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Synthesis of Small Carboranylsilane Dendrons as Scaffolds for Multiple Functionalizations

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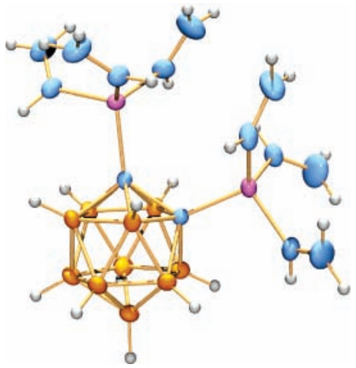
ABSTRACT



Small carbosilane dendrons in which a *closo*-carborane is located at the focal point have been prepared by a sequence of steps involving hydrosilylation and reduction reactions. These compounds are used as scaffolds for peripheral functionalization with styrene, chlorovinylstyrene, or suitable carboranes, while keeping the $C_{cluster}$–Si (C_c–Si) bond. Modification of the core by reduction of the carborane with Mg/$BrCH_2CH_2Br$ was also achieved.

Dendrimers are important due to their very attractive features and allow the design of macromolecules with tailored properties through the incorporation of suitable functions at the core or the periphery sites.[1] Dendrons are dendrimer "wedges" that contain a specific functional group at the core, which generally is different from the end groups on the periphery. The use of dendritic wedges or dendrons, having functionalities on the surface and another single functionality at the core, has not been widely developed. Generally, because of their conical shape, dendrons are used to produce shape-controlled nanostructures and nanoobjects.[2] The 1,2-dicarba-*closo*-dodecaborane and its derivatives show exceptional characteristics,[3] such as chemical and thermal stability,[4]

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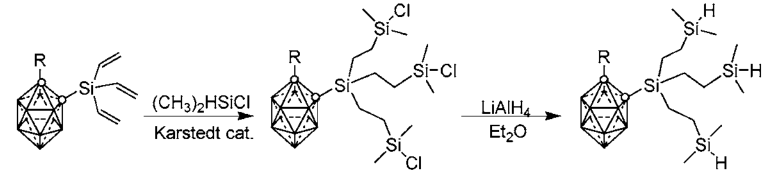
Scheme 1. Preparation of Chloro-Terminated Carboranylsilanes **4**−**6** and Subsequent Reduction to Obtain Compounds **7**−**9**



R = $Si(CHCH_2)_3$, **1**
R = CH_3, **2**
R = C_6H_5, **3**

R = $Si[(CH_2)_2(CH_3)_2SiCl]_3$, **4**
R = CH_3, **5**
R = C_6H_5, **6**

R = $Si[(CH_2)_2(CH_3)_2SiCl]_3$, **7**
R = CH_3, **8**
R = C_6H_5, **9**

low nucleophilicity,[5] electron-withdrawing properties,[6] and a highly polarizable σ-aromatic character, that have stimulated the development of a wide range of potential applications.[7] Their rigid geometry and the relative ease of derivatization at the carbon and boron atoms have allowed the preparation of a broad number of compounds.[8] Recently, we became interested in the synthesis of carborane-containing star-shaped molecules in which a carbosilane core is used as a scaffold.[9] Following our work dealing with the synthesis and study of properties of carborane-containing carbosilanes, we wish to report some examples of dendrons, in which the clusters have been the focal point or core. The versatility of the carborane cluster allows it to act as a scaffold to extend the dendron from the carbon atoms to the periphery or to be modified as a focal point.

Compounds **1**−**3** were prepared from the reaction of the dilithium or monolithium salts of the respective carboranes, 1,2-$C_2B_{10}H_{12}$, 1-CH_3-1,2-$C_2B_{10}H_{11}$, and 1-C_6H_5-1,2-$C_2B_{10}H_{11}$, respectively, with the stoichiometric amount of $(CH_2{=}CH)_3$-SiCl in Et_2O/toluene solutions at room temperature. All three compounds were purified and isolated as pure crystalline air-stable solids in moderate to good yields (52.4, 86.4, and 80.0%, respectively). These compounds present two reactive parts: the carborane cluster (focal point) and the trivinylsilanes (branched points). Thus, compounds **1**−**3** were used as core molecules from which a set of dendrons were prepared by hydrosilylation, reduction, and peripheral functionalization alternate steps.[10]

Hydrosilylations of vinyl functions bonded to the carborane moiety were performed with $(CH_3)_2HSiCl$ in the absence of solvent at room temperature and in the presence of the Karstedt catalyst (3−3.5% Pt) (Scheme 1). The ^1H NMR olefinic resonances were used to follow the complete hydrosilylation reaction by the disappearance of the vinylic protons. The chloro-terminated carboranylsilane dendrons **4**−**6** were recovered in high yield (80−95%). The presence of Si−Cl in the periphery should allow the divergent growth of the dendrons to subsequent generations by successive allylation and hydrosilylation steps.[10] However, our interest has been oriented toward the introduction of different functions on the periphery and the study of the C_c−Si bond stability, to use the carborane cluster as a focal point and a silicon-core protector. Thus, reductions of Si−Cl functions in **4**−**6** were achieved with $LiAlH_4$ in Et_2O, at room temperature overnight, to give **7**−**9** in 60−80% yield, as spectroscopically pure oils (Scheme 1).

Different ligand systems were coupled to dendron peripheries to demonstrate the possibility of a further functionalization. Compounds **7**−**9** with Si−H functions are used as hydrosilylation reagents. The hydrosilylation of styrene using **8** in a solvent-free reaction, in the presence of the Karstedt catalyst, at room temperature overnight, leads quantitatively to compound **10**. Likewise, the functionalization has also been achieved by the hydrosilylation reaction of chlorovinylstyrene with **9** in the same conditions to give compound **11** (99%) (Scheme 2). Compounds **10** and **11** provide a means of activation of dendrons for further reactions, such as transition-metal η^6-arene complexes[11] or coupling agents for Suzuki cross-coupling reactions,[12] respectively.

Furthermore, chloro-terminated dendrons **5** and **6** reacted with the lithium salts of 1-CH_3-1,2-$C_2B_{10}H_{11}$ and 1-C_6H_5-1,2-$C_2B_{10}H_{11}$, in an Et_2O/toluene (1:2) solution at room

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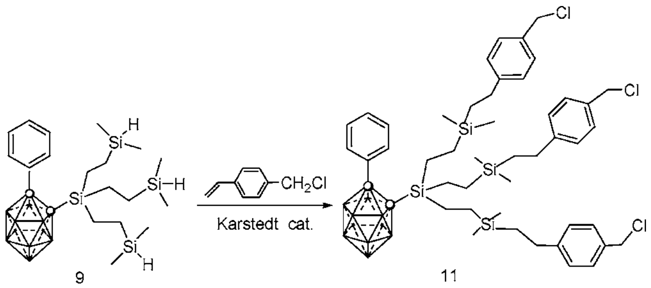
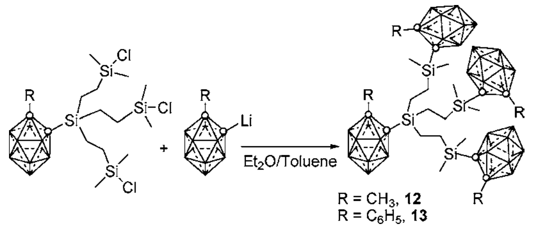
Scheme 2. Preparation of **11** by Hydrosilylation of Chlorovinylstyrene with Compound **9**

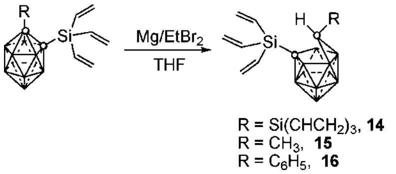


temperature, to give the peripheral carborane-functionalized **12** and **13**, respectively (Scheme 3). These compounds represent an example in which the cluster versatility has led to the preparation of carbosilane dendrons functionalized with carboranes in the focal point and on the periphery. We have studied several strategies to functionalize the surface and obtain molecules having original structures. The chemical reactivity of the cluster located at the core and its compatibility with the functionalities of the surface are of great interest. Thus, in this work, cluster modification was achieved by reduction using a route recently described by our group, in which Mg/BrCH$_2$CH$_2$Br was the reducing agent.[13] Compounds **1**−**3** were reacted with Mg/BrCH$_2$CH$_2$Br in THF at room temperature for 15 h (Scheme 4). Residues were treated with water and [NMe$_4$]Cl to give compounds **14**−**16** as white solids, in which the C$_c$−Si bond was not cleaved. This reducing method can lead to the formation of two isomers: the kinetic and the thermodynamic.[13] In our case, only the corresponding thermodynamic isomer was observed, as will be later confirmed by NMR spectroscopy.

Scheme 3. Preparation of Peripheral Carboranyl-Functionalized Dendrons **12** and **13** from **5** and **6** and Carborane Lithium Salts



Scheme 4. Reduction of the Carborane Located at the Focal Point with Mg/EtBr$_2$



All compounds were characterized by IR, ^{1}H{^{11}B}, ^{13}C{^{1}H}, ^{11}B, and ^{29}Si NMR mass spectrometry, and compounds **1**−**3** were confirmed by X-ray diffraction analysis. The IR spectra for compounds containing *closo* clusters, **1**−**13**, present typical υ(B−H) strong bands between 2584 and 2574 cm^{-1}, whereas in *nido* compounds **14**−**16**, the corresponding band appears in the range 2515−2525 cm^{-1}. For **7**−**9**, the typical υ(Si−H) band at 2110 cm^{-1} is observed. Conversely, the disappearance of this band in the IR spectra of **10** and **11** corroborates their formation. The ^{1}H NMR spectra for **1**−**3** and **14**−**16** exhibit resonances for vinyl protons in the region 6.39−5.58 ppm and other resonances for protons of the related *exo*-cluster groups. All vinylic protons have been unambiguously assigned for each molecule (Table 1, Supporting Information). Moreover, the ^{1}H NMR spectra of **4**−**13** display resonances corresponding to the $-CH_2-CH_2-$ groups in the region 0.49−0.95 ppm and a signal due to the Si−C*H*$_3$ protons. For compounds **7**−**9**, the presence of the Si−*H* bond in the molecule was confirmed by a septuplet at $\delta = 3.87$ ppm (^3J(H,H) = 3.7 Hz) for **7** and **8** and at $\delta = 3.77$ ppm for **9**. In compounds **10** and **11**, resonances attributed to −C*H*$_2$−Ph and additional −C*H*$_2$−Si protons are observed. For **12** and **13**, the ^{1}H NMR spectra show resonances corresponding to the *exo*-cluster groups C$_c$−C*H*$_3$ and C$_c$−C$_6$*H*$_5$ at 2.02 and 7.68−7.36 ppm, respectively. Finally, for **15** and **16**, the appearance and chemical shift of the −C*H*R proton confirm the position of each group in the thermodynamic isomer.[14] For **15**, this proton appears as a multiplet at 3.68 ppm due to the coupling with the C*H*$_3$ group, and in **16**, it appears as a singlet at 4.47 ppm.

In parallel, the ^{13}C{^{1}H} NMR spectra of **1**−**3** and **14**−**16** show resonances between 138.0 and 131.0 ppm attributed to the *C*H$_2$═*C*H carbons. For the rest of the compounds, the ^{13}C NMR spectra show resonances, in the corresponding regions, related to the Si−*C*H$_3$ and Si−*C*H$_2$−*C*H$_2$−Si carbons. Other resonances attributed to the *exo*-cluster carbons and peripheral functions are also exhibited for the corresponding compounds.

The ^{11}B{^{1}H} NMR resonances for **1**−**13** correspond to *closo* species, from δ +1.5 to −11.4 ppm. Compound **1** and derivatives (**4** and **7**) show the pattern 2:2:6. However, different patterns are exhibited for precursor **2** and their derivatives: 1:1:4:4 for **2**, 1:1:6:2 for **5** and **8**, and 1:1:4:2:2 for **10** and for **12**. Compound **3** and derivatives (**6**, **9**, and **11**) exhibit the same pattern of 1:1:4:2:2, and **13** shows the pattern 1:1:8. On the other hand, the ^{11}B resonances of reduced *nido*-compounds **14**−**16** appear in the region −20.0 to 20.0 ppm with the pattern 2:1:1:2:2:2, which is characteristic of the thermodynamic isomer.

The ^{29}Si{^{1}H} NMR spectra of compounds **1**−**3** exhibit a unique signal for all three compounds, around $\delta = -19.0$ ppm. For compounds **4**−**13**, the ^{29}Si{^{1}H} NMR spectra

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exhibit two resonances assigned on the basis of the chemical shifts and the peak intensities. The C_c−Si resonance appears in all compounds in the region 8.06−10.75 ppm. Additionally, the spectra of **4**−**6** exhibit a second peak corresponding to the peripheral *Si*−Cl (ca. 32 ppm), whereas for **7**−**9**, the presence of the Si−H group is confirmed by a resonance in the region −9.62 to −10.04 ppm.

The electrospray (ESI) mass spectra of **10**−**13** and MALDI-TOF-MS of the rest of the compounds have confirmed their formation (see Supporting Information).

X-ray analyses of **1**−**3** confirmed the expected 1,2-C_2 substitutions for the compounds. The molecular structures of **1**−**3** are presented in Figures 1 and 2. The asymmetric unit of **1** contains one molecule, and those of **2** and **3** contain two molecules each having crystallographic C_1 symmetry. In all compounds, the silicon atoms are bonded to three $-CH{=}CH_2$ groups with the C═C double bonds showing normal values of 1.301(3)−1.330(3) Å. The C_c−C_c distances of 1.715(3) Å for **1**, of 1.674(2) and 1.676(2) for **2**, and of 1.708(3) and 1.713(3) Å for **3** are in the expected range for the 1,2-C_2 substituted *ortho*-carboranes and confirm that contribution of substituents at the cluster carbons increases the C_c−C_c distances.[15]

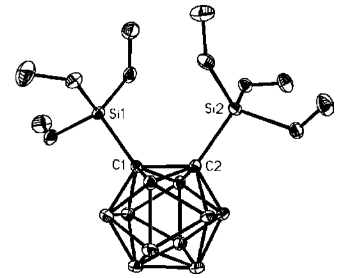

Figure 1. Molecular structure of **1**. Displacement ellipsoids are drawn at 30% probability level.

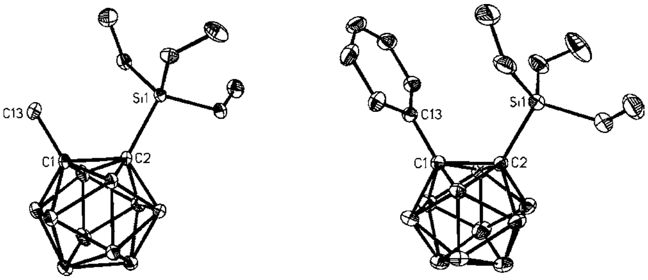

Figure 2. Molecular structures of **2** and **3** displaying just one molecule from the asymmetric unit. Displacement ellipsoids are drawn at 30% probability level.

Dendritic wedges or dendrons had usually been used in the convergent strategy for the growth of dendrimers, in which the dendrimer is assembled from the periphery, and the final reaction involves the attachment of the dendritic wedges to a core molecule. This study has opened a new route to synthesize dendrimeric compounds,[16] or nanomaterials,[17] in which the focal point can act as a protecting group during dendrimer growth and can be eliminated at the end of the growing process. In carbosilane dendrimers, the phenyl group has been used as a silicon-core protector (Si−Ph), which can be cleaved with protic acids, such as HCl or TfOH, to give Si−OTf. In the latter, TfO^- is a good leaving group, allowing the linking of functional nucleophiles.[18] Likewise, the reaction involving nucleophilic attack by fluoride or other nucleophiles, and the subsequent cleavage of C_c−Si bonds, is a well-documented process in carboranylsilane chemistry.[19,20] Thus, the possibility to use carboranes as a platform for dendron functionalization and cluster elimination by nucleophilic cleavage of the C_c−Si bond offers a new strategy to introduce other functions at the core. Furthermore, the possibility of modification of the core cluster by reducing agents, while keeping the C_c−Si bonds, represents another alternative to prepare new carboranylsilane dendrons. Further modifications are under study.

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Supporting Information Available: Experimental data for **1**−**16** and crystallographic data (CIF) for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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