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A Study of the Sequential Acid-Catalyzed Hydroxylation of Dodecahydro-*closo*-dodecaborate(2−)

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The *closo*-$[B_{12}H_{12-n}(OH)_n]^{2-}$ ($n = 1-4$) ions have been synthesized by the reaction of cesium dodecahydro-*closo*-dodecaborate(2−), Cs_2**1**, with aqueous sulfuric acid. Variation of the reaction temperature, time, and acid concentration results in the stepwise introduction of from one to four hydroxyl groups. Each individual hydroxylation step proceeds regioselectively, affording only one isomer per step. Further substitution of the hydroxylated cluster preferentially takes place at a B−H vertex meta to a B−OH vertex. The *closo*-$[B_{12}H_{12-n}(OH)_n]^{2-}$ ($n = 1-4$) species, designated **2**−**5**, respectively, are characterized by one- and two-dimensional ^{11}B NMR spectroscopy, IR spectroscopy, and high-resolution fast atom bombardment (FAB) mass spectrometry. A rationale that qualitatively explains the influence of the hydroxyl group on the chemical shifts of the individual boron vertices is developed. Furthermore, the solid state structures of *closo*-$[B_{12}H_{11}(OH)]^{2-}$, **2**, and *closo*-1,7-$[B_{12}H_{10}(OH)_2]^{2-}$, **3**, are determined by X-ray diffraction. Crystallographic data are as follows: For $[MePPh_3]_2$**2**, monoclinic, space group $P2_1/n$, $a = 890.1(5)$ pm, $b = 1814(1)$ pm, $c = 1270.5(7)$ pm, $\beta = 101.66(2)°$, $Z = 2$, $R = 0.055$; for $[MePPh_3]_2$**3**, monoclinic, space group $P2_1/n$, $a = 887.6(4)$ pm, $b = 1847.2(8)$ pm, $c = 1271.1(5)$ pm, $\beta = 101.17(1)°$, $Z = 2$, $R = 0.065$. In addition, synthetic routes to O-derivatized species of the anions **2**−**5** such as *closo*-$[B_{12}H_{11}(OTiCpCl_2)]^{2-}$, **7**, *closo*-1,7-$[B_{12}H_{10}(OTiCpCl_2)_2]^{2-}$, **8**, *closo*-1,7,9-$[B_{12}H_9(OTiCpCl_2)_3]^{2-}$, **9**, *closo*-$[B_{12}H_{11}(OCONHPh)]^{2-}$, **10**, and *closo*-1,7-$[B_{12}H_{10}(OSO_2Me)_2]^{2-}$, **11**, are described. The crystal structures of **7** and **11** are determined by single-crystal X-ray diffraction. Crystallographic data are as follows: For $[MePPh_3]_2$**7**, monoclinic, space group Cc, $a = 2530.5(2)$ pm, $b = 1653.3(1)$ pm, $c = 1281.3(1)$ pm, $\beta = 118.79(2)°$, $Z = 4$, $R = 0.085$; for $[HPy]_2$**11**, monoclinic, space group $P2_1/n$, $a = 1550.9(8)$ pm, $b = 993.1(5)$ pm, $c = 1726.5(9)$ pm, $\beta = 112.36(2)°$, $Z = 4$, $R = 0.061$.

Introduction

Polyhedral *closo*-borane dianions and *closo*-carboranes are regarded as three-dimensional aromatic species.[1] Consequently, their reactivity and bonding properties have received attention because of the analogy to arenes. Electrophilic substitutions of arenes have been studied extensively, and these studies established the effect of substituents on reactivity and regiospecificity of reactions at the aromatic ring. Few investigations, however, have been conducted regarding the influence of substituents on subsequent reactions of the *closo*-$[B_{12}H_{12}]^{2-}$ cluster, **1**, which was first reported[2] in 1960 and is considered to be the parent species of polyhedral boranes and carboranes.[3]

The substitution chemistry of **1** was intensively investigated by Muetterties and co-workers.[4] Generally, the multisubstituted derivatives of **1** were characterized by IR spectroscopy and elemental analysis; hence their isomeric compositions remained undetermined. For example, anion **1** was halogenated by being reacted with either elemental fluorine, chlorine, bromine, or iodine.[5] These reactions led to a variety of mono-, poly-, and perhalogenated compounds, but, except for the mono- and the persubstituted anions, the structure and the isomeric purity of the products are unclear. Later, the synthesis of the chlorinated *closo*-$[B_{12}H_{12-n}Cl_n]^{2-}$ ($n = 1-3$) derivatives was reinvestigated and the structures of the di- and the trichloro anions were deduced from ^{11}B NMR data.[6] To date, a detailed study has been performed only for the sequential fluorination of **1**.[7] By reaction of **1** with hydrogen fluoride, the *closo*-$[B_{12}H_{12-n}F_n]^{2-}$ ($n = 2$, 4−8, 10, 12) species were obtained and characterized by ^{19}F and ^{11}B NMR spectroscopy. The solid state structure of the heptafluorinated *closo*-1,2,7,8,9,10,11-$[B_{12}H_5F_7]^{2-}$ anion was elucidated by single-crystal X-ray diffraction. To our knowledge, this is the only crystal structure of a polysubstituted derivative of **1** reported to date.

The hydroxylated derivatives of **1** may have a more intriguing chemistry because of their greater reactivity relative to the inert halogenated *closo*-$[B_{12}H_{12-n}X_n]^{2-}$ (X = F, Cl, Br, I) species.[5] Recently, we reported the perhydroxylated anion *closo*-$[B_{12}(OH)_{12}]^{2-}$, which was obtained through reaction of **1** with hydrogen peroxide.[8] The monosubstituted *closo*-$[B_{12}H_{11}(OH)]^{2-}$ anion, **2**, and the disubstituted derivative *closo*-$[B_{12}H_{10}(OH)_2]^{2-}$, **3**, have been previously described.[9] Both compounds were

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prepared by the reaction of **1** with 1-methyl-2-pyrrolidinone (NMP) and hydrochloric acid at 180 and 205 °C, respectively. Subsequent alkaline hydrolysis of the intermediates *closo*-$[B_{12}H_{12-n}(NMP)_n]^{n-2}$ ($n = 1, 2$) gave species **2** and **3**, but the yields of these two-step syntheses were low. Again, it is not known whether one isomer or an isomeric mixture of the dihydroxy species **3** was obtained. Later, Preetz and co-workers obtained **3** as the meta isomer through the reaction of **1** with ethylene glycol.[10]

The chemistry of hydroxylated derivatives of **1** has various interesting aspects that derive from the reactivity and the relative positions of the hydroxyl groups. The chemistry of the hydroxyl function of **2** has been studied previously in reactions with electrophiles such as alkyl halides and acyl chlorides.[11] Alkylation and acylation of the hydroxyl function of **2** occurs. The reaction of **2** with 1,5-dibromopentane, however, afforded the tetrahydropyran derivative *closo*-$[B_{12}H_{11}(OC_5H_5)]^-$.

This paper reports the sulfuric acid catalyzed hydroxylation of **1** yielding *closo*-$[B_{12}H_{12-n}(OH)_n]^{2-}$ ($n = 1-4$) anions, **2**−**5**, as isomerically pure species. One- and two-dimensional ^{11}B NMR spectroscopy revealed the degree of hydroxylation as well as the isomeric relationship of the polyhydroxylated species. Also investigated were the reactions of the anions **2**−**5** with electrophiles such as methanesulfonyl chloride, phenyl isocyanate, and titanocene dichloride, which led to novel O-derivatized *closo*-$[B_{12}H_{12}]^{2-}$ species.

Experimental Section

General Considerations. The ^{11}B NMR data (160 MHz) obtained on a Bruker ARX-500 spectrometer are referenced to external $BF_3 \cdot Et_2O$. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX-400 spectrometer, and the NMR data of the cations are not reported. Infrared data were obtained from KBr pellets. Melting points were determined in a sealed tube and are uncorrected. High-resolution fast atom bombardment (FAB) mass spectra were obtained using a VG-ZAB spectrometer.

Synthesis of Bis(methyltriphenylphosphonium) Hydroxy-undecahydro-*closo*-dodecaborate(2−), $[MePPh_3]_2$2. A 0.50 g (1.23 mmol) sample of Cs_2**1** was suspended in 12 mL of water. Cautiously, 8 mL of 95.7% sulfuric acid was added. Evolution of a gas was observed. The suspension was heated at 90 °C for about 45 min, leading to a clear solution (To determine the end of the reaction, it was monitored by ^{11}B NMR spectroscopy). The solution was slowly added with stirring to a slurry of 20 g of $CaCO_3$ in 200 mL of water. When the suspension was neutralized, the $CaSO_4$ was removed by filtration. The volume of the filtrate was reduced to about 100 mL, and 1.80 g (5.04 mmol) of methyltriphenylphosphonium bromide was added. The resulting precipitate was separated by filtration and dried in a desiccator. The yield of $[MePPh_3]_2$**2** was 0.68 g (0.95 mmol, 78%). The product was recrystallized from acetonitrile/ethanol (mp = 320 °C). HRMS (negative FAB) for $[MePPh_3$**2**$]-$ (m/z): calcd, 435.3236; found, 435.3231. ^{11}B NMR (DMSO): 6.9 (s, B1); −14.4 (d, B2−5, $^1J_{BH}$ = 108.5 Hz); −16.6 (d, B6−11, $^1J_{BH}$ = 119.7 Hz); −22.7 (d, B12, $^1J_{BH}$ = 119.5 Hz). IR [cm^{-1}]: 3653 (sharp, ν O−H), 2489 (ν B−H).

Synthesis of Bis(methyltriphenylphosphonium) 1,7-Dihydroxy-decahydro-*closo*-dodecaborate(2−), $[MePPh_3]_2$3. A 0.50 g (1.23 mmol) sample of Cs_2**1** was suspended in 10 mL of water. Cautiously, 10 mL of 95.7% sulfuric acid was added. Evolution of a gas was observed. The suspension was heated at 90 °C for 90 min, leading to a clear solution. The solution was slowly added with stirring to a slurry of 20 g of $CaCO_3$ in 200 mL of water. When the suspension was neutralized, the $CaSO_4$ was removed by filtration. The volume of the filtrate was reduced to about 50 mL and filtered, and 1.80 g (5.04 mmol) of methyltriphenylphosphonium bromide was added. Immediately a solid precipitated. After cooling in a refrigerator overnight, the solid was separated by filtration and dried in a desiccator. The yield of $[MePPh_3]_2$**3** was 0.56 g (0.77 mmol, 63%). The product was recrystallized from acetonitrile/ethanol (mp = 305 °C). HRMS (negative FAB) for $[MePPh_3$**3**$]^-$ (m/z): calcd, 451.3185; found, 451.3192. ^{11}B NMR (DMSO): 3.4 (s; B1, B7); −15.2 (d; B2, B3; $^1J_{BH}$ = 108.8 Hz); −17.4 (d; B4, B6, B8, B11; $^1J_{BH}$ = 108.5 Hz); −20.0 (d; B9, B10; $^1J_{BH}$ = 119.1 Hz); −23.6 (d; B5, B12; $^1J_{BH}$ = 113.9 Hz). IR [cm^{-1}]: 3653, 3645 (sharp, ν O−H), 2486, 2452 (ν B−H).

Synthesis of Bis{bis[(triphenylphosphoranylidene)ammonium]} 1,7,9-Trihydroxy-nonahydro-*closo*-dodecaborate(2−), $[PPN]_2$4. A 0.50 g (1.23 mmol) sample of Cs_2**1** was suspended in 10 mL of water. Cautiously, 10 mL of 95.7% sulfuric acid was added. Evolution of a gas was observed. The suspension was heated at 110 °C for 20 h, leading to a clear solution. The solution was slowly added with stirring to a slurry of 20 g of $CaCO_3$ in 100 mL of water. When the suspension was neutralized, the $CaSO_4$ was removed by filtration. The volume of the filtrate was reduced to about 30 mL and filtered. To the filtrate was added 1.41 g (2.46 mmol) of PPN-Cl, and the suspension was stirred overnight. The resulting precipitate was separated by filtration and dried in a desiccator. The product was recrystallized from ethanol (mp = 332 °C). The yield of $[PPN]_2$**4** was 1.10 g (0.87 mmol, 71%). HRMS (negative FAB) for $[PPN$**4**$]^-$ (m/z): calcd, 728.3851; found, 728.3851. ^{11}B NMR (DMSO): 0.8 (s; B1, B7, B9); −18.0 (d; B3, B4, B8; $^1J_{BH}$ = 109.3 Hz); −20.7 (d; B6, B10, B11; $^1J_{BH}$ = 113.4 Hz); −24.5 (d; B2, B5, B12; $^1J_{BH}$ = 111.7 Hz). IR [cm^{-1}]: 3457 (broad, ν O−H), 2474 (ν B−H).

Synthesis of Cesium 1,2,8,10-Tetrahydroxy-octahydro-*closo*-dodecaborate(2−), $Cs_2$5. A 0.50 g (1.23 mmol) sample of $Cs_2$1 was suspended in 8 mL of water. Cautiously, 12 mL of 95.7% sulfuric acid was added. Evolution of a gas was observed. The suspension was heated at 175 °C for 5 h, leading to a clear solution. The solution was diluted with water and neutralized by the addition of about 70 g of $Ba(OH)_2 \cdot 8H_2O$. When the suspension was neutralized, the $BaSO_4$ was removed by filtration. The filtrate was evaporated to yield 0.25 g (0.53 mmol, 43%) of Cs_2**5** (mp > 350 °C). HRMS (negative FAB) for $[$**5**$]^-$ (m/z): calcd, 206.1926; found, 206.1926. ^{11}B NMR (H_2O): −2.0 (s; B1, B2); −3.6 (s; B8, B10); −20.7 (d; B4, B5, B7, B11; $^1J_{BH}$ = 97.4); −25.0 (d; B3, B6, B9, B12; $^1J_{BH}$ = 95.0 Hz). IR [cm^{-1}]: 3419 (broad, ν O−H), 2485 (ν B−H).

Synthesis of Bis(1-methylpyrrolidinonium)-decahydro-*closo*-dodecaborate(2*B*−*O*), 6. 6 was synthesized according to ref 9. ^{11}B NMR (DMSO): 4.4 (s); −16.6 (d); −19.9 (d).

Synthesis of Cesium 1,7-Dihydroxy-decahydro-*closo*-dodecaborate(2−), $Cs_2$3 from 6. Cs_2**3** was synthesized from **6** according to ref 9. Its ^{11}B NMR data are the same as for **3** obtained by the method originated here.

Synthesis of Bis(methyltriphenylphosphonium) Dichloro(cyclopentadienyl)titaniumoxy-undecahydro-*closo*-dodecaborate(2−), $[MePPh_3]_2$7. A 0.77 g (1.07 mmol) sample of $[MePPh_3]_2$**2** and 0.53 g (2.14 mmol) of Cp_2TiCl_2 were dissolved in dry acetonitrile under nitrogen. The solution was refluxed for 24 h and then added to dry toluene. The resulting precipitate was recrystallized from dry acetonitrile (mp = 273 °C dec) to give yellow crystals of $[MePPh_3]_2$**7**. The yield of 7 was 0.72 g (0.80 mmol, 75%). ^{11}B NMR (MeCN): 11.8 (s, B1); −14.2 (d, B2−5); −16.1 (d, B6−11); −19.6 (d, B12). ^1H NMR (MeCN-d_3): 6.65 (s, 5 H, Cp). ^{13}C NMR (MeCN-d_3): 118.1 (Cp).

Synthesis of Bis(methyltriphenylphosphonium) 1,7-Bis[dichloro-(cyclopentadienyl)titaniumoxy]-decahydro-*closo*-dodecaborate-(2−), $[MePPh_3]_2$8. A 0.30 g sample (0.41 mmol) of $[MePPh_3]_2$**2** and 0.41 g (1.65 mmol) of Cp_2TiCl_2 were dissolved in dry acetonitrile (20 mL) under nitrogen. The solution was refluxed for 24 h. The volume of the resulting solution was reduced, dry toluene (20 mL) was added, and the solution was cooled overnight in a refrigerator. The precipitated syrup was again dissolved in dry acetonitrile (5 mL) and precipitated by dry toluene (20 mL). The syrup was then dissolved in dichloromethane, the solution was filtered, and the filtrate was evaporated to give $[MePPh_3]_2$**8** as a yellow solid. The yield of **8** was 0.18 g (0.16 mmol, 40%). ^{11}B NMR (MeCN): 9.1 (s, B1, B7); −15.0 (d, B2, B3);

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Table 1. Details of Crystallographic Data Collection for Anions **2**, **3**, **7**, and **11**

	$[MePPh_3]_2$**2**	$[MePPh_3]_2$**3**	$[MePPh_3]_2$**7**	$[HPy]_2$**11**
formula	$C_{38}H_{48}B_{12}OP_2$	$C_{38}H_{48}B_{12}O_2P_2$	$C_{43}H_{52}B_{12}Cl_2OP_2Ti$	$C_{12}H_{28}B_{12}N_2O_6S_2$
fw	712.48	728.48	895.3	490.22
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	Cc	$P2_1/n$
a (pm)	890.1(5)	887.6(4)	2530.5(2)	1550.9(8)
b (pm)	1814(1)	1847.2(8)	1653.3(1)	993.1(5)
c (pm)	1270.5(7)	1271.1(5)	1281.3(1)	1726.5(9)
β (deg)	101.66(2)	101.17(1)	118.79(2)	112.36(2)
V (nm^3)	2.009	2.046	4.698	2.459
Z	2	2	4	4
μ (cm^{-1})	1.30	1.35	3.5	2.32
R^a	0.055	0.065	0.085	0.061
$R_w{}^b$	0.069	0.084	0.248	0.079

^{a} $R = \sum||F_o| - |F_c||/|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]^{1/2}$.

−16.5 (d, B4, B6, B8, B11); −18.6 (d, B9, B10); −20.2 (d, B5, B12). ^{1}H NMR (MeCN-d_3): 6.66 (s, 10 H, Cp). ^{13}C NMR (MeCN-d_3): 118.3 (Cp).

Synthesis of Bis{bis[(triphenylphosphoranylidene)ammonium]} 1,7,9-Tris[dichloro(cyclopentadienyl)titaniumoxy]-nonahydro-*closo*-dodecaborate(2−), [PPN]$_2$9. A 0.50 g sample (0.40 mmol) of [PPN]$_2$**4** and 0.34 g (1.38 mmol) of Cp_2TiCl_2 were dissolved in dry acetonitrile under nitrogen. The solution was refluxed for 24 h. The acetonitrile was reduced to about 5 mL, and dry toluene (20 mL) was added. The red solution was cooled overnight in a refrigerator. The resulting precipitate was again dissolved in a small amount of acetonitrile and precipitated by toluene. The obtained syrup was dissolved in dichloromethane, the solution was filtered, and the filtrate was evaporated to give a yellow powder of [PPN]$_2$**9**. The yield of **9** was 0.35 g (0.20 mmol, 51%). ^{11}B NMR (MeCN): 6.8 (s; B1, B7, B9); −16.9 (d; B3, B4, B8); −18.8 (d; B6, B10, B11); −20.7 (d; B2, B5, B12). ^{1}H NMR (MeCN-d_3): 6.60 (s, 15 H, Cp). ^{13}C NMR (MeCN-d_3): 118.4 (Cp).

Synthesis of Bis(trimethylammonium) [(Phenylamino)carbonyloxy]-undecahydro-*closo*-dodecaborate(2−), [HN(Me)$_3$]$_2$10. A 0.50 g (0.78 mmol) sample of $[N(n\text{-}C_4H_9)_2]_2$**2** and 0.17 mL (1.29 mmol) of phenyl isocyanate were refluxed in dry pyridine (10 mL) under nitrogen for 24 h. All volatiles were removed in vacuo, and the residue was dissolved in ethanol (10 mL). Trimethylamine hydrochloride (0.20 g) was added to precipitate a solid, which was redissolved by heating and addition of a small amount of acetonitrile. The solution was cooled, and [HN(Me)$_3$]$_2$**10** (mp = 258 °C dec) crystallized out. The yield of **10** was 0.24 g (0.60 mmol, 78%). ^{11}B NMR (DMSO): 4.0 (s; B1); −15.4 (d; B2−5); −16.3 (d; B7−11); −19.5 (d; B12). ^{1}H NMR (DMSO-d_6): 8.68 (s, 1 H, CONH); 7.35−6.84 (m, 5 H, Ph). ^{13}C NMR (DMSO-d_6): 153.6 (C=O); 140.9 (Ph, C1); 129.0 (Ph, C3); 121.7 (Ph, C4); 117.9 (Ph, C2). IR [cm^{-1}]: 3360, 3107, 3027 (m, ν CON−H), 2487 (ν B−H), 1653 (m, Amid I), 1537 (m, Amid II).

Synthesis of Dipyridinium 1,7-Bis(methanesulfonyloxy)-decahydro-*closo*-dodecaborate(2−), [HPy]$_2$11. A 1.20 g (2.73 mmol) sample of Cs$_2$**3** and 2.0 mL (25.8 mmol) of methanesulfonyl chloride were refluxed for 24 h in dry pyridine (20 mL) under nitrogen. All volatiles were removed in vacuo, and 25 mL of water was added to the resulting solid. The suspension was filtered and the filtrate was cooled overnight to precipitate 0.45 g (0.92 mmol, 34%) of [HPy]$_2$**11** (mp = 168 °C). ^{11}B NMR (MeCN): 2.1 (s; B1, B7); −16.4 (d; B2, B3); −17.3 (d; B4, B6, B8, B11); −18.6 (d; B9, B10); −20.8 (d; B5, B12). ^{1}H NMR (MeCN-d_3): 2.91 (s, 6 H, Me). ^{13}C NMR (MeCN-d_3): 37.9 (Me).

X-ray Crystallography. Table 1 summarizes the crystallographic data pertaining to compounds [MePPh$_3$]$_2$**2**, [MePPh$_3$]$_2$**3**, [MePPh$_3$]$_2$**7**, and [HPy]$_2$**11**.

Crystal Structure Determination of [MePPh$_3$]$_2$2. A colorless crystal of [MePPh$_3$]$_2$2, obtained from acetonitrile/diethyl ether, was placed on a fiber and mounted on a Huber diffractometer. Unit cell parameters were determined from a least-squares fit of 51 accurately centered reflections (9.3° < 2θ < 20.6°). Data were collected at 25 °C in the θ−2θ scan mode. Of the 5624 unique reflections measured, 2473 were considered observed [$I > 3\sigma(I)$] and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction and absorption. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculations and full-matrix least-squares refinement; SHELX76 (Sheldrick), a crystal structure package; SHELX86 (Sheldrick), a crystal structure solution package; and ORTEP (Johnson).

Atoms were located by use of heavy atom methods. All non-hydrogen atoms were refined with anisotropic parameters. The unit cell contains four cations and two centrosymmetric anions, although the anion **2** is noncentrosymmetric. The oxygen atom has been included at half occupancy. The hydrogen atom bonded to this oxygen was not located. All other hydrogen atoms have been refined. All phenyl groups were included as rigid C$_6$ hexagons, C−C = 139.5 pm, angles 120°. Methyl hydrogen atoms were included in located positions, C−H 100 pm, H−C−H 109.5°. Hydrogen atoms were assigned isotropic displacement values based approximately on the value of the attached atom. Scattering factors for hydrogen were obtained from ref 12.

Crystal Structure Determination of [MePPh$_3$]$_2$3. A colorless crystal of [MePPh$_3$]$_2$**3**, obtained from ethanol/water, was placed on a fiber and mounted on a Huber diffractometer. Unit cell parameters were determined from a least-squares fit of 35 accurately centered reflections (9.6° < 2θ < 20.2°). Data were collected at 25 °C in the θ−2θ scan mode. Of the 3838 unique reflections measured, 2034 were considered observed [$I > 3\sigma(I)$] and were used in the subsequent structure analysis that was performed as described for **2**.

Atoms were located by use of direct methods. All non-hydrogen atoms were refined with anisotropic parameters. The unit cell contains four cations and two centrosymmetric anions, although the anion **3** is noncentrosymmetric. One oxygen atom has been included at half occupancy. The other oxygen atom is further disordered and has been refined at 0.37 and 0.13 occupancy for O(1) and O(4′), respectively. The hydrogen atoms bonded to these oxygens were not located. All other hydrogen atoms have been refined.

Crystal Structure Determination of [MePPh$_3$]$_2$7. A yellow crystal of [MePPh$_3$]$_2$**7**, obtained from diethyl ether/acetonitrile, was placed on a fiber and mounted on a Huber diffractometer. Unit cell parameters were determined from a least-squares fit of 41 accurately centered reflections (15.5° < 2θ < 39.0°). Data were collected at 25 °C in the θ−2θ scan mode. Of the 3228 unique reflections measured, 2355 were considered observed [$I > 2\sigma(I)$] and were used in the subsequent structure analysis that was performed as described for **2**. Atoms were located by use of direct methods. All non-hydrogen atoms were refined with anisotropic parameters.

Crystal Structure Determination of [HPy]$_2$11. A crystal of [HPy]$_2$**11**, obtained from water, was placed on a fiber and mounted on a Huber diffractometer. Unit cell parameters were determined from a least-squares fit of 51 accurately centered reflections (9.6° < 2θ < 20.1°). Data were collected at 25 °C in the θ−2θ scan mode. Of the 5446 unique reflections measured, 3226 were considered observed [$I > 3\sigma(I)$] and were used in the subsequent structure analysis that was performed as described for **2**. Atoms were located by use of direct methods. All non-hydrogen atoms were refined with anisotropic parameters.

Results

Heating Cs$_2$**1** for 40 min in 38% sulfuric acid at 90 °C afforded, after workup, crystalline [MePPh$_3$]$_2$**2** in 78% yield. The IR spectrum of **2** contains a sharp peak at 3653 cm^{-1} that represents the O−H bond vibration. The ^{11}B{^{1}H} NMR spectrum of **2** displays four signals at 6.9, −14.4, −16.6, and −22.7 ppm in the 1:5:5:1 ratio that is typical for monosubstituted B$_{12}$ derivatives. The signal at 6.9 ppm is assigned to the substituted or *ipso*-boron atom, because it is a singlet in the ^{11}B NMR spectrum. The crystal structure of **2** (Figure 1) was obtained from its methyltriphenylphosphonium salt.

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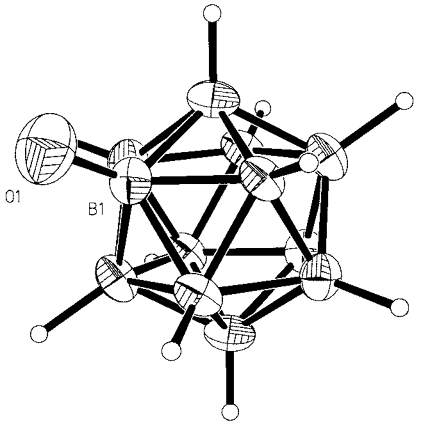


Figure 1. ORTEP representation (30% ellipsoids) of anion **2**.

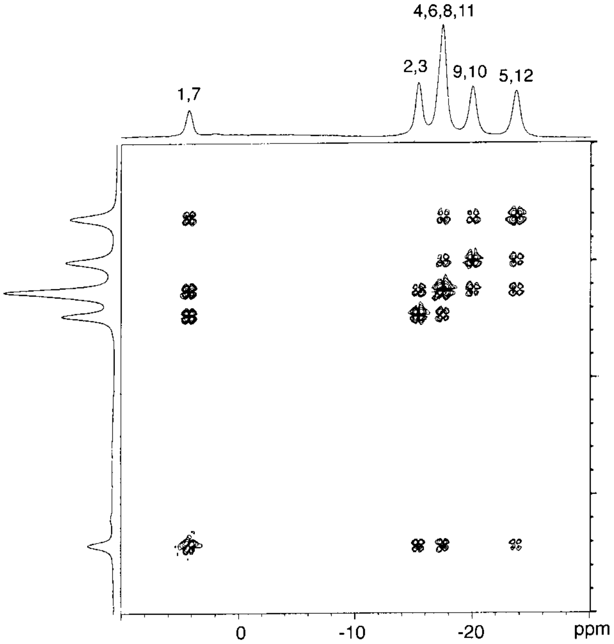


Figure 2. Two-dimensional ^{11}B NMR spectrum of anion **3**.

Stirring Cs$_2$**1** in 48% sulfuric acid at 90 °C for 90 min resulted in a disubstituted derivative, **3**, as judged by its FAB mass spectrum. Two sharp peaks at 3653 and 3645 cm^{-1} in the IR spectrum of **3** are assigned to the O−H bond vibrations. The ^{11}B{^{1}H} NMR spectrum consists of five signals in the ratio 2:2:4:2:2 at 3.4, −15.2, −17.4, −20.0, and −23.6 ppm, and the ^{11}B NMR spectrum indicates a singlet at 3.4 ppm and four doublets. In general, three (1,2 or ortho; 1,7 or meta; 1,12 or para) isomers of **3** are possible. Both the ortho and the meta isomer have C_{2v} symmetry, which would result in five peaks in the ^{11}B NMR spectrum, whereas the para isomer has C_{5v} symmetry (two peaks in the ^{11}B NMR). Because five signals are observed, the compound is either the ortho or the meta isomer. The structure of **3** is determined from its two-dimensional ^{11}B NMR spectrum (Figure 2). The singlet attributable to the B−OH vertices at 3.4 ppm has three cross peaks with the signals of the B−H vertices. This is consistent with the structure of the meta isomer, whereas one would expect two cross peaks for the ortho isomer. The two-dimensional ^{11}B NMR spectrum enabled us as well to assign the other four B−H signals [−15.2 ppm B(2,3); −17.4 ppm B(4,6,8,11); −20.0 ppm B(9,10); −23.6 ppm B(5,12)]. The crystal structure of **3** was obtained from its methyltriphenylphosphonium salt (Figure 3). The *closo*-[B$_{12}$H$_{10}$(OH)$_2$]$^{2-}$ anion was prepared by Muetterties's method, as well.[9] The ^{11}B NMR data characteristic of this compound are identical to those found for **3** obtained by the method described here.

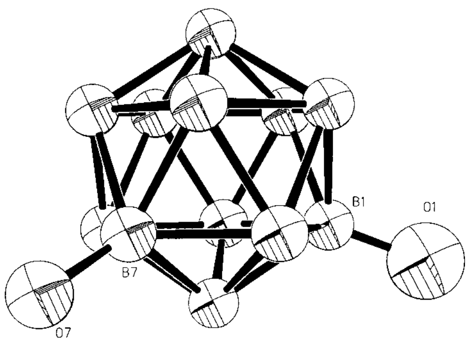


Figure 3. ORTEP representation (30% ellipsoids) of anion **3**.

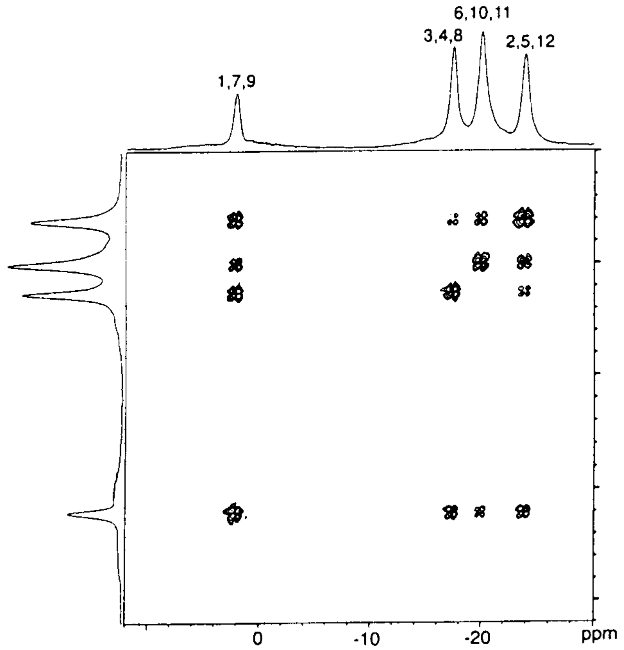


Figure 4. Two-dimensional ^{11}B NMR spectrum of anion **4**.

Heating Cs$_2$**1** at 110 °C in 48% sulfuric acid for 20 h afforded a trisubstituted derivative *closo*-[B$_{12}$H$_9$(OH)$_3$]$^{2-}$, **4**. A broad signal at 3457 cm^{-1} in the IR spectrum of **4** is recorded for ν(O−H). The ^{11}B{^{1}H} NMR spectrum of **4** consists of four signals at 0.8, −18.0, −20.7, and −24.5 ppm in a 3:3:3:3 ratio. The singlet at 0.8 ppm is assigned to the three isochronic *ipso*-boron atoms. Five trisubstituted B$_{12}$ isomers are possible, but only the 1,2,3 and the 1,7,9 isomer have C_{3v} symmetry that is in accordance with the one-dimensional ^{11}B NMR spectrum. The structure of **4** is elucidated by its two-dimensional ^{11}B NMR spectrum (Figure 4). The singlet of the B−OH vertices has cross peaks with each of the three signals of the B−H vertices, which corresponds to the 1,7,9 isomer. For the 1,2,3 isomer, one would expect to observe a single cross peak. The signals of the B−H vertices are also assigned [−18.0 ppm B(3,4,8); −20.7 ppm B(6,10,11); −24.5 ppm B(2,5,12)].

Stirring Cs$_2$**1** in 57% sulfuric acid at 175 °C for 5 h yielded the tetrasubstituted *closo*-[B$_{12}$H$_8$(OH)$_4$]$^{2-}$ anion, **5**, as determined by its FAB mass spectrum. In the ^{11}B{^{1}H} NMR spectrum four signals at −0.7, −2.3, −20.4, and −25.2 ppm in a 2:2:4:4 ratio are present. The two high-field singlets appear as doublets in the hydrogen-coupled ^{11}B NMR spectrum. Because the trisubstituted anion **4** is observed by ^{11}B NMR spectroscopy as an intermediate in the synthesis of **5**, only three tetrasubstituted

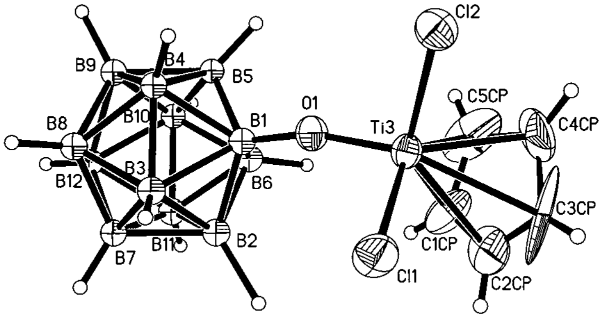


Figure 5. ORTEP representation (30% ellipsoids) of anion **7**.

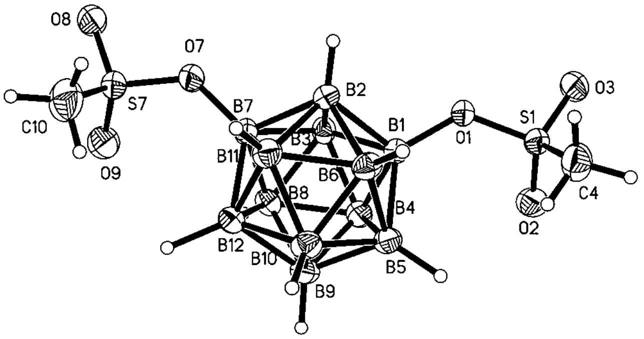


Figure 6. ORTEP representation (30% ellipsoids) of anion **11**.

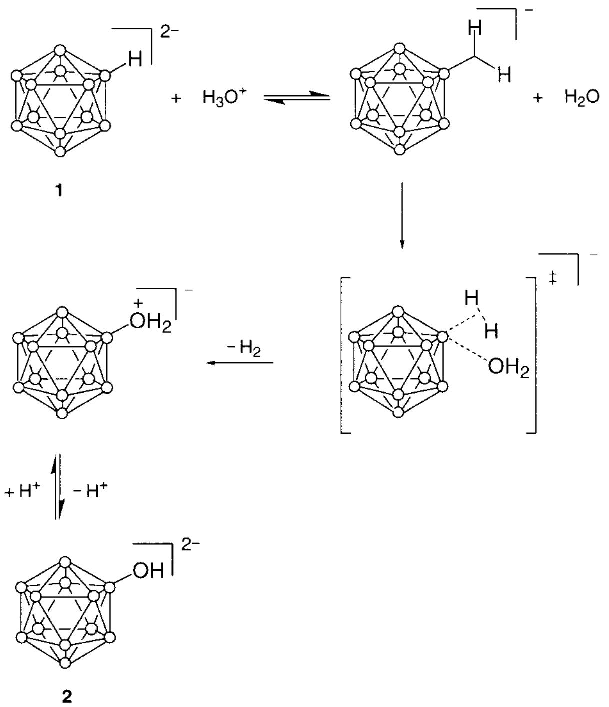
isomers are possible: the *closo*-1,2,8,10-$[B_{12}H_8(OH)_4]^{2-}$ (C_{2v}), the *closo*-1,2,4,12-$[B_{12}H_8(OH)_4]^{2-}$ (C_s), and the *closo*-1,2,4,-10-$[B_{12}H_8(OH)_4]^{2-}$ (C_s) isomer. Of these, only the 1,2,8,10 isomer has two groups of two isochronic B−OH vertices as observed in the ^{11}B NMR spectrum of **5**. Its ^{11}B{^{1}H} NMR spectrum should display three signals for the B−H vertices in a 2:2:4 ratio. Only two doublets are observed and attributable to the boron atoms bound to hydrogen, because two signals accidentally overlap. Furthermore, no cross peaks are observed in the two-dimensional ^{11}B NMR spectrum of **5** between the two sets of B−OH vertices. Therefore compound **5** is the *closo*-1,2,8,10-$[B_{12}H_8(OH)_4]^{2-}$ isomer, because the signals of the *ipso*-boron atoms of both the 1,2,4,12 and the 1,2,4,10 isomer would have cross peaks with each other. The assignment of the individual boron atoms to the peaks in the ^{11}B NMR spectrum was not accomplished, despite the acquisition of two-dimensional ^{11}B NMR data.

Heating anion **2** with titanocene dichloride in acetonitrile at the reflux temperature yielded *closo*-$[B_{12}H_{11}(OTiCpCl_2)]^{2-}$, **7**, in 75% yield. Its ^{11}B NMR spectrum displays the characteristic 1:5:5:1 pattern of a monosubstituted B_{12} cluster. The structure of the titanium species, which was elucidated by single-crystal X-ray analysis (Figure 5), contains only one Cp ligand. The second Cp ligand and not a chloride anion has been displaced by the hydroxyborate cage. The species *closo*-1,7-$[B_{12}H_{10}(OTiCpCl_2)_2]^{2-}$, **8**, and *closo*-1,7,9-$[B_{12}H_9(OTiCpCl_2)_3]^{2-}$, **9**, were prepared accordingly from **3** and **4**, respectively. The reaction of **2** with phenyl isocyanate in pyridine afforded the derivative *closo*-$[B_{12}H_{11}(OCONHPh)]^{2-}$, **10**, as determined by its IR, ^{11}B, and ^{1}H NMR data. Finally, the heating of **3** with methanesulfonyl chloride in pyridine resulted in *closo*-1,7-$[B_{12}H_{10}(OSO_2Me)_2]^{2-}$, **11**, as confirmed by NMR data and X-ray analysis (Figure 6).

Discussion

A convenient method for the hydroxylation of **1** has been established by reacting it with aqueous sulfuric acid. This method is superior to the NMP route described by Muetterties et al.,[9] because it is a high-yield one-step reaction that employs easily acquired chemicals and provides an easily controlled preparation of polyhydroxylated species. The monosubstituted anion, **2**, was synthesized in 78% yield. The dihydroxylation of **1** proceeded regioselectively to give the meta isomer.

Scheme 1. Mechanism of the Acid-Catalyzed Hydroxylation of *closo*-$[B_{12}H_{12}]^{2-}$ by Water



In the reaction of **1** with NMP under acidic conditions, we found that the second carbonyl oxygen of NMP attacks the meta position as well. Repetition of Muetterties's synthesis[9] of **3** proved it to be the meta isomer by comparison of its ^{11}B NMR spectrum with that of **3** synthesized by the hydroxylation with sulfuric acid.

The hydroxylation of *closo*-1,7-$[B_{12}H_{10}(OH)_2]^{2-}$ may lead to four trisubstituted anions (1,2,4; 1,2,8; 1,7,9; 1,2,9) with the statistical probabilities 2:4:2:2. Although the formation of the 1,7,9 isomer is only 20% probable, it is the only product formed. The third hydroxyl group favors the position meta to both of the substituted boron atoms. Placing a fourth hydroxyl substituent in the cluster surface may result in the formation of three possible isomers (1,2,7,10; 1,2,4,12; 1,2,8,10). In the first case, the fourth hydroxyl function is attached to the boron atom that is ortho/ortho/meta to the other three B−OH vertices. In the second isomer, the relevant boron atom is ortho/ortho/para to the *ipso*-boron atoms. In the third possible anion, the fourth B−OH vertex is ortho/meta/meta to the hydroxylated boron vertices. The latter *closo*-1,2,8,10-$[B_{12}H_8(OH)_4]^{2-}$ isomer has the most meta contacts and is formed exclusively.

It is assumed that the hydroxylation of the aromatic B_{12} cluster proceeds via an acid-catalyzed mechanism. First (Scheme 1), sulfuric acid protonates dianion **1** to give *closo*-$[B_{12}H_{13}]^-$. This step reduces the charge of the cluster to −1 and generates a good leaving group, dihydrogen. The second step involves the nucleophilic attack of a water oxygen on the protonated species displacing molecular hydrogen. Further hydroxylation occurs accordingly. The proposed mechanism for the acid-catalyzed hydroxylation of the B_{12} cluster is supported by the observation

Table 2. Selected Bond Lengths [pm] for Anion **2**[a]

B(1)−B(4)	176.8(6)	B(1)−B(5)	177.6(6)
B(1)−B(2)	176.3(6)	B(1)−B(6)	177.5(6)
B(2)−B(6)	177.4(6)	B(2)−B(3)	178.0(6)
B(4)−B(5)	178.1(6)	B(3)−B(4)	175.9(6)
B(5)−B(3) ,2	178.6(6)	B(5)−B(6)	177.9(6)
B(2)−B(4) ,2	178.1(6)	B(6)−B(3) ,2	177.1(6)
B(3)−B(5) ,2	178.6(6)	B(2)−B(5) ,2	177.3(6)
B(4)−B(2) ,2	178.1(6)	B(3)−B(6) ,2	177.1(6)
B(5)−B(2) ,2	177.3(6)	B(4)−B(6) ,2	177.5(6)
B(6)−B(4) ,2	177.5(6)		
B(1)−O(1)	142.6(8)		

[a] Atoms denoted by ,2 are symmetry-related.

Table 3. Selected Bond Lengths [pm] for Anion **3**[a]

B(1)−B(4)	176.4(9)	B(3)−B(7)	175.1(9)
B(1)−B(2)	177.6(9)	B(1)−B(6)	178.2(9)
B(2)−B(6)	176.1(9)	B(2)−B(3)	178.5(9)
B(2)−B(7)	177.1(9)	B(3)−B(4)	179.6(9)
B(1)−B(3)	175.3(9)	B(7)−B(4) ,2	177.5(9)
B(2)−B(4) ,2	175.0(9)	B(6)−B(3) ,2	178.1(9)
B(7)−B(1) ,2	178.1(9)	B(7)−B(6) ,2	177.3(9)
B(4)−B(2) ,2	175.0(8)	B(4)−B(7) ,2	177.5(9)
B(1)−B(7) ,2	178.1(9)	B(6)−B(7) ,2	177.3(9)
B(3)−B(6) ,2	178.1(9)	B(4)−B(6) ,2	177.1(9)
B(6)−B(4) ,2	177.1(9)		
B(1)−O(1)	138(1)	B(7)−O(7)	145(1)
B(4)−O(4′)	134(3)		

[a] Atoms denoted by ,2 are symmetry-related.

Table 4. Selected Bond Lengths [pm] for Anion **7**

B(1)−B(2)	178(2)	B(1)−B(3)	181(2)
B(1)−B(5)	178(2)	B(1)−B(6)	182(2)
B(2)−B(11)	181(2)	B(2)−B(6)	179(2)
B(3)−B(8)	179(2)	B(3)−B(4)	179(2)
B(4)−B(9)	177(2)	B(4)−B(5)	175(2)
B(5)−B(10)	176(2)	B(5)−B(6)	180(2)
B(7)−B(8)	174(2)	B(6)−B(10)	177(2)
B(8)−B(9)	180(2)	B(7)−B(11)	176(2)
B(9)−B(12)	180(2)	B(8)−B(12)	177(2)
B(11)−B(12)	174(2)	B(10)−B(11)	179(2)
B(1)−B(4)	177(2)	B(2)−B(7)	179(2)
B(4)−B(8)	179(2)	B(3)−B(7)	174(2)
B(5)−B(9)	174(2)	B(6)−B(11)	177(2)
B(9)−B(10)	178(2)	B(7)−B(12)	177(2)
B(10)−B(12)	180(2)		
B(1)−O(1)	145(2)	Ti(3)−Cl(1)	227.2(5)
Ti(3)−Cl(2)	228.3(5)	Ti(3)−O(1)	171(1)
Ti(3)−C(1)	232(2)	Ti(3)−C(2)	236(3)
Ti(3)−C(3)	242(3)	Ti(3)−C(4)	234(3)
Ti(3)−C(5)	231(3)		

Table 5. Selected Bond Lengths [pm] for Anion **11**

B(1)−B(4)	176.8(6)	B(3)−B(7)	178.1(6)
B(1)−B(2)	176.3(6)	B(1)−B(6)	177.1(6)
B(2)−B(6)	176.2(7)	B(2)−B(3)	180.2(6)
B(2)−B(7)	178.3(6)	B(3)−B(4)	178.4(6)
B(1)−B(3)	176.1(6)	B(2)−B(11)	177.2(6)
B(3)−B(8)	178.4(6)	B(4)−B(9)	177.8(6)
B(5)−B(10)	178.8(6)	B(7)−B(8)	175.8(6)
B(8)−B(9)	177.0(7)	B(9)−B(12)	179.0(6)
B(11)−B(12)	178.4(6)	B(1)−B(5)	176.7(6)
B(4)−B(5)	178.7(6)	B(5)−B(6)	179.2(6)
B(6)−B(10)	178.7(7)	B(7)−B(11)	177.6(6)
B(8)−B(12)	177.7(6)	B(10)−B(11)	178.0(7)
B(4)−B(8)	178.2(6)	B(5)−B(9)	178.7(6)
B(6)−B(11)	177.3(7)	B(7)−B(12)	176.1(6)
B(9)−B(10)	178.5(7)	B(10)−B(12)	178.7(6)
B(1)−O(1)	149.5(5)	B(7)−O(7)	149.2(5)
S(1)−O(1)	153.1(3)	S(1)−O(2)	153.1(3)
S(1)−O(3)	142.7(3)	S(7)−O(7)	152.0(3)
S(7)−O(8)	142.7(4)	S(7)−O(9)	141.9(3)
S(1)−C(4)	173.2(5)	S(7)−C(10)	174.8(6)

of gas evolution and by the fact that Cs_2**1** is hydroxylated as well by 85% phosphoric acid to give **2**.[13] Moreover, a similar mechanism, in which the fluoride ion functions as a nucleophile, has been proposed previously for the fluorination of **1** by hydrogen fluoride.[7] The predominance of meta substitution to an existing substituent may result from a combination of steric and, in some cases, electronic driving forces.

The meta substitution, which was observed in this hydroxylation study, is common for reactions at the B_{12} framework. Recently, the dithiocyanation of **1** was accomplished using KSCN and an oxidizer (H_2O_2 or $K_2Cr_2O_7$).[14] The main product obtained was the meta isomer, accompanied by small amounts of the para derivative. The difluorination of **1** in molten KHF_2 is reported to give exclusively the meta isomer.[15] The structure of the tetrafluorinated product obtained in the reaction of **1** and hydrogen fluoride was determined to be the 1,2,8,10 isomer,[7] analogous to the tetrahydroxy compound reported in this study.

Crystal Structures of the Anions 2, 3, 7, 11. The solid state structures of the anions **2**, **3**, **7**, and **11** as determined by X-ray diffraction are depicted in Figures 1, 3, 5, and 6, respectively. Table 1 lists the crystallographic data pertaining to these compounds, and Tables 2−5 give selected bond distances. The unit cell dimensions of $[MePPh_3]_2$**2** and $[MePPh_3]_2$**3**, both of which crystallize in the space group $P2_1/n$, are nearly identical. Both anions have a crystallographically imposed center of inversion and are therefore disordered. Slight distortion of the icosahedral geometry is found for the boron cluster of **2**. The B−B bond distances span a narrow range of 175.9(6)−178.6(6) pm. The B(1)−O(1) bond of **2** is 142.6(8) pm long, which is similar to the distance of 144.2(5) pm reported for *closo*-$[B_{12}H_{11}(OCH_2CH_3)]^{2-}$.[11] B−B and B−O bond distances associated with anion **3** [B−B = 175.0(9)−179.6(9) pm; B(1)−O(1) = 138(1) pm; B(7)−O(7) = 145(1) pm] are similar to those of **2**.

Compared with **2** the B−O bond distances of the mesylated anion **11** are elongated by about 5 pm [B(1)−O(1) = 149.5(5) pm; B(7)−O(7) = 149.2(5) pm]. This elongation may be due to the repulsion between the dinegative cluster and the oxygen lone pairs of the mesyl groups. The B−O bond length of the titanocene derivative **7** [B(1)−O(1) = 145(2) pm] is almost identical to that of the alcohol **2**. The other bond distances of **7** are similar to the ones of the analogous titanocene derivative Cp(*i*-PrO)$TiCl_2$.[16]

^{11}B NMR Spectroscopy of the *closo*-$[B_{12}H_{12-n}(OH)_n]^{2-}$ (n = 1−4) Anions. One- and two-dimensional ^{11}B NMR spectroscopy has proven to be the most powerful tool for the structural determination of the *closo*-$[B_{12}H_{12-n}(OH)_n]^{2-}$ (n = 1−4) anions. An individual signal in the ^{11}B NMR spectra (with one exception for $n = 4$, vide infra) is recorded for each set of boron vertices. The singlets of the B−OH vertices are shifted significantly downfield compared with the doublets of the B−H vertices. By integrating these separated peaks, the degree of

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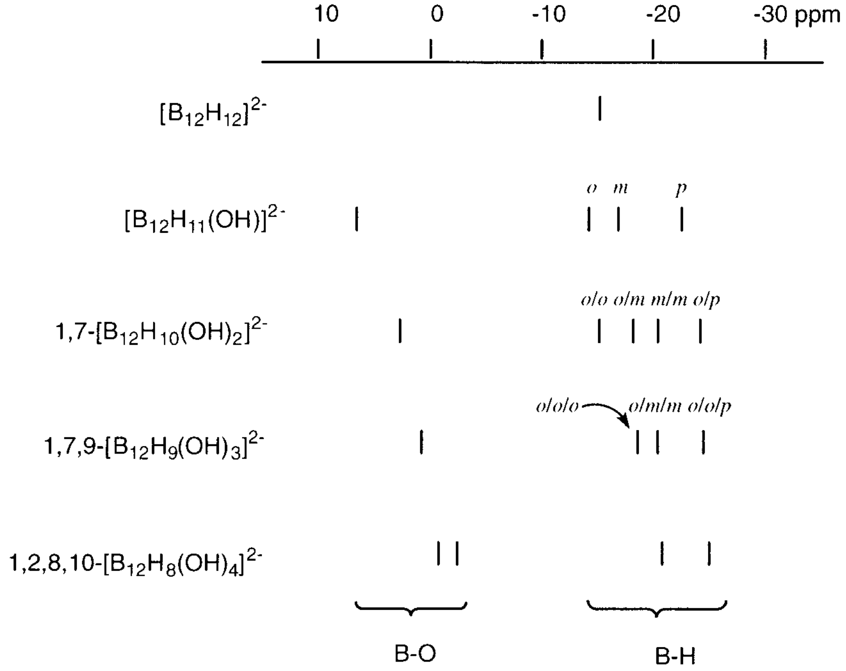
(15) Solntsev, K. A.; Kuznetsov, N. T.; Ivanov, S. V.; Sakharov, S. G. *Program and Abstracts*, Ninth International Meeting on Boron Chemistry, Heidelberg, Germany, July 14−18, 1996; p 191.

(16) Weller, T.; Rubenstahl, T.; Dehnicke, K. Z. *Kristallogr.* **1995**, *210*, 369.

Scheme 2. Overview of the ^{11}B NMR Data of Species **1**−**5**



hydroxylation of the cluster was estimated. Once the number of hydroxyl groups was established, their position relative to each other was derived from the symmetry of the recorded spectrum. If two isomers have the same point group, the cross peaks in the two-dimensional ^{11}B NMR spectrum offer further information to identify the isomer.

Three effects influence the ^{11}B NMR resonances of the *closo*-$[B_{12}H_{12-n}(OH)_n]^{2-}$ ($n = 1-4$) family.[17] The downfield shift of the B−OH singlets is attributable to the negative inductive effect (−I) of the hydroxyl group. The −I effect diminishes rapidly with distance. Second, the chemical shifts are influenced by the resonance effect (+R) that arises from substituents with lone pairs. The +R effect shields the boron vertices due to the electron donation of the substituent to the cluster as a whole. Finally, the antipodal effect describes the upfield shift of a signal of a boron vertex that is trans to an *ipso*-boron atom. In *closo*-$[B_{12}H_{11}(OH)]^{2-}$, the −I effect deshields the *ipso*-boron atom (−6.9 ppm) and causes the signals of the ortho B−H vertices [B(2−6), −14.4 ppm] to be shifted downfield relative to the ones of the meta B−H vertices [B(7−11), −16.6 ppm]. The antipodal effect shifts the resonance of vertex B(12), which is para to the B−OH vertex, upfield (−22.7 ppm). Compared with the parent anion *closo*-$[B_{12}H_{12}]^{2-}$ (−15.3 ppm) the signal is shifted by −7.4 ppm. The analysis is more complex for the polyhydroxylated anions because of the presence of multiple B−OH vertices. For example, the dihydroxylated anion **3** has four sets of B−H groups at −15.2 ppm (B2,3), −17.4 ppm (B4,6,8,11), −20.0 ppm (B9,10), and −23.6 ppm (B5,12). Their relation with respect to the two B−OH vertices B(1,7) at 3.4 ppm is ortho/ortho, ortho/meta, meta/meta, and ortho/para, respectively. As expected, the signal for the two B−H vertices of **3** that are ortho to both of the two electron-withdrawing *ipso*-boron atoms is deshielded the most. On the other hand, the signal of the B−H vertices that are para to one of the B−OH vertices appears upfield and is shifted by −8.3 ppm relative to **1**. The signal of the boron atoms B(4,6,8,11) resonates at higher frequency than that of the vertices B(9,10) because the latter are not bound to an *ipso*-boron atom. The same rules explain the spectrum of the trihydroxylated species **4**. Here, the B−H vertices B(3,4,8) that are ortho to the three *ipso* atoms B(1,7,9) are deshielded the most and the boron atoms B(2,5,12) that are para to one of the three *ipso*-boron atoms resonate at the lowest frequency. For the anion **5**, we were unable to assign the four peaks by two-dimensional ^{11}B NMR spectroscopy. By applying the rules, however, that became apparent from the ^{11}B NMR data of the anions **2**−**4** to compound **5** we tentatively assigned the peaks. The two groups of *ipso*-boron atoms B(1,2) and B(8,10) are positioned ortho/meta/meta and meta/meta/meta relative to each other. Therefore, the singlet at −2.0 ppm arises from the B−OH vertices with the one ortho contact, B(1,2). Of the three sets of B−H vertices, two [(B(3,6) and B(9,12)] have one para contact. They resonate at the lowest frequency. The resonance of the boron atoms B(4,5,7,11) that are not para to any *ipso*-boron atom is assigned to the signal at −20.7 ppm.

Scheme 2 exhibits the effect of the subsequent substitution of a hydrogen by a hydroxyl group on the $^{11}B\{^1H\}$ NMR spectrum of the *closo*-$[B_{12}H_{12-n}(OH)_n]^{2-}$ ($n = 0-4$) anions. The singlets of the B−OH vertices are shifted downfield compared with the signal of **1** because of the −I effect. With each additional hydroxyl function, however, the singlets of the B−OH vertices are shifted upfield relative to **2** because of the increasing electron density due to the +R effect. A similar trend is observed for the B−H vertices as well. The signals of the B−H vertices of **2** and **3** that are ortho to the *ipso*-boron atoms are deshielded relative to the signal of **1**; but the signal of the B−H vertices B(3,4,8) of **4**, which are ortho to three *ipso*-boron atoms, is already shielded compared with **1**. As more hydroxyl groups are attached to the icosahedron, the deshielding due to the −I effect of the hydroxyl substituent is reduced by the electron-donating +R and antipodal effect.

Conclusion

The hydroxylation of the *closo*-$[B_{12}H_{12}]^{2-}$ cluster proceeds stepwise, which allows the synthesis and isolation of the polysubstituted *closo*-$[B_{12}H_{12-n}(OH)_n]^{2-}$ ($n = 1-4$) anions. The described method employing sulfuric acid is convenient and

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[17] Heřmánek, S. *Chem. Rev.* **1992**, *92*, 325.

allows high-yield one-step hydroxylations of **1**. Furthermore, the hydroxylation proceeds regioselectively. Three effects of the hydroxyl group on the chemical shifts of the boron vertices are distinguished and qualitative rules are developed to explain the recorded ^{11}B NMR data.

The reaction of the hydroxyl function of the *closo*-$[B_{12}H_{12-n}(OH)_n]^{2-}$ ($n = 1-4$) species with the electrophiles methanesulfonyl chloride, phenyl isocyanate, and titanocene dichloride, respectively, results in O-derivatized dodecaborate(2−) anions.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $[MePPh_3]_2$**2**, $[MePPh_3]_2$**3**, $[MePPh_3]_2$**7**, and $[HPy]_2$**11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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