Organometallics **2005,** *24,* 6351−6357

Boron-Functionalized Carbosilanes: Insertion of Carborane Clusters into Peripheral Silicon Atoms of Carbosilane Compounds

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Received July 29, 2005

Two families of carborane-containing star-shaped carbosilane molecules have been synthesized. Three different carborane cages 1-R-1,2-$C_2B_{10}H_{11}$, in which the R group possesses different bulkiness (R = H, Me, Ph), have been introduced on the carbosilane periphery through $C_{cluster}$−Si bonds. The first family, **1**−**3**, is derived from a chlorosilane that contains two carbon atoms as the branch point (1G_V-Cl), whereas in the second one, **4**−**6**, the branch length has been changed (1G_A-Cl) in order to study the size and flexibility of the compound in both the reaction with carboranes and the final products. Two different methods have been used for their preparation: (a) the nucleophilic substitution of the periphery Si−Cl functions with the corresponding carborane monolithium salt; (b) the hydrosilylation reaction of tetravinyl or tetraallylsilane with the carboranylsilanes 1-Me_2HSi-2-Me-1,2-$C_2B_{10}H_{10}$ (**7**) and 1-Me_2HSi-2-Ph-1,2-$C_2B_{10}H_{10}$ (**8**) catalyzed by Karsted's catalyst. The first method leads to compounds that incorporate four carboranyl moieties covalently bonded to the peripheral Si atoms of a carbosilane core; nevertheless, differences in the final product yields are observed depending on the carborane derivatives and the starting chlorosilane. The hydrosilylation reaction was a highly efficient method to obtain **2** and **3** in large yield; nevertheless, this process was not successful to prepare **5** and **6**. In addition, it is important to emphasize that **1**−**3** were successfully isolated in crystalline form suitable for X-ray diffraction analyses. Furthermore, the X-ray crystal structure of the carboranylsilane 1-Me_2HSi-2-Ph-1,2-$C_2B_{10}H_{10}$ (**8**) is also reported.

Introduction

The *closo*-1,2-$C_2B_{10}H_{12}$ carborane cluster, known as *o*-carborane, is chemically and thermally stable with a rigid three-dimensional structure.[1] The $C_{cluster}$−H protons in carboranes can be easily removed[2] by strong bases, generating nucleophile anions that have the ability to react with a wide range of electrophilic reagents.[3] The steric bulk of the carboranes requires that the electrophiles be reasonably reactive and unhindered in order to achieve good yields. Because of their unique physical and chemical properties, carboranes have been used to prepare a great variety of coordination compounds and have been suitable for a wide range of applications such as catalysis,[4] extraction of radionuclides,[5] and radiopharmaceuticals.[6] Although the field of carborane chemistry has been developed for over 40 years, few carborane-containing dendrimers have been reported.[7] In view of the emerging importance of dendrimers[8] as a new class of materi-

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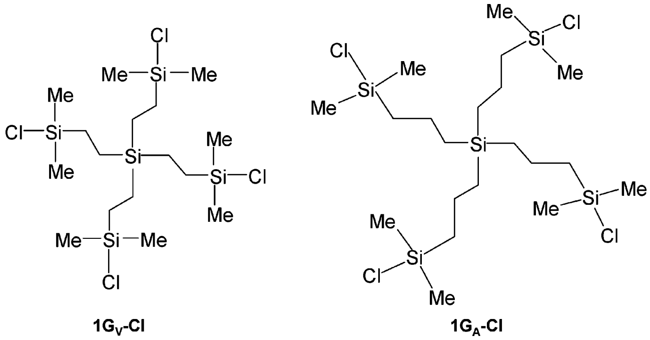

Figure 1. Chlorosilanes derived from the tetravinylsilane ($1G_V$-Cl) and tetraallylsilane ($1G_A$-Cl).

als and the versatility of carboranes in both synthesis and applications, we are interested in functionalizing the periphery of dendrimers with carborane clusters. The carbosilane dendrimers are well-suited for this purpose, because they are kinetically and thermodynamically very stable and their structures can be easily modified according to the required application.[9] In this way we are interested in creating active multifunctional nanosystems using carbosilane compounds as an inert scaffold in which carborane derivatives are attached on the periphery in the aim for subsequent cluster metalation/functionalization.[4,5]

We have early reported the first assembly of carborane moieties linked by a carbosilane scaffold.[10] Here we present two sets of boron-functionalized star-shaped carbosilane molecules, in which different *o*-carborane derivatives have been anchored. These may be taken as model compounds whose purpose was to test synthetic routes for a subsequent development of carborane-containing carbosilane dendrimers. To investigate the effect of size, flexibility, and reactivity of chlorosilanes toward carboranes, chlorosilane derivatives with two carbon-atom spacers $\{Si[(CH_2)_2Si(CH_3)_2Cl]_4\}$, $1G_V$-Cl,[11] or three carbon-atom spacers $\{Si[(CH_2)_3Si(CH_3)_2Cl]_4\}$, $1G_A$-Cl,[12] have been prepared (Figure 1). The X-ray crystal structures of compounds **1** and **2** are also reported, contributing to the few examples of crystalline structures determined by single-crystal X-ray diffraction studies of carbosilane compounds.[10,13]

Results and Discussion

Synthesis of Carborane-Containing Star-Shaped Carbosilane Molecules. (a) From Chlorosilane Derivatives. The chlorosilanes $1G_V$-Cl[11] and $1G_A$-Cl[12] were synthesized according to literature methods, using tetravinyl or tetraallylsilane as initiator core and dimethylchlorosilane (Me_2HSiCl) in the Pt-catalyzed hydrosilylation step. Carborane-containing star-shaped molecules $1G_V$-*o*-carborane (**1**)**,** $1G_V$-methyl-*o*-carborane (**2**), and $1G_V$-phenyl-*o*-carborane (**3**) were prepared in an analogous manner from the nucleophilic substitution of chlorine atoms in $1G_V$-Cl with the respective monolithio derivatives of *o*-carborane, 1-Me-*o*-carborane, and 1-Ph-*o*-carborane (Scheme 1). The reaction conditions were optimized and different solvent mixtures were used depending on the cluster: Et_2O/toluene (1:2 or 1:1.5) was used for the preparation of **2** and **3**, respectively, while dimethoxyethane/toluene (1:2) was the best solvent mixture for preparing **1**. Subsequently, $1G_A$-*o*-carborane (**4**), $1G_A$-methyl-*o*-carborane (**5**), and $1G_A$-phenyl-*o*-carborane (**6**) were prepared by reaction of a toluene solution of $1G_A$-Cl with an ether solution of the monolitium salts of the corresponding carborane cluster. In each case, compounds were isolated from the crude product by addition of cold Et_2O, giving by filtration spectroscopically pure crystalline air-stable solids in 38, 45, and 62% yields for **1**, **2**, and **3**, respectively. Nevertheless, **5** and **6** were obtained as waxlike solid compounds in 14 and 17% yields, respectively, while **4** was a white solid obtained in 22% yield.

(b) From Carboranylsilanes. The preparation of previous compounds was also attempted by direct hydrosilylation of tetravinyl or tetraallylsilane with the appropriate carboranylsilane in the presence of the Karstedt catalyst. For this purpose, 1-Me-2-Me_2HSi-1,2-$C_2B_{10}H_{10}$ (**7**) and 1-Ph-2-Me_2HSi-1,2-$C_2B_{10}H_{10}$ (**8**)[10] were prepared (Scheme 2). The synthesis of **7** has been completed by the reaction of Li[1-Me-1,2-$C_2B_{10}H_{10}$] with Me_2HSiCl in THF, following a similar procedure as that reported for **8**. Compound **7** was isolated as an oil in 95% yield.

To prepare **2** and **3**, the Pt-catalyzed hydrosilylation reaction of tetravinylsilane with the respective **7** and **8** was attempted using the reaction conditions reported for conventional organosilane compounds.[14] In this respect, different solvents (THF, toluene), catalysts (Karstedt catalyst in xylene, Speier's, Pt/C), temperatures, and reaction times were checked. The reactions were monitored by IR, and ^1H NMR spectroscopy in solution, tracing the evolution of the Si−H signal; however no reaction was observed in any case. Conversely, in the absence of solvent, compounds **2** and **3** were obtained in high yields, 70 and 85%, respectively, by hydrosilylation mostly in the β position of tetravinylsilane with **7** and **8** at 50 °C overnight and using the Karstedt catalyst (3−3.5% platinum) (Scheme 3).

As for **2** and **3**, attempts were made to prepare **5** and **6** by hydrosilylation of tetraallylsilane with the respective carboranylsilanes **7** and **8**, without solvent and in

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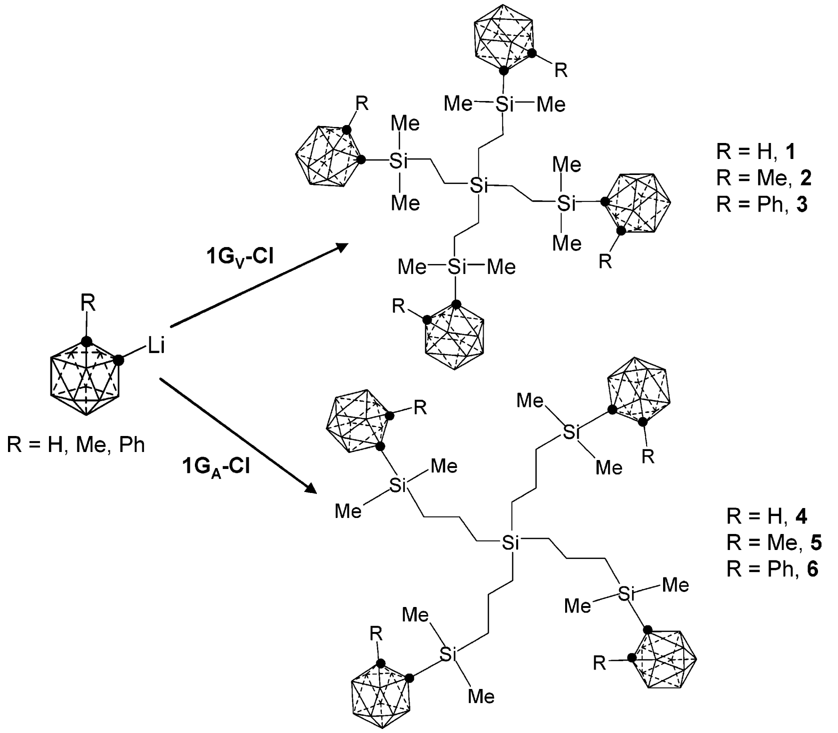
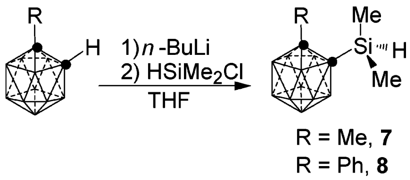
Scheme 1. Preparation of 1−6 by Nucleophilic Substitution of Si−Cl Functions in 1G$_V$-Cl and 1G$_A$-Cl with Monolithium Salts of Carboranes



Scheme 2. Preparation of Carboranylsilanes 7 and 8



the presence of the Karstedt catalyst (3−3.5% platinum); however the reaction did not occur.

Characterization of the Star-Shaped Molecules 1−6. The structures of **1**−**6** were established on the basis of elemental analysis, IR, ^{1}H, ^{13}C, ^{11}B, and ^{29}Si NMR, and mass spectroscopies and for **1**−**3** unequivocally confirmed by X-ray diffraction analysis. The IR spectra present typical ν(B−H) strong bands for *closo* clusters between 2568 and 2576 cm^{-1} and intense bands near 1255 cm^{-1} corresponding to δ(Si−CH$_3$). The ^{1}H NMR spectra for **1**−**3** exhibit resonances for Si−CH$_3$ protons in the region −0.13 to 0.35 ppm and methylene protons between 0.14 and 0.66 ppm. All these protons have been shifted to higher field with respect to the precursor 1G$_V$-Cl, due to the presence of the cluster in the compound. The ^{13}C{^{1}H} NMR spectra show resonances for Si−CH$_3$ carbons in the region δ −2.2 to −3.7 ppm, shifted to higher field with respect to the precursor 1G$_V$-Cl (0.9 ppm). The ^{11}B{^{1}H} NMR resonances are observed in a typical region for *closo*[15] clusters, from δ +1.40 to −13.85 pmm, with a 1:1:2:4:2 pattern for **1** and 1:1:4:4 for **2** and **3**. The ^{29}Si{^{1}H} NMR spectra exhibit two signals assigned on the basis of the chemical shifts and the peak intensities. The Si−C$_{\text{cluster}}$ atoms appear at 10.31, 9.38, and 10.36 for, **1**, **2**, and **3**, respectively, shifted to higher field with respect to the peripheral Si−Cl (32.71 ppm) in 1G$_V$-Cl. The core Si atoms appear between 10.42 and 10.57 ppm, close to the position in the precursor 1G$_V$-Cl (10.09 ppm).

Due to the similarities in the characterization of **4**−**6** with those derived from 1G$_V$-Cl, only some relevant information will be specified. The ^{1}H NMR spectra exhibit two triplets between δ 0.39 and 0.89 ppm attributed to the different Si−CH$_2$ protons and multiplets in the region δ 1.11 to 1.39 ppm due to the remaining CH$_2$ protons. The ^{13}C{^{1}H} NMR spectra show resonances attributed to CH$_2$ carbon atoms, in the region δ 17.1 to 21.2 ppm, shifted to lower field compared with **1**−**3**. The ^{11}B NMR resonances are displayed in the region δ +1.29 to −13.93 ppm, with patterns 1:1:2:4:2 for **4** and 1:1:4:4 for **5** and **6**. The ^{29}Si{^{1}H} NMR spectra exhibit the external Si−C$_{\text{cluster}}$ between δ 9.02 and 8.09 ppm, while the core Si atoms appear in the range 0.45−0.79 ppm, at higher field compared with **1**−**3** (10.42−10.57 ppm).

Two different mass spectrometry techniques have been used for the characterization of compounds: electrospray (ESI) and ammonia chemical ionization (CI). The CI mass spectrum of **1** exhibits a peak at *m*/*z* = 963.0, which corresponds to [M + NH$_4$]$^+$, while the peak at *m*/*z* = 74.0 attributed to the fragment [SiCH$_2$CH$_2$ + NH$_4$]$^+$ is that of 100% abundance. Nevertheless, the ESI was recorded in CHCl$_3$/CH$_3$OH and used for the higher molecular weight compounds **2**−**6**. The ESI mass spectrum of **2** shows two signals, at *m*/*z* = 1064.0 corresponding to [M + 2(CH$_3$OH)]$^-$ and at *m*/*z* = 157.2 due to the [C$_3$B$_{10}$H$_{13}$]$^-$ fragment, attributed to the 1-Me-*o*-carborane. The ESI mass spectrum of **4** shows one peak at *m*/*z* = 1036.8 corresponding to [M + 2(H$_2$O)]$^-$, in which the two H$_2$O molecules come from the CH$_3$OH. In contrast, the ESI mass spectrum of **5** and **6** shows

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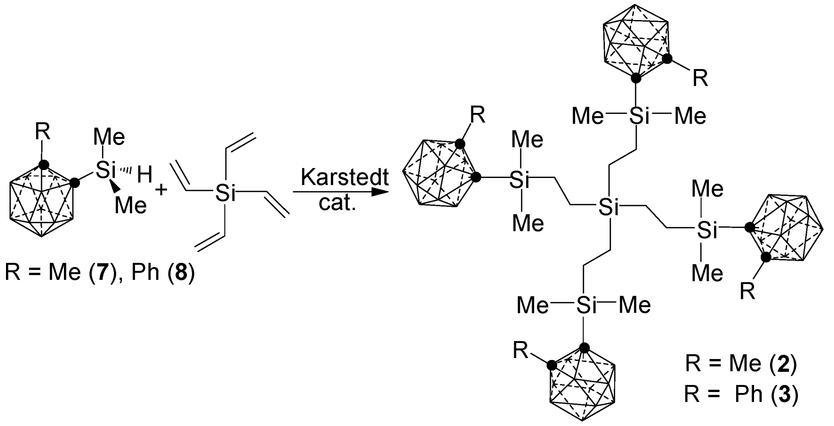
Scheme 3. Synthesis of 2 and 3 by Hydrosilylation of Tetravinylsilane with 7 and 8 Using Karsted's Catalyst



one signal at m/z = 1120.5 and 1368.5, respectively, which are assigned to $[M + 2(CH_3OH)]^-$ and signals corresponding to the 1-Me-*o*-carborane and 1-Ph-*o*-carborane, respectively.

X-ray Crystal Structures of 1, 2, 3, and 8. Star-shaped molecules **1**−**3** were isolated as monocrystals suitable for X-ray structural determination by hexane vapor diffusion into a $CHCl_3$ solution of them. Compound **8** was isolated from a Et_2O solution.

X-ray analyses of **1**, **2**, and **3**[10] confirmed the expected star-shaped structures peripherally functionalized by *o*-carborane derivatives for each compound. The molecular structure of **1** is presented in Figure 2. Although the structures seem very similar, the crystallographic symmetry of the molecules is different. In **1** the central silicon atom is located at a 4-fold improper axis; thus the asymmetric unit of the structure consists of one-fourth of the molecule. In **2** the central silicon atom occupies a 2-fold axis; therefore the asymmetric unit of the structure consists of half of the molecule. The structure of **2** is partially disordered (see Supporting Information). In two of the four carborane clusters, the methyl groups connected to C_c atoms are each occupying two positions. In **3**,[10] orientations of the clusters are mutually different, resulting in C_1 symmetry for the molecule.

Table 1. Selected Bond Lengths (Å) for 1, 2, 3, and 8

	1	2	3	8
$Si-C_{Me}$	1.855(3) 1.856(5)	1.846(5) 1.866(6)	1.844(5) 1.861(5)	1.849(2) 1.853(2)
$Si-C_c$	1.916(4)	1.931(4) 1.932(5)	1.924(4) 1.937(4)	1.914(2)
C_c-C_c	1.678(6)	1.650(8)[b]	1.694(5) 1.720(5)	1.703(3)
$Si_{core}-C_{CH2}$	1.878(3)	1.869(5) 1.870(4)	1.871(4) 1.880(4)	

[a] If more than one bond exists, shortest and longest values are gathered one on top of the other. C_c denotes cluster carbon. [b] Only ordered bond length listed.

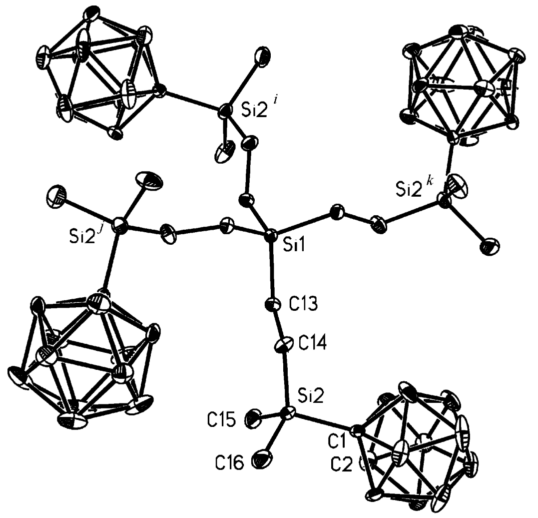


Figure 2. Molecular structure of $1G_V$-*o*-carborane (**1**). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level. Superscripts *i*, *j*, and *k* refer to equivalent positions $-x$, $-y+1/2$, z; $y-1/4$, $-x+1/4$, $-z+1/4$; and $-y+1/4$, $x+1/4$, $-z+1/4$.

Despite the different symmetries of **1**, **2**, and **3**, the corresponding bond parameters are very similar: $Si_{core}-C_{CH_2}$ bond lengths vary from 1.869(5) to 1.878(3) Å and are shorter that the $Si-C_c$ distances of 1.916(4)−1.937(4) Å (see Table 1). The only significant differences can be seen in the C_c-C_c distances [1.650(8)−1.720(5) Å], the distance in **3** being the longest. This is in accord with the observation that a phenyl substituent at a cluster carbon in *o*-carboranes expands the C_c-C_c distance more than hydrogen or aliphatic substituents.[16,17] Bond lengths and angles of **1**, **2**, and **3** are typical for this kind of compound, and the values agree well with those reported for 1,1′,2,2′-bis-μ-dimethylsilylbis[1,2-dicarba-*closo*-dodecaborane(12)].[18] The C_c-C_c-Si angle varies slightly depending on the cluster, being 118.5° for **1**, 121.3° for **2**, and 122.8° for **3**. Thus, the increase of bulkiness of the substituent in the cluster provides an enlargement of the dihedral angle, probably to avoid steric hindrance.

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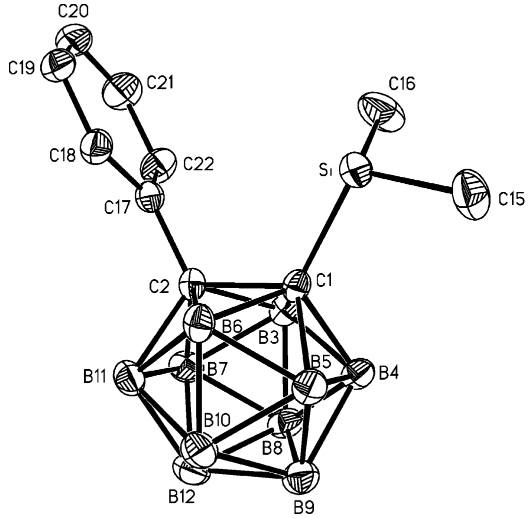

Figure 3. Molecular structure of 1-Me_2HSi-2-Ph-1,2-$C_2B_{10}H_{10}$ (**8**). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

The molecular structure of **8** is presented in Figure 3. Bond lengths and angles in **8** are very similar to those of **3**.[10] The C_c-C_{Ph}, C_c-C_c, and $Si-C_{Me}$ bonds of 1.507(3), 1.703(3), and 1.849(2)/1.853(2) Å in **8** agree very well with the corresponding values of 1.498(5)−1.511(6), 1.694(5)−1.720(5), and 1.844(5)−1.861(5) in **3**.

Discussion

The preparation of the star-shaped compounds **1**−**6** from chlorosilane derivatives was monitored by $^{11}B\{^1H\}$ NMR, which indicated that the expected compounds were immediately generated after the addition of $1G_V$-Cl or $1G_A$-Cl to the corresponding carborane lithium salts at 0 °C. Additional reaction times did not improve the yield of final products because a reversal of the reaction toward the generation of the nonlithiated carborane was observed. Our understanding is that buildup of Cl^- during the reaction could be the limiting factor. From the reaction crude it is always possible to recover unreacted starting carboranes by sublimation; however, yields are given with regard to the initial added amount. For compounds **4**−**6**, the reaction conditions were the same as those used in the preparation of the star-shaped molecules derived from $1G_V$-Cl; however a lower yield was observed in all cases. All attempts (change of solvents, use of TMEDA, etc.) to improve their yield was unsuccessful. This was attributed to intrinsic properties of the starting chlorosilane, such as larger spacers and higher instability,[19] the different reactivity of these with each cluster, and the physical properties of the final product.

The preparation of compounds **2**, **3**, **5**, and **6** was also attempted by Pt-catalyzed hydrosilylation reaction of vinyl- or allylsilanes, using reported reaction conditions for conventional organosilane compounds.[14] However, only compounds **2** and **3** were obtained in the absence of solvent at 50 °C overnight and using a higher Pt concentration. These results were attributed to the different nature and reactivity of the carboranyl moiety in the carboranylsilanes, (carboranyl)$(Me)_2SiH$, compared with conventional organic groups, such as phenyl or methyl, in $Ph(Me)_2SiH$ or $(Me)_3SiH$. To study the different charge of the Si^+ and H^- in the carboranylsilanes 1-$SiMe_2H$-2-Me-1,2-$C_2B_{10}H_{10}$, 1-$SiMe_2H$-2-Ph-1,2-$C_2B_{10}H_{10}$, and their aromatic counterparts $Ph(Me)_2SiH$ and $(Me)_3SiH$, theoretical calculations using the GAUSSIAN98 suite of programs were performed. The results indicate that the H of carboranylsilanes **7** and **8**, computed at the B3LYP/6-31G level of theory, presents calculated NPA charges of −0.196 and −0.189, respectively, compared with −0.210 and −0.216 for $Ph(Me)_2SiH$ and $(Me)_3SiH$. Thus, the electron-withdrawing character of the cluster together with its bulkiness renders the Si−H bond less reactive, and vigorous reaction conditions are required. In addition, for the preparation of **5** and **6** by hydrosilylation of tetraallylsilane, it seems that these conditions were not good enough probably also due to the higher electronic delocalization in the allyl group.

Conclusions

Two sets of carborane-containing star-shaped carbosilanes, **1**−**3** and **4**−**6**, have been synthesized. The synthetic methodology described here may be suitable for carbosilane dendrimers of higher generations and other carborane derivatives. Further functionalization of the peripheral carborane clusters and the formation of metallodendrimers are under study.

Experimental Section

Instrumentation. Microanalyses were performed in the analytical laboratory using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded with KBr pellets or NaCl on a Shimadzu FTIR-8300 spectrophotometer. The electrospray-ionization mass spectra (ESI-MS) were recorded on a Bruker Esquire 3000 spectrometer using a source of ionization and an ion trap analyzer. The chemical ionization mass spectrum was recorded in a Hewlet Packard 5989 spectrometer by introduction of NH_3 gas. The ^1H, $^1H\{^{11}B\}$ NMR (300.13 MHz), ^{11}B, $^{11}B\{^1H\}$ NMR (96.29 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz), and ^{29}Si NMR (59.62 MHz) spectra were recorded on a Bruker ARX 300 spectrometer equipped with the appropriate decoupling accessories at room temperature. All NMR spectra were recorded in $CDCl_3$ solutions at 22 °C. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3\cdot OEt_2$, and those for ^1H, $^1H\{^{11}B\}$, $^{13}C\{^1H\}$ NMR, and ^{29}Si NMR spectra were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in hertz.

Materials. All manipulations were carried out under a dinitrogen atmosphere using standard Schlenck techniques. Solvents were reagent grade and were purified by distillation from appropriate drying agents before use. 1,2-$C_2B_{10}H_{12}$, 1-Me-1,2-$C_2B_{10}H_{11}$, and 1-Ph-1,2-$C_2B_{10}H_{11}$ were supplied by Katchem Ltd. (Prague) and used as received. Me_2HSiCl, $SiCl_4$ and Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex, 3−3.5% platinum in vinyl-terminated poly(dimethylsiloxane)) were purchased from ABCR and used as received. The $[Si(CH{=}CH_2)_4]$ was purchased from Across. The *n*-BuLi solution (1.6 M in hexanes) was purchased from Lancaster or Aldrich and $CH_2{=}CHCH_2MgCl$ from Aldrich. The $[Si(CH_2CH{=}CH_2)_4]$ and chlorosilanes $1G_V$-Cl and $1G_A$-Cl were prepared according to the literature.[11,12] The carboranylsilane 1-Ph-2-Me_2HSi-1,2-$C_2B_{10}H_{10}$ (**8**) and **3** were previously prepared.[10]

Preparation of 1-Me-2-$SiMe_2H$-1,2-$C_2B_{10}H_{10}$ (7). To a solution of 1-Me-1,2-$C_2B_{10}H_{11}$ (1.0 g, 6.3 mmol) in dry THF

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[19] van der Made, A. W.; van Leewen, P. W. N. M., de Wilde, J. C.; Brances, R. A. C. *Adv. Mater.* **1993**, *5*, 466.

(20 mL) at 0 °C was added dropwise a 1.6 M solution of *n*-BuLi in hexane (4.1 mL, 6.6 mmol). The mixture was stirred for 30 min at room temperature, then cooled to 0 °C, and $HSiMe_2Cl$ (0.9 mL, 8.0 mmol) was added dropwise with stirring, yielding a suspension, which was stirred at room temperature overnight. Next, the mixture was quenched with 10 mL of an aqueous solution saturated with NH_4Cl, transferred to a separatory funnel, and diluted with 40 mL of Et_2O. The aqueous layer was separated and extracted with additional Et_2O (60 mL). The organic layers were then dried over anhydrous $MgSO_4$ and concentrated in vacuo to give **7** as a yellow oil. Yield: 1.3 g, 95%. ^{1}H NMR: δ 0.42 (d, J(H,H) = 3.7, 6H, Si−CH_3), 2.05 (s, $C_{cluster}$−CH_3), 4.26 (sept, J(H,H) = 3.7, 1H, Si−*H*). ^{1}H{^{11}B} NMR: δ 0.42 (d, J(H,H) = 3.7, 6H, Si−CH_3), 2.05 (s, $C_{cluster}$−CH_3), 2.11 (br s, B−*H*), 2.18 (br s, B−*H*), 2.26 (br s, B−*H*), 2.42 (br s, B−*H*), 4.26 (sept, J(H,H) = 3.7, 1H, Si−*H*). ^{29}Si NMR: δ −6.83 (d, ^1J(Si,H) = 206 Hz). ^{11}B NMR: δ 1.4 (d, ^1J(B, H) = 146, 1B, B(9)), −4.1 (d, ^1J(B, H) = 150, 1B, B(12)), −7.4 (d, ^1J(B, H) = 134, 4B, B(4,5,8,10)), −8.7 (d, ^1J(B, H) = 156, 2B, B(3,6)), −9.6 (2B, B(7,11)). ^{13}C{^{1}H} NMR: δ −3.2 (Si−CH_3), 24.9 ($C_{cluster}$−CH_3), 68.5 (*C*$_{cluster}$), 75.3 (*C*$_{cluster}$). FTIR (NaCl), ν cm^{-1}: 2562 (ν(B−H)), 2164 (ν(Si−H)), 1257 (δ(Si−CH_3)). Anal. Calcd for $C_5H_{20}B_{10}Si$: C, 27.75; H, 9.31. Found: C, 27.70; H, 9.24.

Preparation of 1G$_V$-*o*-carborane (1). To a solution of 1,2-$C_2B_{10}H_{12}$ (0.61 g, 4.23 mmol) in toluene (4.0 mL) and dimethoxyethane (3.0 mL) at 0 °C was added a 1.6 M solution of *n*-BuLi in hexane (2.7 mL, 4.32 mmol) dropwise. The mixture was stirred for 1 h at room temperature. After cooling it to 0 °C, a solution of 1G$_V$-Cl (0.45 g, 0.87 mmol) in toluene (4.0 mL) and dimethoxyethane (2.0 mL) was added dropwise with stirring. The suspension was stirred for 5 min at 0 °C and filtered off through Celite. The solvent was removed and the residue treated with cold Et_2O (8.0 mL) to isolate **1** as a white solid. Yield: 0.31 g, 37.8%. Hexane vapor diffusion into a $CHCl_3$ solution of **1** gave single crystals suitable for X-ray analysis. ^{1}H NMR: δ 0.27 (s, 24H, Si−CH_3), 0.54 (m, 16H, Si−CH_2), 3.36 (br s, 4H, $C_{cluster}$−*H*). ^{1}H{^{11}B} NMR: δ 0.27 (s, 24H, Si−CH_3), 0.54 (m, 16H, Si−CH_2), 2.06 (br s, B−*H*), 2.20 (br s, B−*H*), 2.25 (br s, B−*H*), 2.35 (br s, B−*H*), 3.36 (br s, 4H, $C_{cluster}$−*H*). ^{29}Si NMR: δ 10.31 (s, *Si*−$C_{cluster}$), 10.57 (s, *Si*$_{core}$). ^{11}B NMR: δ −0.5 (br s, 1B, B(9)), −1.8 (d, ^1J(B, H) = 145, 1B, B(12)), −7.2 (d, ^1J(B, H) = 148, 2B, B(8,10)), −11.8 (br s, 4B, B(4,5,7,11)) −13.9 (d, ^1J(B, H) = 175, 2B, B(3,6)). ^{13}C{^{1}H} NMR: δ −3.7 (Si−*C*H_3), 2.5 (Si−*C*H_2), 7.4 (Si−*C*H_2), 59.6 (*C*$_{cluster}$), 65.6 (*C*$_{cluster}$). FTIR (KBr), cm^{-1}: 3063 (ν($C_{cluster}$−H), 2568 (ν(B−H)), 1256 (δ(Si−CH_3)). Anal. Calcd for $C_{24}H_{84}B_{40}Si_5$: C, 30.50; H, 8.90. Found: C, 31.15; H, 8.81. MS-chemical ionization, (NH_3) *m/z*: calcd for $C_{24}H_{84}B_{40}Si_5$, 945.0; found, 963.0 [(M + NH_4)$^+$, 18%], 734.0 [($C_{18}H_{63}B_{30}Si_4$ + NH_4)$^+$, 8%], 160.0 [($C_2B_{10}H_{10}$ + NH_4)$^+$, 32%], 74.0 [($SiCH_2CH_2$ + NH_4)$^+$, 100%].

Preparation of 1G$_V$-methyl-*o*-carborane (2). *Method A*: To a solution of 1-Me-1,2-$C_2B_{10}H_{11}$ (0.76 g, 4.81 mmol) in Et_2O (6.0 mL) and toluene (3.0 mL) at 0 °C was added a 1.6 M solution of *n*-BuLi in hexane (3.1 mL, 4.96 mmol) dropwise. The mixture was stirred for 30 min at room temperature. After cooling it to 0 °C, a solution of 1G$_V$-Cl (0.62 g, 1.20 mmol) in toluene (6.0 mL) and Et_2O (3.0 mL) was added dropwise with stirring. The workup was the same as for 1G$_V$-*o*-carborane to give **2** as a white solid. Yield: 0.53 g, 44.2%. *Method B*: **7** (0.25 g, 1.15 mmol) was introduced into a Schlenck and heated to 50 °C; subsequently tetravinylsilane (0.1 mL, 0.59 mmol) and 2 drops of Karstedt catalyst were added. The mixture was stirred at 50 °C for 40 h, then the volatiles were evaporated in the vacuum line. Compound **2** was separated by chromatographic workup in 70% yield. Hexane vapor diffusion into a $CHCl_3$ solution of **2** gave single crystals suitable for X-ray analysis. ^{1}H NMR: δ 0.35 (s, 24H, Si−CH_3), 0.59 (m, 16H, Si−CH_2), 2.02 (s, 12H, $C_{cluster}$−CH_3). ^{1}H{^{11}B} NMR: δ 0.35 (s, 24H, Si−CH_3), 0.59 (m, 16H, Si−CH_2), 2.02 (s, 12H, $C_{cluster}$−CH_3), 2.25 (br, B−*H*), 2.43 (br, B−*H*). ^{29}Si NMR: δ 9.38 (s, *Si*−$C_{cluster}$), 10.42 (s, *Si*$_{core}$). ^{11}B NMR: δ 0.5 (d, ^1J(B, H) = 116, 1B, B(9)), −4.9 (d, ^1J(B, H) = 154, 1B, B(12)), −8.3 (d, ^1J(B, H) = 147, 4B, B(4,5,8,10)), −10.3 (br s, 4B, B(3,6,7,11)). ^{13}C{^{1}H} NMR: δ −2.2 (Si−CH_3), 2.7 (Si−*C*H_2), 9.0 (Si−*C*H_2), 25.8 ($C_{cluster}$−*C*H_3), 71.0 (*C*$_{cluster}$), 75.3 (*C*$_{cluster}$). FTIR (KBr), cm^{-1}: 2576 (ν(B−H)), 1257 (δ(Si−CH_3)). Anal. Calcd for $C_{28}H_{92}B_{40}Si_5$: C, 33.60; H, 9.30. Found: C, 34.33; H, 9.55. MS-electrospray (ESI), solution of $CHCl_3$/CH_3OH (1:1) *m/z*: calcd for $C_{28}H_{92}B_{40}Si_5$, 1001.9; found, 1064.0 [(M + 2CH_3OH)$^-$, 100%], 157.2 [($C_3B_{10}H_{13}$)$^-$, 9%].

Preparation of 1G$_A$-*o*-carborane (4). The procedure was the same as for 1G$_V$-*o*-carborane (**1**) using 1,2-$C_2B_{10}H_{12}$ (0.55 g, 3.81 mmol) and *n*BuLi (2.4 mL, 3.84 mmol) in a solution of toluene (5.0 mL)/dimethoxyethane (2.0 mL), and 1G$_A$-Cl (0.55 g, 0.96 mmol) in toluene (5.0 mL)/dimethoxyethane (2.0 mL). The suspension was stirred for 10 min at 0 °C and filtered off through Celite. The solvent was removed and the residue treated with cold Et_2O (10 mL) to isolate **4** as a white solid. Yield: 0.21 g, 21.9%. ^{1}H NMR: δ 0.26 (s, 24H, Si−CH_3), 0.61 (t, ^3J(H, H) = 8.3, 8H, Si−CH_2), 0.80 (t, ^3J(H, H) = 8.3, 8H, Si−CH_2), 1.34 (m, 8H, CH_2), 3.35 (br s, 4H, $C_{cluster}$−*H*). ^{1}H{^{11}B} NMR: δ 0.26 (s, 24H, Si−CH_3), 0.61 (t, ^3J(H, H) = 8.3, 8H, Si−CH_2), 0.80 (t, ^3J(H, H) = 8.3, 8H, Si−CH_2), 1.34 (m, 8H, CH_2), 2.06 (br s, B−*H*), 2.18 (br s, B−*H*), 2.32 (br s, B−*H*), 3.35 (br s, 4H, $C_{cluster}$−*H*). ^{29}Si NMR: δ 8.78 (s, *Si*−$C_{cluster}$), 0.56 (s, *Si*$_{core}$). ^{11}B NMR: δ −0.6 (br, 1B, B(9)), −1.9 (d, ^1J(B, H) = 143, 1B, B(12)), −7.3 (d, ^1J(B, H) = 149, 2B, B(8,10)), −11.9 (br s, 4B, B(4,5,7,11)) −13.9 (d, ^1J(B, H) = 171, 2B, B(3,6)). ^{13}C{^{1}H} NMR: δ −3.0 (Si−CH_3), 17.2 (*C*H_2), 18.3 (*C*H_2), 19.7 (*C*H_2), 59.6 (*C*$_{cluster}$), 65.9 (*C*$_{cluster}$). FTIR (KBr), cm^{-1}: 3071 (ν($C_{cluster}$−H), 2573 (ν(B−H)), 1257 (δ(Si−CH_3)). Anal. Calcd for $C_{28}H_{92}B_{40}Si_5$: C, 33.57; H, 9.26. Found: C, 34.08; H, 9.38. MS-electrospray (ESI), solution of $CHCl_3$/CH_3OH (1:1) *m/z*: calcd for $C_{28}H_{92}B_{40}Si_5$, 1001.9; found, 1036.8 [(M + 2H_2O)$^-$, 100%], 180.0 [($C_2B_{10}H_{10}$ + 2H_2O)$^-$, 38%], 143.0 [($C_2B_{10}H_{10}$)$^-$, 29%].

Preparation of 1G$_A$-methyl-*o*-carborane (5). The procedure was the same as for 1G$_V$-methyl-*o*-carborane (**2**) using 1-Me-1,2-$C_2B_{10}H_{11}$ (0.71 g, 4.49 mmol) and *n*-BuLi (2.8 mL, 4.48 mmol) in Et_2O (4.0 mL)/toluene (8.0 mL). After cooling to 0 °C, a solution of 1G$_A$-Cl (0.60 g, 1.05 mmol) in toluene (8.0 mL) and Et_2O (4.0 mL) was added dropwise with stirring. The suspension was stirred for 10 min at 0 °C and filtered off through Celite. The solvent was removed and the residue treated with hexane for 2 h. The insoluble part was separated and treated with petroleum ether to give **5** as a transparent oil. Yield: 0.15 mg, 13.5%. ^{1}H NMR: δ 0.32 (s, 24H, Si−CH_3), 0.64 (t, ^3J(H, H) = 7.7, 8H, Si−CH_2), 0.89 (t, ^3J(H, H) = 7.7, 8H, Si−CH_2), 1.39 (m, 8H, CH_2), 2.02 (s, 12H, $C_{cluster}$−CH_3). ^{1}H{^{11}B} NMR: δ 0.32 (s, 24H, Si−CH_3), 0.64 (t, ^3J(H, H) = 7.7, 8H, Si−CH_2), 0.89 (t, ^3J(H, H) = 7.7, 8H, Si−CH_2), 1.39 (m, 8H, CH_2), 2.02 (s, 12H, $C_{cluster}$−CH_3), 2.23 (br, B−*H*), 2.42 (br, B−*H*). ^{29}Si NMR: δ 8.09 (s, *Si*−$C_{cluster}$), 0.70 (s, *Si*$_{core}$). ^{11}B NMR: δ 0.4 (d, ^1J(B, H) = 130, 1B, B(9)), −5.0 (d, ^1J(B, H) = 153, 1B, B(12)), −8.4 (d, ^1J(B, H) = 148, 4B, B(4,5,8,10)), −10.4 (br s, 4B, B(3,6,7,11)). ^{13}C{^{1}H} NMR: δ −1.3 (Si−*C*H_3), 17.4 (*C*H_2), 18.4 (*C*H_2), 21.2 (*C*H_2), 25.7 ($C_{cluster}$−*C*H_3), 71.3 (*C*$_{cluster}$), 75.3 (*C*$_{cluster}$). FTIR (KBr), cm^{-1}: 2582 (ν(B−H)), 1257 (δ(Si−CH_3)). Anal. Calcd for $C_{32}H_{100}B_{40}Si_5$: C, 36.33; H, 9.52. Found: C, 36.84; H, 9.64. MS-electrospray (ESI), solution of $CHCl_3$/CH_3OH (1:1) *m/z*: calcd for $C_{32}H_{100}B_{40}Si_5$, 1056.5; found, 1120.5 [(M + 2CH_3OH)$^-$, 29%], 892.5 [($C_3B_{10}H_{13}$ + 2H_2O)$^-$, 41%], 157.0 [($C_3B_{10}H_{13}$)$^-$, 100%].

Preparation of 1G$_A$-phenyl-*o*-carborane (6). The procedure was the same as for 1G$_V$-phenyl-*o*-carborane (**3**) using 1-Ph-1,2-$C_2B_{10}H_{11}$ (0.63 g, 2.86 mmol) and *n*-BuLi (1.8 mL, 2.88 mmol) in dry Et_2O (4.0 mL). After cooling to 0 °C, a solution of freshly prepared 1G$_A$-Cl (0.41 g, 0.72 mmol) in toluene (6.0 mL) was added dropwise with stirring. The workup was the same as for **5** to give **6** as a transparent oil. Yield: 0.16 mg,

Table 2. Crystallographic Parameters for 1G$_V$-*o*-carborane (1), 1G$_V$-methyl-*o*-carborane (2), 1G$_V$-phenyl-*o*-carborane (3), and 1-SiMe$_2$H-2-Ph-1,2-C$_2$B$_{10}$H$_{10}$ (8)

	1	**2**	**3**	**8**
empirical formula	$C_{24}H_{84}B_{40}Si_5$	$C_{28}H_{92}B_{40}Si_5$	$C_{48}H_{100}B_{40}Si_5$	$C_{10}H_{22}B_{10}Si$
fw	945.76	1001.87	1250.13	278.47
cryst syst	tetragonal	orthorhombic	orthorhombic	monoclinic
space group	$I4_1/a$ (no. 88)	$Pba2$ (no. 32)	$Pc2_1b$ (no. 29)	$P2_1/n$ (14)
a (Å)	20.7053(4)	13.9813(5)	12.7957(1)	13.6454(8)
b (Å)	20.7053(4)	17.6592(5)	18.2036(2)	6.9216(2)
c (Å)	13.5310(5)	12.7224(4)	33.0523(5)	18.1622(10)
β (deg)	90	90	90	107.739(2)
V (Å^3)	5800.9(3)	3141.14(17)	7698.80(16)	1633.82(14)
Z	4	2	4	4
T (°C)	−100	−100	−100	−100
λ (Å)	0.71073	0.71073	0.71073	0.71073
ρ (g cm^{-3})	1.083	1.059	1.079	1.132
μ (cm^{-1})	1.48	1.40	1.26	1.24
goodness-of-fit[a] on F^2	1.099	1.054	1.051	1.027
R1[b] [$I > 2\sigma(I)$]	0.0768	0.0777	0.0674	0.0423
wR2[c] [$I > 2\sigma(I)$]	0.1700	0.1952	0.1028	0.1016
Flack parameter x		0.2(2)	0.38(10)	

[a] $S = [\sum(w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

17.0%. ^{1}H NMR: δ −0.16 (s, 24H, Si−CH_3), 0.39 (t, ^3J(H, H) = 8.1, 8H, Si−CH_2), 0.51 (t, ^3J(H, H) = 8.1, 8H, Si−CH_2), 1.11 (m, 8H, CH_2), 7.43−7.28 (m, 20H, C$_6H_5$). ^{1}H{^{11}B} NMR: δ −0.16 (s, 24H, Si−CH_3), 0.39 (t, ^3J(H, H) = 8.1, 8H, Si−CH_2), 0.51 (t, ^3J(H, H) = 8.1, 8H, Si−CH_2), 1.11 (m, 8H, CH_2), 2.18 (br s, B−*H*), 2.39 (br s, B−*H*), 2.69 (br s, B−*H*), 2.90 (br s, B−*H*), 7.43−7.28 (m, 20H, C$_6H_5$). ^{29}Si NMR: δ 9.02 (s, *Si*−C$_{cluster}$), 0.45 (s, Si_{core}). ^{11}B NMR: δ 1.3 (br, 1B, B(9)), −2.9 (d, ^1J(B, H) = 143, 1B, B(12)), −8.2 (d, ^1J(B, H) = 139, 4B, B(4,5,8,10)), −10.9 (br s, 4B, B(3,6,7,11)). ^{13}C{^{1}H} NMR: δ −2.3 (Si−*C*H$_3$), 17.1 (*C*H$_2$), 18.2 (*C*H$_2$), 20.6 (*C*H$_2$), 76.2 ($C_{cluster}$), 83.4 ($C_{cluster}$), 128.5 (Ph−C_{para}), 130.5 (Ph−C_{ortho}), 131.2 (Ph−C_{meta}), 132.7 (Ph−C_{ipso}). FTIR (KBr), cm^{-1}: 2583 (ν(B−H)), 1253 (δ(Si−CH$_3$)). Anal. Calcd for $C_{52}H_{108}B_{40}Si_5$: C, 47.81; H, 8.33. Found: C, 48.05; H, 8.45. MS-electrospray (ESI), solution of CHCl$_3$/CH$_3$OH (1:3) *m/z*: calcd for $C_{52}H_{108}B_{40}Si_5$, 1304.5; found, 1368.5 [(M + 2CH$_3$OH)$^-$, 20%], 219.0 [(C$_8$B$_{10}$H$_{15}$)$^-$, 100%].

X-ray Structure Determinations of 1, 2, 3, and 8. Single crystals of **1**, **2**, and **3** suitable for X-ray analyses were obtained by hexane vapor diffusion into a CHCl$_3$ solution, while compound **8** was isolated as single crystals from an Et$_2$O solution. Single-crystal data collections were performed on a Nonius KappaCCD diffractometer at −100 °C using graphite-monochromatized Mo Kα radiation. Totals of 2748, 5296, 12551, and 2674 unique reflections were collected for **1**, **2**, **3**, and **8**, respectively.

The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[20] None of the structures contain solvents, and all the structures, except **2**, are well-ordered. The asymmetric unit of **2** consists of two carborane cages, and in the other cage the methyl substituent connected to the cluster carbon is disordered, occupying two positions. For each compound, all non-hydrogen atoms, except the disordered methyl carbon of **2**, were refined with anisotropic thermal displacement parameters. Hydrogen atoms for each structure were treated as riding atoms using the SHELX97 default parameters. Crystallographic parameters for compounds **1**, **2**, **3**, and **8** are gathered in Table 2.

Acknowledgment. This work has been supported by the CICYT (MAT2004-01108) and Generalitat de Catalunya, 2001/SGR/00337. A.G. thanks MCyT for a FPI grant annexed to MAT01-1575.

Supporting Information Available: Characterization of carboranylsilanes **7** and **8**, representation of the crystal structure of compound **2**, and crystallographic data (CIF) for **1**, **2**, and **8** are available free of charges via the Internet at http://pubs.acs.org.

OM050651+

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[20] Sheldrick, G. M. *SHELX97*; University of Göttingen: Germany, 1997.