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Synthesis of a New Class of Carborane-Containing Star-Shaped Molecules via Silicon Tetrachloride Promoted Cyclotrimerization Reactions

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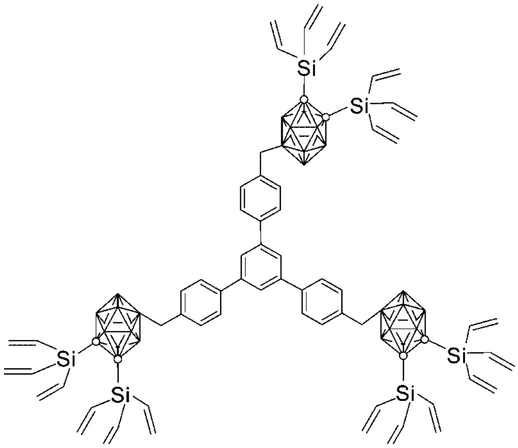
ABSTRACT



Symmetrical star-shaped molecules with carborane clusters on the periphery have been synthesized in good yields via silicon tetrachloride mediated cyclotrimerization reactions of 9-benzyl derivatives of carboranes with acetyl group substitution on the benzene ring. Facile functionalization of these symmetrical core structures with 1-iodoheptane and trivinylchlorosilane produce compounds which could be used as liquid crystalline substances and precursors for synthesis of higher order carbosilane dendrons.

Polyhedral carborane clusters are a class of synthetically useful molecules that have practical applications in areas such as materials science, medicine, and catalysis.[1] They have been widely used in making new boron neutron capture therapy (BNCT) drugs[2] and, more recently, in the syntheses of macromolecular structures such as dendrimers,[3] liquid crystalline substances,[4] and thermally stable polymers.[5] Dendrimers are globular macromolecules consisting of a symmetrical core and layers of branched repeating units extending from the core and end groups on the outer layer of the repeating units. These branched macromolecules have found applications as low-dielectric materials, catalysts,

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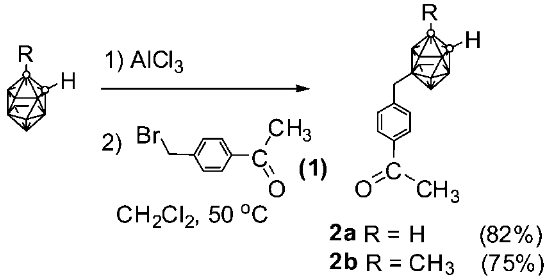
biosensors, magnetic resonance imaging agents, drug delivery vehicles, organic semiconductors, and organic light-emitting diodes.[6] Silicon tetrachloride mediated cyclotrimerization of aryl ketones has been found to be an efficient methodology for the construction of symmetrical dendritic structures.[7] In this paper, we report the syntheses of carborane-containing symmetrical star-shaped molecules which can be used as a core for dendrimers and liquid crystalline substances via silicon tetrachloride mediated trimerization of acetyl-containing benzyl derivatives of carboranes. 1,3,5-Tris(1,12-dicarba-*closo*-dodecaboran-1-yl) benzene, a similar kind of star-shaped molecule containing *p*-carborane, is known.[8]

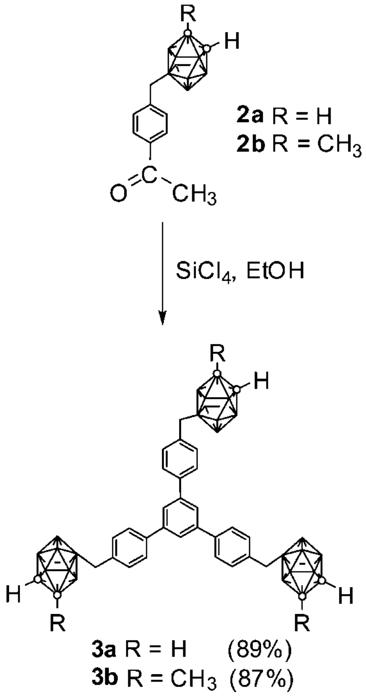
Palladium-catalyzed cross-coupling of three 1,12-dicarba-*closo*-dodecaborane units to a 1,3,5-triiodobenzene afforded 1,3,5-tris(1,12-dicarba-*closo*-dodecaboran-1-yl) benzene in a moderate 56% yield.[8] In addition, another cyclic trimer containing *m*-carborane is also reported to be formed in 5% yield from the reaction between 1,7-$Cu_2C_2B_{10}H_{10}$ and *meta*-diiodobenzene in the presence of pyridine in 1,2-dimethoxyethane.[9]

Organoboranes in which the organic moiety is attached at the boron atom of the *o*- and *m*-carborane cages have been synthesized by electrophilic alkylation of carborane cages with alkyl halides and benzyl halides that contain electron-withdrawing substituents such as NO_2, COOH, COOMe, and COPh in the presence of aluminum chloride.[10] Employing a similar methodology, we synthesized the benzyl derivative of the *o*-carboranes (with benzylation at the B-9 position) containing an acetyl group on the benzene ring, as shown in Scheme 1. Electrophilic benzylation of the *o*-carborane and its derivatives were carried out by refluxing a mixture of 1-(4-(bromomethyl)phenyl)ethanone (**1**)[11] and *o*-carborane in dichloromethane in the presence of aluminum chloride (Scheme 1). Although the boron atoms 8, 9, 10, and 12 of the cage are the most negative, the electrophilic reactions of 1, 2-$C_2B_{10}H_{12}$ in the presence of Lewis acid catalysts such as aluminum chloride preferentially gives B-9 derivatives. The carbon atoms and those borons directly linked to them (3, 6, 4, 5, 7, 11) do not undergo Friedel−Crafts-type reactions.[10,12] The cage appended 9-benzyl carboranes, **2a**−**b**, then underwent facile trimerization with silicon tetrachloride and ethanol to produce compounds **3a**−**b** (Scheme 2). Such symmetrical compounds are useful building blocks for designing more complex target molecules and can also serve as central cores for the design of higher level dendrimeric structures. Some of these star-shaped molecules show luminescence and liquid crystalline properties.[13] Func-

Scheme 1. Benzylation of *o*-Carborane



Scheme 2. Cyclotrimerization of Benzylated Carboranes Containing an Acetyl Group on the Benzene Ring



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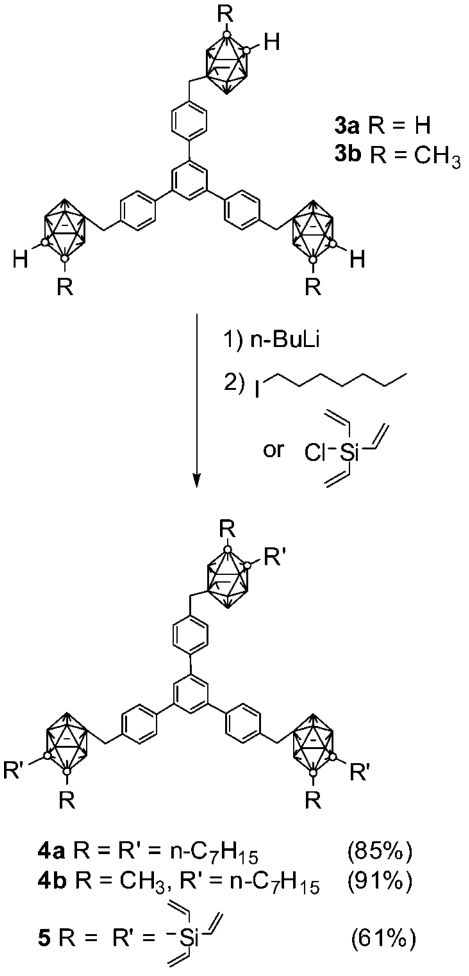
tionalization of the carborane-containing symmetrical trimers **3a** and **3b** may be achieved by reaction with various silanes and aliphatic halides. Scheme 3 illustrates the reaction of lithium salts of **3b** with stoichiometric amounts of 1-iodoheptane in THF and the reaction of the dilithium salt of **3a** with trivinylchlorosilane in THF. These reactions led to the formation of compounds **4a**, **4b**, and **5**, respectively, in good yield. Such heptyl derivatives of carboranes have shown liquid crystalline properties,[14]and compound **5** may be useful for synthesis of higher order carbosilane dendrons via hydrosilylation reactions.[15] All compounds were characterized by ^{1}H, ^{13}C, ^{11}B NMR, and IR, and the melting points of all solid compounds were determined. Cyclotrimers **3a** and **3b** especially have high melting temperatures, 180 and 170 °C, respectively. The IR spectra of compounds containing *closo* clusters **2**−**5** show strong bands between 2597 and 2569 cm^{-1} corresponding to ν (B−H). For compounds **2a** and **2b**, bands were observed at 1663 and 1666 cm^{-1} corresponding to ν (C=O). The ^{1}H NMR spectra of cyclotrimers **3a** and **3b** and their derivatives **4a**, **4b**, and **5** showed resonances in the region δ 7.8−6.9 ppm typical for phenyl protons; compound **5** showed resonances between 6.28 and 5.71 ppm corresponding to vinyl protons. ^{13}C NMR spectra of compounds **3**−**5** showed resonances between 145 and 123 ppm typical for phenyl carbons, and compound **5** showed resonances at 138.0 and 131.9 ppm corresponding to vinyl carbons. The proton-decoupled and proton-coupled ^{11}B NMR spectra of all compounds exhibit a spectral pattern that corroborates substitution at the B-9 position of the carborane cages.[10,12] Finally, the mass spectral data of all compounds from **3**−**5** have confirmed their formation.

Scheme 3. Functionalization of Cyclotrimers



An attempt to trimerize 1-acetyl-*o*-carborane with silicon tetrachloride and ethanol failed to produce the desired cyclotrimer. Mechanistically, the trimerizations proceed via the initial formation of a carbocation on the acetyl group, which then reacts with another acetyl group in its enol form, and ultimately the trimer forms by combining with a third acetyl carbocation.[16] From the investigations of carborane chemistry, it has been concluded that the C−H’s of the carboranes behave as electron-deficient aliphatic moieties, whereas the chemical behavior of the B−H’s has more of an aromatic character.[12] The electron-deficient character of cage C−H’s may not support the formation of an adjacent carbocation. However, trimerization of **2a**,**b** proceeds smoothly.

In summary, we have shown that an acetyl aromatic moiety attached to the boron atom of the carborane cages undergoes trimerization reactions to generate symmetric building blocks for synthesis of higher order dendrimers and liquid crystalline substances, metallacarboranes, and new BNCT agents. Dendrimers are prepared using a divergent or a convergent approach. In the divergent method, dendrimers are made in a stepwise manner from a small polyfunctional core, whereas in the convergent approach, the growth of the molecule starts from the periphery and finally attaches to the core moiety.[17] The present study has opened a new route to synthesize dendritic structures by both convergent and divergent approaches because of the ease of functionalization of the carboranes present on the periphery of the symmetrical core. A new class of carborane-containing carbosilane dendrons can also be synthesized starting from **5** and lithiated carboranes via hydrosilylation reactions.[18] Furthermore, compounds **3a** and **3b** can be used to make a new class of

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metallacarboranes via decapitation of carborane cages.[19] A new class of BNCT agents may be possible by making these compounds water soluble.[20] Further work is now underway to synthesize higher generation dendrimers containing multiple carborane clusters, derivatization of the carborane clusters on the periphery of the trimers, as well as making a new class of metallacarboranes and BNCT agents.

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Supporting Information Available: Detailed description of typical experimental procedures and characterization data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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