Camouflaged Carboranes as Surrogates for C_{60}: Syntheses of Functionalized Derivatives by Selective Hydroxyalkylation

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Introduction

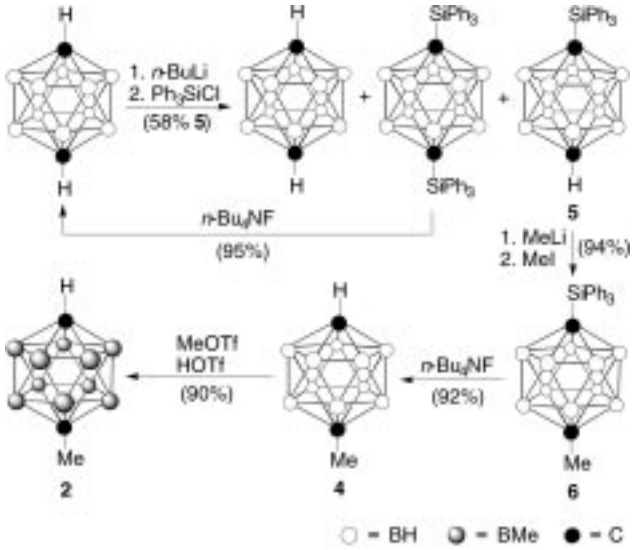
Recently we reported the methylation of 1,12-dicarba-*closo*-dodecaborane (*p*-carborane) and its *C*-methyl derivatives, using methyl triflate (MeOTf) in the presence of triflic acid (HOTf) to yield the corresponding deca-*B*-methyl-*p*-carborane (**1**), undecamethyl-*p*-carborane (**2**), and dodecamethyl-*p*-carborane (**3**).[1] In these compounds each boron atom bears a methyl group whereby the carborane framework is completely shielded. Preliminary investigation revealed that this shielding effect provides enhanced chemical and thermal stability and enhances hydrophobicity. Thus, these derivatives are important as structural components for molecular scaffolding and supramolecular constructs[2] as well as for use in boron neutron capture therapy (BNCT)[3] and other pharmaceutical applications. Of special significance is the fact that the size of the extremely hydrophobic derivative **3** resembles that of C_{60}. In **3**, the long "vertex-to-vertex" van der Waals diameter is 9.9 Å. In C_{60} the long van der Waals diameter of its C atoms is 10.7 Å.[4] The dodecamethylcarba-*closo*-dodecaborate(−) anion *closo*-$CB_{11}Me_{12}^-$, another example for a permethylated icosahedron, exhibits a long van der Waals diameter of 9.96 Å.[5] Thus, based on the comparable effective sizes of these spherical systems, **3** and *closo*-$CB_{11}Me_{12}^-$ can be viewed as stereochemical C_{60} surrogates, although their surfaces are chemically and physically different from the surface of C_{60}.

The derivatization of **1** is, in principle, possible at the methyl substituents or at the carbon atoms of the cluster. An example of the former is the reaction of **1** with chlorine under UV irradiation, by which two hydrogen atoms of each methyl group are replaced by chlorine atoms.[6] The exclusive functionalization at only one of the ten available methyl groups could be achieved by utilizing the Barton reaction which selectively introduces a single oxime function.[7]

Results and Discussion

As previously reported,[1] **2** is easily accessible by per-*B*-methylation of C-methyl-*p*-carborane (**4**). However, the published synthesis of **4** is not optimal.[8] Consequently an improved synthesis was developed. It is depicted in Scheme 1.

Scheme 1



Since the deprotonation of the CH vertexes of *p*-carborane with RLi leads to mixtures of starting material and mono- and dilithiated species, the subsequent reaction with MeI affords a product mixture which is difficult to separate. Therefore, the introduction of a protecting group is desirable to enable the selective methylation of only a single carbon atom. Adopting a previously described method, we used a silyl group for protection since the SiR_3 moiety can be easily removed by reaction with tetrabutylammonium fluoride (TBAF).[9] Reaction of *p*-carborane with *n*-BuLi followed by the addition of Ph_3-SiCl afforded compound **5** in 58% conversion after

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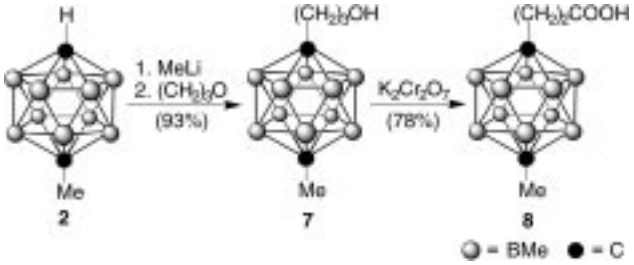
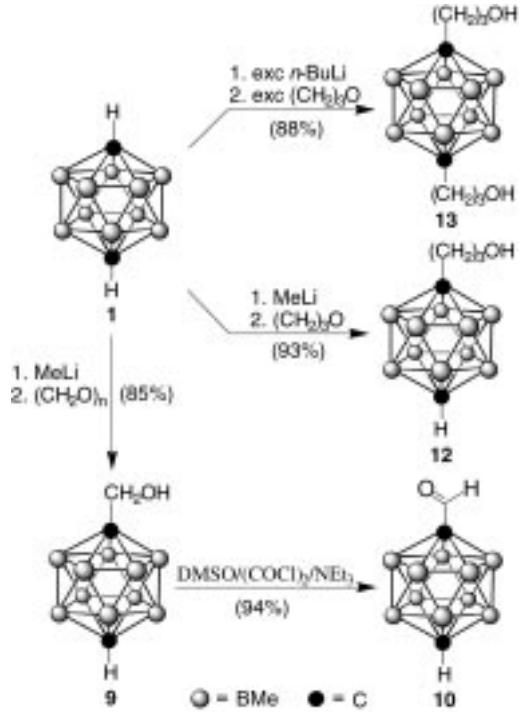
Scheme 2



Scheme 3

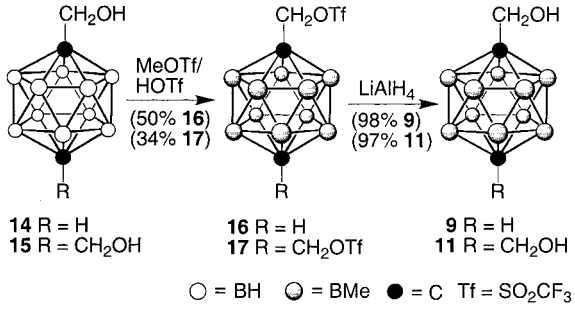


isolation by chromatography. The disilylated product, which is also formed, can be reconverted to *p*-carborane by its reaction with TBAF. Deprotonation of **5** with MeLi followed by reaction with MeI yielded **6** nearly quantitatively. Subsequent reaction with TBAF gave **4**, which was isolated in over 90% yield via chromatography. Permethylation of **4** with MeOTf/HOTf to produce **2** was conducted as previously described.[1]

Deprotonation of the CH vertex in **2** allows the introduction of functional groups. The deprotonation of **2** was accomplished in a THF/Et_2O solvent mixture after 15 h stirring with an excess of MeLi (5−7 equiv) at room temperature. Interestingly, attempts to perform the deprotonation of **2** with MeLi in pure Et_2O were not successful. Addition of trimethylene oxide at 0 °C to lithiated **2** followed by stirring at room temperature for 15 h gave the alcohol **7** as a colorless solid in 93% yield (Scheme 2). The oxidation of **7** using potassium dichromate in a mixture of THF and 2 M sulfuric acid produced carboxylic acid **8**.

Treatment of **1** with MeLi in THF/Et_2O followed by reaction with paraformaldehyde afforded the alcohol **9** in 85% yield after purification (Scheme 3). Aldehyde **10** as well as the hemiacetal of **9** and **10** were identified as byproducts. Aldehyde **10** could be obtained in 95% yield by Swern oxidation of **9**. Surprisingly, no significant amount of the 1,12-bis(hydroxymethyl) derivative **11** is formed in the preparation of **9** whether 1 equiv or an excess of MeLi was used for the deprotonation of **1**. In analogy, deprotonation of **1** using 1 equiv of *n*-BuLi and subsequent addition of trimethylene oxide leads exclusively to the 1-(3-hydroxypropyl) derivative **12**. However, exhaustive metalation of **1** with 4 equiv of *n*-BuLi in THF at 15 °C followed by the addition of 4 equiv of trimethylene oxide leads to the 1,12-bis(3-hydroxypropyl) derivative **13** in high yield.

Scheme 4



The reactions of **14** and **15**[10] with MeOTf/HOTf afforded the per-*B*-methylated triflic acid ester derivatives of **9** and **11**, **16** and **17**, respectively (Scheme 4). Intriguingly, in both methylation reactions reduction of the alcohol function occurs, yielding the corresponding hydrocarbons **2** and **3**, respectively. Attempts to affect nucleophilic substitution of the triflate group by iodide ion undoubtedly failed due to steric hindrance. However, the desired alcohols **9** and **11** were obtained in excellent yields by reduction of **16** and **17**, respectively, using lithium aluminum hydride.

In this communication an improved synthesis of undecamethyl-*p*-carborane (**2**) and the complete deprotonation of its remaining CH vertex is described. Subsequent reaction of the lithiated intermediate with trimethylene oxide provided the 3-hydroxypropyl derivative **7**, which has been oxidized to the corresponding acid **8**.

Treatment of deca-*B*-methyl-*p*-carborane (**1**) with 1 equiv of base followed by reaction with paraformaldehyde and trimethylene oxide gave the monohydroxyalkylated derivatives **9** and **12**, respectively. This result indicates that the equilibrium between **1** and mono- and dilithiated species of **1** (vide supra) is suppressed.[11] Thus, reactivity differences between **1** and *p*-carborane are quite apparent. The full metalation of both CH vertexes of **1** requires an excess of base (*n*-BuLi). Dilithiated **1** was subsequently quenched with trimethylene oxide to give diol **13**.

In an alternative approach to obtain **9** as well as the bis-3-hydroxymethylated derivative **11** in moderate yields, previously mono- and bishydroxymethylated *p*-carborane was reacted with MeOTf and the obtained triflic acid esters **16** and **17** were reduced to yield the corresponding alcohols.

Conclusion

Despite the adverse steric and electronic effect of the methyl groups on each boron atom in **1** and **2**, the

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(11) In verification of these findings, reaction of **1** with 1 equiv of MeLi followed by the reaction with MeI at 0 °C leads to a mixture of 10% starting material, 85% **2**, and 5% **3**.

reactivity of their CH vertexes in deprotonation reactions with alkyllithium reagents has been demonstrated. The compounds obtained may prove useful in the further development of camouflaged carborane chemistry. Since the geometry and size of the permethylated carborane cage closely resembles C_{60}, the compounds described herein represent the first known functionalized C_{60} surrogates based upon a carborane framework.

Experimental Section

Standard Schlenk- and vacuum line techniques were employed for all manipulations of air- and moisture sensitive compounds. Reaction solvents were distilled from appropriate drying agents under nitrogen before use. Deca-*B*-methyl-,[1] undecamethyl-,[1] 1-(hydroxymethyl)-,[10] and 1,12-bis(hydroxymethyl)-*p*-carborane[10] were prepared according to literature methods. Other reagents were used as purchased commercially. Proton (^{1}H NMR) and carbon (^{13}C NMR) spectra were obtained on a Bruker ARX 400 at 400.13 and 100.62 MHz, respectively. Boron (^{11}B−NMR) spectra were obtained at 160.46 MHz on a Bruker ARX 500 spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to $SiMe_4$ and measured with respect to residual protons in deuterated solvents. Chemical shift values for ^{11}B−NMR spectra were referenced relative to external $BF_3{\cdot}Et_2O$. Mass spectra were obtained on a VG AUTOSPEC.

1-(Triphenylsilyl)-1,12-dicarbadodecaborane(12) (5). To a solution of *p*-carborane (2.442 g, 17 mmol) in THF (50 mL) was slowly added *n*-BuLi (12.8 mL, 20.5 mmol, 1.6 M solution in hexanes) at −20 °C. The suspension was allowed to warm to 10 °C and was stirred for 30 min at this temperature. It was cooled again to −20 °C, and a solution of triphenylsilyl chloride (5.0 g, 17 mmol) in THF (30 mL) was added. After stirring for 20 h at room temperature, the solvent was removed under reduced pressure, the residue was quenched with water and extracted three times with Et_2O (50 mL). The combined ether extracts were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. *p*-Carborane was separated via sublimation at room temperature (10^{-2} mm) using a dry ice cooled sublimation finger. The sublimation residue was chromatographed on silica gel using toluene as eluent. The first fraction yielded **5** (3.83 g, 58%) as a colorless solid after removal of the solvent. Mp 165 °C; ^{1}H NMR (C_6D_6) δ 7.1−7.8 (m, 15H, Ar), 0.8−3.8 (br, 10 H, BH), 2.3 (s, 1H, carboranyl-CH); ^{13}C{^{1}H} NMR (C_6D_6) δ 130.4, 130.3, 131.5, 137.6 (Ar), 73.4 (carboranyl-CH), 69.3 (carboranyl-CSi); ^{11}B{^{1}H} NMR (benzene) δ −12.7, −10.6; HRMS (EI) *m*/*z*, calcd 403.2771, found 403.2771 ($M^+ + H$).

1-(Triphenylsilyl)-12-methyl-1,12-dicarbadodecaborane-(12) (6). MeLi (2.5 mL, 3.5 mmol, 1.4 M in Et_2O) was added to a suspension of **5** (1.00 g, 2.5 mmol) in a mixture of benzene (35 mL) and THF (5 mL) at room temperature. After stirring for 24 h, MeI (570 mg, 4.04 mmol) was added, and the colorless solution was stirred for another 1 h. The workup was performed analogously to that of **5** and gave **6** as a white solid (854 mg, 94%). Mp 170 °C; ^{1}H NMR (acetone-d_6) δ 7.3−7.7 (m, 15H, Ar), 1.0−3.2 (br, 10H, BH), 1.4 (s, 3H, CH_3); ^{13}C{^{1}H}-NMR (C_6D_6) δ 129.5, 131.5, 137.5 (Ar), 84.8 (carboranyl-*C*-CH_3), 64.4 (carboranyl-CSi), 26.3 (CH_3); ^{11}B{^{1}H} NMR (benzene) δ -11.8, −10.1; HRMS (EI) *m*/*z*, calcd 417.2924, found 417.2927 ($M^+ + H$).

1-Methyl-1,12-dicarbadodecaborane(12) (4).[8] Tetrabutylammonium fluoride (4 mL, 4.0 mmol, 1 M solution in THF) was added dropwise to a solution of **6** (790 mg, 0.9 mmol) in THF at −78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 1 h, and water (10 mL) was added. After additional stirring for 20 min, the product was extracted with Et_2O (3 × 30 mL). The ethereal solution was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residual crude product was purified via sublimation at room temperature (10^{-2} mm) using a dry ice cooled sublimation finger providing **4**[8] (131 mg, 92%) as a colorless solid. Mp 145 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 2.55 (s, 1H, carboranyl-CH), 2.31 (br, q, J = 185 Hz, 5H, BH), 2.21 (br, q, J = 185 Hz, 5H, BH), 1.40 (s, 3H, CCH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 64.5 (carboranyl-C), 56.6 (carboranyl-C), 27.0 (CH_3); ^{11}B{^{1}H} NMR (pentane) δ −10.8 (s, 5B), −13.8 (s, 5B); ^{11}B{^{1}H-coupled} NMR (pentane) δ −10.8 (d, J = 1123 Hz, 5B), −13.8 (s, J = 1123 Hz, 5B); HRMS (EI) *m*/*z*, calcd 159.4082, found 159.4080 (M^+).

1-(3-Hydroxypropyl)-2,3,4,5,6,7,8,9,10,11,12-undecamethyl-1,12-dicarbadodecaborane(12) (7). MeLi (26 mL, 36.8 mmol, 1.4 M in Et_2O) was added to a solution of undecamethyl-*p*-carborane (**2**) (1.6 g, 5.4 mmol) in THF (40 mL) at room temperature. After the solution was stirred for 16 h, the reaction flask was cooled to 0 °C, and 2.15 g (37.0 mmol) trimethylene oxide was added dropwise. The mixture was warmed to room temperature and stirred for additional 5 h. After removal of the solvent under reduced pressure, water (20 mL) was added to the remaining residue followed by the addition of pentane (10 mL) and Et_2O (10 mL). The reaction mixture was neutralized by adding aqueous HCl. The water layer was separated and washed three times with pentane/Et_2O (1:1). The organic layers were collected and dried over anhydrous $MgSO_4$, and the solvents were removed under reduced pressure. Impurities were removed from the crude product by sublimation at 120 °C/10^{-2} mm. Subsequent crystallization from pentane gave **7** as a colorless solid (1.86 g, 93%). Mp 280 °C. ^{1}H NMR ($CDCl_3$) δ 3.4 (t, 2H, CH_2OH), 1.5 (m, 4H, CH_2CH_2), 0.8 (s, 3H, CCH_3), 0.1 (s, 15H, BCH_3), −0.1 (s, 15H, BCH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 74.1, 76.0 (carboranyl C), 63.1 (CH_2OH), 28.1, 29.7 (CH_2CH_2), 13.2 (CH_3), −3.0 (br, BCH_3); ^{11}B{^{1}H-coupled} NMR ($CDCl_3$) δ −7.8; HRMS (EI) *m*/*z*, calcd 356.4082, found 356.4080 (M^+).

2,3,4,5,6,7,8,9,10,11,12-Undecamethyl-1,12-dicarbado-decaboranyl(12)-1-(3-propionic acid) (8). To a solution of **7** (267 mg, 0.75 mmol) in THF (20 mL) was added a solution of potassium dichromate (2.21 g, 7.5 mmol) in 2 M H_2SO_4 (20 mL) dropwise at ambient temperature. After stirring for 48 h, Et_2O (20 mL) was added. The water layer was separated and washed three times with Et_2O. The organic layers were collected and dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. Impurities were removed from the crude product by sublimation at 120 °C/10^{-2} mm to yield **8** as a colorless solid (245 mg, 78%). Mp 275 °C. ^{1}H NMR ($CDCl_3$) δ 2.2 (m, 2H, CH_2), 1.8 (m, 2H, CH_2), 0.8 (s, 3H, CCH_3), 0.0 (s, 15H, BCH_3), −0.1 (s, 15H, BCH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 178.1 (CO), 75.4, 76.2 (carboranyl-C), 30.9 (CH_2CO_2H), 26.2 (CCH_2-CH_2), 13.3 (CCH_3), −3.0 (BCH_3, br); ^{11}B{^{1}H-coupled} NMR ($CDCl_3$) δ −7.8; FT-IR ν 1712 (CO); HRMS (EI) *m*/*z*, calcd 370.3839, found 370.3844 (M^+).

1-(Hydroxymethyl)-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane (12) (9). Variation a: To a solution of deca-*B*-methyl-*p*-carborane (**1**) (1.00 g, 3.5 mmol) in THF (30 mL) at room temperature was added MeLi (2.64 mL, 3.7 mmol, 1.4 molar solution in Et_2O) dropwise, and the mixture was stirred for 5 h at room temperature. Solid paraformaldehyde (111 mg, 3.7 mmol) was added, and the mixture was allowed to react for 30 min at room temperature and for an additional 15 min at 50 °C. After hydrolysis of the mixture with aqueous HCl, the organic layer was separated from the water phase and extracted twice with Et_2O. The combined organic phases were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified via chromatography on silica gel (Et_2O/pentane 4:1) yielding **9** (R_f = 0.55, 937 mg, 85%) as a colorless solid. Mp 364 °C (decomp); ^{1}H NMR ($CDCl_3$) δ 3.5 (s, 2H, CH_2-OH), 2.1 (s, 1H, CH), 1.2 (br s, 1H, OH), 0.1, 0.0 (s, 2 × 15H, BCH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 78.4 (CCH_2OH), 75.2 (CH), 61.3 (CH_2OH), −4.0 (br, BCH_3); ^{11}B{^{1}H-coupled} NMR (Et_2O) δ − 7.3, − 8.6 (2s, BCH_3); IR (KBr pellet) ν 3444, 2963, 2908, 1434, 1322, 1261, 1099, 1044, 1018, 800; HRMS (E/I) (*m*/*z*), calcd 314.3613, found 314.3615 (M^+).

1-Formyl-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (10). DMSO (1.19 g, 15.30 mmol) was added dropwise to a solution of oxalyl chloride (0.99 g, 7.64 mmol) in CH_2Cl_2 at −78 °C. The mixture was allowed to warm to −55 °C, and the alcohol **9** (1. 20 g, 3.82 mmol) was added. The suspension was allowed to warm to −10 °C, and NEt_3 (1.74 g, 17.20 mmol) was added. The reaction mixture was stirred at room temperature for an additional 1 h and was quenched with water. The separated water layer was extracted with CH_2Cl_2, and the combined organic fraction was dried under vacuum. Water was added to the residue and extracted twice with pentane. The combined pentane extracts were dried over calcium chloride, filtered, and dried to provide **10** (1.13 g, 95%) as an

off-white solid. Mp 328 °C; ^{1}H NMR ($CDCl_3$) δ 8.85 (s, 1H, CHO), 2.27 (s, 1H, carboranyl-CH), 0.11 (s, 15H, BCH_3), 0.09 (s, 15H, BCH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 190.1 (s, CHO), 80.4 (s, carboranyl-C), 78.1 (s, carboranyl-C), −4.6 (br, m, BCH_3); ^{11}B{^{1}H-coupled} NMR (Et_2O) δ −7.4, −8.1 (2s, BCH_3); HRMS (E/I) *m*/*z*, calcd 312.3456, found 312.3457 (M^+).

1-(3-Hydroxypropyl)-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (12). To a solution of deca-*B*-methyl-*p*-carborane (**1**) (1.00 g, 3.5 mmol) in THF at 0 °C was added *n*-BuLi (1.5 mL, 3.6 mmol, 2.5 M solution in hexanes) dropwise, and the mixture was stirred for 4 h at 20 °C. The reaction flask was cooled to 0 °C, and trimethylene oxide (215 mg, 3.7 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature. After removal of the solvent under reduced pressure, water was added to the remaining residue and the resulting suspension was acidified by adding aqueous HCl followed by extraction with Et_2O. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. Subsequent crystallization from Et_2O/pentane afforded **13** as a colorless solid (1.05 g, 88%). Mp 257 °C. ^{1}H NMR ($CDCl_3$) δ 3.39 (t, J = 8 Hz, 2H, CH_2OH), 2.29 (s, 1H, carboranyl-CH), 2.01 (s, 1H, OH), 1.45 (m, 4H, carboranyl-C−CH_2CH_2), −0.03 (s, 30H, BCH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 78.4, 74.6 (carboranyl-C), 63.0 (CH_2OH), 29.7 (CCH_2), 28.4 (*C*H_2-CH_2OH), −3.7 (br, BCH_3); ^{11}B{^{1}H-coupled} NMR (pentane) δ −6.9 (s, 5B), −8.4 (s, 5B); HRMS (EI) *m*/*z*, calcd 342.39258, found 342.39279 (M^+).

1,12-Bis(3-hydroxypropyl)-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (13). To a solution of deca-*B*-methyl-*p*-carborane (**1**) (1.00 g, 3.5 mmol) in THF at 0 °C was added *n*-BuLi (5.6 mL, 14.0 mmol, 2.5 M solution in hexanes) dropwise, and the mixture was stirred for 5 h at 15 °C and an additional 1 h at room temperature. The reaction flask was cooled to 0 °C, and trimethylene oxide (870 mg, 15.0 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature. After removal of the solvent under reduced pressure, water was added to the remaining residue and the resulting suspension was acidified by adding aqueous HCl followed by extraction with Et_2O. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. Subsequent crystallization from Et_2O/pentane afforded **13** as a colorless solid (1.31 g, 93%). Mp 295 °C. ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 30H, BCH_3), 1.45 (m, 4H, carboranyl-C−CH_2CH_2), 3.41 (t, J = 8 Hz, 2H, CH_2OH); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 77.9 (carboranyl-C), 63.2 (CH_2OH), 29.8 (CCH_2), 28.4 (*C*H_2-CH_2OH), −3.8 (br, BCH_3); ^{11}B{^{1}H-coupled} NMR (Et_2O) δ −7.3; HRMS (EI) *m*/*z*, calcd 400.4352, found 400.4344 (M^+).

1-(Hydroxymethyl)-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12)trifluoromethanesulfonic Acid Ester (16). 1-(Hydroxymethyl)-*p*-carborane (**14**) (1.00 g, 5.7 mmol), dissolved in a mixture of MeOTf (7.2 mL, 10.40 g, 63.1 mmol) and HOTf (2.00 mL, 3.45 g, 23.0 mmol), was heated at 140 °C until the condensation of MeOTf at the reflux condenser stopped (∼48 h). The reaction mixture was poured onto ice−water, neutralized with K_2CO_3, and extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under vacuum. The residue was flashed through silica gel with pentane to afford undecamethyl-*p*-carborane (**2**) in 45% yield after removal of the solvent (771 mg, 2.6 mmol). The column was then eluted with Et_2O. The volume of Et_2O was reduced to 20 mL, pentane (30 mL) was added, and **16** was crystallized by slow evaporation of the solvents. Yield 45% (1.15 g, 2.58 mmol), mp > 350 °C; ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 4.18 (s, 2H, CH_2OTf), 2.21 (s, 1H, carboranyl-CH), 0.09, 0.08 (2s, 2 × 15H, BCH_3); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 118.6 (q, CF_3, J 312 Hz), overlap with $CDCl_3$-signal (*C*CH_2OTf), 72.4 (*C*H_2OTf), 72.0 (carboranyl-CH), −4.0 (br, BCH_3); ^{11}B{^{1}H-coupled} NMR (Et_2O) δ −7.9, −8.6 (2s, BCH_3); HRMS (E/I) *m*/*z*, calcd 446.3106, found 446.3105 (M^+).

1,12-Bis-(hydroxymethyl)-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane (12)-bis-trifluoromethane sulfonic acid ester (17). 1.00 g (4.9 mmol) of 1,12-bis(hydroxymethyl)-*p*-carborane (**15**) was allowed to react in a mixture of MeOTf (6.7 mL, 9.65 g, 58.8 mmol) and HOTf (1.30 mL, 2.21 g, 14.7 mmol) at 140 °C for 48 h. The workup was performed analogously to that of **16**. Flash chromatography of the crude product mixture on silica gel using pentane afforded dodecamethyl-*p*-carborane (**3**)[1] (612 mg, 40%). The Et_2O eluent of this column contained **17** (1.04 g, 35%) which precipitated as colorless crystals after diminishing the volume of the solvent slowly. Mp > 350 °C; ^{1}H NMR ($CDCl_3$) δ 4.18 (s, 4H, CH_2OTf), 0.18 (s, 30H, BCH_3); ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 118.6 (q, CF_3, J = 312 Hz), 74.4 (CCH_2OTf), 72.0 (*C*H_2OTf), −4.4 (br, BCH_3); ^{11}B{^{1}H-coupled} NMR (Et_2O) δ −7.5 (10B, BCH_3); HRMS (EI) *m*/*z*, calcd 608.2704, found 608.2696 (M^+).

1-(Hydroxymethyl)-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane (12) (9). Variation b: Triflate **16** (1.00 g, 2.2 mmol) and $LiAlH_4$ (425 mg, 11.2 mmol) were refluxed in THF for 8 h. After the THF had been removed under vacuum, the residue was hydrolyzed with cold water, and the resulting suspension was acidified with HCl. The aqueous phase was extracted with Et_2O, and the organic phase was dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue was purified via silica gel chromatography (Et_2O/pentane 1:1) providing colorless **9** (688 mg, 98%).

1,12-Bis(hydroxymethyl)-2,3,4,5,6,7,8,9,10,11-decamethyl-1,12-dicarbadodecaborane(12) (11). In analogy to the preparation of **9**, variation b, bis triflic acid ester **17** (1.00 g, 1.6 mmol) and $LiAlH_4$ (626 mg, 16.5 mmol) were reacted. Purification via silica gel chromatography (Et_2O/pentane 3:1) provided colorless **11** (548 mg, 97%). Mp > 350 °C; ^{1}H NMR (acetone-d_6) δ 3.62 (t, J = 8 Hz, 4H, CH_2O*H*), 3.54 (d, J = 8 Hz, 4H, CH_2OH), 0.08 (s, 30H, BCH_3); ^{13}C{^{1}H}-NMR (acetone-d_6) δ 80.1 (carboranyl-C), 61.5 (CH_2OH), −4.1 (br, BCH_3); ^{11}B{^{1}H-coupled} NMR (Et_2O) δ −7.8 (s, BCH_3); HRMS (EI) *m*/*z*, calcd 344.3718, found 344.3722 (M^+).

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Supporting Information Available: X-ray structure analysis data for the compounds **6** and **17** (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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