(2)	1178(1)	33(1)
B(9)	6819(2)	−134(2)	807(1)	35(1)
B(10)	7808(2)	−969(2)	1098(1)	33(1)
B(11)	7850(2)	−551(2)	1652(1)	29(1)
B(12)	6557(2)	−555(3)	1345(1)	33(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 9. Selected Bond Lengths (pm) and Angles (deg) for **5**

O(1)−C(1)	132.5(3)	O(1)−B(1)	148.5(3)
O(2)−C(1)	119.4(3)	C(1)−C(2)	150.2(4)
B(1)−B(2)	176.3(4)	B(1)−B(5)	177.2(4)
B(1)−B(3)	177.5(4)	B(1)−B(4)	177.8(4)
B(1)−B(6)	178.1(4)	B(2)−B(6)	176.8(4)
B(2)−B(11)	177.1(4)	B(2)−B(7)	177.7(4)
B(2)−B(3)	179.0(4)	B(3)−B(8)	177.6(4)
B(3)−B(7)	177.7(4)	B(3)−B(4)	178.4(4)
B(4)−B(8)	177.6(4)	B(4)−B(9)	177.8(4)
B(4)−B(5)	178.3(4)	B(5)−B(6)	176.6(4)
B(5)−B(10)	177.0(4)	B(5)−B(9)	179.5(4)
B(6)−B(11)	176.2(4)	B(6)−B(10)	177.5(4)
B(7)−B(11)	176.3(4)	B(7)−B(12)	176.7(4)
B(7)−B(8)	177.2(4)	B(8)−B(9)	176.5(4)
B(8)−B(12)	177.4(4)	B(9)−B(12)	177.7(4)
B(9)−B(10)	177.8(4)	B(10)−B(11)	178.1(4)
B(10)−B(12)	178.1(4)	B(11)−B(12)	176.7(4)
C(1)−O(1)−B(1)	124.4(2)	O(2)−C(1)−O(1)	126.9(2)
O(2)−C(1)−C(2)	121.1(2)	O(1)−C(1)−C(2)	111.9(2)
O(1)−B(1)−B(2)	126.1(2)	O(1)−B(1)−B(5)	115.5(2)
O(1)−B(1)−B(3)	126.2(2)	O(1)−B(1)−B(4)	119.5(2)
O(1)−B(1)−B(6)	119.6(2)		

Crystallographic Data Collection and Refinement of the Structure of $[N(n\text{-}C_4H_9)_4]_2[CH_3CO_2\text{-}closo\text{-}B_{12}H_{11}(2-)]$ (5). The diffraction intensities of a colorless crystal of approximate 1.1 × 0.3 × 0.1 mm were collected on a Siemens P4 diffractometer in a fashion similar to that used for **2**. A total of 17289 reflections were measured, of which 8019 ($R_{int} = 0.1434$) were unique. The cell parameters were obtained from 35 centered reflections with θ in the range 5.5−16.0°. The refinement similar to **2** converged with R1 = 0.0642 and wR$_2$ = 0.1462 for 8019 reflections and 464 parameters. Crystallographic data are summarized in Table 1. Atomic positional parameters of **5** are listed in Table 8.

Results

Syntheses. Alkylation and acylation of the hydroxy group attached to the boron cluster could be achieved as shown in Scheme 1 by standard procedures. The alkylation reactions were carried out in dimethyl sulfoxide using potassium hydroxide as a base. Alkylation of **1** with benzyl chloride gave the *O*-benzyl derivative **7**, and the ethyl derivative **2** was obtained by reaction with ethyl iodide. The crystal structure of **2** was determined by X-ray diffraction analysis. Alkylation of **1** using 1,5-dibromopentane afforded the cyclic oxonium salt **3**. This was proven by the proton decoupled ^{13}C-NMR spectrum showing three singlets, which is consistent with the C_s symmetry of **3**, and by its solid state structure determined by X-ray analysis.

Colorless crystals of the acetate **5** and the benzoate **4** were obtained similar to the procedure described for thioesters of **6**[5] in the reaction of **1** with the corresponding acid chlorides/pyridine in acetonitrile. The molecular structures of **4** and **5** were determined by single-crystal X-ray diffraction.

The structures of the cations tetrabutylammonium and (μ-nitrido)bis(triphenylphosphorus)(1+) are not unusual and will not be discussed further. Table 3 lists selected bond length and angles of $[CH_3CH_2O\text{-}closo\text{-}B_{12}H_{11}(2-)]$ (**2**), and a plot showing the molecular structure of **2** is given in Figure 1. The molecule consists of an icosahedral boron cluster with one ethoxy ligand. The pseudoicosahedral geometry of the cluster is distorted. The B−B bond lengths range from 175.2(7) to 180.9(6) pm. The B(1)−O(1) distance is 144.2(5) pm which is similar to the reported bond length for 4-Me_2S-7-MeO−B_9H_{12} (**8**) (143.5 pm).[10] Significant difference from sp^3 geometry is found for the B(1)−O(1)−C(1) angle [115.9(3)°]. Similar deviation is observed for **8** (114.5°). The B(12)−B(1)−O(1) angle (175.8°) deviates by 4.2° from linearity.

Selected bond lengths and angles of $[C_5H_{10}O\text{-}closo\text{-}B_{12}H_{11}(1-)]$ (**3**) are given in Table 5. A view of the solid state structure is shown in Figure 2. The crystal structure confirms the presence of the oxonium salt. The six-membered ring exists in the chair conformation. The most striking feature is the planar coordination of the oxygen (the sum of the bond angles is 356.1°). The coordination of the tetrahydropyrane ligand to $[closo\text{-}B_{12}H_{11}(1-)]$ changes bond lengths of the ring only slightly. Compared to the molecular structure of gaseous tetrahydropyrane determined by electronic diffraction,[11] longer C−O(1) bonds [145.6(4), 147.3(4) pm for **3**; 142.0(2) pm for tetrahydropyrane] for **3** are found whereas C−C bonding is similar. The B−B bonds lie in the range of 174.0(5) to 180.6(5) pm proving cluster distortion from icosahedral symmetry. The B(1)−O(1) distance of **3** is quite long with 152.8(4) pm, probably due to the higher coordination number of oxygen.

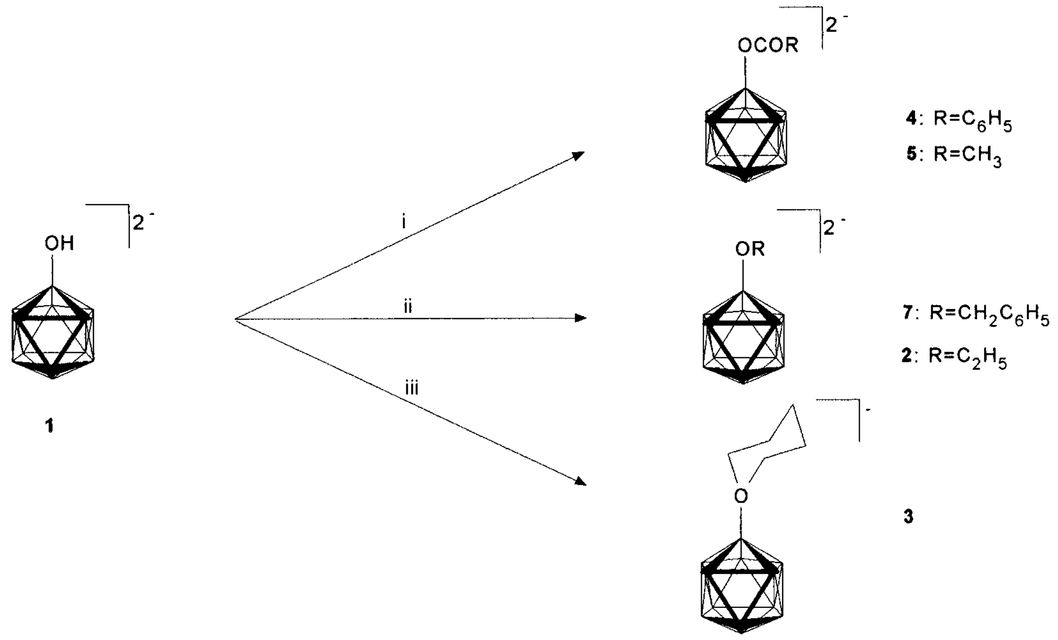
Table 7 lists the bond length and selected bond angles of the anion $[C_6H_5CO_2\text{-}closo\text{-}B_{12}H_{11}(2-)]$ (**4**), and a plot of the structure is shown in Figure 3. The three bond angles at the carboxylate carbon are 127.3(9)° [O(2)-C(1)-O(1)], 112.0(10)°

---

(10) Subrtova, V. *Collect. Czech. Chem. Commun.* **1971**, *36*, 4034.

(11) Breed, H. E.; Gundersen, G.; Seip, R. *Acta Chem. Scand.* **1979**, *A33*, 225.

Scheme 1



i) RCOCl, Py, MeCN; ii) RX, KOH, DMSO; iii) Br-$(CH_2)_5$-Br, KOH, DMSO

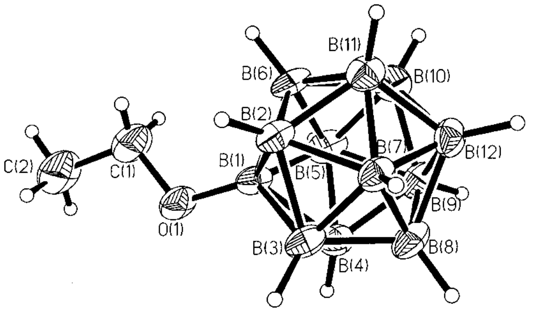


Figure 1. Structure of $[CH_3CH_2O-B_{12}H_{11}(2-)]$ (thermal ellipsoids at 50% probability).

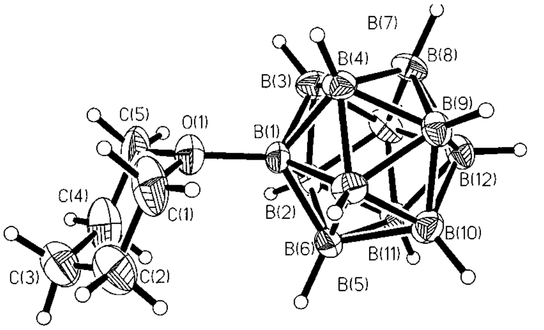


Figure 2. Structure of $[C_5H_{10}O-B_{12}H_{11}(1-)]$ (thermal ellipsoids at 50% probability).

$[C(2)-C(1)-O(1)]$, and 120.7(10)° $[O(2)-C(1)-O(1)]$, respectively. The C(1)−O(2) double bond is 119.9(10) pm long; the C(1)−O(1) single-bond is 130.2(10) pm. The B−B bond distance varies from 173.3(14) to 180.6(14) pm, again showing deviation from the icosahedral geometry. The length of the B(1)−O(1) bond [149.4(12) pm] is a little shorter than the one found in **3**. Noticeable is the difference for the B(12)−B(1)−O(1) angle (173.7°) from the ideal 180°. The B(1)−O(1)−C(1) bonding angle of 126.8(8)° of compound **4** diverges from the tetrahedral, sp^3-hybridized geometry of oxygen.

The X-ray structure of $[CH_3CO_2$-*closo*-$B_{12}H_{11}(2-)]$ (**5**) (Table 9, Figure 4) shows features similar to those of **4** with a B(1)−O(1) distance of 148.5(3) pm, bonding angles at the carboxylate

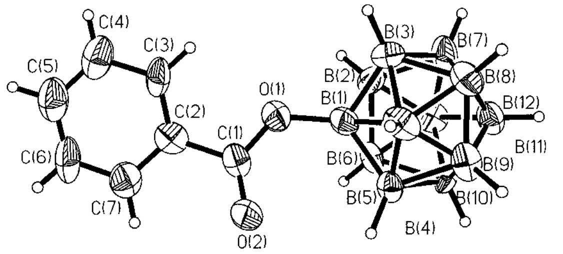


Figure 3. Structure of $[C_6H_5CO_2-B_{12}H_{11}(2-)]$ (thermal ellipsoids at 50% probability).

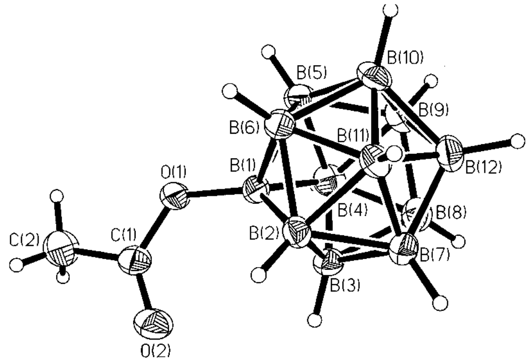


Figure 4. Structure of $[CH_3CO_2-B_{12}H_{11}(2-)]$ (thermal ellipsoids at 50% probability).

carbon of 126.9(2)° $[O(2)-C(1)-O(1)]$, 111.9(2)° $[C(2)-C(1)-O(1)]$, and 121.1(2)° $[O(2)-C(1)-O(1)]$, respectively. The B(1)−O(1)−C(1) bonding angle is 124.4(2)°, the B(12)−B(1)−O(1) angle is 174.7°, in the range of compound **4**.

IR Spectra. The vibrational frequency of the B−H bond ν(B−H) or the B−B bond ν(B−B) was not found to be sensitive to derivation of the boron cluster. For compounds **2**, **3**, **4**, **5**, and **7** ν(B−H) lies in the range of 2491 to 2477 cm^{-1}, while ν(B−B) varies from 1052 to 1045 cm^{-1}. Compared to the frequencies of $[B_{12}H_{12}]^{2-}$ [ν(B−B) = 2486, 2462 cm^{-1}; ν(B−H) = 1073, 1057 cm^{-1}][12] only slight differences were found, indicating that intracluster bonding is not perturbed by substitu-

---

(12) Srebny, H. G.; Preetz, W. *Z. Naturforsch.* **1984**, *39b*, 189.

Table 10. ^{11}B NMR Chemical Shifts (ppm) of Compounds **2**, **3**, **4**, **5**, and **7**

substituent	compd no.	B(1)	B(2−6)	B(7−11)	B(12)	ref
H		−15.3	−15.3	−15.3	−15.3	18
OC_2H_5	**2**	11.7	−11.3	−12.7	−17.5	
$OCH_2C_6H_5$	**7**	12.3	−11.2	−12.6	−17.3	
$OCOCH_3$	**5**	7.9	−10.7	−12.2	−15.4	
$OCOC_6H_5$	**4**	8.2	−10.6	−12.2	−15.4	
$O(-CH_2-)_5$	**3**	13.6	−10.7	−10.7	−15.5	

tion of the icosahedron. Similar results were obtained by comparison of the IR spectra of monohalohydrododecaborates.[12]

^{11}B NMR Spectra. Table 10 presents the chemical shifts of compounds **2**, **3**, **4**, **5**, and **7**. The spectra show a 1:5:5:1 pattern typical for monosubstituted B_{12}-derivatives. Chemical shifts of different O-substituted derivatives of **1** show only small variations. Compared to $[B_{12}H_{12}]^{2-}$ the B-1 atom is strongly effected by substitution due to the $-I$ effect of oxygen. Because of the positively charged oxygen, the B-1 of the oxonium salt **3** shows the greatest downfield shift. Since the deshielding of the $-I$ effect decreases with distance, vertices B(2−6) resonate at higher frequency than vertices B(7−11).

Discussion

The alkylation of $[HS-B_{12}H_{11}]^{2-}$, **6**, had been realized by reaction with alkyl halides in acetonitrile.[5] Since the hydroxy group of $[HO-B_{12}H_{11}]^{2-}$, **1**, is less nucleophilic than the thiol group of **6**, potassium hydroxide was necessary in the case of alkylation of **1**. As opposed to **6**, alkylation of **1** generally afforded monoalkylated derivatives. This is probably due to sterical hindrance since the B−O bond is 40 pm shorter than the B−S bond, and lower nucleophilicity of oxygen. Solely reaction with 1,5-dibromopentane gave the cyclic oxonium salt **3**, probably because entropical and kinetic reasons favor formation of the six-membered ring.

Compound **3** is very stable and can be recrystallized from water without decomposition. It can be interpreted as an adduct of tetrahydropyrane with the unknown boron hydride undecahydro-*closo*-dodecaborate(1−). ^{1}H-NMR data of **3** on the other hand are similar to the chemical shifts of protonated tetrahydropyrane. The chemical shift of the α-CH_2-group of tetrahydropyrane, for example, changed from 3.6 ppm to 5.0 ppm for its protonated form.[13] For compound **3** a downfield shift of 0.8 ppm to 4.4 ppm was found. Also the ^{13}C-NMR spectra showed a downfield shift of 12.6 ppm for the α-ring carbon of **3** (82.1 ppm), compared to tetrahydropyrane (69.5 ppm). NMR data of **3** do at least indicate a positively charged oxygen.

Compounds **2**, **3**, **4**, and **5** are the first oxygen-substituted *closo*-boron clusters whose crystal structures have been determined. The only determined X-ray structures of monosubstituted $[B_{12}H_{12}]^{2-}$ derivatives are those of triethylamine−*closo*-undecahydrododecaborate(1−) (**9**)[14] and **6**.[15] All boron clusters show distortion from the pseudo-icosahedral geometry, probably because of packing interactions. A similar variance has been observed for **9** where the B−B lengths vary from 173.0(14) to 179.6(14) pm.[14] The B(1)−O(1) distance seems to be influenced by steric interactions between boron cluster and ligand rather than by O−B π donation. The longest B(1)−O(1) distances are found for the tri-coordinated oxygen in **3**, and the esters **4** and **5**, which could be due to repulsion between the carbonyl group and the β-hydrogens of the icosahedron. Widening of the B(1)−O(1)−C(1) bonding angle can be explained by the same reason. For the ester derivatives **4** and **5** with a bonding angle of 126.8(8) and 124.4(2)° the deviation is considerable larger than for **2** [115.9(3)°]. The sum of bonding angles of the tricoordinated oxygen of **3** is 356.1°, suggesting that the oxygen has a nearly planar geometry. This has been observed for other tricoordinated oxygens attached to boron clusters, as for example in tetrahydrofurane adducts to carboranes.[16] The oxygen of the triphenyloxonium ion was found to be planar as well,[17] which has been explained by steric requirements of the oxygen ligands rather than by lone-pair effects.

Conclusions

A novel route to anions of the type $[RO-B_{12}H_{11}]^{2-}$ with R = alkyl and acyl and $[C_5H_{10}O-B_{12}H_{11}]^{-}$ has been devised by the reaction of $[HO-B_{12}H_{11}]^{2-}$ with alkyl halides and acid chlorides. X-ray structural analysis and IR spectra of compounds **2**, **3**, **4**, and **5** suggest that no change in cluster bonding takes place. Differences in the pseudoicosahedral geometry of the boron cluster are explained by cation polarisation whereas the bonding situation of the oxygen ligands differs in dependency on sterical hindrance. Reactions of **1** with compounds of possible clinical interest can now be investigated.

Acknowledgment. The authors thank Prof. Binder and his group in Stuttgart (Germany) for recording of the ^{11}B NMR spectra and Johannes Stelten for the other NMR experiments. Financial support for this work was provided by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the North Atlantic Treaty Organisation.

Supporting Information Available: Listings of crystal and structure refinement data, bond distances, bond angles, positional parameters, and anisotropic thermal parameters and structural diagrams (34 pages). Ordering information is given on any current masthead page.

IC951111F

---

(13) Olah, G. A.; Szilagyi, P. J. *J. Org. Chem.* **1970**, *36*, 1121.

(14) Mitchell, G. F.; Welch, A. J. *Acta Crystallogr.* **1986**, *C42*, 101.

(15) Shiro, M.; Aono, K.; Watanabe, H. *Chem. Ind.* **1970**, 564.

(16) (a) Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A.; Woolam, S. F. *Organometallics.* **1994**, *13*, 157. (b) Wang, Z.; Sinn, E.; Grimes, R. *Inorg. Chem.* **1985**, *24*, 834.

(17) Watkins, M. I.; Ip, W. M. I.; Olah, G. A.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 2365.

(18) Hermanek, S. *Chem. Rev.* **1992**, *92*, 325.