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The CH-functionalization of *B*-substituted organosilicon derivatives of polyhedral carboranes as a way to obtain new materials

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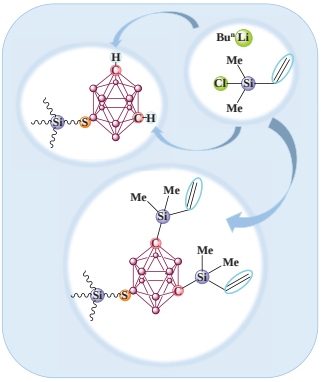
The metallation of CH-groups in carboranyl polyhedra with *n*-butyllithium followed by end-capping with chloro(dimethyl)vinylsilane was explored using a model *B*-substituted organosilicon derivative obtained previously, the optimal conditions being Et_2O, –10 → 20 °C, total processing time 125 min. This procedure was applied to prepare a zero-generation polyfunctional *B*-substituted carborane-carbosilane dendrimer G_0-4 cages.



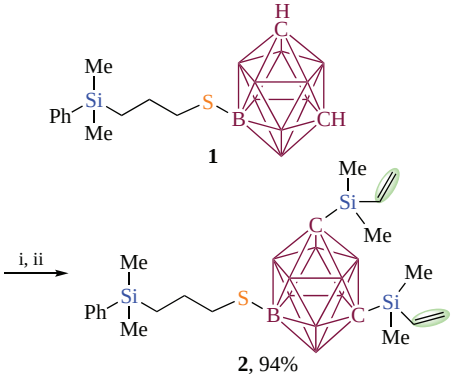
Keywords: carbosilanes, dendrimers, carboranes, CH-functionalization, metallation, core–shell, organosilicon compounds.

One of the most actual tasks of modern materials science is the creation of hybrid materials with a well-defined structure based on organic–inorganic systems. Among such materials, organosilicon compounds and polymers based on them containing various modifying fragments are of particular interest.[1–11] The advantage of such compounds lies in the wide variety of possible structures, which makes it possible to significantly expand the range of useful properties of new materials and, as a result, to increase the potential for their application. Currently, one of the effective approaches to obtaining new organosilicon compounds with desired properties is their modification with organoelement fragments.[12–18] Among the wide range of such fragments, functional derivatives of polyhedral carboranes are highlighted. Icosahedral carboranes possess rigid geometry, aromaticity, rich derivative chemistry, thermal and chemical stability, and exceptional hydrophobic character.[19–25] Due to this, an interest in the use of icosahedral carboranes for application in material chemistry is growing.[26–28] Carborane-equipped organosilicon polymers possess good thermal and radiation stability, they are non-toxic and biologically inert.[29–31]

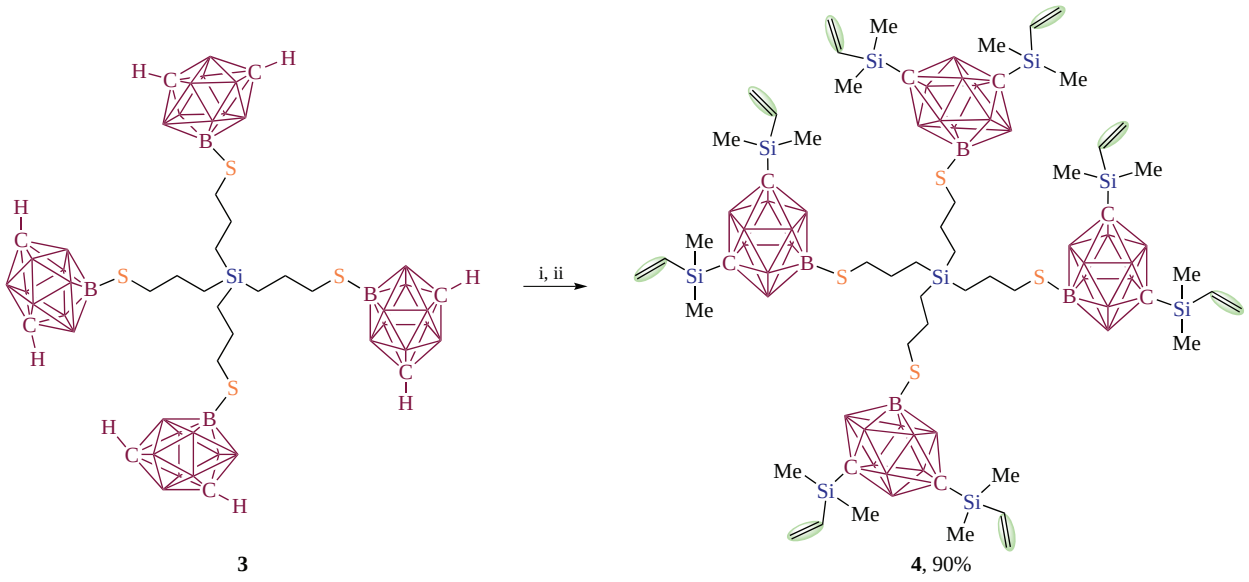
At present, numerous syntheses of organosilicon derivatives of polyhedral carboranes,[32–37] including those with a dendritic structure, have been described.[38–41] However, the attention is mainly focused on the preparation of *C*-substituted derivatives of carboranes, while *B*-substituted derivatives are practically not described, the first boron-substituted carborane-containing dendrimers were obtained only in 2020.[42] We suppose that *B*-substituted organosilicon derivatives of carboranes have a high practical potential since they incorporate reactive CH-groups of the carborane polyhedron. The reduced electron density on the carbon atoms of the polyhedron causes a high acidity of the C–H bond and, accordingly, provides a possibility of metallation of their CH-groups. The metallation reaction is commonly employed for the synthesis of various functionalized organic and organometallic compounds with carboranyl groups.[20,43]

In this work, we studied the possibility of obtaining new functional compounds based on boron-substituted organosilicon derivatives of polyhedral carboranes. We chose the classical lithiation reaction[44–47] as a tool for the functionalization of the CH-groups in carborane moieties.[19,48] At the first step, we studied the possibility of functionalizing the carborane polyhedron using model compound **1** as an example.[35] Lithiation of CH-groups in **1** with *n*-butyllithium followed by end-capping with chloro(dimethyl)vinylsilane resulted in derivative **2** (Scheme 1).

The optimal conditions for the functionalization were selected using this reaction as an example. First, THF was chosen as a



Scheme 1 *Reagents and conditions*: i, Bu^nLi, Et_2O, –10 → 20 °C, 1 h; ii, $Me_2Si(CH{=}CH_2)Cl$, room temperature, 2 h.



Scheme 2 *Reagents and conditions*: i, Bu^{n}Li, Et_2O, –10 → 20 °C, 1 h; ii, $Me_2Si(CH{=}CH_2)Cl$, room temperature, 2 h.

solvent for the lithiation of CH-groups in carboranyl polyhedra. In THF solutions, the aggregation of *n*-butyllithium is significantly weaker due to coordination of lithium with the oxygen atoms of ethereal solvents (Bu^{n}Li exists as tetramer in THF). However, in the course of the reaction darkening of the reaction mixture was observed, and the subsequent analysis of the products by ^{1}H NMR spectroscopy did not reveal the target compound. This could be due to the fact that at room temperature THF is prone of α-deprotonating to decompose into ethylene and acetaldehyde enolate. For this reason, we moved to diethyl ether which is more resistant to Bu^{n}Li and promotes its disaggregation, so the reaction could be carried out at room temperature. In diethyl ether, the target compound, 1,7-bis[dimethyl(vinyl)silyl]-9-{3-[dimethyl(phenyl)silyl]propylthio}-*m*-carborane **2**, was really obtained, which was confirmed by ^{1}H, ^{11}B{H}, ^{13}C and ^{29}Si NMR spectroscopy and elemental microanalysis (see Online Supplementary Materials). It is also worth noting that the use of Et_2O makes it possible to significantly simplify the end-capping stage (there is no need to heat the reaction mixture) as well as the process of isolating the target product.

Further, under selected experimental conditions, we carried out the reaction with a more complex system, zero-generation boron-substituted carborane-carbosilane dendrimer **3**[42] (Scheme 2). According to ^{1}H NMR spectroscopy, the conversion of CH-groups in target product tetrakis(3-{1,7-bis[dimethyl(vinyl)silyl]-*m*-carboranylthio}propyl)silane **4** reached 90%. Thus, on example of the functionalization of the CH-groups of the carborane polyhedra of the dendrimer G_0-4 cages, we have shown the possibility of obtaining functional compounds based on boron-substituted carborane-carbosilane dendrimers.

In conclusion, we present an approach to the modification of boron-substituted organosilicon derivatives of polyhedral carboranes using the lithiation reaction. On a model compound containing two CH-groups in the carborane polyhedron, the optimal conditions were selected. The possibility of modifying a polyfunctional compound, a zero-generation *B*-substituted carborane-carbosilane dendrimer, was shown. This is the first example of the functionalization of *B*-substituted carborane-carbosilane dendrimers. This approach opens a way to the production of a new generation of hybrid organoelement dendrimers. Moreover, this functionalization of hybrid carborane-containing dendrimers and appending of vinyl functional groups make them promising for various applications, for example, as precursors for the production of organoelement aerogels, as cores for the synthesis of star-shaped polymers, and as molecular fillers for organoelement composite materials.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.01.014.

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