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Camouflaged Carborane Amphiphiles: Synthesis and Self-Assembly

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A series of amphiphilic amine hydrochloride salts of B-polymethylated (camouflaged) (aminoalkyl)- and bis(aminoalkyl)-carboranes have been designed and synthesized in high yield for the purpose of constructing novel carborane-based nanomaterials. Due to the distinct separation of the hydrophobic and hydrophilic regions within each salt, the mono- and disubstituted amphiphiles spontaneously self-assembled upon sonication into rod-shape micro/nanostructures in aqueous solutions. The effects of concentration, method of dispersion, solvent, chain length, counterion, ionic charge, and underlying carborane cage structure on the formation of the these rod products were investigated. The microrods have been studied by transmission electron microscopy (TEM), optical microscopy, X-ray powder diffraction (XRD), thermogravimetric/differential thermal analysis (TG/DTA), and FTIR. For the first time, this work clearly demonstrates the self-assembly of B-polymethylated carboranes into supramolecular structures.

Introduction

The possibility that the three isomeric icosahedral $C_2B_{10}H_{12}$ carboranes could be used as structural components in the creation of supramolecular assemblies has long been suggested,[1−3] including reports of new chemistry derived from complexes of electrophilic mercuracarborands[4−9] and hydrophobic carboracycles.[10−12] For the first time, however, the self-assembly of this class of compounds into micro- and nanosized supramolecular structures is now presented. The completely shielded B-polymethylated *ortho*-, *meta*-, and *para*-carboranes (also known as camouflaged carboranes) often used for such applications are synthesized by exhaustive electrophilic alkylation of the boron vertices of the parent icosahedral carboranes. For example, the use of methyl triflate in the presence of catalytic triflic acid gives the corresponding *B*-dodecamethyl-1,12-derivative,[13] while neat methyl iodide with aluminum trichloride is used to create the *B*-octamethyl-1,2- and *B*-octamethyl-1,7-derivatives.[14,15] Additionally, given the correct conditions, it is also possible for further functionalization at both the methyl substituents and carbon atoms of the *para*-substituted methylated clusters,[16] including methyl-group hydroxylation through adaptation of a Barton reaction.[17] These sterically shielded derivatives possess dramatically increased hydrophobicity, enhanced chemical and thermal stability, and excellent solubility in common organic solvents when compared to the correspond-

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ing parent carboranes. For example, the free amine derivatives of camouflaged carboranes can be easily isolated in high yield[18] due to the much enhanced stability of the B-permethylated scaffold, in contrast to amine derivatives of 1,2-$C_2B_{10}H_{12}$, which are notoriously unstable under basic conditions and required conversion to the corresponding ammonium ion to avoid autodegradation to the analogous *nido*-7,8-$C_2B_9H_{12}^-$ derivative.[19,20]

Camouflaged carboranes have been designated as stereochemical surrogates[14,18] of C_{60} because of their similarities in hydrophobicity, globular shape, and size, with van der Waals diameters of 10.7[21,22] and 9.9 Å, respectively. Amphiphilic fullerene derivatives have been found to self-organize into a variety of nanorods and small vesicles upon ultrasonication of dispersions or when cast into films in the presence of water.[23−28] It is believed that the distinct amphiphilic balance of the fullerene derivatives plays a crucial role in directing the formation of the nanostructures, as the hydrophobic effect is widely seen as a vital driving force in self-organization processes found in nature.[29−32] However, the likelihood for random aggregation of C_{60} amphiphiles in nearly all solvents[33] presents difficulty in controlling the architecture of supramolecular products.

Although the surfaces of C_{60} and methylated carboranes are chemically and physically different, due to their structural similarities, one can envision that camouflaged carborane amphiphiles may also possess interesting self-assembly behavior. Initial work with the previously reported[18] amphiphilic carborane, 1-(octa-*B*-methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-4-aminobutane hydrochloride, indicated that aggregates ranging in length from 50 nm to 1 μm could be produced by ultrasonication of the carborane derivative in dilute aqueous solutions. To test the possibility that this and other camouflaged carborane derivatives could self-organize into well-defined micro/nanostructures, a variety of structurally and isomerically diverse carborane amphiphiles was synthesized. Upon ultrasonication the size and shape of the resulting aggregates was found to be dependent on the number and position of hydrophilic side chains, the counterion, and the external environment (e.g., solvent and temperature). Here the complete synthesis and characterization of this novel class of camouflaged carborane amphiphiles is reported, together with micrographic evidence of their self-assembly behavior in solution.

Experimental Section

General Procedures. Probe sonication was performed with a Vibra Cell ultrasonicator from Sonics & Materials Inc. Transmission electron microscopy was performed on a JEOL 100CX TEM electron microscope. Copper grids (300 square mesh) Formvar stabilized with carbon were purchased from Ted Pella, Inc. Microscopic images were taken with an Axiotech 100 microscope (AxioCam MR camera) from Carl Zeiss Vision GmbH. X-ray powder diffraction spectra were taken on a locally built machine with Cu-radiation sources and a graphite monochromator, in the $\theta/2\theta$ mode. TG/DTA was recorded on Pyris Diamond TG/DTA from Perkin-Elmer Instruments. NMR spectra were recorded on a Bruker ARX 500 MHz spectrometer. Column chromatography was performed on silica gel 60 (Geduran, EMD). Mass spectroscopic analyses were performed by the UCLA mass spectroscopy facility. EI were measured on a Micromass GCT. MALDI was measured on an IonSpec 7.0T Ultima FTMS. MALDI-TOF was measured on an Applied Biosystems DE-STR. Melting points are uncorrected and determined in an open capillary.

Syntheses were normally carried out under an argon atmosphere when they were sensitive to air and moisture. Reagents were reagent-grade and used without further purification unless otherwise stated. THF and Et_2O were freshly distilled from sodium benzophenone ketyl; CH_2Cl_2 was from CaH_2 under nitrogen.

Transmission Electron Microscopy (TEM). A few milligrams of the amphiphile were dispersed in 6 mL of distilled water. The mixture was probe sonicated for 5 min. One drop of the sonicated carborane-substituted alkylamine hydrochloride/water suspension was transferred to a TEM grid. After the sample was air-dried, TEM images were taken with a JEOL 100CX TEM electron microscope at an accelerating voltage of 100 kV.

General Alkylation Procedure for the Synthesis of 11−13. To a stirred solution of the appropriate poly-*B*-methylcarborane (7.38 mmol) in THF was added BuLi (8.27 mmol, 2.2 M in hexane) under an argon atmosphere at −5 °C. The mixture was stirred for 0.5 h before being allowed to warm to room temperature, and stirring continued for 1 h. This mixture was again cooled to −5 °C for the addition of trimethylene oxide (8.15 mmol) and allowed to warm again to room temperature while stirring overnight. Saturated aqueous $NaHCO_3$ (50 mL) was added to the mixture, and it was extracted with diethyl ether. The organic layer was dried over $MgSO_4$. After filtration, the filtrate was concentrated under vacuum and the residue flashed through a short pad of silica gel with hexane followed by hexane/ethyl acetate (3:1). The residual unreacted starting material was recovered from hexane in this manner. The hexane/ethyl acetate eluate was concentrated under vacuum to afford the product as a white solid. 1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-3-hydroxypropane, **13**: yield 2.50 g (99%); mp 257 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.41 (t, 2 H, J = 5.85 Hz, CH_2OH), 1.998 (s, 1H, C*H*), 1.43 (m, 4 H, CH_2CH_2CH_2OH), 0.038 (s, 15 H, BCH_3), 0.026 (s, 15 H, BCH_3); ^{13}C NMR (125 MHz,

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$CDCl_3$): δ 78.09 (CCH_2, br), 74.38 (*C*H, br), 62.91, 29.61, 28.09, −4 (br, B*C*H_3); ^{11}B NMR (160 MHz, $CDCl_3$) δ −8.27 (s), −9.70 (s); HRMS (EI) for $C_{15}H_{38}B_{10}O$ (*m*/*z*) calcd 342.3934, found 342.3928 (M^+, 100%).

Bromination Method for the Synthesis of 14−16. To a stirred solution of propanol **11**, **12**, or **13** (3.71 mmol) and carbon tetrabromide (4.19 mmol) in methylene chloride (50 mL) was added triphenylphosphine (5.3 mmol) in portions at 0 °C. The solution was slowly warmed to room temperature and stirred under nitrogen overnight. After removal of the solvent by vacuum the residue was flashed through a silica gel column with hexane. The eluate was concentrated under vacuum to afford a white solid. 1-(Octa-*B*-methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-3-bromopropane, **14**: yield 1.3 g (92%); mp 93−94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (t, 2 H, J = 6 Hz, CH_2Br), 3.11 (s, 1H, C*H*), 2.23 (m, 2 H, CH_2CH$_2$Br), 1.93 (m, 2 H, CH_2CH$_2$CH$_2$Br), 0.12 (s, 6 H, BCH_3), 0.062 (s, 6 H, BCH_3), −0.022 (s, 6 H, BCH_3), −0.24 (s, 3 H, BCH_3), −0.26 (s, 3 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.70 (br), 54.49 (br), 31.67, 31.38, 30.94, −4 (br, BCH_3); ^{11}B NMR (160 MHz, ether) δ 7.91 (s, 1 B), 5.19 (s, 1 B), −1.06 (s, 2 B), −6.22 (s, 2 B), −6.90, (s, 2 B), −13.13 (d, 2 B); HRMS (EI) for $C_{13}H_{33}B_{10}Br$ (*m*/*z*) calcd 377.2725, found 377.2708 (M^+, 100%). 1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-3-bromopropane, **16**: yield >90%; mp 200 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.19 (t, 2 H, J = 6 Hz, CH_2Br), 2.02 (s, 1H, C*H*), 1.70 (m, 2 H, CH_2CH$_2$Br), 1.57 (m, 2 H, CH_2CH$_2$CH$_2$Br), 0.050 (s, 15 H, BCH_3), 0.037 (s, 15 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 77.56 (CCH_2, br), 74.65 (*C*H, br), 33.79, 30.54, 29.35, −3.8 (br, B*C*H_3); ^{11}B NMR (160 MHz, $CDCl_3$) δ −7.15 (s), −8.51 (s); HRMS (EI) for $C_{15}H_{37}B_{10}Br$ (*m*/*z*) calcd 405.3076, found 405.3070 (M^+, 100%).

General Method for the Synthesis of Azides 17−19. To a mixture of bromopropane **14**, **15**, or **16** (3.4 mmol), sodium azide (10.6 mmol), and tetrabutylammonium bromide (0.34 mmol) was added benzene (10 mL) and water (15 mL). The reaction mixture was refluxed for 72 h. After being cooled to room temperature, the mixture was extracted with three portions of pentane. The combined organic phase was dried over magnesium sulfate and filtered. The filtrate was concentrated under vacuum, and the residue was flashed through a short silica gel column with hexane. The eluate was concentrated under vacuum to afford a white solid. 1-(Octa-*B*-methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-3-azidopropane, **17** yield: 1.0 g (90%); mp 65−66 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.32 (t, 2 H, J = 6.4 Hz, CH_2N$_3$), 3,12 (s, 1H, C*H*), 2.12 (m, 2 H, CH_2CH$_2$N$_3$), 1.65 (m, 2 H, CH_2CH$_2$CH$_2$N$_3$), 0.12 (s, 6 H, BCH_3), 0.054 (s, 6 H, BCH_3), −0.022 (s, 6 H, BCH_3), −0.24 (s, 3 H, BCH_3), −0.26 (s, 3 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.78 (br), 54.30 (br), 50.40 (*C*H$_2$N$_3$), 29.34, 27.89, −4 (br, BCH_3); ^{11}B NMR (160 MHz, ether) δ 7.91 (s, 1 B), 5.20 (s, 1 B), −1.01 (s, 2 B), −6.18 (s, 2 B), −6.86, (s, 2 B), −13.08 (d, 2 B); HRMS (EI) for $C_{13}H_{33}B_{10}N_3$ (*m*/*z*) calcd 339.3684, found 339.3681 (M^+, 100%). 1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-3-azidopropane, **19**: yield >90%; mp 146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.08 (m, 2 H, −CH_2N$_3$), 2.02 (s, 1H, C*H*), 1.45 (m, 4 H, CH_2CH_2CH$_2$N$_3$), 0.046 (s, 15 H, BCH_3), 0.037 (s, 15 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 77.72 (CCH_2, br), 74.66 (*C*H, br), 51.64 (-*C*H$_2$N$_3$), 29.07, 26.06, −3.9 (br, B*C*H_3); ^{11}B NMR (160 MHz, $CDCl_3$) δ −9.86 (s), −11.16 (s); HRMS (EI) for $C_{15}H_{37}B_{10}N_3$ (*m*/*z*) calcd 367.3998, found 367.3988 (M^+, 100%).

Reduction of Azides to the Corresponding Amines 20−22. Under a nitrogen atmosphere to a stirred suspension of lithium aluminum hydride (1.7 mmol in 8 mL of ether) was slowly added a solution of the azidopropane **17**, **18**, or **19** (0.34 mmol) in ether (4 mL) at 0 °C. The mixture was slowly warmed to room temperature and stirred overnight. After the mixture was cooled to 0 °C, water followed by NaOH (2 M, 3 mL) was added to quench the excess LAH. After separation of the organic layer the aqueous layer was extracted with ether 3 times. The combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration, the filtrate was dried under vacuum to afford the white solid as pure product. 1-(Octa-*B*-methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-3-aminopropane, **20**: yield 100 mg (94%); mp 115−117 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3,18 (s, 1H, C*H*), 2.71 (m, 2 H, CH_2NH$_2$), 2.09 (m, 2 H, CH_2CH$_2$CH$_2$NH$_2$), 1.51 (m, 2 H, CH_2CH$_2$NH$_2$), 0.12 (s, 6 H, BCH_3), 0.055 (s, 6 H, BCH_3), −0.064 (s, 6 H, BCH_3), −0.24 (s, 3 H, BCH_3), −0.26 (s, 3 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 65.74 (br), 54.61 (br), 41.51 (*C*H$_2$NH$_2$), 32.50, 29.50, −4.15 (br, BCH_3); ^{11}B NMR (160 MHz, $CDCl_3$) δ 6.71 (s, 1 B), 4.08 (s, 1 B), −2.02 (s, 2 B), −7.17 (s, 2 B), −7.98, (s, 2 B), −14.33 (d, 2 B); HRMS (EI) for $C_{13}H_{35}B_{10}N$ (*m*/*z*) calcd 313.3773, found 313.3717 (M^+). 1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-3-aminopropane, **22**: yield >90%; mp 280 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.44 (t, 2 H, J = 6.8 Hz, −CH_2NH$_2$), 1.98 (s, 1H, C*H*), 1.38 (m, 4 H, CH_2CH_2CH$_2$NH$_2$), 0.018 (s, 15 H, BCH_3), 0.0058 (s, 15 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.30 (CCH_2, br), 74.41 (*C*H, br), 42.67, 30.55, 29.21, −4.0 (br, B*C*H_3); ^{11}B NMR (160 MHz, $CDCl_3$) δ −8.57 (s), −10.03 (s); HRMS (MALDI) for $C_{15}H_{39}B_{10}N$ (*m*/*z*) calcd 342.4161, found 342.4161 ($[M + H]^+$, 100%).

General Procedure for Conversion of Alkylamines to the Corresponding Amine Hydrochloride Salts 1−3. The aminopropane (**20**, **21**, or **22**) was dissolved in a small amount of diethyl ether through which a stream of dry HCl gas was passed. The resulting carborane-substituted amine hydrochloride salt precipitated from solution and was collected by filtration, or if no precipitate formed, the solvent was removed by vacuum to yield the product as a white solid. 1-(Octa-*B*-methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-3-aminopropane hydrochloride, **1**: mp 216 °C (dec); ^{1}H NMR (500 MHz, CD_3OD) δ 3.98 (s, 1H, C*H*), 2.94 (t, 2 H, J = 7.4 Hz, CH_2NH$_3$Cl), 2.23 (m, 2 H, CH_2CH$_2$NH$_3$Cl), 1.83 (m, 2 H, CH_2-CH$_2$CH$_2$NH$_3$), 0.15 (s, 6 H, BCH_3), 0.10 (s, 6 H, BCH_3), −0.024 (s, 6 H, BCH_3), −0.25 (s, 3 H, BCH_3), −0.27 (s, 3 H, BCH_3); ^{13}C NMR (125 MHz, CD_3OD) δ 66.48 (br), 56.68 (br), 39.97, 30.34, 27.67, −4 (br, BCH_3); ^{11}B{^{1}H} NMR (160 MHz, CH_3OH) δ 7.07 (1 B), 4.44 (1 B), −1.78 (2 B), −6.88 (4 B), −13.46 (2 B); HRMS (MALDI) for $C_{13}H_{36}B_{10}N^+$ (M^+) (*m*/*z*) calcd 314.3847, found 314.3850 (M^+, 100%). 1-(Octa-*B*-methyl-1,7-dicarba-*closo*-dodecaboran-1-yl)-3-aminopropane hydrochloride, **2**: mp 250 °C (dec); ^{1}H NMR (500 MHz, CD_3OD) δ 2.92 (t, 2 H, J = 7.8 Hz, CH_2-NH$_3$Cl), 2.70 (s, 1H, C*H*), 1.81 (m, 2 H, CH_2CH$_2$NH$_3$Cl), 1.66 (m, 2 H, CH_2CH$_2$CH$_2$NH$_3$), 0.18 (s, 6 H, BCH_3), 0.13 (s, 6 H, BCH_3), −0.032 (s, 3 H, BCH_3), −0.14 (s, 6 H, BCH_3), −0.16 (s, 3 H, BCH_3); ^{13}C NMR (125 MHz, CD_3OD) δ 66.96 (br), 56.91 (br), 40.32, 28.21, 26.63, −4.0 (br, BCH_3); ^{11}B{^{1}H} NMR (160 MHz, CH_3OH) δ 3.19 (1 B), 1.00 (1 B), −2.11 (2 B), −5.67 (2 B), −7.45 (2 B), −17.60 (2 B); HRMS (MALDI) for $C_{13}H_{36}B_{10}N^+$ (M^+) (*m*/*z*) calcd 314.3853, found 314.3859 (M^+, 100%). 1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-3-aminopropane hydrochloride, **3**: mp 270 °C (dec); ^{1}H NMR (500 MHz, CD_3OD) δ 2.69 (t, 2 H, J = 7.6 Hz, CH_2NH$_3$Cl), 2.33 (s, 1H, C*H*), 1.58 (m, 2 H, CH_2CH$_2$NH$_3$Cl), 1.52 (m, 2 H, CH_2CH$_2$CH$_2$NH$_3$), 0.097 (s, 15 H, BCH_3), 0.061 (s, 15 H, BCH_3); ^{13}C NMR (125 MHz, CD_3OD) δ 76.45, 66.91, 40.78, 29.83, 26.13, −4 (br, BCH_3); ^{11}B {^{1}H}NMR (160 MHz, CH_3OH) δ −7.65 (5 B), −8.90 (5 B); HRMS (MALDI) for $C_{15}H_{40}B_{10}N^+$ (M^+) (*m*/*z*) calcd 342.4172, found 342.4172 (M^+, 100%).

1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-3-cyanopropane, 23. A mixture of **16** (266 mg, 0.656 mmol) and sodium cyanide (110 mg, 2.2 mmol) in 10 mL of DMSO was heated to 85 °C for 18 h, and saturated ammonium chloride solution was added to quench the reaction. The mixture was extracted with diethyl ether. The organic layer was washed with water and brine and then dried over anhydrous magnesium sulfate. After filtration, the filtrate was concentrated under vacuum and the residue flushed through a short pad of silica gel with ether. The eluate was concentrated to afford white solid as pure product (230 mg, 100%): mp 170−171 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (m, 2 H, CH_2CH$_2$CN), 2.03 (s, 1H, C*H*), 1.53 (m, 4 H, CH_2CH$_2$CH_2-CN), 0.048 (s, 15 H, BCH_3), 0.038 (s, 15 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 118.77, 74.87 (*C*CH$_2$, br), 31.00, 22.63, 17.69, −3.6 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ −8.60 (s), −9.82 (s); HRMS (EI) for $C_{16}H_{37}B_{10}N$ (*m*/*z*) calcd 351.3937, found 351.3954 (M^+, 100%).

1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-4-aminobutane hydrochloride, 4. To a stirred suspension of lithium aluminum hydride (1.5 mmol in 4 mL of ether) under an argon atmosphere was slowly added a solution of the cyanopropane **23** (0.30 mmol) in ether (4 mL) at 0 °C. The mixture was warmed to room temperature and stirred 40 h. After the mixture was cooled to 0 °C, water followed by NaOH (2 M, 3 mL) was added to quench the excess LAH. The product was isolated by column chromatography with ether through which a stream of dry HCl gas was directly passed. The resulting carborane-substituted amine hydrochloride salt precipitated out of solution and was collected by filtration to yield the product as a white solid: mp 260 °C (dec); ^{1}H NMR (500 MHz, CD_3OD) δ 2.77 (t, 2 H, J = 7.6 Hz, CH_2NH$_3$Cl), 2.22 (s, 1H, C*H*), 1.42 (m, 4 H), 1.24 (m, 2 H), 0.017 (s, 15 H, BCH_3), −0.0075 (s, 15 H, BCH_3); ^{13}C NMR (125 MHz, CD_3OD) δ 79.41, 76.13 (br), 40.27, 32.76, 29.16, 24.99, −4 (br, B*C*H$_3$); ^{11}B{^{1}H} NMR (160 MHz, CH_3OH) δ −7.85 (5 B), −9.19 (5 B); HRMS (MALDI) for $C_{16}H_{42}B_{10}N^+$ (M^+) (*m*/*z*) calcd 356.4318, found 356.4331 (M^+).

1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-5-bromopentane, 24. To a stirred solution of deca-*B*-methyl-*para*-carborane (0.496 g, 1.74 mmol) in THF (15 mL) was added BuLi (1.4 mL, 1.5 mmol, 1.1 M in hexane) under an argon atmosphere at −5 °C. The mixture was stirred for 0.5 h, warmed to room temperature, and stirred for 2.5 h. Excess 1,5-dibromopentane (0.9 mL, 6 mmol) was added to the mixture at −78 °C and then warmed to room temperature and refluxed for 40 h. The reaction mixture was concentrated under vacuum, and the crude product was extracted with hexane. The organic layer was washed with water and brine and then dried over $MgSO_4$. After filtration, the filtrate was concentrated under vacuum. The resulting yellow oil was heated to 75 °C under vacuum to remove the excess 1,5-dibromopentane. The residue was purified by silica gel column chromatography with hexane. After concentration of the appropriate fractions the pure product was obtained as a white solid (500 mg, 66%): mp 158.5−159.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.33 (t, 2 H, J = 6.8 Hz, CH_2Br), 1.99 (s, 1H, C*H*), 1.76 (m, 2 H, CH_2CH$_2$Br), 1.38 (m, 2 H, CCH_2), 1.19 (m, 4 H), 0.027 (s, 30 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.64 (*C*CH$_2$, br), 74.46 (*C*H, br), 33.56, 32.24, 31.86, 28.95, 25.84, −4.0 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ −8.61 (s), −10.01 (s); HRMS (EI) for $C_{17}H_{41}B_{10}Br$ (*m*/*z*) calcd 433.3390, found 433.3380 (M^+, 100%).

1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-6-bromohexane, 25. Under an argon atmosphere, to a stirred solution of deca-*B*-methyl-*para*-carborane (0.995 g, 3.50 mmol) in THF (40 mL) was added BuLi (3.5 mL, 3.7 mmol, 1.06 M in hexane) slowly at −5 °C. The mixture was stirred for 0.5 h, allowed to warm to room temperature, and stirred for an additional 2 h. Excess 1,6-dibromohexane (2.5 mL, 16 mmol) was added to the mixture at −78 °C, and the reaction mixture was warmed to room temperature and refluxed for 2 days. Water was added to quench the reaction, and the mixture was extracted with hexane. The organic layer was washed with water and brine and then dried over $MgSO_4$. After filtration, the filtrate was concentrated under vacuum. The resulting yellow oil was heated to 89 °C under vacuum distillation to remove the excess 1,6-dibromohexane. The residue was purified by silica gel column chromatography with hexane. After concentration of the appropriate fractions, the pure product was obtained as a white solid (1.18 g, 75%): mp 113−114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (t, 2 H, J = 6.8 Hz, CH_2Br), 1.99 (s, 1H, C*H*), 1.78 (m, 2 H, CH_2CH$_2$Br), 1.36 (m, 4 H, CCH_2), 1.16 (m, 2 H), 1.07 (m, 2 H), 0.027 (s, 30 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.81 (*C*CH$_2$, br), 74.41 (*C*H, br), 33.66, 32.66, 31.92, 29.56, 27.69, 26.43, −3.8 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ −8.05 (s), −9.48 (s); HRMS (EI) for $C_{18}H_{43}B_{10}Br$ (*m*/*z*) calcd 4 47.3547, found 447.3551 (M^+, 100%).

1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-5-azidopentane, 26. A mixture of bromopentane **24** (0.326 g, 0.752 mmol), sodium azide (180 mg, 2.77 mmol), tetrabutylammonium bromide (45 mg, 0.14 mmol), benzene (3 mL), and water (5 mL) was heated to reflux for 72 h. After being cooled to room temperature, the mixture was extracted with three portions of pentane. The combined organic phase was dried over magnesium sulfate and filtered. The filtrate was concentrated under vacuum, and the residue was purified by a silica gel column chromatography with hexane. After concentration of the appropriate fractions the pure product was obtained as a white solid (204 mg, 69%): mp 97−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.20 (t, 2 H, J = 6.9 Hz, CH_2N$_3$), 1.99 (s, 1H, C*H*), 1.50 (m, 2 H, CH_2CH$_2$N$_3$), 1.38 (m, 2 H, CCH_2), 1.17 (m, 4 H), 0.031 (s, 30 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.62 (*C*CH$_2$, br), 74.46 (*C*H, br), 51.34 (*C*H$_2$N$_3$), 31.88, 28.46, 27.50, 26.19, −3.7 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ −9.87 (s), −11.24 (s); HRMS (EI) for $C_{17}H_{41}B_{10}N_3$ (*m*/*z*) calcd 395.4312, found 395.4314 (M^+).

1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-6-azidohexane, 27. A mixture of bromohexane **25** (0.424 g, 0.948 mmol), sodium azide (260 mg, 4.0 mmol), tetrabutylammonium bromide (40 mg, 0.12 mmol), benzene (2 mL), and water (3.3 mL) was heated to reflux for 72 h. After being cooled to room temperature, the mixture was extracted with three portions of diethyl ether. The combined organic phase was dried over magnesium sulfate and filtered. The filtrate was concentrated under vacuum, and the residue was flashed through a short pad of silica gel with hexane. Concentration of the eluate afforded the pure product as a white solid (388 mg, 99%): mp 44−45 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.22 (t, 2 H, J = 6.9 Hz, CH_2N$_3$), 1.99 (s, 1H, C*H*), 1.52 (m, 2 H, CH_2CH$_2$N$_3$), 1.37 (m, 2 H, CCH_2), 1.27 (m, 2 H), 1.16 (m, 2 H), 1.07 (m, 2 H), 0.025 (s, 30 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.80 (*C*CH$_2$, br), 74.42 (*C*H, br), 51.34, 31.92, 29.92, 28.75, 26.48, 26.27, −3.8 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ −11.27 (s), −12.69 (s); HRMS (EI) for $C_{18}H_{43}B_{10}N_3$ (*m*/*z*) calcd 409.4469, found 409.4472 (M^+, 100%).

1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-5-aminopentane, 28. To a stirred suspension of lithium aluminum hydride (50 mg, 1.25 mmol in 2 mL of ether) under an argon atmosphere was added slowly the solution of the azidopentane **26** (115 mg, 0.29 mmol) in ether (2 mL) at 0 °C. The mixture was slowly warmed to room temperature and stirred overnight. After the mixture was cooled to 0 °C, water followed by NaOH (2 M, 3

mL) was added to quench the excess LAH. After passage through a short pad of Celite the filtrate was extracted with ether 3 times. The combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration, the filtrate was dried under vacuum to afford the white solid as pure product (100 mg, 93%): mp 154−155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.62 (br, 2 H, CH_2NH$_2$), 1.97 (s, 1H, C*H*), 1.35 (m, 4 H), 1.16 (m, 2 H), 1.07 (m, 2 H), 0.010 (s, 30 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.87 (*C*CH$_2$, br), 74.37 (*C*H, br), 42.03 (*C*H$_2$NH$_2$), 33.27, 31.98, 27.66, 26.47, −3.9 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ −11.30 (s), −12.74 (s); HRMS (MALDI) for $C_{17}H_{43}B_{10}N$ (*m*/*z*) calcd 370.4475, found 370.4461 $(M + H)^+$.

1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-6-aminohexane, 29. Under an argon atmosphere, to a stirred suspension of lithium aluminum hydride (118 mg, 2.95 mmol) in 4 mL of ether was added slowly the solution of the azidohexane **27** (249 mg, 0.6 mmol) in ether (6 mL) at 0 °C. Then the mixture was slowly warmed to room temperature and stirred overnight. After cooling of the reaction mixture to 0 °C, water was added to quench the excess LAH, and the mixture was filtered through a short pad of Celite. The filtrate was extracted with ether and dried over anhydrous magnesium sulfate. After filtration, the filtrate was vacuum-dried to afford the white solid as a pure product (190 mg, 83%): mp 122−123 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.64 (br, CH_2NH$_2$), 1.96 (s, 1H, C*H*), 1.34 (m, 4 H), 1.16 (m, 2 H), 1.12 (m, 2 H), 1.03 (m, 2 H), −0.0005 (s, 30 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 78.94 (*C*CH$_2$, br), 74.33 (*C*H, br), 41.93, 33.76, 31.98, 30.30, 29.67, 26.60, 26.46, −3.8 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ −9.95 (s), −11.40 (s); HRMS (MALDI) for $C_{18}H_{45}B_{10}N$ (*m*/*z*) calcd 384.4632, found 386.4631 ($[M + H]^+$, 100%).

General Procedure for Conversion of Alkylamines to the Corresponding Amine Hydrochloride Salts 5 and 6. The alkylamines **28** and **29** were converted to the corresponding amine hydrochloride salts as outlined previously for the formation of **1**−**3** and isolated as white solids after filtration. 1-(Deca-*B*-methyl-1,-12-dicarba-*closo*-dodecaboran-1-yl)-5-aminopentane hydrochloride, **5**: mp >270 °C (dec); ^{1}H NMR (500 MHz, CD_3OD) δ 2.84 (t, 2 H, J = 7.6 Hz, CH_2NH$_3$Cl), 2.26 (s, 1H, C*H*), 1.55 (m, 2 H), 1.47 (m, 2 H), 1.26 (m, 2 H), 1.16 (m, 2 H), 0.052 (s, 15 H, BCH_3), 0.036 (s, 15 H, BCH_3); ^{13}C NMR (125 MHz, CD_3OD) δ 79.75 (br), 76.13 (br), 40.63, 32.93, 28.18, 28.01, 27.61, −3.1 (br, B*C*H$_3$); ^{11}B{^{1}H} NMR (160 MHz, CD_3OD) δ −7.71 (5 B), −9.01 (5 B); HRMS (MALDI) for $C_{17}H_{44}B_{10}N^+$ (*m*/*z*) calcd 370.4475, found 370.4477 (M^+, 100%). 1-(Deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-6-aminohexane hydrochloride, **6**: mp 240 °C (dec); ^{1}H NMR (500 MHz, CD_3OD) δ 2.89 (t, 2 H, J = 7.6 Hz, CH_2-NH$_3$Cl), 2.26 (s, 1H, C*H*), 1.61 (m, 2 H), 1.47 (m, 2 H), 1.32 (m, 2 H), 1.25 (m, 2 H), 1.15 (m, 2 H), 0.067 (s, 15 H, BCH_3), 0.054 (s, 15 H, BCH_3); ^{13}C NMR (125 MHz, CD_3OD) δ 80.07 (br), 76.10 (br), 40.65, 33.17, 30.90, 28.53, 27.87, 27.10, −3.7 (br, B*C*H$_3$); ^{11}B{^{1}H} NMR (160 MHz, CD_3OD) δ −7.36 (5 B), −8.71 (5 B); HRMS (MALDI) for $C_{18}H_{46}B_{10}N^+$ (*m*/*z*) calcd 384.4632, found 384.4639 (M^+, 100%).

1,7-Bis(3-hydroxy-1-propyl)octa-*B*-methyl-1,7-dicarba-*closo*-dodecaborane, 30. To a stirred solution of octa-*B*-methyl-*meta*-carborane (2.0 g, 7.8 mmol) in THF (80 mL) was added BuLi (3.6 mL, 7.9 mmol, 2.2 M in hexane) under an argon atmosphere at −10 °C. The mixture was stirred for 0.5 h before being allowed to warm to room temperature with continued stirring for 4 h. This mixture was again cooled to −10 °C for addition of trimethylene oxide (0.51 mL, 7.8 mmol) and then was allowed to warm again to room temperature for stirring overnight. At the conclusion of this time saturated aqueous $NaHCO_3$ (50 mL) was added to the mixture and it was extracted with diethyl ether. The organic layer was dried over $MgSO_4$. After filtration, the filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography with hexane followed by an increasing ratio of ethyl acetate of the eluent. The residual unreacted starting material was recovered in this manner. The hexane/ethyl acetate eluate was concentrated under vacuum to afford the product as a white solid (0.6 g, 44%): mp 146−147 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.61 (t, 4 H, CH_2OH), 1.63 (m, 8 H, CH_2CH_2CH$_2$OH), 0.069 (s, 12 H, BCH_3), −0.18 (s, 6 H, BCH_3), −0.21 (s, 6 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 65.46 (*C*CH$_2$, br), 62.45 (CH_2OH), 32.12, 25.13, −4 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ −0.52 (s, 2 B), −3.91 (s, 2 B), −7.38 (s, 4 B), −18.11 (d, 2 B). HRMS (EI) for $C_{16}H_{40}B_{10}O_2$ (*m*/*z*): calcd 372.4040, found 372.4040 (M^+); calcd 373.4009, found 373.3998 $[M + H]^+$.

1,7-Bis(3-bromo-1-propyl)octa-*B*-methyl-1,7-dicarba-*closo*-dodecaborane, 31. To a stirred solution of dihydroxypropane **30** (0.169 g, 0.452 mmol) and carbon tetrabromide (478 g, 1.44 mmol) in methylene chloride (15 mL) was added triphenylphosphine (480 g, 1.83 mmol) in portions at 0 °C. After being slowly warmed to room temperature, the reaction was stirred under nitrogen overnight. All solvents were removed by vacuum, and the residue was flashed through a silica gel column with hexane/dichloromethane (5/1). The eluate was concentrated under vacuum to afford a white solid (220 g, 96%): mp 101−102 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (t, 4 H, J = 6.3 Hz, CH_2Br), 1.92 (m, 4 H), 1.68 (m, 4 H), 0.085 (s, 12 H, BCH_3), −0.17 (s, 6 H, BCH_3), −0.19 (s, 6 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 64.82 (*C*CH$_2$, br), 32.75 (CH_2Br), 31.88, 27.38, −4.3 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$) δ 2.22 (s, 2 B), −2.13 (s, 2 B), −5.76 (s, 4 B), −16.74 (d, 2 B); HRMS (EI) for $C_{16}H_{38}B_{10}Br_2$ (*m*/*z*) calcd 498.2330, found 498.2261 (M^+, 100%).

1,7-Bis(3-cyano-1-propyl)octa-*B*-methyl-1,7-dicarba-*closo*-dodecaborane, 32. A mixture of dibromopropane **31** (0.22 g, 0.44 mmol), sodium azide (172 mg, 2.65 mmol), tetrabutylammonium bromide (28 mg, 0.09 mmol), benzene (3 mL), and water (5 mL) was heated to reflux for 72 h. After being cooled to room temperature, the mixture was extracted with three portions of hexane. The combined organic phase was dried over magnesium sulfate and filtered. The filtrate was concentrated under vacuum to afford a colorless oil (186 mg, 99%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.26 (t, 4 H, J = 6.3 Hz, CH_2N$_3$), 1.65 (m, 4 H), 1.58 (m, 4 H), 0.077 (s, 12 H, BCH_3), −0.17 (s, 6 H, BCH_3), −0.20 (s, 6 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 65.06 (*C*CH$_2$, br), 51.07 (*C*H$_2$N$_3$), 28.45, 25.98, −4.4 (br, B*C*H$_3$); ^{11}B NMR (160 MHz, $CDCl_3$): δ 0.99 (s, 2 B), −3.39 (s, 2 B), −7.09 (s, 4 B), −18.16 (d, 2 B); HRMS (EI) for $C_{16}H_{38}B_{10}N_6$ (*m*/*z*) calcd 422.4161, found 422.4155 (M^+).

1,7-Bis(3-amino-1-propyl)octa-*B*-methyl-1,7-dicarba-*closo*-dodecaborane, 33. To a stirred suspension of lithium aluminum hydride (100 mg, 2.5 mmol in 5 mL of ether) under a nitrogen atmosphere was added slowly the solution of bis(azidopropane) **32** (186 mg, 0.44 mmol) in ether (12 mL) at 0 °C. The mixture was slowly warmed to room temperature and stirred overnight. After the mixture was cooled to 0 °C, water followed by NaOH (2 M, 3 mL) was added to quench the excess LAH. After separation of the organic layer the aqueous layer was extracted with ether 3 times. The combined organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration, the filtrate was dried under vacuum to afford the white solid as pure product (140 mg, 86%): mp 119−120 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 2.66 (br, 4 H, CH_2NH$_2$), 1.63 (m, 4 H), 1.62 (m, 4 H), 0.12 (s, 12 H, BCH_3),

−0.16 (s, 12 H, BCH_3); ^{13}C NMR (125 MHz, CD_3OD) δ 67.07 (CCH_2, br), 42.00 (CH_2NH_2), 32.35, 27.28, −4.0 (br, BCH_3); ^{11}B NMR (160 MHz, CD_3OD) δ 2.11 (s, 2 B), −2.27 (s, 2 B), −5.75 (s, 4 B), −16.37 (d, 2 B); HRMS (EI) for $C_{16}H_{42}B_{10}N_2$ (*m*/*z*) calcd 370.4359, found 370.4326 (M^+, 100%).

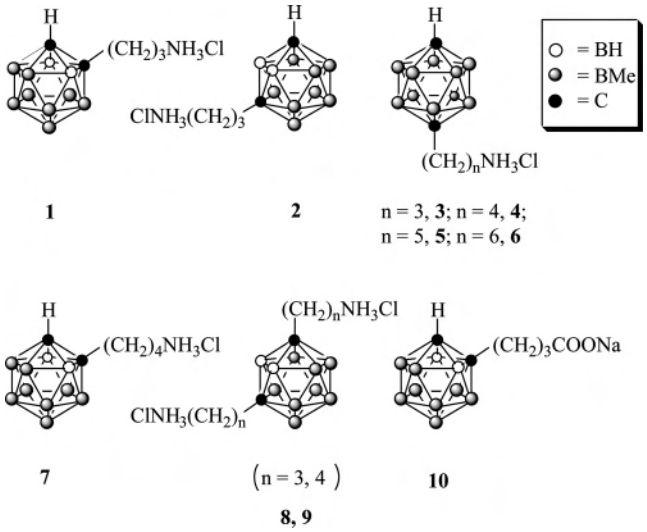
1,7-Bis(3-amino-1-propyl)octa-*B*-methyl-1,7-dicarba-*closo*-dodecaborane Hydrochloride, 8. The diaminopropane **33** was converted to the corresponding amine hydrochloride salt as outlined previously for the formation of **1**−**3** and isolated as a white solid after filtration: mp 275 °C (dec); ^1H NMR (500 MHz, DMSO) δ 2.77 (t, 4 H, J = 6.1 Hz, CH_2NH_3), 1.59 (m, 8 H), 0.045 (s, 12 H, BCH_3), −0.24 (s, 12 H, BCH_3); ^{13}C NMR (125 MHz, DMSO) δ 65.36 (CCH_2, br), 38.50 (CH_2NH_3), 26.62, 25.38, −4.2 (br, BCH_3); ^{11}B NMR (160 MHz, DMSO) δ 2.06 (s, 2 B), −2.62 (s, 4 B), −5.65 (s, 2 B), −16.77 (d, 2 B); HRMS (MALDI) for $[C_{16}H_{43}B_{10}N_2]^+$ (*m*/*z*) calcd 371.4438, found 371.4441 $[M^{2+} - H^+]^+$.

1,7-Bis(3-cyano-1-propyl)octa-*B*-methyl-1,7-dicarba-*closo*-dodecaborane, 34. A mixture of the dibromopropane **31** (166 mg, 0.33 mmol), sodium cyanide (98 mg, 2 mmol), and DMSO (9 mL) was heated to 80 °C for 24 h. Saturated ammonium chloride solution was then added to quench the reaction at room temperature. The mixture was extracted with diethyl ether. The combined organic layer was washed with water and brine and then dried over anhydrous magnesium sulfate. After filtration, the filtrate was vacuum-dried and the residue was flushed through a short pad of silica gel with ether. The eluate was concentrated to afford white solid as the pure product (118 mg, 91%): mp 127−128 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.34 (t, 4 H, J = 6.8 Hz, CH_2CN), 1.74 (m, 4 H), 1.65 (m, 4 H), 0.090 (s, 12 H, BCH_3), −0.16 (s, 6 H, BCH_3), −0.19 (s, 6 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 118.70, 64.40 (CCH_2, br), 27.78, 24.86, 17.18, −4.4 (br, BCH_3); ^{11}B NMR (160 MHz, $CDCl_3$) δ 1.22 (s, 2 B), −3.17 (s, 2 B), −7.02 (s, 4 B), − 18.34 (d, 2 B); HRMS (EI) for $C_{18}H_{38}B_{10}N_2$ (*m*/*z*) calcd 391.4002, found 391.4010 (M^+, 100%).

1,7-Bis(4-amino-1-butyl)octa-*B*-methyl-1,7-dicarba-*closo*-dodecaborane, 35. Under an argon atmosphere to a stirred suspension of lithium aluminum hydride (60 mg, 1.5 mmol in 4 mL of ether) was added slowly the solution of the dicyanopropane **34** (116 mg, 0.297 mmol) in ether (4 mL) at 0 °C. The mixture was slowly warmed to room temperature and stirred 40 h. After the mixture was cooled to 0 °C, water followed by NaOH (2 M, 3 mL) was added to quench the excess LAH. The mixture was filtered through a pad of Celite, and the filtrate was extracted with ether. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. After filtration, the filtrate was vacuum-dried to afford the white solid as a pure product (124 mg, 89%): mp 124−126 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.68 (br, 4 H, CH_2NH_2), 1.45 (m, 4 H), 1.37 (m, 8 H), 0.023 (s, 12 H, BCH_3), −0.21 (s, 6 H, BCH_3), −0.25 (s, 6 H, BCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 65.82 (CCH_2, br), 41.78 (CH_2NH_2), 33.69, 28.58, 26.29, −4.0 (br, BCH_3); ^{11}B NMR (160 MHz, $CDCl_3$) δ 0.74 (s, 2 B), −3.74 (s, 2 B), −7.26 (s, 4 B), −18.04 (d, 2 B); HRMS (MALDI) for $[C_{18}H_{47}B_{10}N_2]^+$ (*m*/*z*) calcd 399.4741, found 399.4724 ($[M + H]^+$, 100%).

1,7-Bis(4-amino-1-propyl)octa-*B*-methyl-1,7-dicarba-*closo*-dodecaborane hydrochloride, 9. The diaminobutane **35** was converted to the corresponding amine hydrochloride salt as outlined previously for the formation of **1**−**3** and isolated as a white solid after filtration: mp 230 °C (dec); ^1H NMR (500 MHz, CD_3OD) δ 2.95 (br, 4 H, CH_2NH_3), 1.65 (m, 4 H), 1.58 (m, 8 H), 0.077 (s, 12 H, BCH_3), −0.21 (s, 12 H, BCH_3); ^{13}C NMR (125 MHz, CD_3OD) δ 66.89 (CCH_2, br), 40.78 (CH_2NH_3), 29.47, 28.46, 27.36, −4.0 (br, BCH_3); ^{11}B NMR (160 MHz, CD_3OD) δ 2.32 (2 B), −2.28 (2 B), −5.62 (4 B), −16.13 (2 B); HRMS (MALDI) for $[C_{18}H_{47}B_{10}N_2]^+$ (*m*/*z*) calcd 399.4741, found 399.4734 ($[M^{2+} - H^+]^+$, 100%).

Chart 1. Polymethylated Carborane Amphiphiles

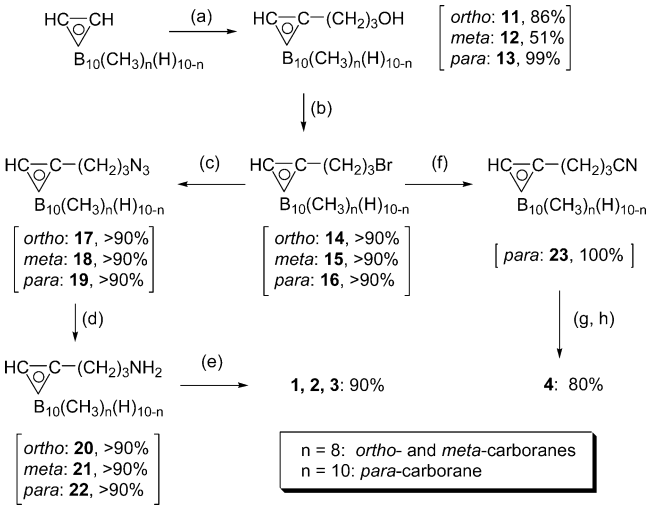


Sodium 1-(Octa-*B*-methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-4-butyrate, 10. A mixture of the cyanopropane **23** (66 mg, 0.2 mmol) and NaOH (2 N, 0.25 mL, 0.5 mmol) in MeOH (2.3 mL) was heated to reflux overnight. HCl (2 M, 0.14 mL) was added carefully until the pH reached 8. The precipitate was collected, washed carefully with a small amount of cold water, and dried to yield the desired product (50 mg, 70%): mp 230 °C (dec); ^1H NMR (500 MHz, $CO(CD_3)_2$) δ 4.05 (s, 1H, C*H*), 2.05 (m, 4 H), 1.66 (m, 2 H), 0.13 (s, 6 H, BCH_3), 0.060 (s, 6 H, BCH_3), −0.033 (s, 6 H, BCH_3), −0.26 (s, 3 H, BCH_3), −0.28 (s, 3 H, BCH_3); ^{13}C NMR (125 MHz, $CO(CD_3)_2$) δ 180.27, 68.04 (CCH_2, br), 56.39 (*C*H, br), 36.86, 32.62, 25.64, −3.7 (br, BCH_3); ^{11}B NMR (160 MHz, $CDCl_3$) δ 6.74 (s, 1 B), 4.19 (s, 1 B), −1.91 (s, 2 B), −6.85 br, 4 B), −13.26 (br, 2 B); HRMS (MALDI) for $[C_{14}H_{33}B_{10}O_2]^-$ (*m*/*z*) calcd 341.3491, found 341.3501 (M^-, 100%).

Results and Discussion

Ten B-polymethylated carborane-containing amphiphiles, **1**−**10** (Chart 1), bearing various hydrophilic side chains were synthesized and characterized by ^1H, ^{13}C, and ^{11}B NMR and high-resolution mass spectrometry (HRMS). Since the parent $C_2B_{10}H_{12}$ carboranes exist as *ortho*-, *meta*-, and *para*-isomers, compounds **1**−**3**, which differ in spatial arrangement of the cage carbon atoms, were synthesized to determine what effect, if any, the symmetry and cage dipole moment of the monomer imposes upon the resulting assembled structures. Compounds **3**−**6**, deca-*B*-methyl-*para*-carborane amphiphiles with linker lengths increasing from three to six methylene units, respectively, were investigated to ascertain the degree to which increasing chain length impacted rod formation during ultrasonication and assembly of the rod structures. Compound **7**, an *ortho*-carborane derivative functionalized with a protonated 4-amino-1-butyl side chain, was synthesized according to procedures previously reported.[13] Though aggregation of this amphiphile in solution has already been noted,[13] TEM images of the micro/nanorods are presented here. In contrast to the single-chained amphiphiles, compounds **8** and **9** each have two hydrophilic side chains conjugated to the *meta*-carborane scaffold. Last, compound **10** was synthesized as an example of an anionic species to

Scheme 1. Synthesis of Amphiphiles **1**−**3** and **4**[a]



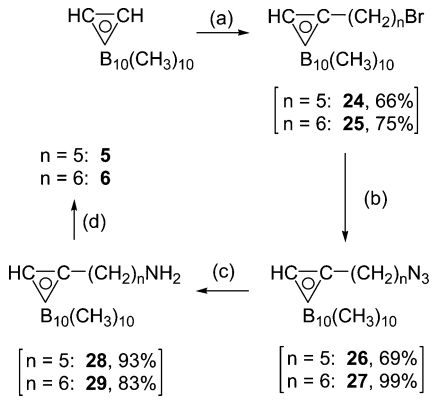
[a] Reagents and conditions: (a) (1) 1 equiv of BuLi, −12 °C to 25 °C, (2) $(CH_2)_3O$, 25 °C; (b) CBr_4, PPh_3, 25 °C; (c) NaN_3, Bu_4NBr, H_2O, benzene; (d) $LiAlH_4$, Et_2O, 0−25 °C, 12 h; (e) HCl; (f) NaCN; (g) $LiAlH_4$, Et_2O, 0−25 °C, 12 h; (h) HCl.

facilitate the investigation of amphiphile polarity on micro/nanorod self-assembly. While the distinction between crystallization and self-assembly is somewhat ambiguous, the TEM images of the rods formed from these carborane amphiphiles clearly show the formation of micro/nanostructures that resulted from the reorganization of these species upon sonication.

Trimethylene-Linked Amphiphiles, 1−3. The syntheses of hydrochloride salts of three 3-amino-1-propylcarborane derivatives were adapted from the synthetic strategy previously developed[5] for use with *meta*-carborane substrates, as shown in Scheme 1. Beginning with the three isomeric B-polymethylated carboranes,[13−15] each was treated with 1 equiv of BuLi followed by trimethylene oxide to form propanol derivatives in 90, 51, and 90% yield for the *ortho*-, *meta*, and *para*-compounds, respectively. The low yield of the *meta*-carborane product was due to the formation of the corresponding disubstituted product, formed in a nearly 1:1 ratio with the monosubstituted compound. The formation of disubstituted products was seen when utilizing *meta*-substrates and is likely due to a combination of electronic effects and steric hindrance, either of which would lead preferentially to the synthesis of monosubstituted derivatives of *ortho*- and *para*-carborane. Once derivatized, the hydroxyl moiety was transformed into a bromine functional group by carbon tetrabromide with triphenylphosphine in methylene chloride. In the presence of tetrabutylammonium bromide, the halogenated carboranes reacted with NaN_3 in a phase-transfer solvent mixture consisting of benzene and water to form the corresponding azide. Reduction of the azido functionalites by lithium aluminum hydride yielded primary amines, which were converted into the corresponding amphiphilic alkylamine chlorides **1**−**3**.

Tetramethylene-Linked Amphiphiles, 4 and 7. The synthesis of **7** was based on a known procedure.[18] The synthesis of compound **4**, shown in Scheme 1, started from 1-(deca-*B*-methyl-1,12-dicarba-*closo*-dodecaboran-1-yl)-3-bromopropane, **16**, which was treated with sodium cyanide in DMSO to produce the nitrile, **23**. Reduction of **23** with lithium aluminum hydride in ether gave the corresponding aminobutane, which was treated with HCl to afford the carborane-substituted amine hydrochloride salt **4**.

Scheme 2. Synthesis of *para*-Carborane Penta- and Hexamethylene-Linked Amphiphiles **5** and **6**[a]



[a] Reagents and conditions: (a) (1) 1 equiv of BuLi, −5 °C to 25 °C, 2 h; (2) $Br(CH_2)_nBr$, −78 °C−reflux, 48 h; (b) NaN_3, Bu_4NBr, H_2O, benzene; (c) $LiAlH_4$, Et_2O, 0−25 °C; (d) HCl, Et_2O, 25 °C.

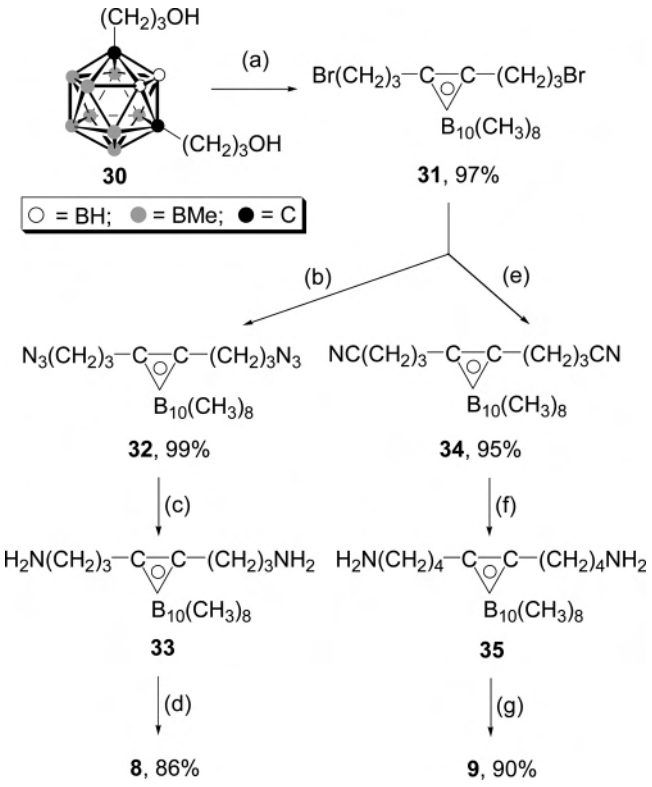
Deca-*B*-methyl-*para*-carborane Amphiphiles, 5 and 6. Penta- and hexamethylene-linked **5** and **6** share the same synthetic route, as shown in Scheme 2. Deca-*B*-methyl-*para*-carborane was deprotonated with BuLi, and the active lithiated species was reacted with excess 1,5-dibromopentane or 1,6-dibromohexane to form the corresponding bromide. The syntheses continued as described previously for the formation of compounds **1**−**3**, with the conversion of the bromine functionalities to azides and their subsequent reduction with lithium aluminum hydride to produce the corresponding amines.

Dual-Chain Amphiphiles, 8 and 9. As mentioned previously, the base-facilitated functionalization of octa-*B*-methyl-1,7-dicarba-*closo*-dodecaborane as its lithiated reagent yields both mono- and disubstituted products. For the synthesis of compounds **8** and **9** the bis(propanol) derivative (**30**) was converted to the corresponding dibromide upon reaction with carbon tetrabromide and triphenylphosphine. Following the same synthetic pathways used for compounds **1**−**4**, the dibromide was converted to the substituted aminopropane **33** through an azide, while compound **9** was formed through reduction of a nitrile precursor, as shown in Scheme 3.

Anionic Amphiphile, 10. The one-step synthesis of the negatively charged, monosubstituted, deca-*B*-methyl-1,12-dicarba-*closo*-dodecaborane **10** was achieved by alkaline hydrolysis of nitrile **23**. Neutralization of the excess NaOH with HCl upon conclusion of the reaction resulted in precipitation of the pure product as a sodium salt in good yield.

External Factors Affecting Rod Formation. At room temperature, compounds **1**−**7** are soluble in methanol and ethanol but insoluble in water. For studies of self-assembly, several milligrams of each sample were dispersed in sufficient water to achieve concentrations between 4 and 5 mM, if dissolved. Ultrasonication of each mixture yielded a translucent milky suspension that was transferred to a transmission electron microscopy (TEM) grid and air-dried to obtain samples for morphological studies. TEM images revealed that compounds **1**−**7** formed one-dimensional

Scheme 3. Synthesis of Dual-Chain Amphiphiles **8** and **9**[a]



[a] Reactions and conditions: (a) CBr_4, PPh_3; (b) NaN_3, Bu_4NBr, H_2O, benzene; (c) $LiAlH_4$, Et_2O, 0−25 °C, 12 h; (d) HCl; (e) NaCN, 77 °C, 44 h; (f) $LiAlH_4$, Et_2O, 0−25 °C; (g) HCl.

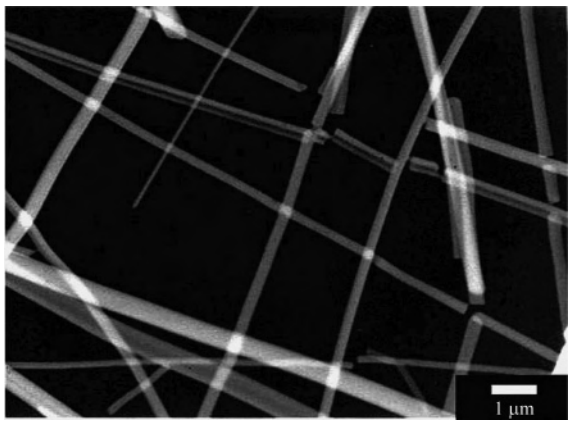


Figure 1. Typical transmission electron microscopy image showing carborane amphiphile microrods.

rodlike structures approximately 70 μm in length with average diameters of 300 nm (Figure 1). Amphiphiles **2** and **7** appeared to produce the longest rods with the most uniform distribution of diameters. All of the rod structures tended to further agglomerate into micrometer-sized rods that could be observed using an optical microscope.

To clarify whether rod formation was due to self-assembly of the amphiphiles in water or induced by water evaporation, the "milky" suspensions were inspected directly using an optical microscope. Uniform microrods were observed throughout the droplet, indicating that the microrods were formed in water during sonication rather than as a result of water evaporation. For comparison, the microscopic images of a sample of compound **2**, before and after sonication, are shown in Figure 2.

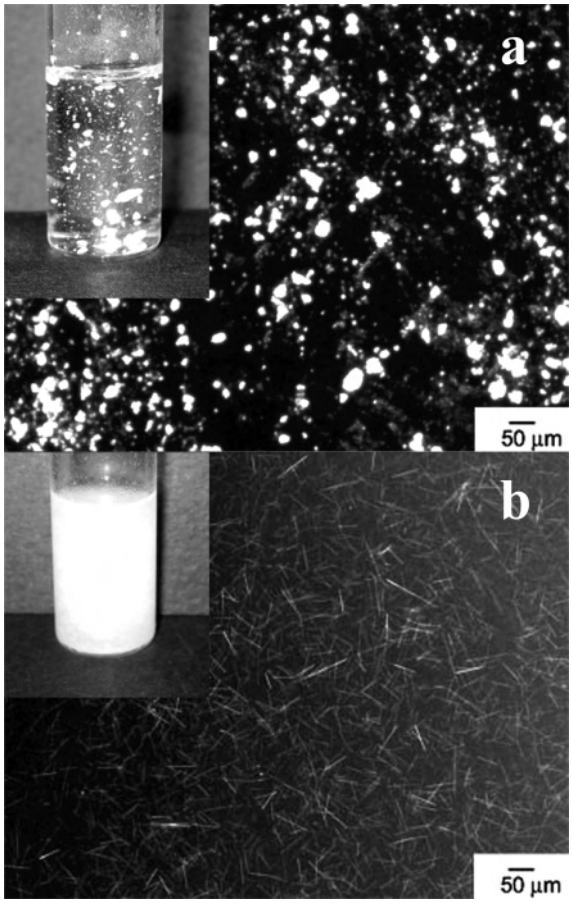


Figure 2. Optical microscopy images showing the morphologies of **2** suspended in water droplets before (a) and after (b) sonication. The transition from irregularly shaped particulates (a) to uniform microrods (b) is evident. The insets show the actual dispersion.

Compound **7** was used as a model to study the effect of concentration on microrod formation. Sonication of samples in water, which would yield 1, 2, 4, 5, and 9 mM solutions, if dissolved, each resulted in the formation of rodlike structures; rods formed at 9 mM were the shortest.

Since the microrods were obtained during dispersion, it was of interest to know whether sonication was critical for their formation. In control experiments, compounds **2** and **7** were heated in water until the solids dissolved to form clear solutions at approximately 90 °C. After cooling of the solutions to room temperature, two milky suspensions were obtained. Microscopy studies showed that rodlike structures were present in both samples; in addition to self-assembly of the solid species by sonication, the carborane amphiphiles are also able to form microrods through a conventional crystallization process. Though both methods of rod formation are possible, the self-assembly process provided a faster way to create the same rodlike architecture observed upon bulk heating and cooling of dilute solutions of the amphiphiles. Sonication may also decrease the size of the microrods, possibly leading to nanoscale rods.

It is well-known that the shapes of crystals vary depending upon the conditions of growth. To determine if the same was true of the self-assembled macromolecular aggregates of these amphiphiles, efforts were made to grow X-ray diffraction-quality crystals of **2** and **7** by employing different solvent systems with different assembly techniques, such as

slow evaporation, vapor diffusion, and solvent diffusion. As expected, the amphiphiles self-assembled into rods upon reprecipitation from a variety of solvents including methanol−water, acetonitrile−ethyl acetate, acetone, acetone−water, ethanol−water, chloroform, and chloroform−ether. Although the one-dimensional nature of the rods prevented the collection of X-ray diffraction data, it indicated that these single-chain, B-polymethylated carborane amphiphiles possess a great propensity to self-assemble into one-dimensional rods upon separation from solution under a variety of conditions.

Inherent Features Affecting Self-Assembly. In addition to the external conditions, such as concentration, temperature, and method of dispersion, internal structural factors were also explored that might affect the assembly of carborane amphiphiles. The inherent features investigated included the *ortho*-, *meta*-, or *para*-orientation of the side chains, affecting the dipole moment, side-chain length, counterion identity, the number of the side chains attached, and hydrophobicity.

The trimethylene-linked amphiphiles **1**−**3**, representing the three isomeric carborane derivatives of the same monosubstituted compound, possess similar self-assembly properties; the substitution pattern of the cage carbons and the associated dipole moment of the cages has little effect on their innate assembly properties. On the basis of the TEM microscopic images, it was found that, in relation to each other, **1** formed the thinnest rods, while **3** assembled into the shortest rod structures.

As with carborane cage identity, the length of the side chain had little effect on the assembly of the monosubstituted amphiphiles. Increasing the chain length of the *para*-substituted amphiphiles from three to six methylene units, compounds **3**−**6**, resulted in all cases in the formation of microrods upon sonication. Optical microscopic images indicate that the length of microrods formed from compounds **4**−**6** decreased as the side-chain length was increased (Figure 3), while compound **3** formed the shortest rods.

Counterions are known to significantly influence micelle formation from surfactants.[34] To determine if counterion identity would affect amphiphilic self-assembly, rod formation of the alkylammonium bromide, nitrate, sulfate, and three phosphate salts of 1-(octa-*B*-methyl-1,2-dicarba-*closo*-dodecaboran-1-yl)-4-aminobutane were compared. As solids, these four compounds were sonicated in water and the resultant suspensions were examined using optical microscopy. Uniform rods were formed in each case with the exception of the sulfate, which still exhibited self-assembly but tended to form less stable rods that were not easily visualized with optical or TEM microscopy.

The cationic, monosubstituted, B-polymethylated carborane amphiphiles exhibit a significant tendency to self-assemble into one-dimensional rods. For comparison, the anionic amphiphile **10** was synthesized by the basic hydrolysis of 1-(octa-*B*-methyl-1,2-dicarba-closo-dodecaboran-1-yl)-3-cyanopropane[18] with sodium hydroxide. The surfactant **10** is a white solid that is slightly soluble in water at room temperature. The same ultrasonication procedure was performed on the water suspension of **10**, and very short rods were observed using optical microscopy.

(34) Myers, D. *Surfactant Science and Technology*; VCH: New York, 1988.

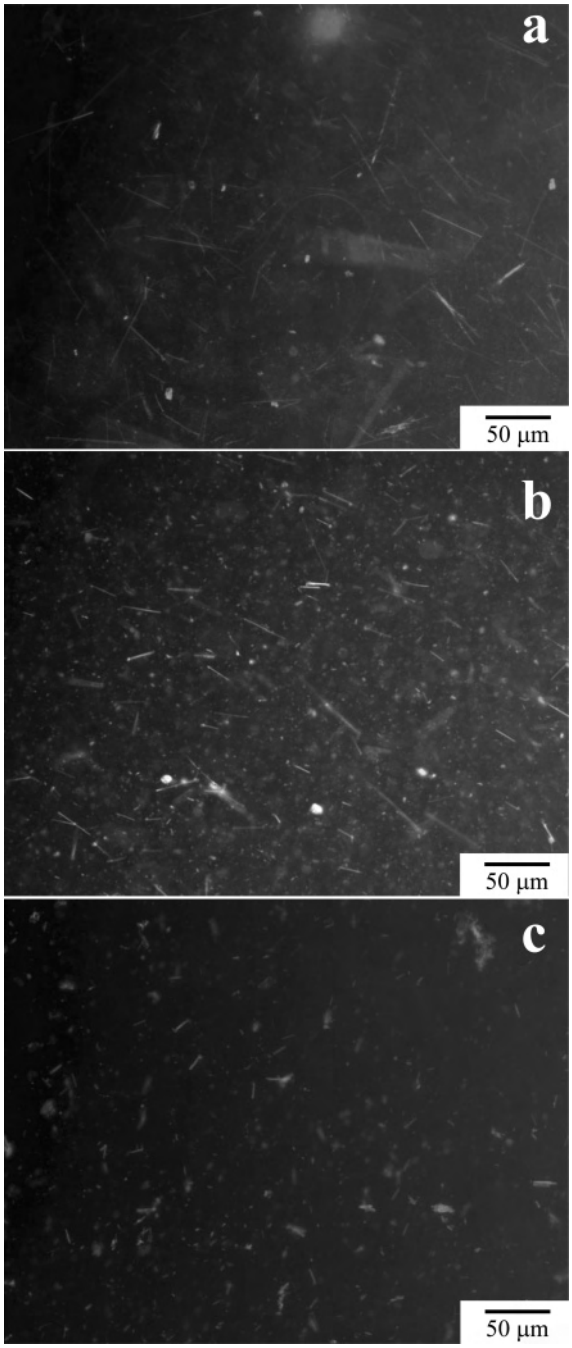


Figure 3. Optical microscopic images of amphiphile **4** (a), **5** (b), and **6** (c) suspended in water droplets showing the decreasing length of microrods from **4** to **6**.

It is known that [60]fullerene derivatives having one hydrophilic alkylamine hydrochloride side chain demonstrate significantly different self-organization behavior in water when compared to those functionalized with two hydrophilic alkylamine hydrochloride chains.[25] The dual-chain amphiphiles **8** and **9**, with increased hydrophilicity over their monosubstituted counterparts, were synthesized to investigate their aggregation behavior. As expected, they both have greater solubility in water than that of the single-chained analogues **1**−**7**. The ultrasonicated suspensions were examined using optical microscopy, but no rods were observed; only some small spheres with no defined structure were noted. After the suspensions were air-dried, hexagonal

assemblies were detected in the 1.6 mM suspension of compound **8**, rectangular structures were observed when the suspension concentration was increased to 8.3 mM, and featherlike aggregation was observed for dried 8 mM samples of **9**.

Of all the factors investigated, the critical packing parameter (the relative size of the hydrophilic to hydrophobic portions), as exemplified by dual-chain compounds **8** and **9**, had the greatest effect on the self-assembly of the B-polymethylated carboranes. Further investigation of these dual-chain amphiphiles is in progress.

Like self-assembled [60]-fullerene amphiphiles that possess strong hydrophobicity, the hydrophobic interactions could serve as the main attractive force for the assembly of B-polymethylated carboranes, as well. As a test of this hypothesis, the known compound 1-(1,2-dicarba-*closo*-dodecaboran-1-yl)-3-aminoproprane hydrochloride was synthesized and dispersed in water as previously described. This compound is significantly more hydrophilic than its B-polymethylated analogues and has good water solubility; upon sonication no milky suspension was formed, even when the concentration was doubled. Optical and TEM images indicated that no rods were formed. Only irregularly shaped solids were observed. In this study, rods were formed only from amphiphiles derived from B-polymethylated carboranes, forming assemblies that were stable for at least several months. Like [60]-fullerene derivatives, B-polymethylated carboranes have a tendency to aggregate or self-assemble, and the hydrophobic interaction played an important role in forming supramolecular micro/nanostructures.

X-ray Powder Diffraction Studies. Rods comprised of species **1**−**7** were studied by powder X-ray diffraction. All the B-polymethylated carboranes have major peaks in the region of $2\theta = 10-13°$. The *d* spacing was calculated to be nearly 9 Å, which closely corresponds to the size of the B-polymethylated *para*-carborane cage, with a reported van der Waals diameter of 9.9 Å.[14] The maximum *d* spacing calculated from the corresponding peak for species **1**−**7** was 21.4, 26.3, 19.3, 26.8, 27.9, 26.4, and 28.9 Å, respectively, which is twice their molecular size. A relationship between maximum *d* spacing and the size of the self-assembled rods from compounds **1**−**3** was also apparent: B-polymethylated *meta*-carborane has the largest d_{max} and formed the longest rods, while the *para*-compound had the smallest d_{max} and formed the shortest rods; compound **4**, with a d_{max} greater than that of compound **3**, experimentally formed the longer rods expected on the basis of these theoretical predictions.

Since the d_{max} spacing of compounds **1**−**7** is approximately twice the molecular length of each, the hydrophobic B-polymethylated carborane amphiphiles could be packing in a head-to-head fashion. To investigate further, HRTEM was employed with rods formed from compounds **2** and **7** at a voltage of 120 kV, but no molecular packing information could be obtained because the samples melted under the conditions necessary for image acquisition.

TG/DTA and IR Studies. The TG/DTA thermograms were recorded for rod samples of compounds **2**, **3**, and **7** to determine if hydrogen bonds to water molecules not only exist but possibly assisted in the formation of the assembled structures. The thermograms of the three compounds were similar—all indicated the loss of more than half of the sample mass between 200 and 300 °C, signifying endothermic decomposition. This result was consistent with observations made while recording the melting points of the samples; no obvious weight loss corresponding to water volatilization was observed between 30 to 150 °C. The FTIR spectrum of rod sample **2** as a Nujol mull exhibited a very weak and broad absorption between 3500 and 3300 cm^{-1} which suggested the possible presence of water since the $\nu(RNH_2Cl^+)$ signal is typically found from 3100 to 3000 cm^{-1}. This is not conclusive.

Conclusion

A series of novel, hydrophobic, polymethylated carborane-containing amphiphiles, **1**−**10**, have been synthesized, and it was demonstrated for the first time that such species undergo self-assembly to form micro/nanostructures under a variety of conditions. The pronounced tendency for self-assembly is mainly due to the enhanced hydrophobicity and size of the B-polymethylated carboranes and their consequent hydrophobic interaction. Many factors have been investigated which affected the supramolecular assembly of amphiphilic carborane surfactants in different environments, including carborane cage substitution pattern, solvent, counterion identity, and chain length. To better control the size and shape of carborane aggregates, further study is required to delineate the detailed structure of the assembled rods at the molecular level and the mechanism of their assembly. The self-assembly of these B-polymethylated carboranes provides additional prospects in the search for novel materials having interesting structural properties and potential applications in advanced materials technologies and biomedicine. The highly methylated icosahedral carboranes may prove to be the most effective hydrophobes capable of simple synthetic manipulation. They are representative of "organoboranes of the second kind".[35−37]

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Supporting Information Available: Full experimental and spectroscopic details for all compounds reported (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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