

An Icosahedral Array of Methyl Groups Supported by an Aromatic Borane Scaffold: The $[closo-B_{12}(CH_3)_{12}]^{2-}$ Ion

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The quest for globular structures possessing both hydrophobic surfaces and extraordinary kinetic stability stems from the search for novel modules with which to synthesize supramolecular structures,¹ weakly coordinating anions,² and space-controlling drug components.³ The fullerenes, characterized by unique chemistry and physical properties, represent one family of such precursors.⁴ Another family of globular hydrophobes, described by us as “camouflaged” carboranes,⁵ has been described.^{6,7} These species may approach the van der Waals diameter of C_{60} by attachment of methyl groups and functionalized methyl substituents to the icosahedral scaffolding of the aromatic $[closo-C_nB_{12-n}H_{12}]^{n-2}$ ($n = 0-2$). Whereas hydrophobic and amphiphilic derivatives of this sort are known with $n = 1$ and 2, the fully methylated derivative of the parent species, dodecamethyl-*closo*-dodecaborate(2-), **1** ($n = 0$), is now reported for the first time.

Here we describe a new permethylation technique for icosahedral *closo*-boranes employing trimethylaluminum and methyl iodide in the absence of a solvent (Scheme 1). This method produced **1** when applied to the parent anion of the polyhedral borane family, aromatic $[closo-B_{12}H_{12}]^{2-}$, **2**. The anion **1** was characterized by 1H and ^{11}B NMR spectroscopy, high-resolution fast atom bombardment (FAB) mass spectrometry, cyclic voltammetry, and single-crystal X-ray diffraction.

Applying two electrophilic permethylation techniques employed for carboranes⁵⁻⁷ to $[N(n-Bu)_4]_2$ resulted in partial triflation (using methyl trifluoromethanesulfonate) or halogenation (using aluminum chloride/methyl iodide). However, a solution of **2**, trimethylaluminum, and methyl iodide kept at 45 °C for 1 day led to various polyiodinated species $[closo-B_{12}Me_{12-x}I_x]^{2-}$ ($x \leq 5$). Additional heating of the suspension for 5 days gave **1** and $[closo-B_{12}Me_{11}I]^{2-}$, **3**. This mixture was isolated and again heated at the reflux temperature in neat trimethylaluminum to convert the byproduct **3** into **1**.

Apparently, the iodine atoms of the B–I vertexes are successively exchanged by methyl groups when the species $[closo-B_{12}Me_{12-x}I_x]^{2-}$ ($x \leq 5$) are heated in trimethylaluminum. To verify this hypothesis, the monoiodinated anion $[closo-B_{12}H_{11}I]^{2-}$, **4**, was heated to reflux in neat trimethylaluminum, and $[closo-B_{12}H_{11}(CH_3)]^{2-}$, **5**, was obtained in 55% yield. This procedure provides an alternate route to monoalkylated $[closo-B_{12}H_{11}R]^{2-}$ anions, which are usually obtained through palladium-catalyzed alkylation

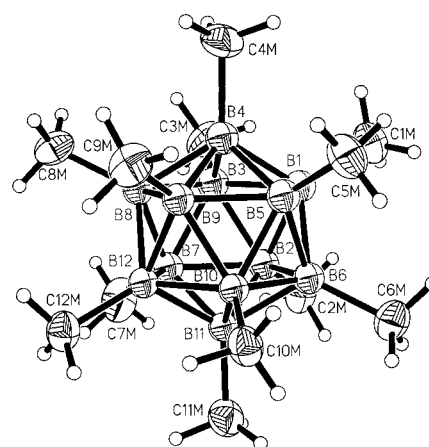
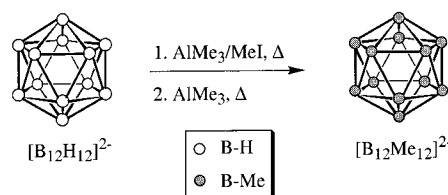


Figure 1. Molecular structure of the dodecamethyl-*closo*-dodecaborate(2-) anion **1** (thermal ellipsoids represent a 30% probability level). Selected bond distances (pm) of the anion: B–B = 174(11)–181(11); B–C = 159(11)–170(11).

Scheme 1



of **4** with Grignard reagents.⁸ No reaction was observed when $[PPh_4]_2[closo-B_{12}I_{12}]$ was heated for 4 days in neat trimethylaluminum at the reflux temperature.

The NMR data pertaining to **1** (^{11}B NMR: singlet at -10.8 ppm, 1H NMR: broad singlet at -0.48 ppm) are in accordance with its symmetry (point group I_h). Because of the quadrupole moment of the boron nucleus, a ^{13}C NMR resonance for the B–CH₃ carbon atoms of **1** is not observed. High-resolution FAB mass spectrometry confirms the mass of the permethylated derivative **1** (centered at $m/z = 310.4020$ with the correct isotopic distribution). The cyclic voltammogram of $[Et_4N]_2$ **1** (100 mM Et_4NPF_6 , $Ag/AgCl$, acetonitrile) shows a reversible one-electron oxidation process $[closo-B_{12}(CH_3)_{12}]^{2-}/[closo-B_{12}(CH_3)_{12}]^-$ at $E_{1/2} = 0.41$ V. The dinegative species **1** is more easily oxidized than the monoanion $[closo-CB_{11}(CH_3)_{12}]^-$ ($E_{pa} = 1.6$ V).⁶

Blood-red single crystals of $[(C_5H_5N)_2CH_2]_2$ **1**·CH₃CN were obtained from acetonitrile/ethanol.⁹ The crystal structure of **1** (Figure 1) confirms the permethylation of the B_{12} icosahedron with some distortion of its icosahedral geometry. The B–B bond lengths of **1** [174(1)–181(1) pm] are similar to those of the unsubstituted anion **2** [175.5(7)–178.0(7) pm].¹⁰ The B–C bond distances of **1** [159(1)–170(1) pm] are longer than the B–C bond of **5** [158(2) pm]⁸ and the exo B–C bonds of $[closo-CB_{11}(CH_3)_{12}]^-$ [159(2)–160.1(6) pm]⁶ and *closo*-1,12- $C_2B_{10}(CH_3)_{12}$ [158.3(6) pm].⁵ The red color of $[(C_5H_5N)_2CH_2]_2$ **1** is apparently due to a charge-transfer interaction of the anion **1** with the pyridinium rings of the dipositive cation. The plane through the triangle B1, B4, and B5 is nearly parallel to the plane established by a pyridinium ring N1 and C2–C6. The angle between the

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(9) Crystal data for $[(C_5H_5N)_2CH_2]_2$ **1**·CH₃CN: blood-red; orthorhombic; $Pc2_1n$, $a = 971.5(7)$ pm, $b = 1505(11)$ pm, $c = 2282(2)$ pm; $Z = 4$; $R = 0.074$, $R_w = 0.184$; GOF = 1.04.

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normals of these two planes is 7.3° . The distances of the boron atoms B1, B4, and B5 from the latter plane are 508(1), 486(1), and 504(1) pm, respectively; the distances of the methyl carbon atoms C1M, C4M, and C5M are 389(1), 338(1), and 378(1) pm, respectively.

The longest across-cage methyl carbon–methyl carbon distances of **1** average 668 pm; the corresponding maximum methyl hydrogen–methyl hydrogen distance is 761 pm compared to 707 pm for C_{60} .¹¹ This property coupled with water solubility should provide a novel prosthetic group for drug design. Preliminary results indicate that the permethylated dianion **1** may be oxidized in a fashion analogous to that of the monocarborane monoanion¹²

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$[closo-CB_{11}(CH_3)_{12}]^-$ to give the radical $\{[closo-B_{12}(CH_3)_{12}]^*\cdot\}^-$.¹³ We are currently investigating the permethylation of other polyhedral borane anions and exploring the organic chemistry of the hydrocarbon surface of **1**.

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Supporting Information Available: Synthetic details, 400 MHz 1H and 160 MHz ^{11}B NMR data of **1**, and X-ray structural information on $[(C_5H_5N)_2CH_2]1 \cdot CH_3CN$ (PDF). An X-ray crystallographic file, in CIF format, is available through the Internet only. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(13) The radical monoanion $\{[closo-B_{12}(CH_3)_{12}]^*\cdot\}^-$ was observed under FAB conditions as the parent molecular ion of **1**.