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Approaches to the Preparation of Carborane-Containing Carbosilane Compounds

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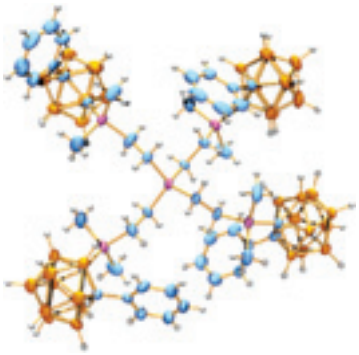
ABSTRACT



A novel type of carborane cluster assembly has been successfully prepared using carbosilane derivatives as a scaffold. Two synthetic routes have been used: One involves the reaction of a carbosilane containing terminal Si−Cl functions with the lithium salt of the phenyl-*o*-carborane, and the second one consists of a highly efficient hydrosilylation of tetravinylsilane with the corresponding carboranylsilane. The crystal structure of this carborane-containing carbosilane compound has been determined by X-ray diffraction.

The *o*-carborane and its derivatives present properties such as high stability, hydrophobicity, so-called three-dimensional "aromaticity", and synthetic versatility.[1] This makes them suitable for a wide range of applications in organometallic chemistry and materials science such as extraction of radionuclides,[2] BNCT,[3] and catalysis,[4] among others. Although some carborane-containing dendrimers have been reported, none of them have been integrated into carbosilane structures.[5] Dendrimers[6] constitute a class of spherical and monodisperse macromolecules that can be constructed from a multifunctional central core and expand to a periphery. Today, the technology of dendrimers is focused on the modification of their properties and potential applications by introduction of reactive functional groups[7] or metals in their interior or on their periphery.[8,9] Of the multitude of

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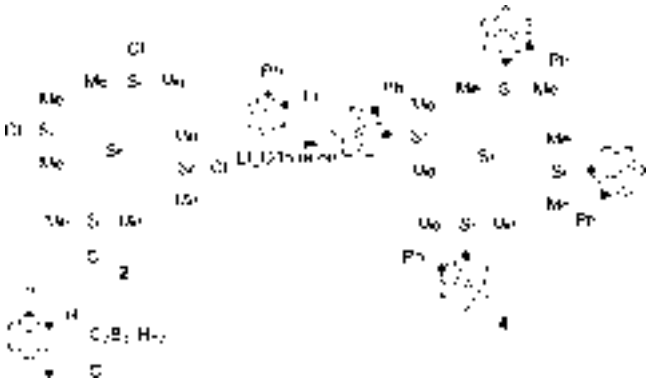
dendrimers reported, we are interested in those having a Si atom as the branch point, with strong Si−C bonds as the connecting structure. These perfect and robust carbosilane dendrimers are kinetically and thermodynamically very stable molecules that can be further functionalized according to the required application.[10] Our aim is to generate new macromolecules using carbosilane dendrimers as an inert scaffold in which carborane derivatives are attached on the periphery. Here, we present the first example of an assembly of carborane moieties linked by a carbosilane scaffold. This compound may be taken as a model for subsequent development of carborane-containing carbosilane dendrimers. The synthetic methodology used is suitable for applitcation in the synthesis of various generations of carbosilane dendrimers and other carborane derivatives.

Our first approach for attaching clusters onto organosilicon cores involved the reaction of the lithium salt of phenyl-*o*-carborane (**1**) and the carbosilane derivative **2**[11] by a nucleophilic substitution reaction (Scheme 1). Thus, a

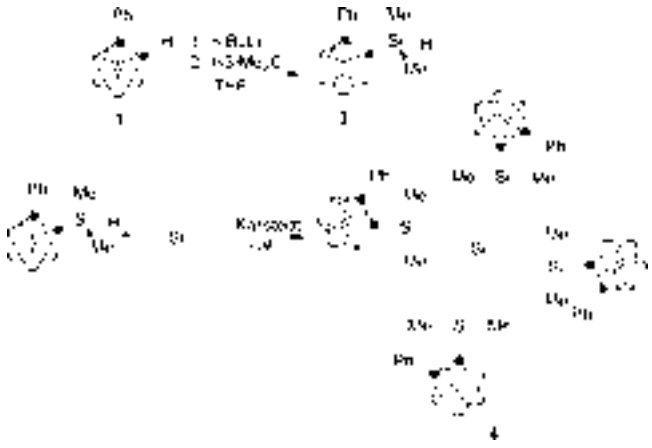
Scheme 1. Preparation of **4** from **2** and Li[1-Ph-1,2-$C_2B_{10}H_{10}$]



solution of **1** in diethyl ether was treated with *n*-buthyllithium at 0 °C to afford the monolithiated species, and subsequently a solution of **2** in toluene was added. The mixture was stirred for 5 min at 0 °C and then filtered. After evaporation of solvents, the residue was treated with cold diethyl ether (0 °C), affording compound **4** as an air-stable white solid in 62% yield.

Analysis (vide infra) shows that a carbosilane core with four phenyl-*o*-carborane clusters on the periphery was obtained. In principle, compound **4** could be prepared by a hydrosilylation reaction following Cuadrado and collaborators' procedure.[12] Thus, considering the properties of carboranes, the hydrosilylation of tetravinylsilane with the corresponding carboranylsilane was investigated. For this purpose, 1-dimethylsilyl-2-phenyl-1,2-dicarba-*closo*-dodecaborane (**3**) was prepared. The synthesis of **3** was achieved by reaction of the lithium salt of **1** with $HSiMe_2Cl$ in THF (Scheme 2). Compound **3** was isolated as a white solid in

Scheme 2. Preparation of **3** and Subsequent Hydrosilylation Reaction of Tetravinylsilane with **3** to Achieve **4**



96% yield. The IR spectrum shows bands at 2572 and 2161 cm^{-1} attributed to ν(B−H) and ν(Si−H), respectively. The ^1H NMR spectrum displays a doublet at 0.07 ppm (Si−Me) and a septuplet at 3.67 ppm (Si−H). A singlet at −4.69 ppm was displayed by the $^{29}Si\{^1H\}$ NMR spectrum, which was split into a doublet (^1J(Si, H) = 217 Hz) in the ^{29}Si NMR spectrum. The $^{11}B\{^1H\}$ NMR spectrum shows five signals, in the range δ −10.56 to +2.11 ppm, assigned to the corresponding B atoms by a two-dimensional COSY $^{11}B\{^1H\}-^{11}B\{^1H\}$ NMR spectrum.

No reaction was observed, however, when **3** was mixed with tetravinylsilane in the reported reaction conditions using Pt catalysts.[11,12] The permanence of the Si−H signal in the IR and ^1H NMR spectra indicated its lack of reactivity under those conditions. Formation of **4** in 85% yield was successfully achieved by the addition of **3** to tetravinylsilane in the absence of solvent, at 50 °C overnight, using the Karstedt catalyst[13] (Scheme 2). In view of these results, the hydrosi-

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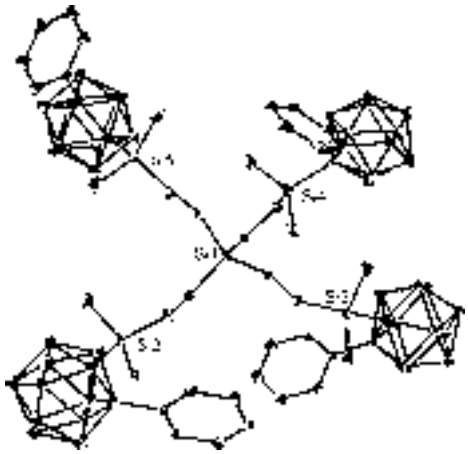

Figure 1. Structure of **4**. Thermal ellipsoids are drawn at the 20% probability level.

lylation reaction of carboranylsilanes with appropriate vinyl or allyl derivatives under catalytic conditions in the absence of solvent could lead to novel dendrimers or macromolecular structures in which the carboranyl units were attached.

The structure of **4** was straightforwardly established on the basis of IR, ^{1}H, $^{13}C\{^{1}H\}$, ^{11}B, and ^{29}Si NMR, elemental analysis, and electrospray-ionization mass spectrometry (ESI-MS) and unequivocally confirmed by X-ray diffraction analysis. The IR spectrum shows two bands at 2568 and 1253 cm^{-1} corresponding to ν(B−H) and δ(Si−Me), respectively. The ^{1}H NMR spectrum exhibits a singlet at −0.13 ppm assigned to the Si−Me protons and a multiplet at 0.14 ppm due to the Si−$(CH_2)_2$−Si protons. Such protons appear at higher field with respect to precursor **2** (from 0.44 to −0.13 ppm for Si−Me and from 0.65 to 0.14 ppm for Si−CH_2). This effect has been attributed to the influence of the ring electronic currents with these protons (vide infra).[14] The $^{13}C\{^{1}H\}$ NMR resonances of the CH_2 and CH_3 groups have also been shifted to higher field with respect to **2**. The $^{11}B\{^{1}H\}$ NMR spectrum of **4** shows four resonances in a range δ −10.14 to +1.41 ppm that were assigned by comparison with **3**. The $^{29}Si\{^{1}H\}$ NMR spectrum displays two close signals at 10.56 ppm (Si core) and 10.36 ppm (Si periphery). The latter corresponds to the Si atom bonded to the $C_{cluster}$. The corresponding Si resonance is shifted to higher field with respect to the peripheral Si−Cl (32.71 ppm) for **2**, due to the presence of the cluster. The ESI mass spectrum of **4** shows various peaks, among them one at m/z = 1312.1 corresponding to $[M + 2(CH_3OH)]^-$. Crystals suitable for X-ray structural determination were isolated, and the structure is shown in Figure 1. The molecule assumes C_1 symmetry with mutually different orientations of the clusters. The $C_{cluster}$−$C_{cluster}$ distances of 1.649(4)−1.720(4) Å are comparable to values found for 1,1′,2,2′-$(SiMe_2)_2$- and 1,2-Ph_2-disubstituted *o*-carborane derivatives [1.688(5) and 1.720(4), and 1.733(4) Å, respectively].[15] The Si−$C_{cluster}$ distances are around 1.93 Å, longer than the dendrimeric Si−C distance (1.85 Å). The $C_{cluster}$−$C_{cluster}$−Si angle is 122.8°.

In conclusion, two different synthetic routes have been developed for the incorporation of carboranyl moieties onto oganosilicon cores. The first approach involves the reaction of a Si−Cl-functionalized carbosilane derivative with the monolithium salt of phenyl-*o*-carborane. The second one consists of the hydrosilylation reaction of tetravinylsilane with the corresponding carboranylsilane. Both methods afford a cluster compound that incorporates four phenyl-*o*-carborane moieties covalently bonded to the peripheral silicon atoms of a carbosilane core. If we consider the many reactions that the carborane clusters can undergo, it is clear that compound **4**, as well as later to be developed carborane-terminated carbosilane dendrimers, offers many opportunities for the functionalization of the periphery. The synthesis of **4** opens the way for such dendrimers considering the availability of periphery vinyl and chlorine-terminated silicon dendrimers. Work is now underway to extend the reported procedures to synthesize multicarborane-containing higher generation dendrimers and proceed toward further derivatization of the carborane clusters.

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Supporting Information Available: Experimental data for **3** and **4** and crystallographic data (CIF) for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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

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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_2-HSi-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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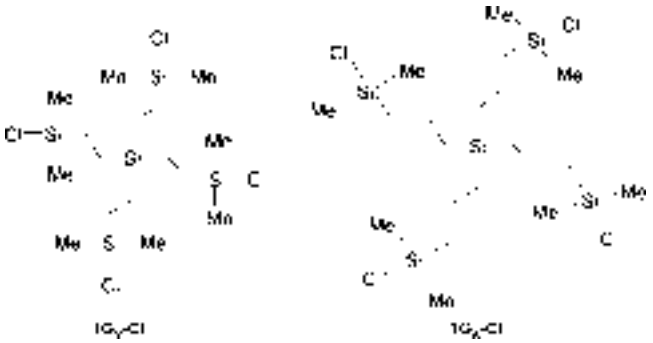

Figure 1. Chlorosilanes derived from the tetravinylsilane ($1G_V$-Cl) and tetraallylsilane ($1G_A$-Cl).

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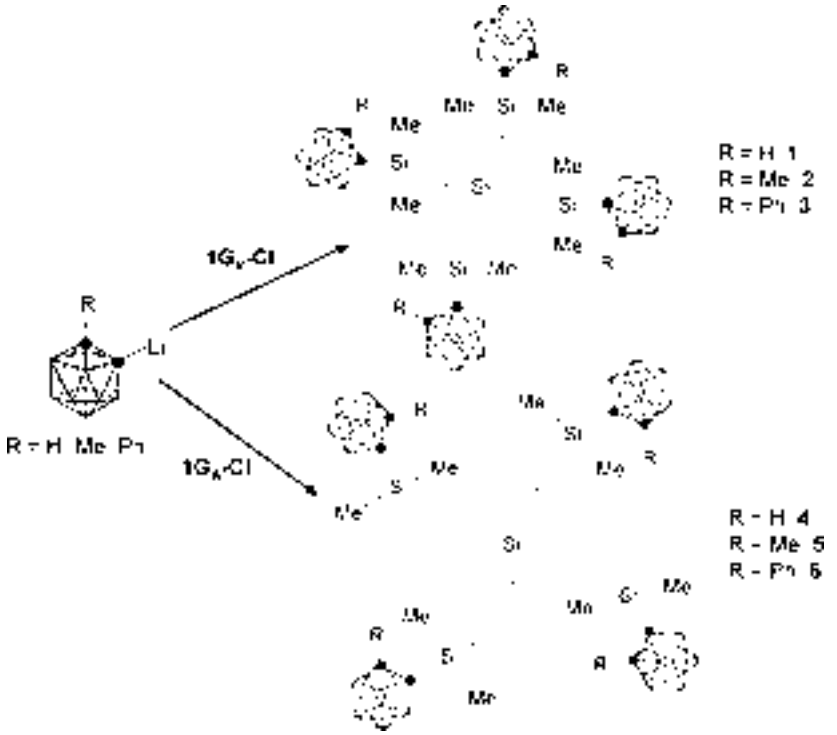
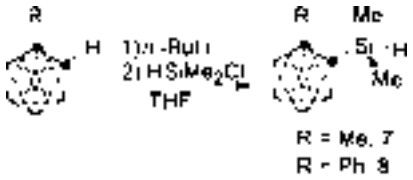
Scheme 1. Preparation of 1−6 by Nucleophilic Substitution of Si−Cl Functions in $1G_V$-Cl and $1G_A$-Cl with Monolithium Salts of Carboranes



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$_{cluster}$ 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$_{cluster}$ 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 $[SiCH_2CH_2 + NH_4]^+$ is that of 100% abundance. Nevertheless, the ESI was recorded in $CHCl_3/CH_3OH$ 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 $[M + 2(CH_3OH)]^-$ and at *m/z* = 157.2 due to the $[C_3B_{10}H_{13}]^-$ fragment, attributed to the 1-Me-*o*-carborane. The ESI mass spectrum of **4** shows one peak at *m/z* = 1036.8 corresponding to $[M + 2(H_2O)]^-$, in which the two H_2O molecules come from the CH_3OH. In contrast, the ESI mass spectrum of **5** and **6** shows

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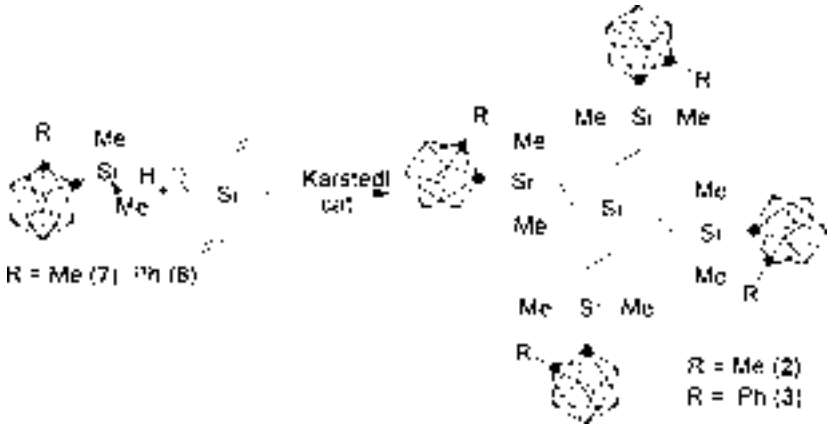
Scheme 3. Synthesis of 2 and 3 by Hydrosilylation of Tetravinylsilane with 7 and 8 Using Karsted's Catalyst



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

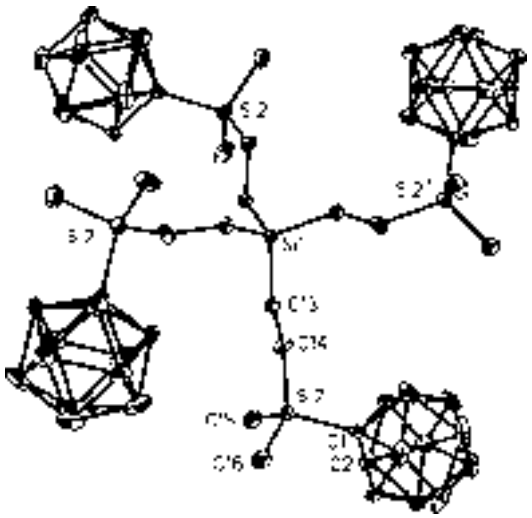


Figure 2. Molecular structure of $1G_V$-*o*-carborane (**1**). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level. Superscripts i, j, and k refer to equivalent positions $-x$, $-y+1/2$, z; $y-1/4$, $-x+1/4$, $-z+1/4$; and $-y+1/4$, $x+1/4$, $-z+1/4$.

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

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

two positions. In **3**,[10] orientations of the clusters are mutually different, resulting in C_1 symmetry for the molecule.

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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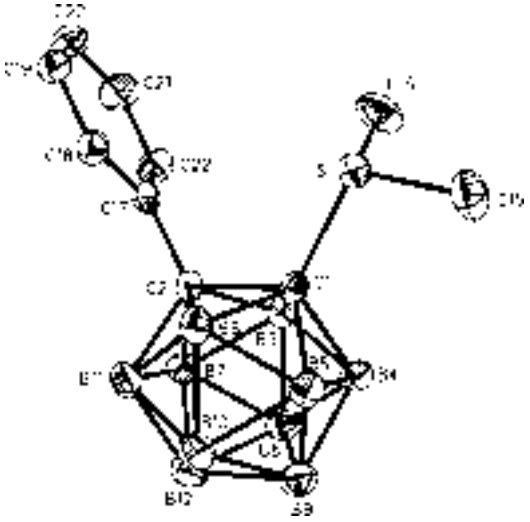

Figure 3. Molecular structure of 1-Me_2HSi-2-Ph-1,2-$C_2B_{10}H_{10}$ (**8**). Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

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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(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−*C*H_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−*C*H_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−*C*H_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-$SiMe_2H$-2-Ph-1,2-$C_2B_{10}H_{10}$ (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_3OH (1:3) *m/z*: calcd for $C_{52}H_{108}B_{40}Si_5$, 1304.5; found, 1368.5 [(M + 2CH_3OH)$^-$, 20%], 219.0 [($C_8B_{10}H_{15}$)$^-$, 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_2O 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.

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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.

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ANNEXOS

ANNEX I-ARTICLES PUBLICATS

(Posteriors Comissió Doctorat 14 de Febrer de 2006)

Synthetic approaches to the preparation of hybrid network materials incorporating carborane clusters

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A novel type of hybrid organic–inorganic class II materials with carborane-containing units have been prepared from a particular trichlorosilylcarborane-containing precursor. Different polymerisation processes were investigated in order to achieve the formation of materials that incorporate the covalently bonded carborane units and exhibit different structural characteristics. Hydrolytic, and non-hydrolytic sol–gel process were used for the preparation of the hybrid materials with an Si–O–Si-based network, whereas the hybrid material with an Si–N═C═N–Si-based network was prepared by a carbodiimide sol–gel process. Structural characterisation was performed by solid state NMR, IR, porosimetry and X-ray powder diffraction that reveal the formation of non-porous to porous materials with a high level of polycondensation, a short-range order organisation and the preservation of the covalent bond between the carborane part and the inorganic network. Alternatively, a solid-state process was used and allows the preparation of materials with a higher level of organisation according to polarized light microscopy. The materials are stable to about 450 °C in inert atmosphere, suggesting good thermal stability.

Introduction

The *closo*-1,2-carborane and its derivatives combine, in a unique three-dimensional symmetrical rigid cluster-like structure, high stability (chemical, photochemical and thermal) with a highly polarizable σ-aromatic character.[1–6] All this make these clusters good candidates for non-linear optical materials;[7–9] liquid crystals with specific mesophase, birefringence and photochemical stability;[10–14] or organic–inorganic hybrid carborane–siloxane polymers and preceramic precursors that exhibit outstanding thermal and oxidative properties.[15–19] In addition, 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,[20–26] radiopharmaceuticals,[27,28] and conducting organic polymers,[29] among others.[30–32]

The carborane cluster could represent an attractive versatile group for the preparation of organic–inorganic hybrid materials due to its intrinsic properties. We found interesting to synthesize some of them that could be seen as models for a subsequent development of carborane-containing hybrid materials. Nowadays, there is significant interest in materials that combine in a hybrid material high dimensional, thermal and oxidative stability.[33] Among them, the *bridged polysilsesquioxanes* are functional organic–inorganic materials prepared by a sol–gel process,[34,35] with the ideal chemical formula R–[$SiO_{1.5}$]$_n$,[33,36–38] which combine the properties of the organic and inorganic parts. In this respect, the organic bridging group attached to the Si atoms can be very different in terms of length, rigidity and functionality, which provides the chance to modulate properties such as porosity, thermal stability, and chemical reactivity, among others. Likewise, the control of porosity, thermomechanical properties and short to long-range order organisation have been some of the main purposes in the selection of an organic spacer.[39]

Thus, we report here an approach to the preparation and characterization of hybrid materials, where the ''organo-functional'' part contains a carborane moiety. In this respect, we study the preparation of carborane–organo-poly(trichlorosilyl), R–[$Si(Cl)_3$]$_2$ (R = carborane–organic part), in order to work with the trichlorosilyl-polymerizable group,[40] which allows the formation of hybrid materials by either hydrolytic or non-hydrolytic sol–gel processes. Additionally, we compare the solvent processes with a solid-state process that leads to more periodically organised materials.[41] This type of trichlorosilyl precursor was recently demonstrated to be useful for the preparation of silsesquicarbodiimide, a type of hybrid material containing Si–N═C═N–Si linkages.[42–44] Therefore, starting with the same precursor we investigate the possibility to prepare carborane-containing silsesquioxanes by four different ways, and to characterize these solids in terms of structure, porosity, level of condensation and thermal stability.

Results and discussion

Synthesis and characterization of precursors

The preparation of the precursors relies on the weak acidity of the $C_{cluster}$–H (C_c–H) protons in carboranes (pK_a = 23.0),[45] that can be removed by strong bases generating nucleophile anions. These have the ability to react with a wide range of electrophilic reagents, such as halogens, alkyl halides,

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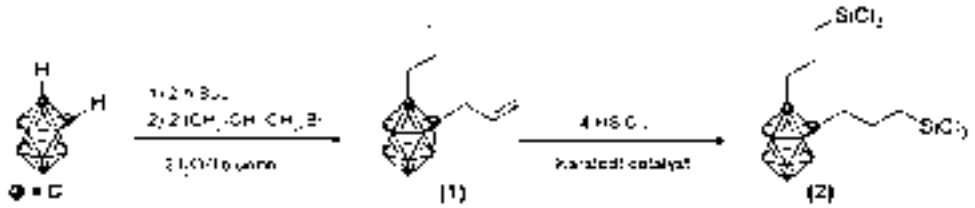


Scheme 1 Synthesis of 1,2-$(CH_2–CH=CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (**1**) and 1,2-$((CH_2)_3SiCl_3)_2$-1,2-$C_2B_{10}H_{10}$ (**2**) from 1,2-$C_2B_{10}H_{12}$.

chlorosilanes, *etc.*[46] Thus, compound **1**, 1,2-$(CH_2–CH=CH_2)_2$-1,2-$C_2B_{10}H_{10}$ was prepared by the reaction of the dilithium salt of the *o*-carborane with the stoichiometric amount of allyl bromide, according to Scheme 1. The resultant yellow oil was characterized by IR, $^1H\{^{11}B\}$, $^{13}C\{^1H\}$ and ^{11}B NMR. Three resonances at 2.9, 5.2 and 5.8 ppm are observed in the $^1H\{^{11}B\}$ NMR spectrum and are attributed respectively to $C_{cluster}–CH_2$, CH and CH_2 of the allyl group. The corresponding resonances at 39.2, 132.5 and 119.5 ppm are also exhibited in the $^{13}C\{^1H\}$ NMR spectrum, whereas the peak at 77.7 ppm is assigned to the $C_{cluster}$ atoms (C_c). The ^{11}B NMR spectrum exhibits two resonances, at −4.5 and −10.6 ppm, with a 2 : 8 pattern.

The hydrosilylation reaction with $HSiCl_3$ of the allylic function bonded to the carborane moiety in **1**, for two hours at room temperature in the presence of Karstedt catalyst, gave quantitatively the trichlorosilane **2** (99% yield) (Scheme 1). Precursor **2** was obtained as a yellow oil, for which $^{29}Si\{^1H\}$ NMR analysis revealed the presence of only one signal at 11.6 ppm. Other NMR data obtained by $^1H\{^{11}B\}$ and $^{13}C\{^1H\}$ NMR indicated almost complete hydrosilylation (98%) in the β position.

Preparation of the hybrid materials

Four different methods using precursor **2** have been used: hydrolytic sol–gel, non-hydrolytic sol–gel, solid-state and carbodiimide processes.

According to a classical hydrolytic sol–gel process, xerogel **3** was prepared by hydrolysis–polycondensation using a stoichiometric amount of water dissolved in THF at room temperature (see Scheme 2). The gel was rapidly formed and allowed to age for 7 days. After washing with the corresponding solvents, the gel was dried to give an insoluble and brittle powder.

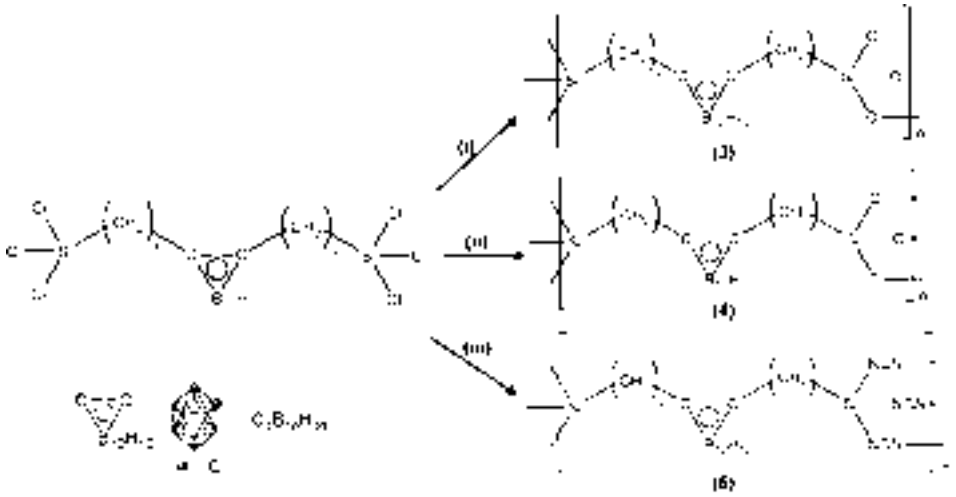
Likewise, a non-hydrolytic sol–gel process was used for the preparation of xerogel **4**, using diisopropyl ether as oxygen donor and $FeCl_3$ (0.1%) as catalyst, under argon at 110 °C for 43 hours (Scheme 2).[47,48]

The solid-state hydrolytic process was usable since chlorosilanes are highly reactive toward water,[49] and xerogel **5** was obtained by exposing the precursor **2** to the air for 19 days.

A carbodiimide sol–gel-like process based on the exchange reaction between Si–N and Si–Cl bonds was also investigated in order to prepare a Si–N=C=N–Si network different from the oxide network that results from the hydrolytic or the non-hydrolytic process. According to Scheme 2, xerogel **6** was obtained by sol–gel polycondensation of **2** with bis(trimethylsilyl)carbodiimide in THF at room temperature in the presence of pyridine as catalyst. The opaque white gel was aged for 7 days at 45 °C, washed with THF to remove by-products and pyridine, and dried under vacuum at 130 °C for 1 day to give xerogel **6**.

Characterization of the hybrid materials

Molecular structure. The IR spectra (KBr pellet) of xerogels **3**, **4** and **5** exhibit strong bands at 2594 cm^{-1} corresponding to the B–H stretching mode, which indicates the presence of the cluster in the material, and those at 1078 cm^{-1} are related to Si–O–Si stretches that indicate the condensation of the precursor Si–Cl functions. Bands at 3400 and 3600 cm^{-1}



Scheme 2 Preparation of xerogels **3**, **4** and **6**; (i) H_2O, THF, (ii) $(^iPr)_2O$, $FeCl_3$, (iii) $Me_3Si–N=C=N–SiMe_3$, THF, pyridine.

corresponding to SiO–H are insignificant and the band near 1600 cm^{-1} due to H_2O is very small for xerogels **3–5**. Other bands observed in the region 2950–2880 and 1250 cm^{-1} corroborate the presence of the alkyl chain in the hybrid material. For **6**, two strong absorption bands at 2592 and 2152 cm^{-1} correspond respectively to the B–H stretching and the carbodiimide group (Si–NCN). Upon contact with moisture, hydrolysis of the Si–NCN groups occurs, with subsequent Si–O–Si polycondensation ($\nu_{Si-O-Si}$ = 1063 cm^{-1}), and cyanamide groups (ν_{N-CN} = 2265 cm^{-1}) that replace the carbodiimide units (Si–NCN).[43]

The ^{13}C CP MAS NMR spectra of xerogels **3** and **4** also confirm that the integrity of the molecular building block survives the sol–gel polymerization, and that the Si–C and C_c–C bonds cleavage does not occur. Three peaks around 14, 24 and 37 ppm corresponding to Si–CH_2–CH_2–CH_2–$C_{cluster}$ alkyl spacers are observed, while a broad peak centred at 80 ppm is attributed to the C_c atoms. For **6**, the ^{13}C CP MAS NMR spectrum exhibits peaks at 18 ppm (*C*H_2–Si), 24 ppm (CH_2–CH_2), 38 ppm (C_c–*C*H_2), 80 ppm (C_c) and 121 ppm (N*C*N). The chemical shifts of the bridging alkylene carbons are very similar to those observed for silica-based xerogels **3** and **4**, partially due to the similar electronegativity of the NCN function and the oxygen atoms.[42]

An evaluation of the degree of condensation of the polysiloxane network was obtained by looking at the ^{29}Si CP MAS NMR spectroscopic analyses. Both xerogels **3** and **4**, exhibit three broad peaks at δ −49, −56 and −65 ppm, corresponding to T^1 [SiC(OH)$_2$(OSi)], T^2 [SiC(OH)(OSi)$_2$] and T^3 [SiC(OSi)$_3$], respectively. No signals in the range of −100 to −110 ppm due to Q^n substructures are observed, which confirms that Si–C bonds are not cleaved during the condensation process. ^{29}Si CP MAS NMR spectroscopy can be used to evaluate quantitatively the level of condensation (LC) according to the formula LC = 1/3 T^1 + 2/3 T^2 + 1 T^3.[50] In both xerogels **3** and **4**, the LC was 75% by deconvolution of the ^{29}Si CP MAS NMR spectra (Table 1). However, xerogel **3** prepared by the hydrolytic sol–gel process shows more T^3 and T^1 substructures than xerogel **4**, which presents negligible T^1 units (6%) and major T^2 and T^3. Altogether, **4** prepared by the non-hydrolytic sol–gel method seems more homogeneous than **3** in terms of substructure units (see Table 1). For **5** the quantity was too small for such analysis. For **6**, a qualitative ^{29}Si CP HPDEC spectrum exhibit a broad peak at −62 ppm similar to that found in poly(organosilsesquioxanes). This corroborates the expected formation of $[(NCN)_{1.5}Si(CH_2)_3(C_2B_{10}H_{10})(CH_2)_3Si(NCN)_{1.5}]_n$ due to the condensation of the material. Additional signals at 11.4 ppm and 1.7 ppm attributed, respectively, to residual uncondensed CH_2–$SiCl_3$ and C═N–$SiMe_3$ functions are also observed. The compositions of xerogels **3**, **4** and **6** were also estimated by elemental analysis, assuming that the organic groups have not been cleaved during the condensation, and completely condensation. For hydrolytic xerogel **3** the calculated analysis is very consistent with the theoretical, however the non-hydrolytic xerogel **4** gives percentages of C and H which should agree with an uncondensed O(^{i}Pr) group. For xerogel **6**, as a result of the high moisture sensitivity of –NCN groups, different elemental analyses performed from the same sample give distinct results.

Table 1 Degree of condensation for xerogels **3** and **4**

	T^1		T^2		T^3		
Xerogel	ppm	%	ppm	%	ppm	%	LC (%)
3	−49.8	22	−57.4	30	−65.1	48	75
4	−49.4	6	−57.0	63	−66.4	31	75

Meso- and microscopic structure. X-Ray powder diffraction analysis was performed to obtain information about the organization at the micro- and mesoscopic scale. The XRD patterns of xerogels **3** and **4** are similar (Fig. 1), they did not exhibit any sharp Bragg peak, but they present two broad bands consistent with a short-range ordered structure. According to a Bragg's law assumption, these bands correspond to *d* spacings of 15.2 and 6.2 Å for **3**, and 13.8 and 6.2 Å for **4**. The first *d* spacing is associated with the high intensity (001) peak, while 6.2 Å could be associated with the second order (002) peak, for each compound. Additionally, a very smooth broad band at *d* = 3.7 Å (Fig. 1b and d) is also observed. For **6**, the XRD diffraction pattern displays two broad bands close to those found in xerogels **3** and **4**. Additional Bragg's signals indicate the presence of a material with an organisation at a long-rang order, however it is not possible at the present time to decide if it is due to a single compound or a mixture of two different products (Fig. 1c). Thus, all our xerogels exhibit in general a short-range order organization at the nanometre scale when compared to other xerogels that remain completely amorphous,[33] which we have attributed to the presence of the rigid *o*-carborane cluster. In this respect, the signals at 13.8 Å and 15.2 Å are related to the presence of the organo–carborane moiety and the broad shoulder at 3.7 Å is generally attributed to the contribution of the Si–O–Si network.[36] The signal at 13.8 Å is in agreement with a periodic distance due to the organic alkylene bridge, specifically to twice the [C_c–$CH_2CH_2CH_2$–SiO–] fragment, which is estimated to measure 6.85 Å, by computer simulation models of organo–carborane packing within silicate sheets to form a lamellar structure (Fig. 2a). The signal at 6.2 Å could correspond to

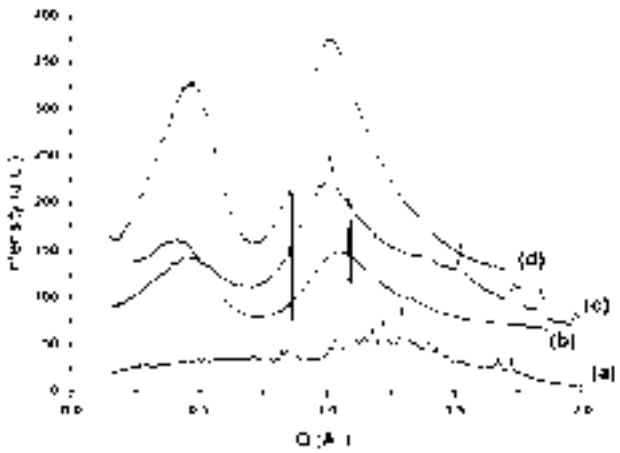


Fig. 1 X-Ray powder diffraction diagrams of: (a) precursor **2**, (b) xerogel **3**, (c) xerogel **6**, (d) xerogel **4**.

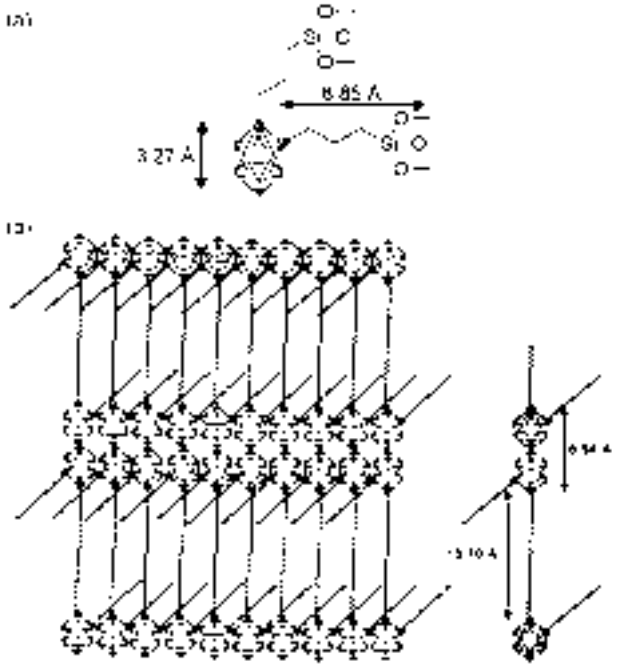


Fig. 2 a) Main distances in the xerogels calculated by computer simulation. b) Proposed organization of the carborane moieties and alkylic chains in xerogels.

a periodic distance of the cluster moiety, since this agrees with twice the distance between the C1 and its antipodes B12 as determined by computer simulation (Fig. 2a), or just to the $[C_c–CH_2CH_2CH_2–SiO–]$ fragment. Likewise, this has been interpreted by us as the formation of a periodic structure with alternating organo–carborane and silica layers which represent an unique nanostructuration of the material (Fig. 2b).

For xerogel **5** obtained using the solid-state hydrolytic process by exposing to air the precursor **2**, the XRD diagram shows the same two broad bands as **3**, at 6.1 and 15.1 Å, and two additional sharp peaks at $d = 3.4$ and 3.3 Å, indicating the presence of a higher level of periodicity (Fig. 3). Compared to the X-ray diffraction powder of the crystallized precursor **2**, there is a difference in the position of the Bragg's peaks of **5**, which exhibits main peaks at 0.86, 1.10, 1.22, 1.30, 1.68, 1.72 $Å^{-1}$ in Q^{-1}. Therefore, although part of the periodical structure is maintained during the solid-state hydrolysis, it is obvious that the initial packing of the precursor is lost and serves as a template leading to the long-range order organization of the xerogel **5** (see Fig. 3).

Transmission electronic microscopy (TEM) studies on the xerogel **4** reveal the great heterogeneity of the materials in terms of organization. Taken from the same sample, a great part of the material appears completely amorphous, while some other parts present a high level of organization. The TEM images presented in Fig. 4 confirm the layered structure of a part of the material in which the interlayer spacing is 3.4 Å. This result might be in agreement with the (004) order with respect to the high intensity (001) peak observed in the XRD pattern. This could be considered as a preliminary result and further studies will be the subject of a future work.

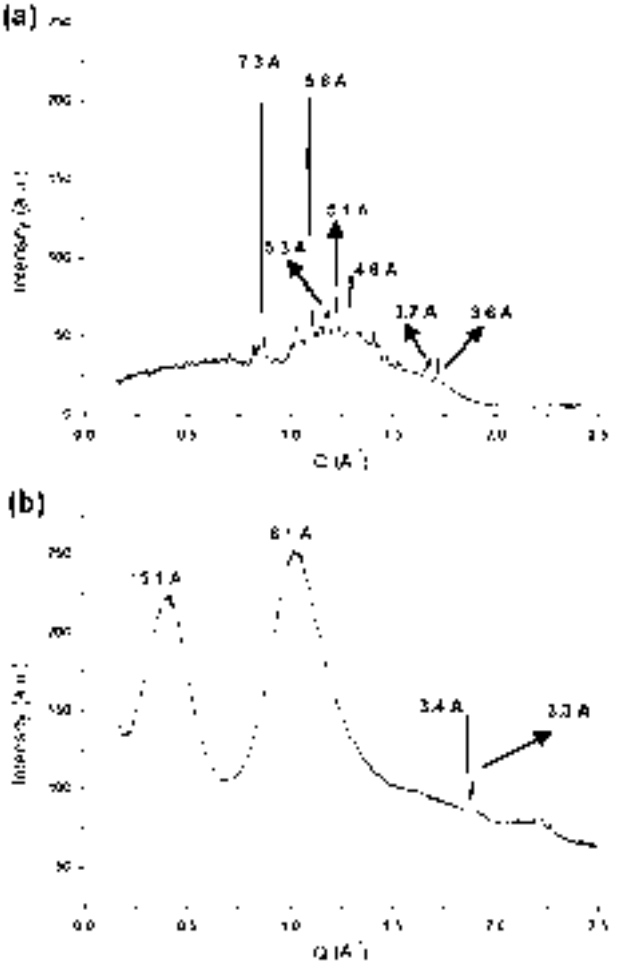


Fig. 3 X-Ray powder diffraction diagrams of: (a) crystallized precursor **2** and (b) xerogel **5**.

Microscopy. Focusing on the hydrolytic solid state condensation of **2**, analysis of the precursor in polarized light agrees with the X-ray data which indicate a crystallised compound highly birefringent and colourful by microscopy. Although part of the colour is lost upon exposure to air, the resulting **5** is still highly birefringent and moreover the shape of the crystalline needles seems to be preserved indicating a very low level of amorphisation during the polycondensation of the crystallised precursor. This is in agreement with the presence of Bragg's signal observed by X-ray diffraction analysis of the material (Fig. 5).

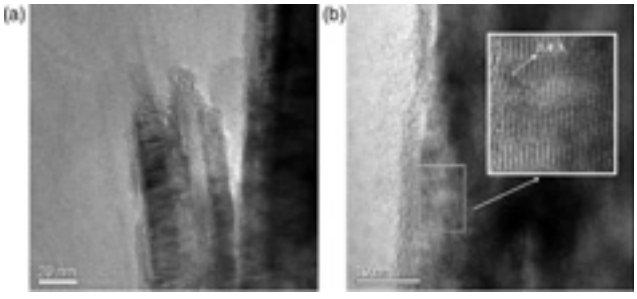


Fig. 4 TEM images for xerogel **4**.

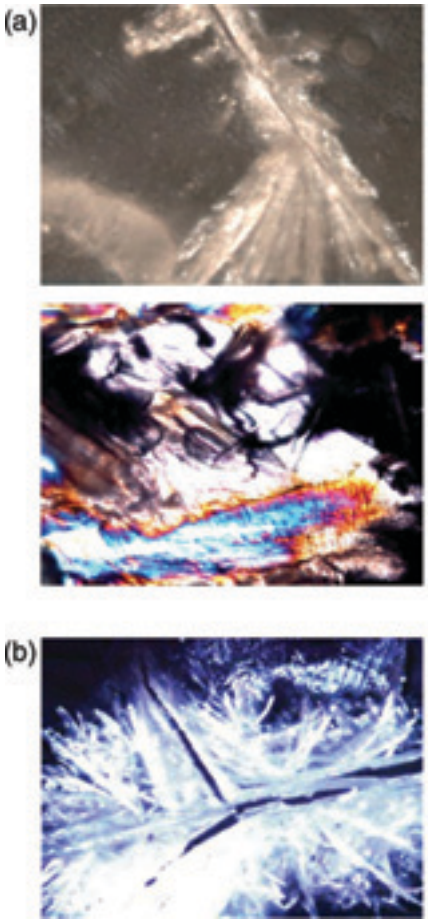


Fig. 5 Optical micrographs in polarized light of: (a) **2** and (b) **5**.

Porosity. The pore structure and the specific surface area of the materials were determined by adsorption/desorption isotherms.[51,52] Xerogels **3** and **4** exhibit very low specific surface areas (<15 m^2 g^{-1}), which could be attributed in a first approach to the presence of the flexible alkyl groups in the material.[37] However, for **6** a much higher specific surface area of 200 m^2 g^{-1} was found by a 5 points porosimetry measurement with BET calculation, which clearly indicates that for the same precursor the type of condensation process and experimental conditions modify the porosity in the gel structure. This may also results from the fact that Si–O–Si bridges are flexible while Si–N=C=N–Si are much more rigid. For **5**, the amount of product was too small for this analysis.

Thermal stability. The thermal behaviour of xerogels studied by thermogravimetric analysis (TGA) in inert argon atmosphere was determined between 20 and 1200 °C at a heating rate of 5 °C min^{-1}, exhibiting high thermal stability. Xerogels **3** and **4** show weight losses between 100 °C and 450 °C, which correspond to 6.1 and 9.6%, respectively, and is attributed to the final condensation of the material (Fig. 6). The main weight loss (around 18%) occurs between 450 and 800 °C, which should correspond to m/z 56, attributed to the loss of two CH_2=CH_2 molecules. Continued heating to temperature

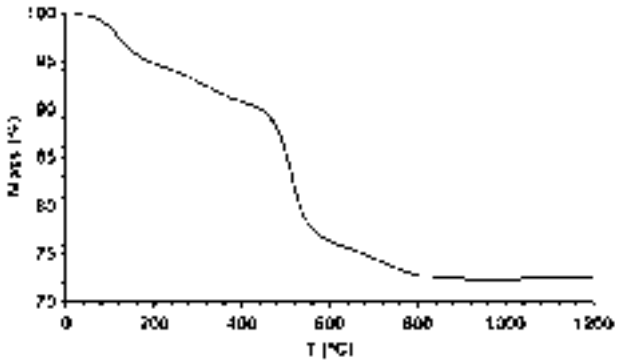


Fig. 6 TGA curve of xerogel **3** under an atmosphere of argon.

of 1200 °C leaves a black residue in 77% yield, whose ATR spectrum exhibits two intense bands at 1370 and 1090 cm^{-1} attributed to ν(B–O) and ν(Si–O), respectively; however no signals corresponding to B–H are observed indicating that the cluster has been completely degraded. In addition, the XRD spectrum of the residue does not exhibit any Bragg's peak, indicating that a completely amorphous material is obtained. In the same conditions, xerogel **6** is stable up to 200 °C, then an 8% weight lost is observed gradually up to 400 °C and could be due to the final condensation of the material, and evaporation of residual bis(trimethylsilyl)carbodiimide.[42] The main weight loss (around 35%) occurs between 400 and 800 °C and is certainly related to the loss of carbon-containing moieties and to the condensation of residual uncondensed groups like $SiCl_3$ and –C=N–$SiMe_3$. In all the cases, elimination of carborane moieties should not be considered since in inert atmosphere *o*-carborane (1,2-$C_2B_{10}H_{12}$) begins to isomerize to *m*-carborane (1,7-$C_2B_{10}H_{12}$) above 425 °C, and above 700 °C the *p*-carborane (1,12-$C_2B_{10}H_{12}$) is obtained.[6]

Conclusions

In the present work we report on the preparation and structural characterization of a new type of carborane-containing class II hybrid material in which the cluster is bonded to the siloxane groups. The key point in the design of such materials has been the introduction of an unusually rigid, chemically and thermally versatile moiety attached through organic spacers to hydrolysable $SiCl_3$ groups ready to condense by different processes. Four hybrid organic–inorganic xerogels (**3–6**) have been prepared using hydrolytic and non-hydrolytic sol–gel polycondensation, the solid-state process and the carbodiimide procedure. Materials prepared by hydrolytic or non-hydrolytic sol–gel methods are very similar in terms of thermal stability, porosity and structure but different in terms of structural T^n subunits. Although a short-range order between the organo–carborane unit can be proposed to describe the structural organisation of these solids, a higher periodicity seems achievable by a solid-state process, in agreement with previous work.[41,53] Finally, the hybrid material **6** prepared from the same precursor exhibits some differences in the porosity, condensation and X-ray structure with respect to

the other materials; all structural characteristics that have to be related to the nature of the Si–N═C═N–Si network. Current work is being carried out to go into the study of the features and behaviour of these and other related materials.

Experimental

Materials

All reactions were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents were purified, dried, and distilled by standard procedures. Trichlorosilane and Karstedt platinum catalyst (3–3.5% Pt) were purchased from ABCR. Allyl bromide (99%) and *n*-BuLi were used as received from Aldrich and Lancaster. $FeCl_3$ and pyridine were purchased from Aldrich. $Me_3Si–NCN–SiMe_3$ was prepared according to literature procedures.[42]

Instrumentation

Infrared spectra were measured in NaCl or KBr pellets on a ThermoNicolet AVATAR 320 FT-IR. Attenuated Total Reflection (ATR) spectra were measured on a Bruker Tensor 27 using a Specac NKII Golden Gate accessory. $^1H\{^{11}B\}$ NMR (300.13 MHz), ^{11}B NMR (96.29 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz) and $^{29}Si\{^1H\}$ NMR (59.62 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. NMR spectra were measured using samples in $CDCl_3$ solution at room temperature. Chemical shifts for ^{11}B NMR were referenced to external $BF_3 \cdot OEt_2$ and those for $^1H\{^{11}B\}$ NMR, $^{13}C\{^1H\}$ NMR and $^{29}Si\{^1H\}$ NMR were referenced to Me_4Si. ^{29}Si CP MAS NMR (at 79.49 MHz) and ^{13}C CP MAS NMR (at 100.63 MHz) spectra were obtained on a Bruker Advance ASX400 using a CP MAS sequence or a HPDEC. Thermogravimetric analyses (TGA) of the network materials were performed on a Netzsch STA 409 PC/PG under a 50 mL min^{-1} argon flow. Samples were heated from 20 to 1200 °C at 5 °C min^{-1}. X-Ray powder diffraction measurements were performed using a spectrometer with a rotating copper anode with an OSMIC monochromator system and an 'Image Plate 2D' detector working with CuKα (λ = 1.542 Å) radiation and a beam size of 0.5 × 0.5 mm and acquisition time of 40 to 50 minutes. Sample were previously crushed and placed in a Lindeman tube (1mm diameter). The specific surfaces areas, porosities, volumes, and pore size distributions were determined by analysing the N_2 adsorption/desorption isotherms according to the BET method using a Micromériticcs Gémini III 2375 and ASAP 2010. TEM images were achieved with a JEOL JEM 2011 (200 Kv) microscope. Elemental analyses were performed in the analytical laboratory using a Flash EA 1112 Series microanalyzer.

Syntheses

1,2-(CH_2–CH═CH_2)$_2$-1,2-$C_2B_{10}H_{10}$ (1). In a Schlenk flask under argon, 1,2-$C_2B_{10}H_{10}$ (1.0095 g, 7.0 mmol) was dissolved in a mixture of toluene (14 ml) and diethyl ether (7 ml). The solution was cooled at 0 °C and *n*-BuLi (9.7 ml, 14.7 mmol) was added dropwise. The mixture was stirred for 1 hour at room temperature, cooled again at 0 °C, and (CH_2═CH–CH_2)Br (1.2 ml, 13.9 mmol) was added. The mixture was stirred for 2 hours at room temperature and refluxed overnight. Then it was cooled to room temperature, and quenched with 20 ml of water, transferred to a separatory funnel and extracted with Et_2O (3 × 10 ml). The organic layer was dried over $MgSO_4$ and concentrated under vacuum to obtain compound **1** (1.51 g, 97%) as a yellow oil. FTIR NaCl/cm^{-1} 3086 ν(═CH_2), 3022 ν(═CH), 2986–2925 ν(C–H)$_{alkyl}$, 1643 ν(C═C) and 1418 δ(═C–H). $^1H\{^{11}B\}$ NMR (δ (ppm)): 2.1 (2H, br s, B–*H*), 2.3 (8H, br s, B–*H*), 2.9 (4H, d, J_1 = 7.3 Hz, C_c–CH_2), 5.1 (2H, d, $J_{1,t}$ = 16.7 Hz, CH═CH_2), 5.2 (2H, d, $J_{1,c}$ = 9.7 Hz, CH═CH_2), 5.8 (2H, m, $J_{1,t}$ = 16.7 Hz, $J_{1,c}$ = 9.7 Hz, J_1 = 7.3 Hz, C*H*═CH_2). ^{11}B NMR (δ (ppm)): −4.5 (2B, d, J_1 = 145.0 Hz), −10.6 (8B, d, J_1 = 153.9 Hz). $^{13}C\{^1H\}$ NMR (δ (ppm)): 132.5 (*C*H═CH_2), 119.5 (CH═*C*H_2), 77.7 (C_c), 39.2 (C_c–*C*H_2).

1,2-[(CH_2)$_3$$SiCl_3$]$_2$-1,2-$C_2B_{10}H_{10}$ (2). In a Schlenk flask under argon, **1** (950 mg, 4.2 mmol), $HSiCl_3$ (1.71 ml, 16.9 mmol) and Karstedt catalyst (16 µl, 0.034 mmol) were mixed and stirred for 2 hours at room temperature. Evaporation of the volatiles and the excess of $HSiCl_3$ gave compound **2** (2.10 g, ≈99%) as yellow oil. $^1H\{^{11}B\}$ NMR (δ (ppm)): 1.46 (4H, t, J_1 = 8.1 Hz, –CH_2–Si), 1.86 (4H, m, –CH_2–CH_2–Si), 2.29 (4H, t, J_1 = 8.1 Hz, B–C_c–CH_2–). ^{11}B NMR (δ (ppm)): −3.6 (2B, d, J_1 = 141.4 Hz), −9.4 (8B, m). $^{13}C\{^1H\}$ NMR (δ (ppm)): 78.5 (C_c), 36.4 (C_c–*C*H_2), 23.7 (*C*H_2–CH_2), 22.6 (*C*H_2–Si). $^{29}Si\{^1H\}$ NMR (δ (ppm)): 11.6.

Hydrolytic xerogel 3. In a Schlenk flask under argon, **2** (792 mg, 1.6 mmol) was dissolved in THF (2 ml). After all the precursor was dissolved, H_2O (0.2 ml, 9.9 mmol) was added dropwise to the solution. Once the addition was completed, a white solid was observed and the suspension was stirred for 30 minutes. The stirring was then stopped to allow gelation. After 5 minutes a gel was formed and was kept for 1 week for aging. The solid and the liquid phases were separated by filtration. The isolated gel was crushed and washed with ethanol (3 × 10 ml), acetone (3 × 10 ml) and diethyl ether (3 × 10 ml), and finally dried under vacuum to obtain xerogel **3** (279 mg, 53%). FTIR KBr/cm^{-1} 2958–2888 ν(C–H)$_{alkyl}$, 2594 ν(B–H), 1458 δ(C–H)$_{alkyl}$, 1196 δ(Si–CH), 1078 ν(Si–O–Si). ^{29}Si NMR CP-MAS (δ (ppm)): −49 (T^1), −56 (T^2), −65 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 80 (C_c), 37 (C_c–*C*H_2), 24 (*C*H_2–CH_2), 14 (*C*H_2–Si). X-Ray powder diffraction shows two broad bands with *d* spacings of 6.2 Å and 15.2 Å. The surface area measure using the N_2 BET technique is 13 m^2 g^{-1}. Anal. Calc. for $C_8H_{22}B_{10}Si_2O_3$: C, 29.1; H, 6.7%. Found: C, 28.9; H, 6.6%.

Non-hydrolytic xerogel 4. In a Schlenk flask under argon, **2** (730 mg, 1.5 mmol) was dissolved in $^iPr_2O$ (0.63 ml) and $FeCl_3$ (0.1%) catalyst was added to the solution. The mixture was stirred for 5 minutes and transferred under N_2 to another tube, which was frozen in liquid nitrogen and sealed under vacuum. The sealed tube was held at 110 °C in an oven for 43 hours and then opened under argon. The obtained gel was crushed and washed with ethanol (3 × 10 ml), acetone (3 × 10 ml) and diethyl ether (3 × 10 ml), and finally dried under vacuum to obtain xerogel **4** (352 mg, 72%). FTIR KBr/cm^{-1} 2950–2880 ν(C–H)$_{alkyl}$, 2592 ν(B–H), 1458 δ(C–H)$_{alkyl}$, 1196 δ(Si–CH),

1063 ν(Si–O–Si). ^{29}Si CP MAS NMR (δ (ppm)): −49 (T^1), −56 (T^2), −65 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 80 (C_c), 37 (C_c–CH_2), 24 (CH_2–CH_2), 14 (CH_2–Si). X-Ray powder diffraction shows two broad bands with *d* spacings of 6.2 Å and 13.8 Å. The surface area measure using the N_2 BET technique is 8 m^2 g^{-1}. Anal. Calc. for $C_8H_{22}B_{10}Si_2O_3$: C, 29.1; H, 6.7%. Found: C, 32.6; H, 7.6%.

Solid-state hydrolytic xerogel 5. Some drops of a solution of **2** in CH_2Cl_2 were deposited on a microscope slide under argon until the formation of some crystals was observed. Then pictures of these crystals were taken using an electronic microscope. After this, the crystals were exposed to air for 19 days to form a white gel, which was insoluble in CH_2Cl_2. Again, some pictures of the solid were taken. FTIR KBr/cm^{-1} 2950–2880 ν(C–H)$_{alkyl}$, 2594 ν(B–H), 1458 δ(C–H)$_{alkyl}$, 1196 δ(Si–CH), 1078 ν(Si–O–Si). X-Ray powder diffraction shows two broad bans with *d* spacings of 6.1 Å, 15.1 Å, 3.4 Å and 3.3 Å.

Silsesquicarbodiimide xerogel 6. In a Schlenk flask under argon, **2** (693 mg, 1.4 mmol) was dissolved in THF (3 ml). Then, Me_3Si–NCN–$SiMe_3$ (0.97 ml, 4.2 mmol) and pyridine (0.06 ml, 0.7 mmol) were added to the solution and stirred at room temperature for 1 hour. After this time, a white gel was obtained and allowed to age for 1 week at 45 °C. The gel was crushed, treated with dry THF (10 ml), filtered and washed with dry THF (2 × 10 ml) under argon. Finally, the solid was dried under vacuum at 130 °C for a day to obtain xerogel **6** (571 mg, 80%). FTIR KBr/cm^{-1} 2950–2880 ν(C–H)$_{alkyl}$, 2592 ν(B–H), 2152 ν(Si–NCN), 1459 δ(C–H)$_{alkyl}$, 1254 δ(Si–CH_2). ^{29}Si CP MAS NMR (δ (ppm)): 11.4, 1.7, −62. ^{13}C CP MAS NMR (δ (ppm)): 121 (NCN), 80 (C_c), 38 (C_c–CH_2), 24 (CH_2–CH_2), 18 (CH_2–Si). X-Ray powder diffraction shows two broad bands with *d* spacings of 5.9 Å and 13.7 Å, and additional Bragg's peaks with *d* spacings of 4.3, 3.8, 3.4, 3.3 and 3.2 Å. The surface area measure using the N_2 BET technique is 200 m^2 g^{-1}.

Acknowledgements

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ANNEX II-ARTICLES ENVIATS O PENDENTS DE PUBLICACIÓ

(Posteriors Comissió Doctorat 14 de Febrer de 2006)

Enviat a *Chemistry of Materials*

Carboranyl units bringing unusual thermal and structural properties to hybrid materials prepared by Sol-Gel process.

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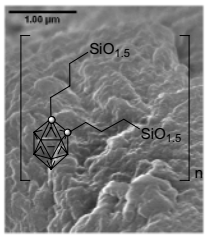
Abstract

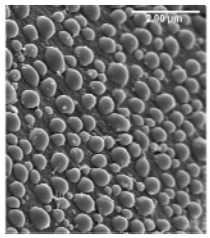
Strategies for the preparation of carboranyl-containing hybrid materials by hydrolytic Sol-Gel process were investigated with carboranyl-containing poly-trialkoxysilyl precursors: 1,2-$[(CH_2)_3Si(OEt)_3]_2$-1,2-$C_2B_{10}H_{10}$ (**P1**) and 1-R-2-$Si[(CH_2)_2Si(OEt)_3]_3$-1,2-$C_2B_{10}H_{10}$ (R = Me, **P2** or Ph, **P3**). Using **P1**, the integrity of the precursor is preserved whatever is the catalyst (F^-, H^+), while for **P2** and **P3**, cleavage of the $C_{cluster}$-Si bond is observed with F^- and OH^- as catalysts. Such Si-$C_{cluster}$ bond cleavage leads to porous hybrid materials templated by the carborane, which is further eliminated from the material and totally recovered. At the opposite, non porous materials are obtained when carborane is preserved in the materials. Part of this hybrid material exhibits a lamellar structure in relation with the presence of the carborane units. In dry air, high thermal stability is observed for such materials and results in a very limited oxidation of the material at 1200°C (weight gain of <5%). In inert atmosphere, high thermal stability combined with several chemical transformation lead to a limited weight loss, graphitisation and oxide and under-oxide mixtures. Materials were characterised by IR, solid state NMR (^{29}Si, ^{13}C), porosimetry, X-ray diffraction, SEM, TEM, TGA and XPS.

Arántzazu González-Campo, Bruno Boury, Francesc Teixidor, Rosario Núñez*

Carboranyl units bringing unusual thermal and structural properties to hybrid materials by hydrolitic Sol-Gel process

Carboranyl-containig class II organic-inorganic hybrid materials prepared by hydrolytic Sol-Gel process exhibit unexpected structural features and outstanding thermal stability. Lamellar structures and possible template effect is related to the presence of the carboranyl units.





Introduction

Boron cluster ligands provide structural and bonding possibilities distinct from conventional organic ligands.[1] The exceptional characteristics exhibited by these icosahedral carboranes,[2,3] such as electron-withdrawing properties,[4] low nucleophilicity, chemical inertness, thermal stability, highly polarizable σ-aromatic character and high hydrophobicity have stimulated research on the development of novel polymeric materials incorporating these boron clusters.[5] Thermal treatment of *ortho*-carborane at 465-500 ºC[6] and in a flow system at 600 ºC[7] produces the *meta* isomer in high yield, while higher temperatures give an equilibrium mixture of *para*-carborane and its *meta* isomer. High temperature stable hybrid polymers containing carborane clusters bonded to siloxane groups have been reported.[8] These have been used as oxidative protection coatings or ceramic polymeric materials that exhibit outstanding thermal and thermo-oxidative properties compared to other silicon polymers.[9] Despite their potential application related to these properties a limited number of carborane-containing hybrid materials are known, and their behaviour in the preparation of Sol-Gel hybrid materials remains to be tested. Therefore we have been attracted to develop class II organic-inorganic hybrid materials incorporating *ortho*-carborane moieties, and we recently reported the preparation and characterization of hybrid materials obtained from a trichlorosilyl precursor.[10] In this report we focus on the elaboration of carborane-containing hybrid materials from Sol-Gel hydrolysis/polycondensation of carborane-containing organosilanes, that are suitable for the immobilisation of the carborane in an inorganic matrix with high chemical and thermal stability. As for other class II hybrid materials where the "organic" moiety is covalently linked to the Si-O-Si network,[11] the organisation, level of condensation, porosity and composition are the key parameters to keep the carboranyl unit accessible to reactivity. Therefore we envisage the preparation

of new carboranyl-bridged polysilsesquioxanes from different precursors by hydrolysis/condensation of $-Si(OEt)_3$ groups included in the precursor structure. In this report we investigate the strategies and limitation for the introduction of the carborane units in such class II hybrid materials. We also check the structural organisation of the material since the neutral carboranyl unit have weaker self-organisation properties,[12] than those reported recently (polar units, ionic units, H-bonding units) and that exhibits self-organised structure.[11h] Finally, because of the thermal stability of the clusters, we investigate the chemical and structural evolutions of such carboranyl-containing material upon thermal treatment in inert and dry air atmosphere.

Results and Discussion

Synthesis and Characterization of Precursors. Precursor **P1** was obtained from the hydrosilylation reaction of the allyl groups in 1,2-$(CH_2\text{-}CH{=}CH_2)_2$-1,2-$C_2B_{10}H_{11}$,[10] using an excess of $HSi(OEt)_3$ in the presence of Karstedt catalyst at room temperature for two hours (Scheme 1a). Precursors **P2** and **P3** were prepared in a similar way from the corresponding vinyl-containing-carborane groups 1-(CH_3)-2-$Si(CH{=}CH_2)_3$-1,2-$C_2B_{10}H_{10}$ and 1-(C_6H_5)-2-$Si(CH{=}CH_2)_3$-1,2-$C_2B_{10}H_{10}$,[13] (Scheme 1b). According to the ^1H and ^{13}C NMR analysis, the hydrosilylation mostly occurs in the β-position and leads to the precursors in very high yield (≈ 99 %). The ^1H NMR spectra show two peaks at 3.84 and 1.25 ppm due to the -OEt functions, the corresponding peaks in the ^{13}C NMR spectra are displayed at 58.9 and 18.6 ppm. The ^{29}Si NMR spectrum of **P1** shows one peak at -46.7 ppm, whereas two resonances are exhibited for **P2** and **P3** corresponding to $Si\text{-}C_{cluster}$ (10.6 ppm for **P2** and 11.6 ppm for **P3**) and C-SiOEt (-46.6 ppm for **P2** and -46.4 ppm for **P3**). Some differences are

observed in the $^{11}B\{^{1}H\}$ NMR spectra patterns of the precursors; 2:8 for **P1**, 1:1:6:2 for **P2** and 1:1:4:2:2 for **P3.**

Preparation of xerogels by Sol-Gel process. The hydrolysis-polycondensation of all precursors was carried out at room temperature (20-25°C), in THF solutions (1M) in the presence of a catalyst with the stoichiometric amount of deionised water at pH=6-7. Three standard catalysts were tested to activate the hydrolysis/polycondensation reaction : a nucleophile (TBAF), an acid (HCl), and a base (NaOH). The ideal equations and the conditions corresponding to the polycondensation of the precursors are represented in Schemes 2 and 3, and in Table 1. Under these conditions, no precipitation was observed and after formation of the gels, they were allowed to age for 7 days, washed and dried. The resulting insoluble and brittle materials were grounded to powders. The gelation time depends clearly on the type of precursor and the catalyst used. In general, the formation of gels was faster for higher concentration of hydrolysable Si-OEt function in the precursor (**P2**, **P3**) and when TBAF was used as catalyst.

Spectroscopic, structural and textural characterization of xerogels obtained from P1. The persistence of the cluster, the presence of the organic spacer and the condensation of the Si-OEt functions, are confirmed by the spectrocopic data: the IR spectra of **X1A** and **X1B** exhibit strong bands at 2590 cm^{-1} (B-H stretching), at 2966-2876 and 1250 cm^{-1} (ν_{-CH2-}), at 1093 cm^{-1} (Si-O-Si stretching), and very low intensity bands at 3400 and 3600 cm^{-1} (ν_{SiO-H}). The ^{13}C CP MAS NMR spectra of xerogels reveal three resonances around 37, 24 and 12 ppm ($–CH_2-CH_2-CH_2$-Si alkyl spacer), a broad peak centred at 80.4 ppm due to $C_{cluster}$ atoms (C_c), and two peaks of low intensity, at 59.0 and 18.3 ppm, due to residual Si(OEt) groups. The ^{29}Si CP MAS NMR spectra for both xerogels display two resonances, at -57 and -66 ppm, attributed to T^2 and T^3

substructures, respectively (Figure 1).[10] The level of condensation (LC) was estimated by deconvolution of spectra and using the formula LC = 1/3 T^1 + 2/3 T^2 + 1 T^3 (Table 2).[14] An exceptionally high LC (≈ 94 %) is measured for materials prepared with **P1** using HCl or TBAF as catalyst, the level of T^3 being considerably higher than the one of T^2 subunits. No Q^n units were detected and we concluded that both ^{29}Si and ^{13}C CP MAS NMR data support that Si-C bonds were not cleaved during the condensation process. Organisation of the solids at the micro- and mesoscopic scale was checked by X-ray powder diffraction analysis, whcih present two broad signals corresponding to a *d* spacing of 6.4 and 15.3 Å for **X1A** and 6.4 and 14.5 Å for **X1B** (Figure 2). These signals are clearly related to the presence of the organo-carboranyl unit and in a first attempt of interpretation, signals at 15.3 and 14.5 Å might be considered as the 001 order and those at 6.4 Å as 002 order of a lamellar structure. Compared to other hybrid materials with short-range order organisation, in these xerogels the signal at 3.8 Å, generally attributed to the Si-O-Si contribution, is not clearly observed.[15] These XRD patterns are very similar to those previously reported for hybrid materials prepared from 1,2-$[(CH_2)_3SiCl_3]_2$-1,2-$C_2B_{10}H_{10}$ that exhibited a lamellar structure.[10] Thus, a lamellar structure with a short-range order organization due to a periodic structure with alternating organo-carboranyl units and silica layers may be proposed.[10] By nitrogen adsorption/desorption isotherms,[16] a low specific surface area (0-11 m^2g^{-1}) was obtained in both cases. This is consistent with a lamellar highly packed structure and with previous observations related to the presence of long alkyl groups in this type of materials.[10,11a] SEM images of **X1A** exhibit dense and heterogeneous particles (Figure 3a). Transmission electronic microscopy (TEM) studies reveal great heterogeneity in terms of microscopic structure for xerogel **X1A**, which presents a large amorphous part, and a minor part with high level of organization. TEM images presented in Figure 4a

confirm the layered structure for the organized part of the material. An interlayer spacing of 3.4 Å can be estimated and might agree with the (004) order respect to the high intensity peak (001) observed in the XRD pattern.

Spectroscopic, structural and textural characterization of xerogels obtained from P2 and P3. Three different catalysts were tested, TBAF for **X2A** and **X3A,** NaOH for **X2B** and **X3B,** and HCl for **X2C** and **X3C** (Table 1). Clear differences must be made between **X2C** and **X3C** on one hand and **X2A**, **X2B, X3A** and **X3B** on the other hand, since for the last ones there are evidences that Si-C_c bonds cleavage occurs during Sol-Gel processes. First, for **X2A**, **X2B, X3A** and **X3B**, methyl-*o*-carborane or phenyl-*o*-carborane *were recovered in high yield (90 %)* from the organic solvents used for washing the gels. IR spectra of those gels do not exhibit bands around 2590 cm^{-1} (B-H stretching), however they show a strong band around 1037 and 1076 cm^{-1} (Si-O-Si stretching). The ^{13}C CPMAS NMR spectra of these xerogels show peaks of low intensity, at 59.0 and 18.3 ppm, (residual non-hydrolyzed Si-OEt groups), a broad resonance at 6.4 ppm (CH_2 groups of the vinyl chain) and *no signal at 80.4 ppm ($C_{cluster}$ atoms).* Finally, ^{29}Si CP MAS NMR spectra of **X2A** and **X2B** show signals corresponding to T^n units, *n* depending on the precursor and condition : for **X2A** (T^2 and T^3), for **X2B** and **X3A** (T^0, T^1, T^2 and T^3), and for **X3B** (T^1, T^2 and T^3 subunits) (values in Table 2). However, the presence of others signals is consistent with the cleavage of the $C_{cluster}$-Si bond during Sol-Gel process, which involves a nucleophilic attack by fluoride ions or strong bases, such as NaOH, on the very electrophilic silicon atom.[17] Low intensity signals in the region of -100 to -110 ppm are consistent with Q^n substructures resulting from Si-C hydrolysis. In addition, a signal at 13.2 ppm was attributed to the Si atom of the moiety $O[\underline{\mathbf{Si}}[(CH_2)_2SiO_{0.5}]_3]_2$ resulting from hydrolysis

and condensation of C_c-Si to give -Si-O-Si- functions (Scheme 3). Because of the Si-C_c cleavage, the level of condensation (LC) of these xerogels has not being considered here. The X-ray diffraction patterns of xerogels **X2A** (Figure 5), **X2B**, **X3A** and **X3B** do not exhibit any Bragg's peaks, indicating the formation of a completely amorphous material. By gas sorption porosimetry, those xerogels have high specific surface area. Xerogel **X2A** shows an specific surface area of approximately 570 m^2g^{-1} with a porosity of H3 type according to the De Boer classification,[18] with an average pore diameter of 32 Å. This solid present largely mesoporous contribution (79%) without narrow pore size distribution and weak microporous contribution (21%). Similarly, **X3A** presents a specific surface area of 170 m^2g^{-1} with a porous size of 28 Å, being mainly mesoporous. All these data indicate that the formation of porous hybrid organic-inorganic materials from **P2** and **P3** was clearly related to the efficiency of the catalyst action for removing the carborane clusters. In this case, the porosity could be accomplished using the templating effect of the methyl- or phenyl-*o*-carboranes that are later removed.[19] This preliminary results could provide an alternative way for preparing porous hybrid materials by the controlled elimination of carborane from the material, exploiting the sensibility of C_c-Si bonds. However, a fine tuning of the porosity will require to control the formation firstly of the Si-O-Si network and followed in a second time by the Si-C_c cleavage.

Xerogels **X2C** and **X3C** prepared in acidic conditions are completely different and they exhibit strong bands at 2590 cm^{-1} due to the B-H stretching by IR analysis. The ^{13}C CP MAS NMR spectra of **X2C** shows one resonance around 25.0 ppm (C_c-CH_3) and **X3C** exhibits broad resonances around 130 ppm, (C_6H_5 group). Additional peaks corresponding to the Si-CH_2 are observed around 6.0 ppm. The ^{29}Si CPMAS NMR spectra of **X2C** (mostly of T^2 subunits) and **X3C** (T^2 and T^3 substructures in a similar

ratio) indicate high levels of condensation of 86 % and 83 %, respectively (Table 2). All these data agree with the preservation of the Si-$C_{cluster}$ covalent bond during the So-Gel process. Moreover, the XRD diagram of **X3C** shows two broad signals corresponding to a *d* spacing of 16.5 and 6.98 Å (Figure 5), which are very close to those observed for xerogels **X1A**. This result clearly confirms that a lamellar structure with a short-range order organization could be assumed for **X3C**, and is an obvious verification that signals observed are related to the presence of the carboranyl units. Xerogels **X2C** and **X3C** were non-porous materials with specific surface areas of < 10 m^2g^{-1} by nitrogen adsorption/desorption isotherms.

Thermal treatment of carboranyl-containing hybrid material X1.

The carboranyl-bridged hybrid materials **X1A** and **X1B** exhibit good thermal stability up to 450 ºC under argon, as other similar hybrid materials with phenyls or arylenes-bridged polysilsesquioxanes.[20] Xerogels looses weight by two waves (2.1 % + 4.1 %) in the range 100-450 ºC, which is usually attributed to desorption of residues and the final condensation of the material. Between 450 and 800ºC an important weight loss of ≈16.5 % occurs. Heating up to 1200 ºC leaves a ceramic char with a 77 % yield (Figure 6). Considering that the elimination of all organic spacers would lead to a theoretical 35 % weight loss, the conservation of an elevated organics quantity in the material is obvious and this behaviour, different from other hybrid material of this type, suggests that carborane provides a high stabilizing effect to the material during the thermolysis in inert atmosphere.

In order to obtain more detailed information of this thermal behaviour, characterisations of **X1A** were done after annealed at 400, 550, 800 and 1200ºC, under

an argon flow, followed by washing with THF and dried, in order to remove all the soluble residual compounds before characterization:

a) Up to 400 ºC, the recovered material **X1A-400** does not show significant changes in the X-ray diagram and in the specific surface area respect to the started xerogel **X1A** (Table 3, Figure 2). However, a higher level of condensation according to the ^{29}Si CP MAS spectra is observed, showing only a broad peak at -66.0 ppm corresponding to T^3 subunits and suggesting a LC ≈100% (Figure 1). The ^{13}C CP MAS NMR spectrum confirms the presence of the alkyl spacers and C_c atoms. At this temperature, the residual condensation has occurred without apparent alteration of the initial structure.

b) **X1A-400** was heated up to 550 ºC and **X1A-550** was recovered after a weight loss of ≈ 8 %, which could be attributed to the elimination of a part of the organic units. The IR spectrum shows a large band at 2586 cm^{-1} due ν(BH) of the *closo* cluster, and bands of lower intensity in the region 2950-2880, that corroborate the presence of alkyl groups. The ^{29}Si CP MAS NMR spectrum is similar to that of **X1A-400,** exhibiting only a broad band at -66.0 ppm (T^3) (Figure 1). Therefore, the Si atoms are still bonded to the C atoms from alkyl groups at this temperature. However, the ^{13}C CP MAS NMR spectrum exhibit new resonances compared to **X1A-400**: a new peak at 128.9 ppm was attributed to the presence of unsaturated C=C in the material, and that at -3.9 ppm assigned to a CH_3 group bonded to a Si atom. Our hypothesis is that thermal treatment leads to the formation of partially $-CH_2=CH_2$ and $CH_3SiO_{1.5}$ units by rearrangement of the $CH_2CH_2CH_2SiO_{1.5}$ radicals that results from one $C_{cluster}$-C bond cleavage. The XRD diagram of **X1A-550** exhibits substantial differences respect to the starting **X1A**, only one broad band corresponding to *d* spacing 16.2 Å was observed, while the band corresponding to *d* spacing 6.2 Å is hardly noticeable (Table 3, Figure 2). Additionally, a shoulder of low intensity with a *d* spacing of 7.9 Å is observed. Simultaneously, **X1A-**

550 exhibits a high specific surface area of 265 m^2g^{-1} being mainly microporous. The SEM images of **X1A-550** reveal the general aspect of the material, which suggests that plastic deformations occur at the same time with gas elimination (Figure 3b). Finally, the TEM analyses confirm the microporosity with an approximated pore size of 4.4 Å (Figure 4b). This thermal behaviour is unusual for related organic-inorganic hybrid materials, thus it might be attributed to the presence of the carborane cluster. All these results indicate that the *closo* cluster is still present in the material, but were not conclusive whether or not the *o*-carborane has isomerised to *meta*-carborane. At this point two experiments were carried out in order to prove the possible isomerization process. Xerogel **X1A** was placed in a sealed tube and heated at 550 and 650 ºC in the oven under vacuum. The recovered materials were washed with THF and the soluble residues monitored by ^{1}H and ^{11}B NMR. The residue after heating at 550 ºC does not show signals concerned to the cluster. However at 650 ºC, the ^{11}B NMR spectrum exhibits a set of broad resonances which can be attributed either to *ortho* or to *meta*-carborane. Thus, at this temperature, a percentage of the carborane is not covalently bonded to the siloxane matrix due to the complete $C_{cluster}$-CH_2 bonds cleavage, and this free carborane proves that the cluster rearrangement process is undergoing.

c) Xerogel **X1A-800** is obtained after heating **X1A-550** up to 800 ºC, and an additional weight loss of ≈ 6 %. The XRD diagram shows only a very broad band with *d* spacing 22.4 Å, and the second band corresponding to a *d* spacing 3.7 Å (Si-O-Si) is practically missing (Figure 2). The ATR spectrum does not present the band corresponding to the B-H stretching, indicating that the *closo* cluster has been completely degraded at this temperature. In addition, broad bands at 1300 and 1035cm^{-1} attributed to B-O and Si-O, respectively, are observed. The **X1A-800** is a non-porous material exhibiting a low specific surface area of *ca.* 22 m^2/g. Evolution of X-ray

diffraction and specific surface area may be tentatively interpreted in terms of reaction of the carborane subunits with a silicon oxicarbide above it glass transition, that collapses and forms alloy, loosing the porosity and the short-range order between carborane units.

d) **X1A-800** was heated up to 1200 ºC to give **X1A-1200** as an amorphous and non-porous black residue, with a specific surface area <10 m^2g^{-1}. The XRD diagram does not show any Bragg's peaks for both large or small angles (Figure 2). The elemental analysis using X-ray photoelectron spectroscopy (XPS) determined an atomic concentration of O (43.02 %), C (35.08 %), Si (11.37 %) and B (10.53 %) in the material surface. The curve fittings (Figure 7) give some information about the bonding within the different elements, the binding energy of C1s core levels found in **X1A-1200** are 285.0, 287.2 and 289.3 eV assigned to C-C aliphatics, C-O and C=O functions, respectively. These have also been observed in carbon-fibre polymer composites or graphitic structures.[21] The binding energy for the O1s is 534.3 eV, for B1s is 194.4 eV assigned to B-O bonds, and for Si2p is 105.1 eV assigned to Si-O in silica.[22] The absence of binding energy at 187 eV corresponding to B-H bonds in the XPS analysis revealed the completely oxidation of the carborane group and the presence of different oxides (B_2O_3 and SiO_2) in the ceramic.[9b] Microscopic analyses reveal an heterogeneous medium at different scales: scanning electron microscopy (SEM) analysis of **X1A-1200** shows the presence of droplet of insoluble mineral material < 1 μm Ø, that seem to have been exuded at the surface of the bulk (Figure 8). Interestingly, the TEM images of these micrometer size droplets reveals highly dense and amorphous materials possibly rich in boron (Figure 9a). At a lower scale, nanoparticles of 2 to 10 nm appear embedded in the amorphous matrix possibly made of boron crystallised as shown by electron diffraction (Figure 9b). In other parts of the material, the presence of graphite

structures are clearly observed in Figure 10c , where the distance between the layer planes approaches 3.3 Å. [23] These results agree well with the previously described surface XPS analyses for the **X1-1200**.

Finally, under dry air, the TGA analysis of **X1A** shows a completely different behaviour: after an usual weight loss of 1.9 % between 20 and 350 ºC, a weight loss of 2 % occurs in two waves up to 1000 ºC, then a weight increase of 2 % occurs from 1000 °C up to 1200 °C to yield a black char (Figure 6). DTA curve indicates that exothermic processes are occurring, probably due to oxidation reactions. All together, the weight loss of **X1A** in air up to 1200°C is lower than 2 %. This very low weight loss is surprising if considering the following oxidation phenomena that can occur: carborane $\Rightarrow B_2O_3$ (+ 72.7 %), $CSiO_{1.5} \Rightarrow SiO_2$ (+ 4.8 %) and ($-CH_2-$ + C) $\Rightarrow CO_2 + H_2O$ (-35.7 %). Indeed, the formation of a SiO_2/B_2O_3 glass by a complete oxidation of the initial material would imply a weigh increase of 41.8 %. Therefore, it can be concluded that only a very small proportion of the material is oxidized in this process. Here again a high stability of the material at high temperature under dry air seems related to the presence of the carboranyl subunit. The ATR spectrum of the char obtained at 1200 ºC exhibits very intense bands at 1400 and 1035cm^{-1} attributed to B-O and Si-O, respectively. The TEM analysis reveals that the structure rearranges into discrete layer planes indicative of graphite structure (Figure 10).[23] Likewise, the presence of such graphite structure is rather surprising since the sample is kept under air at 1200 °C.

Conclusions

Organo-carboranyl bridged polysilsesquioxanes have demonstrated to be a versatile class of materials. They can be prepared from precursors that integrate

carboranyl subunits and $Si(OEt)_3$ groups that can be polymerised by Sol-Gel process. Due to the high sensitivity of the C_c-Si bond, the Sol-Gel process must be achieved in non-nucleophilic conditions or through the use of an organic spacer between C_c and Si atoms, in order to avoid C_c-Si cleavage and keep the carborane as an integrated unit of the hybrid material. In this respect, all carboranyl-containing xerogels, were non-porous solids, with high level of condensation and with mostly a short-range order organisation, detected in form of lamellar structure,and attributed to the presence of the rigid carborane in the material. Furthermore, adaptation of the experimental condition should emphasise the formation of the detected lamellar structure homogeneously in the material. Contrarily, organic-inorganic hybrids obtained after removing the carborane cluster, are completely amorphous and mesoporous materials, with high specific surface areas. In this case, the porosity could be accomplish using the templating effect of the carborane, after its controlled elimination from the material. Further alternative way for preparing porous hybrid materials exploiting the sensibility of C_c-Si bond to the nucleophilic attack is under study. Thermal evolution of carborane-containing hybrid materials in inert atmosphere reveals: (a) inertness up to 450°C, (b) formation of micropores between 450 and 550°C, with limited weight loss and feasible carborane cluster modification (rearrangement or starting isomerization), and (c) up to 1200°C closing of the porosity without weight loss, formation of graphite structures and dense nanoparticles. Thermal evolution of the same material in oxidative atmosphere leads to a very small weight increase (<5%) due to very limited oxidation process that leaves a boron rich material with the presence of graphite structures.

Experimental Section

Materials. All reactions were carried out under an atmosphere of purified argon using standard Schlenk techniques. Solvents were purified, dried, and distilled by standard procedures. $HSi(OEt)_3$ and Karstedt platinum catalyst (3-3.5% Pt) were purchased from ABCR. CH_2CHCH_2Br, TBAF, NaOH and HCl were used as received from Aldrich. 1,2-$(CH_2CH{=}CH_2)_2$-1,2-$C_2B_{10}H_{10}$, 1-CH_3-2-$Si(CH{=}CH_2)_3$-1,2-$C_2B_{10}H_{10}$ and 1-C_6H_5-2-$Si(CH{=}CH_2)_3$-1,2-$C_2B_{10}H_{10}$ were prepared according to literature procedures.[10,13]

Instrumentation. Infrared spectra were measured in NaCl or KBr pellets on a ThermoNicollet AVATAR 320 FT-IR. Attenuated Total Reflection (ATR) were measured on a Bruker Tensor 27 using an accessory Specac NKII Golden Gate. ^1H NMR, $^1H\{^{11}B\}$ NMR (300.13 MHz), ^{11}B NMR (96.29 MHz), $^{13}C\{^1H\}$ NMR (75.47 MHz) and $^{29}Si\{^1H\}$ NMR (59.62 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. NMR spectra were measured in $CDCl_3$ solution at room temperature. Chemical shifts for ^{11}B NMR were referenced to external $BF_3{\cdot}OEt_2$ and those for ^1H NMR, ^{13}C NMR and ^{29}Si NMR were referenced to Me_4Si. ^{29}Si CP MAS NMR (at 79.49 MHz) and ^{13}C CP MAS NMR (at 100.63 MHz) spectra were obtained on a Brucker Advance ASX400 using a CP MAS sequence. Thermogravimetric analysis (TGA) of the network materials were performed on a Netzsch STA 409 PC/PG under a 50 mL min^{-1} Argon flow. Samples were heated from 20 to 1200 ºC at 5 ºC/min. X-ray powder diffraction measurements were performed using spectrometer with a rotating copper anode with an OSMIC monochromator system and an 'Image Plate 2D' detector working with the CuKα(λ= 1,542Å) radiation and a beam size of 0,5 x0,5mm and

acquisition time of 40 to 50 minutes. Sample were previously crushed and placed in a Lindeman tube (1mm ∅). The specific surface areas, porosity, volume, and the pore size distribution were determined by analysing the N_2 adsorption/desorption isotherms according to the BET method using a Micromériticss Gémini III 2375 et ASAP 2010. Scanning electron microscopy (SEM) images were performed in a HITACHI S-570 microscope. Transmission electron microscopy (TEM) images were produced with a JEOL JEM 2011 (200Kv) microscope. Elemental analyses were performed in the analytical laboratory using a Flash EA 1112 Series microanalyzer. X-ray photoelectron spectra are obtained on a PHYSICAL ELECTRONICS mod. 5701 (ESCA) Imaging XPS System.

Synthesis of 1,2-[$(CH_2)_3Si(OCH_2CH_3)_3]_2$-1,2-$C_2B_{10}H_{10}$ (P1). In a Schlenck flask under argon, 1,2-$(CH_2CH{=}CH_2)_2$-1,2-$C_2B_{10}H_{10}$ (1.326 g, 5.9 mmol), $HSi(OCH_2CH_3)_3$ (4.5 mL, 23.6 mmol) and Karstedt's catalyst (10 µl, 0.021 mmol) were mixed and stirred for 2 hour at room temperature. Evaporation of the volatiles and the excess of $HSi(OCH_2CH_3)_3$ at 50 ºC gave 3.23 g of a yellow oil. Yield: ≈ 99 %. $^1H\{^{11}B\}$ NMR (δ (ppm)): 3.84 (q, O-C**H**$_2$, $^3J(H,H)$ = 6.9 Hz, 12H), 2.20 (t, C_c-C**H**$_2$, $^3J(H,H)$ = 7.7 Hz, 4H), 1.66 (m, CH_2-C**H**$_2$-CH_2, 4H), 1.25 (t, CH_2-C**H**$_3$, $^3J(H,H)$ = 6.9 Hz, 18H), 0.62 (t, C**H**$_2$-Si, $^3J(H,H)$ = 6.9 Hz, 4H). ^{11}B NMR (δ (ppm)): -4.9 (d, $^1J(B,H)$ = 145 Hz, 2B), -10.7 (8B). $^{13}C\{^1H\}$ NMR (δ (ppm)): 80.1 (**C**$_c$), 58.9 (O-**C**H_2), 38.0 (C_c-**C**H_2), 23.7 (CH_2-**C**H_2-CH_2), 18.6 (CH_2-**C**H_3), 10.7 (C**H**$_2$-Si). $^{29}Si\{^1H\}$ NMR (δ (ppm)): -46.7.

Synthesis of 1-(CH_3)-2-Si[$(CH_2)_2Si(OCH_2CH_3)_3]_3$-1,2-$C_2B_{10}H_{10}$ (P2). In a Schlenck flask under argon, 1-(CH_3)-2-Si$(CH{=}CH_2)_3$-1,2-$C_2B_{10}H_{10}$ (0.620 g, 2.3 mmol), $HSi(OCH_2CH_3)_3$ (2.7 mL, 14.2 mmol) and Karstedt's catalyst (8 µl, 0.017 mmol) were mixed and heated up to reflux. Then, the mixture was stirred for 91 hours at room

temperature. Evaporation of the volatiles and the excess of $HSi(OCH_2CH_3)_3$ at 50 ºC gave 1.75 g of a yellow oil. Yield: ≈ 99 %. $^1H\{^{11}B\}$ NMR (δ (ppm)): 3.84 (q, O-C**H**$_2$, $^3J(H,H)$ = 7.0 Hz, 18H), 2.04 (s, C_c-C**H**$_3$), 1.25 (t, CH_2-C**H**$_3$, $^3J(H,H)$ = 7.0 Hz, 27H), 0.91 (m, Si-C**H**$_2$-, 6H) 0.60 (m, Si-C**H**$_2$, 6H). ^{11}B NMR (δ (ppm)): 1.5 (d, $^1J(B,H)$ = 130 Hz, 1B), -3.9 (d, $^1J(B,H)$ = 160 Hz, 1B), -7.3 (d, $^1J(B,H)$ = 153 Hz, 6B), -9.6 (2B). $^{13}C\{^1H\}$ (δ (ppm)): 76.2 (**C**$_c$), 71.9 (**C**$_c$), 58.9 (O-**C**H_2), 26.4 (C_c-**C**H_3), 18.6 (CH_2-**C**H_3), 4.7 (Si-**C**H_2), 3.3 (Si-**C**H_2). $^{29}Si\{^1H\}$ NMR (δ (ppm)): 10.6 (C_c-**Si**), -46.6 (**Si**-O).

Synthesis of 1-(C_6H_5)-2-Si[$(CH_2)_2Si(OCH_2CH_3)_3$]$_3$-1,2-$C_2B_{10}H_{10}$ (P3). In a Schlenck flask under argon, 1-(C_6H_5)-2-Si($CH{=}CH_2$)$_3$-1,2-$C_2B_{10}H_{10}$ (902 mg, 2.7 mmol), $HSi(OCH_2CH_3)_3$ (3.1 mL, 16.3 mmol) and Karstedt's catalyst (8 µl, 0.017 mmol) were mixed and stirred for 117 hours at room temperature. Evaporation of the volatiles and the excess of $HSi(OCH_2CH_3)_3$ at 50 ºC gave 2.23 g of a yellow oil. Yield: ≈ 99 %. $^1H\{^{11}B\}$ NMR (δ (ppm)): 7.67-7.27 (m, C_6**H**$_5$, 5H), 3.84 (q, O-C**H**$_2$, $^3J(H,H)$ = 7.0 Hz, 18H), 1.25 (t, CH_2-C**H**$_3$, $^3J(H,H)$ = 7.0 Hz, 27H), 0.48 (m, Si-C**H**$_2$-C**H**$_2$-Si, 12H). ^{11}B NMR (δ (ppm)): 1.5 (d, $^1J(B,H)$ = 142 Hz, 1B), -3.7 (d, $^1J(B,H)$ = 145 Hz, 1B), -8.0 (d, $^1J(B,H)$ = 156 Hz, 4B), -10.1 (2B), -11.4 (d, $^1J(B,H)$ = 151 Hz, 2B). $^{13}C\{^1H\}$ (δ (ppm)): 131.3,131.7,130.8,128.9 (**C**$_6H_5$), 83.5 (**C**$_c$), 76.5 (**C**$_c$), 58.9 (O-**C**H_2), 18.6 (CH_2-**C**H_3), 4.0 (Si-**C**H_2), 3.1 (Si-**C**H_2). $^{29}Si\{^1H\}$ NMR (δ (ppm)): 11.6 (Cc-**Si**), -46.4 (**Si**-O).

Preparation of Xerogels X1A and X1B. The preparation of xerogels was carried out according to the following general procedure, the **X1A** is given as an example. In a tube, 704 mg (1.27 mmol) of **P1** was dissolved in 637 µL of dried THF. Then, 637 µL of a solution containing 25 µL (25.5 µmol) of TBAF (1 M in THF), 69 µL (3.82 mmol) of H_2O and 543 µL of dried THF were added. The suspension was then stirred for 10

seconds. After 192 hours a gel was formed and kept 7 days for aging. The gel obtained was powdered and washed three times with ethanol, acetone and diethyl ether and dried in vacuum for 3 hours to yield 372 mg of a white powder. Yield: 88 %. FTIR (KBr, cm^{-1}) ν $(C\text{-}H)_{alquil}$ 2966-2928, ν (B-H) 2590, δ $(C\text{-}H)_{alquil}$ 1460, ν (Si-O-Si) 1093. ^{29}Si CP MAS NMR (δ (ppm)): -57.7 (T^2); -66.9 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 80.4 ($\mathbf{C_c}$), 59.0 (Si-O$\mathbf{C}H_2$), 37.3 ($\mathbf{C}H_2$), 23.7 ($\mathbf{C}H_2$), 18.3 ($OCH_2\mathbf{C}H_3$), 12.4 ($\mathbf{C}H_2$). $S_{Bet} < 10\ m^2g^{-1}$. X-ray powder diffraction shows two very intense broad bands with *d* spacing of 15.7 Å and 6.4 Å.

X1B: 900 mg (1.63 mmol) of **P1** in 1.63 mL of THF containing 41 µL (0.49 mmol) of HCl (37 %) and 88 µL (4.89 mmol) of H_2O gave 452 mg of a gel after 4320 hours. Yield: 84 %. FTIR (KBr, cm^{-1}) ν $(C\text{-}H)_{alquil}$ 2947-2876, ν (B-H) 2593, δ $(C\text{-}H)_{alquil}$ 1460, ν (Si-O-Si) 1093. ^{29}Si CP MAS NMR (δ (ppm)): -57.6 (T^2); -66.2 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 80.4 ($\mathbf{C_c}$), 59.0 (Si-O$\mathbf{C}H_2$), 37.3 ($\mathbf{C}H_2$), 23.7 ($\mathbf{C}H_2$), 18.3 ($OCH_2\mathbf{C}H_3$), 12.4 ($\mathbf{C}H_2$). S_{Bet} =11 m^2g^{-1}. X-ray power diffraction shows two broad bands with *d* spacing of 14.5 Å, 6.4 Å.

X1A-400: The xerogel **X1A** was heated at 400 ºC under an argon flow of 5 $ºCmin^{-1}$. The white solid produced was analysed, indicating the completed condensation of the starteing material **X1A**. FTIR (KBr, cm^{-1}) ν $(C\text{-}H)_{alquil}$ 2939-2914, ν (B-H) 2586, δ $(C\text{-}H)_{alquil}$ 1460, ν (Si-O-Si) 1031, 690. ^{29}Si CP MAS NMR (δ (ppm)): -66.0 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 80.4 ($\mathbf{C_c}$), 37.3 ($\mathbf{C}H_2$), 23.7 ($\mathbf{C}H_2$), 13.1 ($\mathbf{C}H_2$). S_{Bet} = 3 m^2g^{-1}. X-ray powder diffraction shows two broad bands with *d* spacing of 15.0 Å, 6.4 Å.

X1A-550: Xerogel **X1A-400** was heated up to 550 ºC under an argon atmosphere. The recovered white solid was analysed. FTIR (KBr, cm^{-1}) ν $(C\text{-}H)_{alquil}$ 2950-2880, ν (B-H) 2586, δ $(C\text{-}H)_{alquil}$ 1460, ν (Si-O-Si) 1138, 774. ^{29}Si CP MAS NMR (δ (ppm)): -64.7 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 128.9 (**C**=C), 71.0 ($\mathbf{C_c}$), 20.7 ($\mathbf{C}H_2$), -3.9 (OSi-

CCH_3). S_{Bet} = 265 m^2g^{-1}. X-ray powder diffraction shows one broad bands with *d* spacing of 16.2 Å, and two very low intensity bands corresponding to *d* spacing 7.9 and 3.9 Å.

X1A-800: Xerogel **X1A-550** was heated up to 800 ºC under an argon atmosphere. The recovered black solid was analysed. ATR (cm^{-1}) ν $(C\text{-}H)_{alquil}$ 2950-2880, ν (B-O) 1300, ν (Si-O-Si) 1035. ^{29}Si CP MAS NMR (δ (ppm)): -66.0 (T^3), 110 (Q^n). S_{Bet} = 22 m^2g^{-1}. X-ray powder diffraction shows one broad bands with *d* spacing of 22.4 Å, and a very low intensity band corresponding to *d* spacing 3.7 Å.

X1A-1200: Xerogel **X1A-800** was heated up to 1200 ºC under an argon atmosphere obtaining a black residue. ATR (cm^{-1}) ν (B-O) 1376, ν (Si-O-Si) 1189, 1086. S_{Bet} < 10 m^2g^{-1}. ^{11}B CPMAS NMR (δ (ppm)): 19.9 ppm. X-ray powder diffraction does not show any bands, which indicated the formation of an amorphous material. XPS analysis: O (43.02 %), C (35.08 %), Si (11.37 %), B (10.53 %). The binding energy are for C1s 285 eV, O1s 534 eV, Si2p 105 eV, B1s 194 eV.

Preparation of Xerogels X2. The preparation of xerogels was carried out similarly. The procedure for **X2A** is given as an example. In a tube, 327 mg (0.43 mmol) of **P2** was dissolved in 0.43 mL of dried THF containing 13 µL (13 µmol) of TBAF and 34 µL (1.93 mmol) H_2O. Then the suspension was stirred for 10 seconds. After 20 min. a gel was formed and kept 7 days for aging. The gel obtained was powered and washed three times with ethanol, acetone and diethyl ether and dried in vacuum for 3 hours to yield 129 mg of an off-white power. Yield ≈ 99%, calculated taking into account the total condensation and that carborane has been completely removed (see ideal formula in scheme 2). FTIR (KBr, cm^{-1}) ν $(C\text{-}H)_{alquil}$ 2966-2912, δ(Si-C) 1267, ν (Si-O-Si) 1037, 694. ^{29}Si CP MAS NMR (δ ppm, 60 MHz): 13.2 (CH_2**Si-**O-**Si**CH_2), - 57.3 (T^2), -64.4 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 59.0 (O-**C**H_2), 18.3 (CH_2-**C**H_3), 6.4 (br, Si-**C**H_2).

S_{Bet} = 570 m^2g^{-1}, average pore diameter = 32 Å. The X-ray powder diffraction does not show any Bragg's peak.

X2B: In a tube, 203 mg (0.27 mmol) of **P2** was dissolved in 0.27 mL of dried THF containing 0.33 mg (8.1 μmol) of NaOH and 22 μL (1.22 mmol) of H_2O to give 16 mg of a gel after 1824 hours. Yield: 22 %. calculated taking into account the total condensation and that carborane has been completely removed (see ideal formula in scheme 2). FTIR (KBr, cm^{-1}) ν $(C-H)_{alquil}$ 2972-2912, δ(Si-C) 1267, ν (Si-O-Si) 1076, 1027, 694. ^{29}Si CP MAS NMR (δ ppm, 60 MHz): 13.2 (CH_2**Si-**O-**Si**CH_2), -46.1(T^0), -53.3(T^1), -57.5 (T^2), -64.7 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 59.0 (O-**C**H_2), 18.3 (CH_2-**C**H_3), 6.4 (Si-**C**H_2). The X-ray powdr diffraction does not show any Bragg's peak.

X2C: 190 mg (0.25 mmol) of **P2** was dissolved in 0.25 mL of dried THF containing 11 μL (0.11 mmol) of HCl (32 %) and 20 μL (1.13 mmol) H_2O gave 79 mg of a gel after 744 hours. Yield: 74 %. FTIR (KBr, cm^{-1}) ν $(C-H)_{alquil}$ 2972-2942, δ(Si-C) 1267, ν (Si-O-Si) 1076, 1027, 694. ^{29}Si CP MAS NMR (δ ppm, 60 MHz): 12.0 (C_c-**Si**), -51.5 (T^1), -57.1 (T^2), -64.3 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 59.0 (O-**C**H_2), 25.0 (Cc-CH_3), 18.6 (CH_2-**C**H_3), 0.5-12.0 (br, Si-**C**H_2). S_{Bet}= < 10 m^2g^{-1}. X-ray powder diffraction shows two broad bands with *d* spacing of 16.4 and 6.7 Å.

Preparation of Xerogels X3. The preparation of the xerogels was carried out according to the following general procedure, the **X3A** is given as an example. In a tube, 426 mg (0.52 mmol) of **P3** was dissolved in 0.52 mL of dried THF containing 15.6 μL (15.6 of TBAF and 42 μL (2.34 mmol) of H_2O. Then the suspension was stirred for 10 seconds. After 25 minutes a gel was formed and kept 7 days for aging. The gel obtained was powered and washed three times with ethanol, acetone and diethyl ether and dried to yield 134 mg as a slightly white power. Yield: 93 %. calculated taking into account the

total condensation and that carborane has been completely removed (see ideal formula in scheme 2). FTIR (KBr, cm^{-1}) ν (O-H) 3365, ν $(C-H)_{alquil}$ 2974-2889, δ(Si-C) 1265,ν (Si-O-Si) 1053, 694. ^{29}Si CP MAS NMR (δ ppm, 60 MHz): 13.6 (CH_2**Si-**O-**Si**CH_2), -47.0 (T^0) -50.7 (T^1), -57.1 (T^2), -65.0 (T^3). ^{13}C CP MAS NMR (δ (ppm)): 58.9 (O-**C**H_2), 18.3 (CH_2-**C**H_3), 6.4 (br, Si-**C**H_2). S_{Bet} = 170 m^2g^{-1}, pore size = 28 Å. The X-ray powder diffraction does not show any Bragg's peak.

X3B: 312 mg (0.38 mmol) of **P3** in 0.38 mL of THF containing 0.46mg (11.4 μmol) of NaOH and 31 μL (1.71 mmol) of H_2O gave 73 mg of a gel after 648 hours. Yield: 69 %. calculated taking into account the total condensation and that carborane has been completely removed (see ideal formula in scheme 2). FTIR (KBr. cm^{-1}) ν (O-H) 3386, ν $(C-H)_{alquil}$ 2974-2889, δ $(C-H)_{alquil}$ 1460, δ(Si-C) 1265, ν (Si-O-Si) 1072. ^{29}Si CP MAS NMR (δ ppm, 60 MHz): 13.6. (CH_2**Si-**O-**Si**CH_2), -49.9 (T^1), -57.0 (T^2), -64.9 (T^3). ^{13}C CP MAS NMR (δ (ppm)) = 58.9 (O-**C**H_2), 18.3 (CH_2-**C**H_3), 6.4 (Si-**C**H_2). The X-ray powder diffraction does not show any Bragg's peak. Elemental analysis calculated for $C_6H_{12}O_5Si_4$: C, 26,06; H, 4.37. Found: C, 21,83; H, 5.79.

X3C: 362 mg (0.44 mmol) of **P3** in 0.44 mL of THF containing 20 μL (0.20 mmol) of HCl (32 %) and 36 μL (1.08 mmol) of H_2O gave 143 mg of a gel after 1296 hours. Yield: 67 %. FTIR (KBr. cm^{-1}) ν $(C-H)_{alquil}$ 2958-2928, ν (B-H) 2590, δ $(C-H)_{alquil}$ 1460, ν (Si-O-Si) 1101. ^{29}Si CP MAS NMR (δ ppm, 60 MHz): 12.2 (C_c-**Si**), -57.0 (T^2), -64.1 (T^3). ^{13}C CP MAS NMR (δ (ppm).: 130.5 (**C**$_6$H$_5$), 83.5 (**C$_c$**), 58.4 (SiO**C**H_2), 18.2 (CH_2**C**H_3), 6.2 (**C**H_2). S_{Bet}= < 10 m^2g^{-1}. X-ray power diffraction shows two broad bands with *d* spacing of 16.5 and 6.9 Å.

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

Scheme Caption.

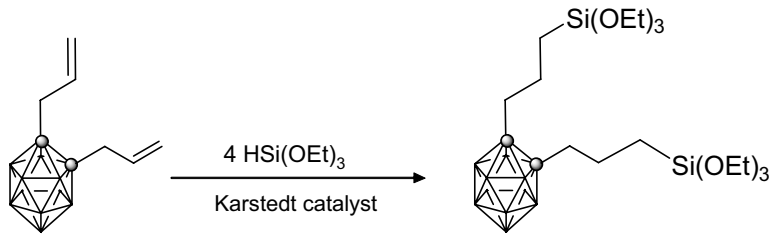
Scheme 1. Synthesis of Precursors: a) **P1**, b) **P2** and **P3**

Scheme 2. Preparation of Xerogels **X1A** (TBA F) **X1B**(HCl)

Scheme 3. Preparation of Xerogels **X2** [**A**(TBAF), **B**(NaOH), **C**(HCl)] and **X3** [**A**(TBAF), **B**(NaOH), **C**(HCl)].

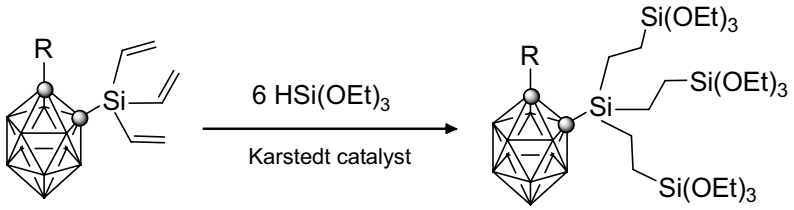
Scheme 1. Synthesis of Precursors: a) **P1**, b) **P2** and **P3**

a)



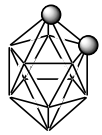
(1) **P1**

b)



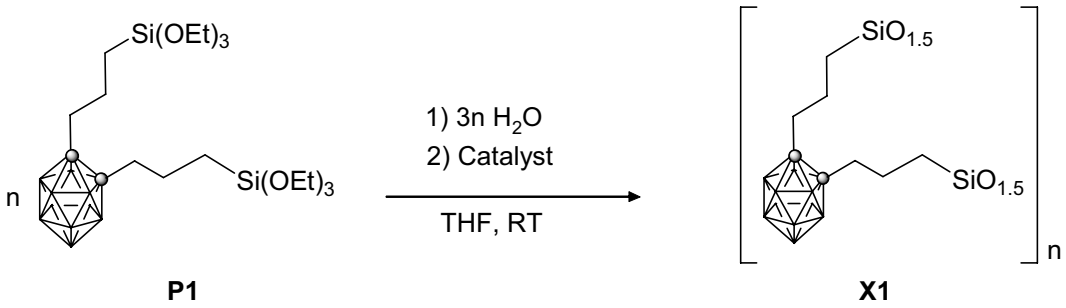
R = Me **(2)**
Ph **(3)**

R = Me **(P2)**
Ph **(P3)**



= $\mathbf{C_2B_{10}H_{10}}$

Scheme 2. Preparation of Xerogels **X1A** (TBAF) **X1B**(HCl)



P1 **X1**

Scheme 3. Preparation of Xerogels **X2** [**A**(TBAF), **B**(NaOH), **C**(HCl)] and **X3** [**A**(TBAF), **B**(NaOH), **C**(HCl)].

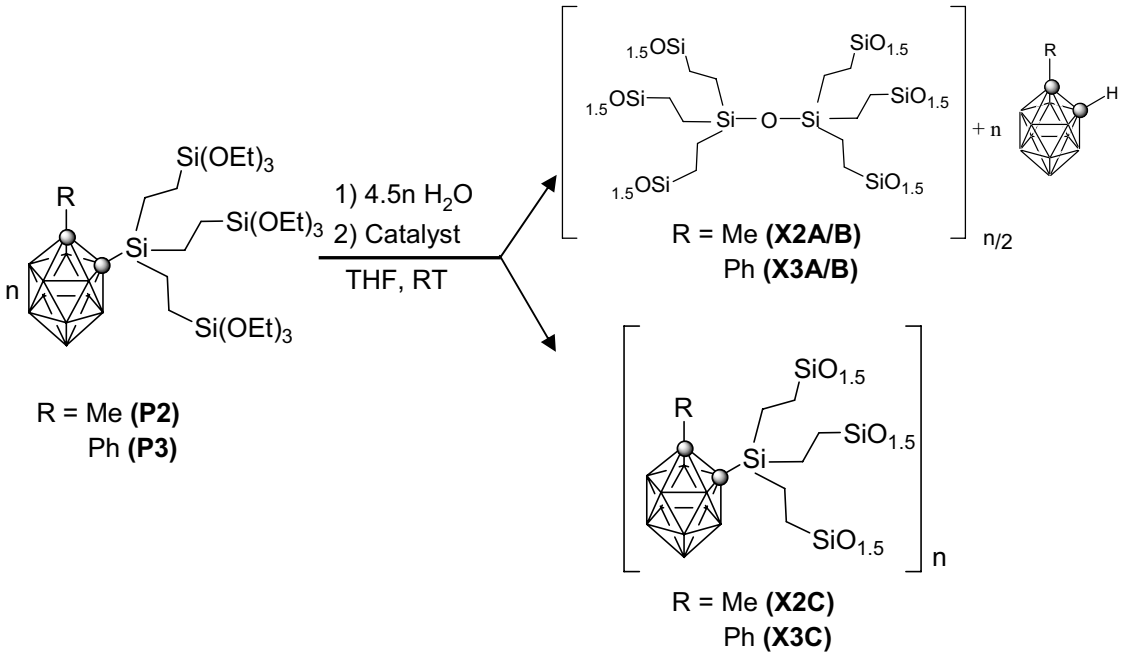


Figure Captions

Figure 1. ^{29}Si CP MAS NMR Spectra for **X1A**, **X1A-400** and **X1A-550**.

Figure 2. XRD Diagram for Xerogel **X1A** Before and After the Thermal Treatment at Different Temperatures: a) **X1A**, b) **X1A-400**, c) **X1A-550**, d) **X1A-800**, e) **X1A-1200**.

Figure 3. SEM Images of **X1A** at Different Temperatures: a) **X1A**, b) **X1A-550**

Figure 4. TEM Images of: a) **X1A** and b) **X1A-550.**

Figure 5. XRD Diagrams for Xerogels **X3A** and **X3C**.

Figure 6. TGA Analyses for Xerogel **X1A**: a) Under Argon, b) Under Dry Air.

Figure 7. C1s, B1s and Si2p Binding Energy Envelopes in the X-ray Photoelectron Spectra of **X1A-1200**.

Figure 8. Scanning Electron Microscopy (SEM) Images of **X1A-1200**

Figure 9. TEM Images of **X1A-1200**

Figure 10. TEM Images For Char Obtained After Heating **X1A** Up To 1200 ºC Under Dry Air.

Figure 1. ^{29}Si CP MAS NMR Spectra for **X1A**, **X1A-400** and **X1A-550**.

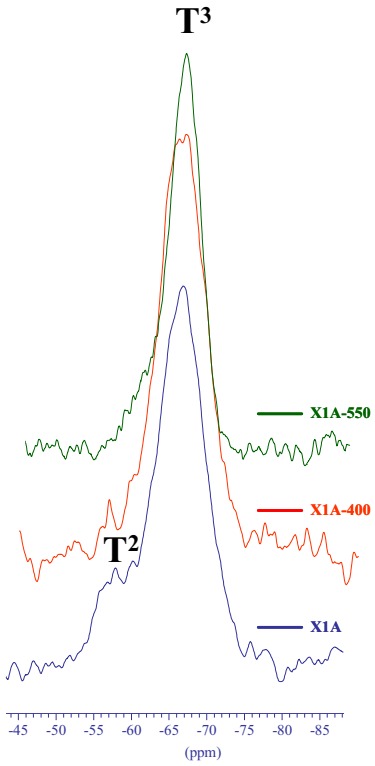


Figure 2. XRD Diagram for Xerogel **X1A** Before and After the Thermal Treatment at Different Temperatures: a) **X1A**, b) **X1A-400**, c) **X1A-550**, d) **X1A-800**, e) **X1A-1200**.

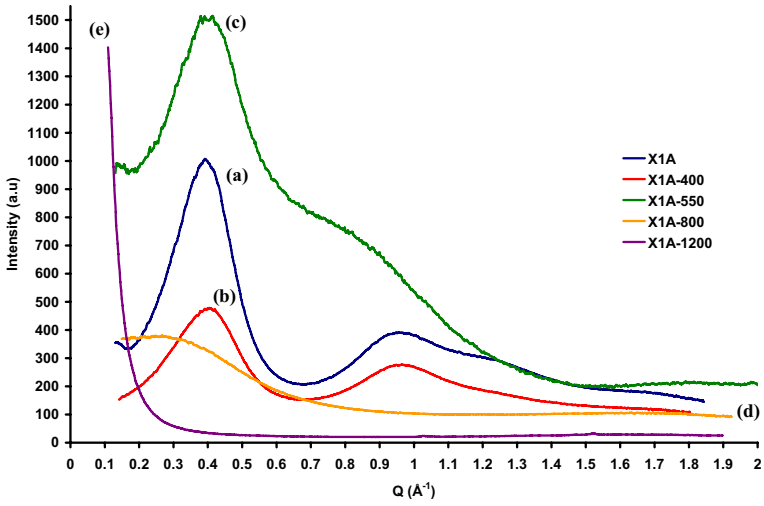


Figure 3. SEM Images of **X1A** at Different Temperatures: a) **X1A**, b) **X1A-550**

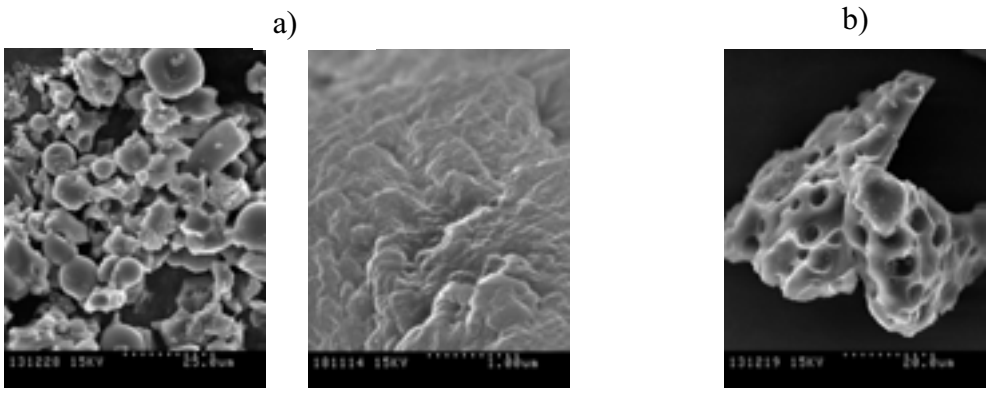
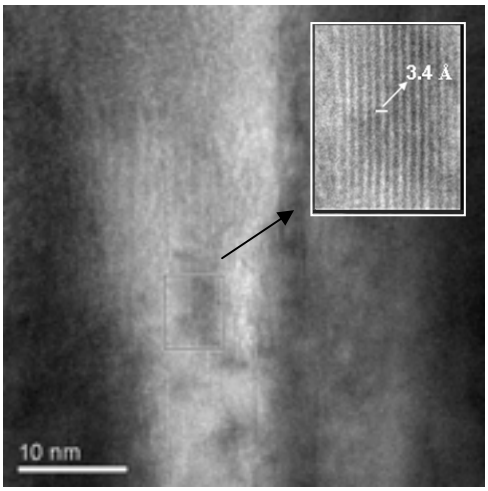


Figure 4. TEM Images of: a) **X1A** and b) **X1A-550.**

a)



b)

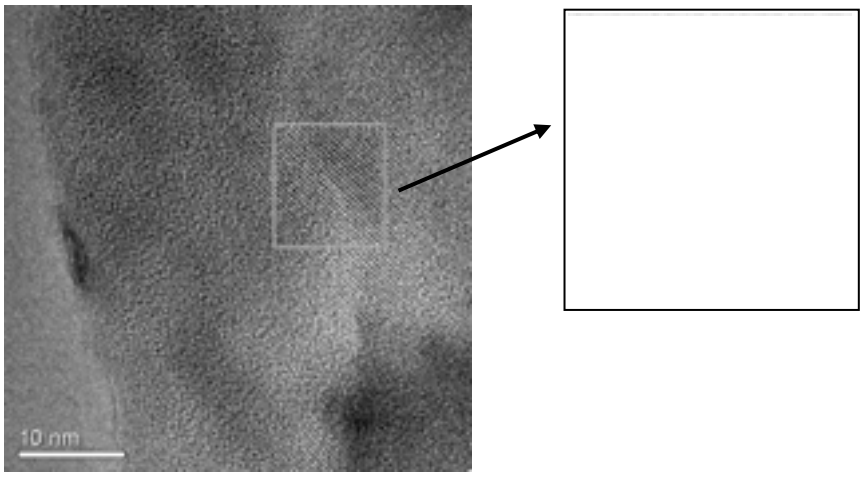


Figure 5. XRD Diagrams for Xerogels **X3A** and **X3C**.

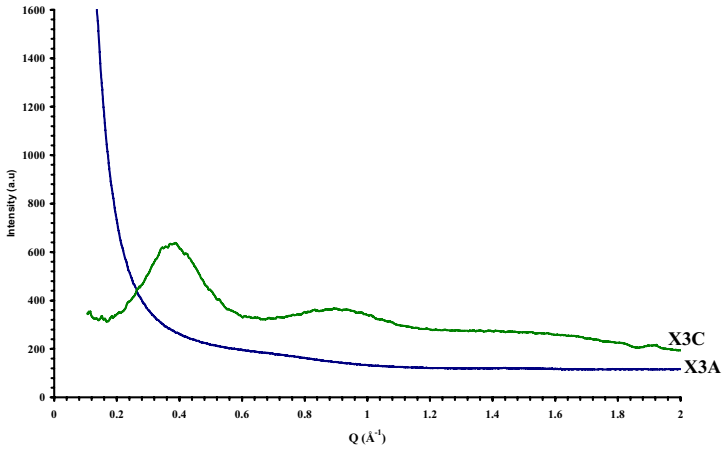


Figure 6. TGA Analyses for Xerogel **X1A**: a) Under Argon, b) Under Dry Air.

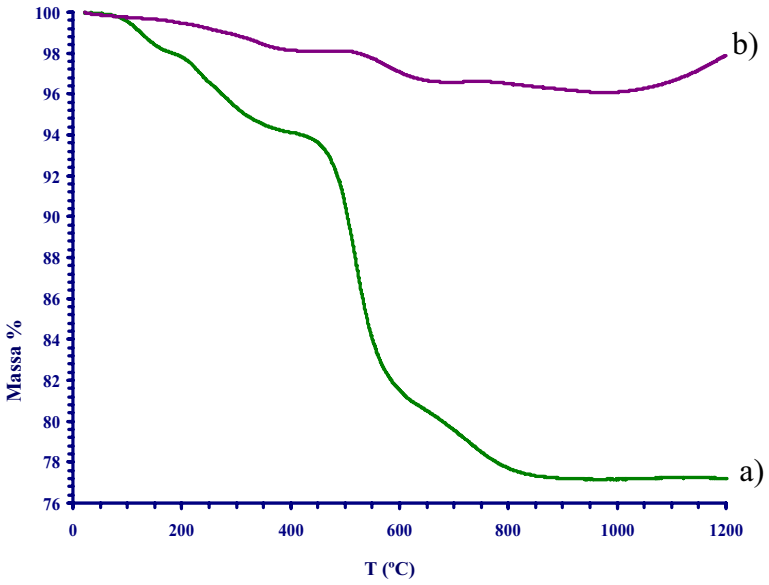


Figure 7. C1s, B1s and Si2p Binding Energy Envelopes in the X-ray Photoelectron Spectra of **X1A-1200**.

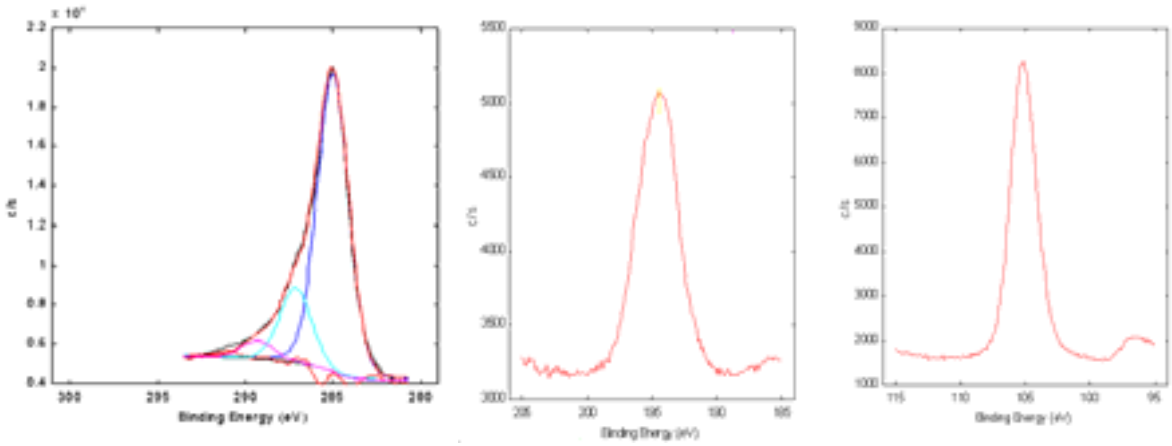


Figure 8. Scanning Electron Microscopy (SEM) Images of **X1A-1200**

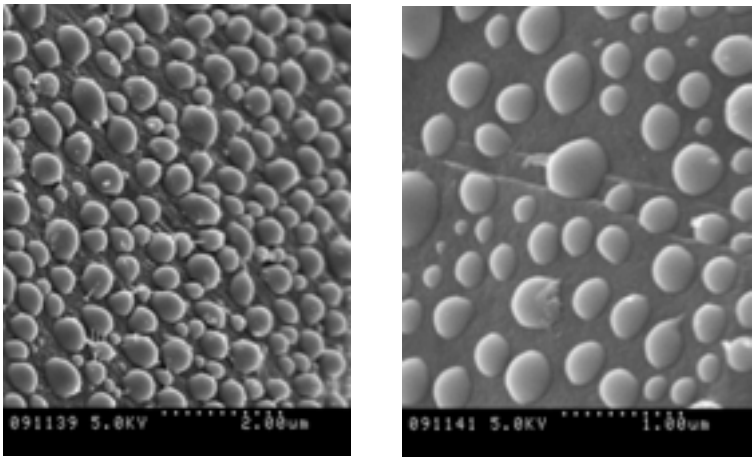


Figure 9. TEM Images of **X1A-1200**

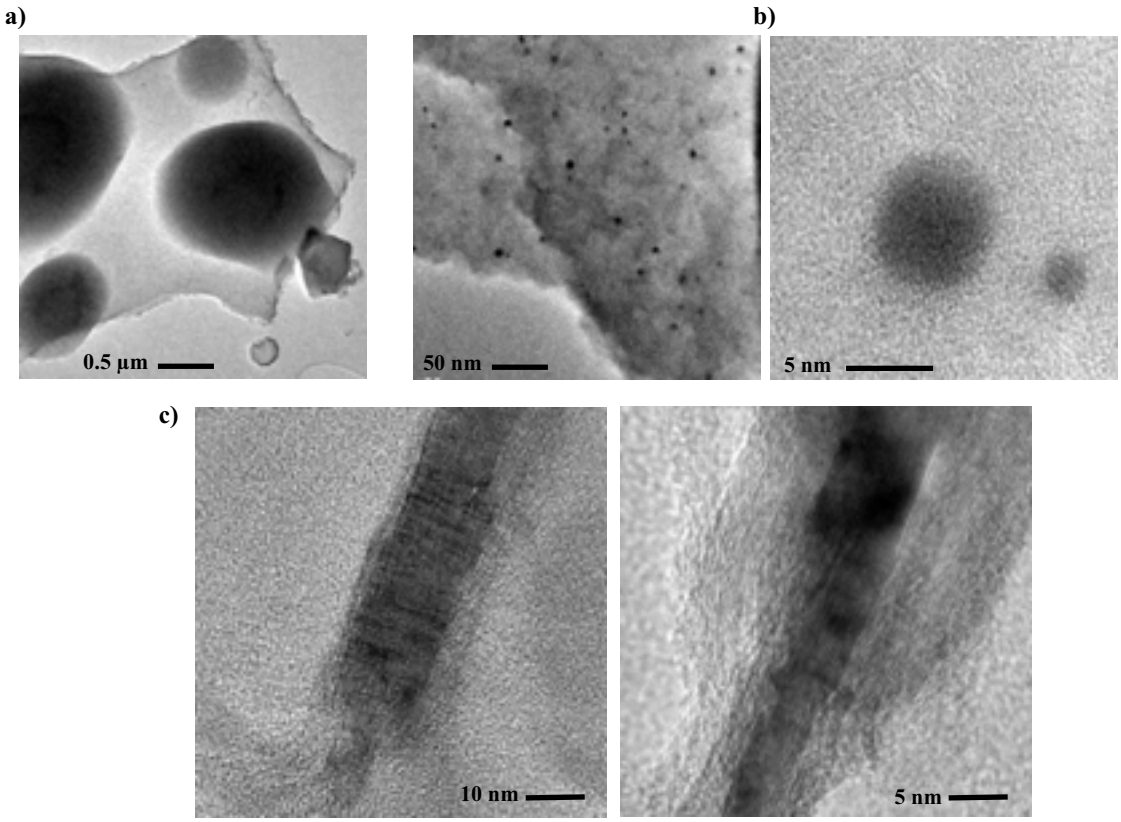


Figure 10. TEM Images For Char Obtained After Heating **X1A** Up To 1200 ºC Under Dry Air.

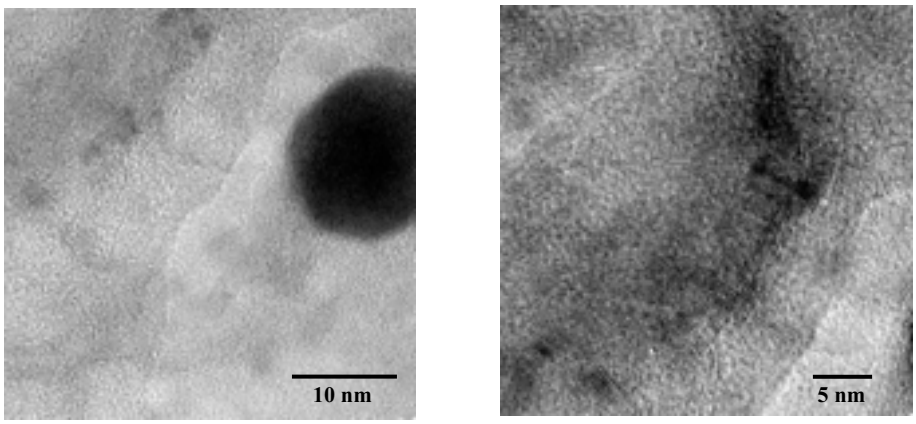


Table 1. Experimental Conditions Xerogels Obtained in THF.

Xerogel	Precursor	Precursor (mol L^{-1})	Catalyst	Catalyst (mol L^{-1})	Gellation time (h)
X1A	P1	1	TBAF	0.02	192
X1B	P1	1	HCl	0.6	4320
X2A	P2	1	TBAF	0.03	0.33
X2B	P2	1	NaOH	0.03	1824
X2C	P2	1	HCl	0.45	744
X3A	P3	1	TBAF	0.03	0.41
X3B	P3	1	NaOH	0.03	648
X3C	P3	1	HCl	0.44	1296

Table 2. ^{29}Si CP MAS NMR Data of Xerogels**.** [a]Level of condensation calculated according to the general equation L.C. = [0.5(T^1 area) + 1.0 (T^2 area) + 1.5 (T^3 area)]/1.5.

Xerogel	^{29}Si NMR CP-MAS								
	T^0		T^1		T^2		T^3		L.C.[a]
	ppm	%	ppm	%	ppm	%	ppm	%	(%)
X1A	-----	0	-----	0	-57.7	17	-66.9	83	94
X1B	-----	0	-----	0	-57.6	22	-66.2	78	93
X2A	-----	0	-----	0	-57.3	47	-64.4	53	--
X2B	-46.1	12	-53.3	35	-57.5	30	-64.7	23	--
X2C	-----	0	-51.5	6	-57.1	30	-64.3	64	86
X3A	-47.0	2	-50.7	3	-57.1	88	-65.0	7	--
X3B	-----	0	-49.9	24	-57.0	45	-64.9	31	--
X3C	-----	0	-----	0	-57.0	53	-64.1	47	82

Table 3. BET and XRD of Carboranyl-Containing Hybrids: **X1A** Before and After Thermal Treatment, **X1B**, **X2C** and **X3C**.

Material	BET(m^2g^{-1})	XRD(Å)
X1A	< 10	15.7/6.4
X1B	11	15.5/6.4
X1A-400	< 10	15.0/6.4
X1A-550	265	16.2
X1A-800	22	22.4
X1A-1200	< 10	--
X2C	< 10	16.4/6.7
X3C	< 10	16.5/6.9

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Synthesis of small carboranyl-silane dendrons as scaffold for multiple functionalizations

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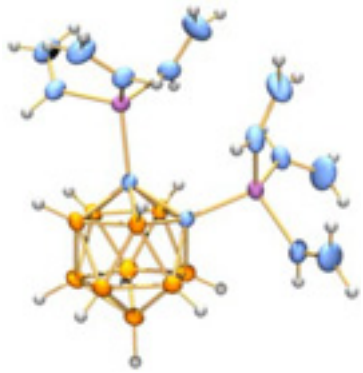
Received Date (will be automatically inserted after manuscript is accepted)

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 scaffold for peripheral functionalization with styrene, chlorovinylstyrene or suitable carboranes, while keeping the C_c-Si bond. Modification of the core by reduction of the carborane with Mg/$BrCH_2CH_2Br$ was also achieved.

Molecules that have a star shape, such as dendrimers, are important due to their very attractive features. Dendrimers allow the design of macromolecules with tailored properties through the incorporation of suitable functions at the suitable site, the core or the periphery.[1] Dendrons are dendrimer "wedges", that contain a precise functional group at the core, which generally is different from the end groups on the periphery. The usefulness of dendritic wedges or dendrons having functionalities on the surface and another single functionality at the core has not been widely developed. Generally, due to their conical shaped, dendrons are used to produce shape-controlled nanostructures and nanoobjects.[2] The 1,2-dicarba-*closo*-dodecaborane and derivatives present

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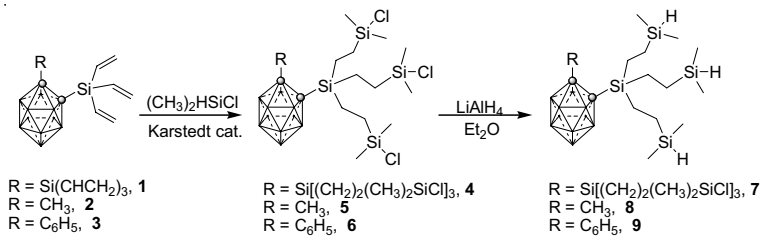
Scheme 1. Preparation of chloroterminated carboranylsilanes **4-6** and subsequent reduction to obtain compounds **7-9.**



R = Si(CHCH$_2$)$_3$, **1**
R = CH$_3$, **2**
R = C$_6$H$_5$, **3**

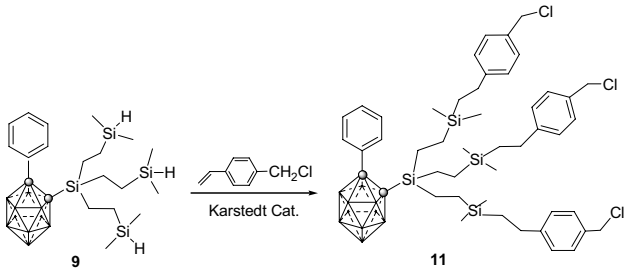
R = Si[(CH$_2$)$_2$(CH$_3$)$_2$SiCl]$_3$, **4**
R = CH$_3$, **5**
R = C$_6$H$_5$, **6**

R = Si[(CH$_2$)$_2$(CH$_3$)$_2$SiCl]$_3$, **7**
R = CH$_3$, **8**
R = C$_6$H$_5$, **9**

exceptional characteristics,[3,4] such as low nucleophilicity, chemical inertness, thermal stability,[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 easiness of derivatization specially at the carbon atoms have allowed the preparation of a wide number of compounds.[8] Recently, we become interested in the synthesis of carborane-containing star-shaped molecules in which a carbosilane core is used as 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 cluster has been the focal point or core. The versatility of the carborane cluster allows to act as scaffold to extend the dendron from the carbon atoms to the periphery, or to be modified as 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 $(CH_2{=}CH)_3SiCl$ in Et_2O/toluene solutions at room temperature. All three compounds were purified and isolated as pure crystalline air-stable solids in moderated 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 alternate hydrosilylation, reduction and peripheral functionalization steps.[10]

Scheme 2. Preparation of **11** via hydrosilylation of chlorovinyllstyrene with compound **9**.



9 **11**

Hydrosilylations of vinyl functions bonded to the carborane moiety were performed with $(CH_3)_2HSiCl$ in the absence of solvent at room temperature, in the presence of Karstedt catalyst (3-3.5% Pt) (Scheme 1). The ^{1}H NMR olefinic resonances were used to follow the complete hydrosilylation reaction by the disappearance of the double bonds 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 to introduce different functions on the periphery and check the resistance of the $C_{cluster}$-Si bond, in order to use the carborane cluster as focal-point and silicon–core protector. Thus, reductions of Si-Cl functions in **4-6** were

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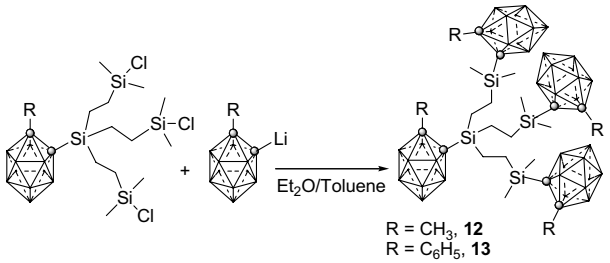
achieved with $Li[AlH_4]$ in Et_2O, at room temperature overnight, to give **7-9** in 60-80 % yield, as spectroscopically pure oils (Scheme 1).

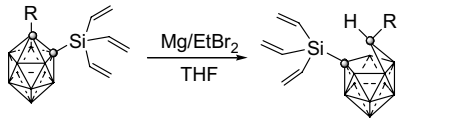
In order to demonstrate the possibility of a further functionalization of dendrons periphery, different ligand systems were attached. Compounds **7-9** with Si-H functions are used as hydrosilylation reagents. The hydrosilylation of styrene using **8** in a solvent-free reaction, in the presence of Karstedt 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 **10-11** 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.

Scheme 3. Preparation of peripheral carboranyl-functionalized dendrons **12-13** from **5-6** and the lithium salts of the carboranes.



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 a Et_2O/toluene (1:2) solution at room temperature, to give the peripheral carborane-functionalized **12** and **13,** respectively (Scheme 3). These compounds represent an example in which the versatility of the cluster has led to prepare carbosilane dendrons functionalized with carboranes in the focal point and on the periphery. Until here we have studied several strategies to functionalize the surface, to obtain molecules having original structures. The chemical reactivity of the cluster located at the core and its compatibility with the functionalities of the surface is of great interest. In this work, we have considered the possibility to modify the cluster by reduction using a route recently described by our group, in which $Mg/BrCH_2CH_2Br$ was the reducing agent.[13] Compounds **1-3** were reacted with $Mg/BrCH_2CH_2Br$ in THF at room temperature for 15 hours (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.[12] In our case, only the corresponding thermodynamic isomer was observed, as will be later confirmed by NMR spectroscopy.

Scheme 4. Reduction of the carborane located at the focal point with $Mg/EtBr_2$.



R = $Si(CHCH_2)_3$, **14**
R = CH_3, **15**
R = C_6H_5, **16**

All resultant structures were characterized by IR, $^1H\{^{11}B\}$, $^{13}C\{^1H\}$, ^{11}B and ^{29}Si NMR, mass spectrometry and confirmed by X-ray diffraction analysis for compounds **1-3**. The IR spectra for compounds containing *closo* clusters, **1-13**, present typical υ(B-H) strong bands between 2584 and 2574 cm^{-1}, while 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 **10-11** corroborates the formation of these compounds. The ^1H 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 ^1H 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-CH_3 protons. For compounds **7-9**, the presence of the Si-*H* in the molecule was confirmed by a septuplet at δ = 3.87 ppm (^3J(H, H) = 3.7 Hz) for **7-8** and at δ = 3.77 ppm for **9**. In compounds **10-11**, resonances attributed to -CH_2-Ph and additional -CH_2-Si protons are observed. For **12-13**, the ^1H NMR spectra show resonances corresponding to the *exo*-cluster groups C_c-CH_3 and C_c-C_6H_5 at 2.02 and 7.68-7.36 ppm, respectively. Finally, for **15-16**, the appearance and chemical shift of the –C*H*R proton confirm the position of each group in the thermodynamic isomer.[12b] For **15**, this proton appears as a multiplet at 3.68 ppm due to the coupling with the CH_3 group, while in **16** is a singlet at 4.47 ppm.

In parallel, the $^{13}C\{^1H\}$ NMR spectra of **1-3** and **14-16** show resonances between 138.0 and 131.0 ppm attributed to the CH_2=*C*H carbons. For the rest of compounds, the ^{13}C NMR spectra show resonances, in the corresponding regions, related to the Si-CH_3 and the Si-CH_2-CH_2-Si carbons. Other resonances attributed to the *exo*-cluster

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(12) (a) Nobre, S. M.; Monteiro, A. L. *Tetrahedron Lett.*, **2004**, *45*, 8225. (b) Casado, M. A.; Stobart, S. R. *Org. Lett.*, **2000**, *2*, 1549.
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groups carbons and peripheral functions are also exhibited for the corresponding compounds.

The $^{11}B\{^1H\}$ NMR resonances for **1-13** correspond to *closo* species,[14] from δ +1.5 to -11.4 ppm. Compound **1** and derivatives (**4**, **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**, 1:1:4:2:2 for **10,** and 1:1:4:2:2 for **12**. Compound **3** and derivatives (**6**, **9**, **11**) exhibit the same pattern 1:1:4:2:2, while **13** shows the pattern 1:1:8. Contrarily, 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 $^{29}Si\{^1H\}$ NMR spectra of compounds **1-3** exhibit a unique signal for all three compounds, around δ = -19.0 ppm. For compounds **4-13** the $^{29}Si\{^1H\}$ NMR spectra 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 compounds have confirmed their formation (see Supporting Information).

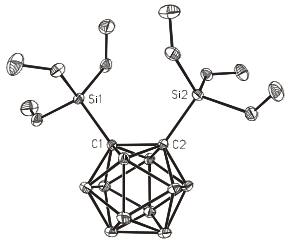

Figure 1. Molecular structure of **1.** Displacement ellipsoids are drawn at 30 % probability level.

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. 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,** 1.674(2) and 1.676(2) for **2**, and 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]Untill now, the dendritic wedges or dendrons had been usually 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. Nowadays, the use of different functions as dendron focal points, which can act as protecting groups during dendrimer growth and can be eliminated at the end of the growing process, has opened a new route to synthesize dendrimeric compounds,[16] or nanomaterials.[17] In carbosilane dendrimers, the phenyl group has been used as silicon-core protector (Si-Ph), which can be cleaved with protic acids, such as HCl or TfOH to give Si-OTf. In the latter, the 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 the carborane as platforms for dendrons functionalization and its further elimination by nucleophilic cleavage of the C_c-Si opens a new strategy to introduce other functions at the focal point. Furthermore, the possibility of modification of the core cluster by reducing agents, while keeping the C_c-Si bond, represents another alternative to prepare new carboranylsilane dendrons. Further modifications are under study.

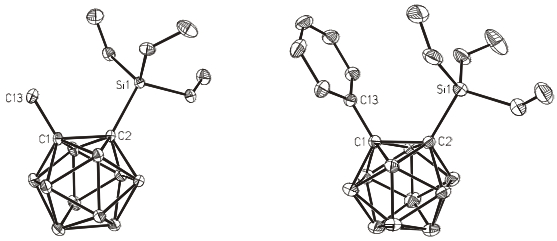

Figure 2. Molecular structures of one of the two molecules in the asymmetric units of **2** and **3.** Displacement ellipsoids are drawn at 30 % probability level.

Acknowledgment This work was supported by CICYT, MAT2004-01108 and the Generalitat de Catalunya, 2001/SGR/00337.

Supporting material available: Synthetic procedures, FT-IR, NMR, elemental analyses and mass spectra of **1-16**. Tables listing detailed crystallographic data, atomic positional and thermal displacement parameters, bond lengths and angles for **1-3**. This material is available free of charge via the Internet at http://pubs.acs.org

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Synthesis of small carboranylsilane dendrons as scaffold for multiple functionalizations.

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Supporting Information

Experimental Section

Instrumentation. IR spectra were recorded with KBr pellets or NaCl on a Shimadzu FTIR-8300 spectrophotometer. Microanalyses were performed in the analytical laboratory using a Carlo Erba EA1108 microanalyzer. The electrospray-ionization mass spectra (ESI-MS) were recorded on a Bruker Esquire 3000 spectrometer using a source of ionization an ion trap analyzer. The MALDI-TOF-MS mass spectra were recorded in the negative ion mode using a Bruker Biflex MALDI-TOF [N_2 laser; λ_{exc} 337 nm (0.5 ns pusles); voltge ion source 20.00 Kv (Uis1) and 17.50 Kv (Uis2)]. The ^{1}H, $^{1}H\{^{11}B\}$ NMR (300.13 MHz), $^{13}C\{^{1}H\}$ NMR (75.47 MHz), ^{11}B, $^{11}B\{^{1}H\}$ NMR (96.29 MHz) and $^{29}Si\{^{1}H\}$ 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 performed in $CDCl_3$ or $(CD_3)_2CO$ solutions at 22 ºC. Chemical shift values for ^{1}H, $^{1}H\{^{11}B\}$, ^{13}C, $^{13}C\{^{1}H\}$ NMR and $^{29}Si\{^{1}H\}$ NMR spectra were referenced to $SiMe_4$, and those for $^{11}B\{^{1}H\}$ and ^{11}B NMR were referenced to external $BF_3{\cdot}Et_2O$. Chemical shifts are reported in units of part per million downfield from the reference, and all coupling constants are reported in Hertz.

Material. All manipulations were carried out under an atmosphere of purified N_2 using standard Schlenk techniques. Solvents were purified, dried, and distilled by standard procedures before use. 1,2-$C_2B_{10}H_{12}$, 1-CH_3-1,2-$C_2B_{10}H_{11}$ and 1,2-C_6H_5-1,2-$C_2B_{10}H_{11}$ were supplied by Katchem Ltd. (Prague) and used as received. $(CH_2{=}CH)_3SiCl$,

$(CH_3)_2HSiCl$, and Karstedt's catalyst in xylene solution (platinum divinyltetramethyldisiloxane complex, 2.1-2.4% platinum in vinyl-terminated poly(dimethylsiloxane)) and I_2 were purchased from ABCR and used as received. The *n*-BuLi solution (1.6 M in hexanes) was used as received from Lancaster. $LiAlH_4$, $C_6H_5CH=CH_2$, $(CH=CH_2)C_6H_4CH_2Cl$, I_2, Mg, $BrCH_2CH_2Br$ and $[N(CH_3)_4]Cl$ were purchased from Aldrich. The Mg was washed with hexane and THF before used.

Synthesis of 1,2-[Si(CH=CH$_2$)$_3$]$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (1). To a solution of 1,2-$C_2B_{10}H_{10}$ (1.00 g, 6.93 mmol) in Et_2O (7 mL) and toluene (14 mL) at 0 ºC was added drop-wise a 1.6 M solution of *n*-BuLi in hexane (9.1 mL, 1.46 mmol). The mixture was stirred for 1 h at room temperature, cooled again at 0 ºC, and $(CH_2=CH)_3SiCl$ (1.2 ml, 13.90 mmol) was added drop-wise. The reaction mixture was then stirred at room temperature for 2 h and filtered off through Celite. The solvent was removed *in vacuo* and the residue treated with cold Et_2O (10 mL) to isolate **1** as a white solid. Yield: 1.31 g, 52.4%. A Et_2O solution of **1** gave single crystals suitable for X-ray analysis. $^1H\{^{11}B\}$ NMR: δ 6.27-6.17 (m, $^3J(H,H)$ = 16.7, $^2J(H,H)$ = 7.0, 12H, C*H*=C*H*$_2$), 5.84 (dd, $^3J(H,H)$ = 16.7, $^2J(H,H)$ = 7.0, 6H, CH=C*H*$_2$), 2.51 (br s, B-*H*), 2.40 (br s, B-*H*), 2.21 (br s, B-*H*). ^{11}B NMR: δ 2.5 (d, $^1J(B, H)$ = 143, 2B), -5.5 (d, $^1J(B, H)$ = 150, 2B), -8.7 (d, $^1J(B, H)$ = 162, 4B), -10.7 (d, $^1J(B, H)$ = 192, 2B). $^{13}C\{^1H\}$ NMR: δ 138.4 (CH=*C*H$_2$), 131.8 (*C*H=CH$_2$), 71.9 ($C_{cluster}$). $^{29}Si\{^1H\}$ NMR: -18.49. FTIR (KBr), cm^{-1}: 3059 ($\nu(C_{vinyl}$-H)), 2985-2950 ($\nu(C_{alkyl}$-H)), 2574 (ν(B-H)). Anal. Calcd. for $C_{14}H_{28}B_{10}Si_2$: C, 46.62; H, 7.83. Found: C, 46.0; H, 7.70. MALDI-TOF-MS (m/z): cald. 360.7 found: 359.3 (M-1), 250.1 [M-Si(CH=CH$_2$)$_3$], 143.0 [M-2(Si(CH=CH$_2$)$_3$)].

Synthesis of 1-CH_3-2-[$Si(CH=CH_2)_3$]-1,2-$C_2B_{10}H_{10}$ (2). The procedure was the same as for compound **1** using 1.00 g (6.32 mmol) of 1-CH_3-1,2-$C_2B_{10}H_{11}$ in Et_2O (7 mL) and toluene (14 mL), 4.1 mL (6.56 mmol) of 1.6 M solution of *n*-BuLi in hexane and 1.0 mL (6.32 mmol) of $(CH_2=CH)_3SiCl$. The reaction mixture was stirred for 50 min and filtered off through Celite. The solvent was removed *in vacuo* giving **2** as white waxy solid. Yield: 1.46 g, 86.4 %. A Et_2O solution of **2** gave single crystals suitable for X-ray analysis. ^{1}H NMR: δ 6.34 (dd, ^{3}J(H,H) = 14.6, ^{2}J(H,H) = 4.1, 3H, CH=C*H*$_2$), 6.22 (t, ^{3}J(H,H) = 19.5, 3H, C*H*=CH_2), 5.92 (dd, ^{3}J(H,H) = 19.5, ^{2}J(H,H) = 4.1, 3H, CH=C*H*$_2$), 3.5-1.5 (br s, B-*H*), 2.02 (s, 3H, $C_{cluster}$-C*H*$_3$). ^{1}H{^{11}B} NMR: δ 6.34 (dd, ^{3}J(H,H) = 14.6, ^{2}J(H,H) = 4.1, 3H, CH=C*H*$_2$), 6.22 (t, ^{3}J(H,H) = 19.5, 3H, C*H*=CH_2), 5.92 (dd, ^{3}J(H,H) = 19.5, ^{2}J(H,H) = 4.1, 3H, CH=C*H*$_2$), 2.95 (br s, B-*H*), 2.45 (br s, B-*H*), 2.02 (s, 3H, $C_{cluster}$-C*H*$_3$), 1.51 (br s, B-*H*). ^{11}B NMR: δ 1.5 (d, ^{1}J(B, H) = 130, 1B), -3.9 (d, ^{1}J(B, H) = 160, 1B), -7.3 (d, ^{1}J(B, H) = 153, 4B), -9.6 (4B). ^{13}C{^{1}H} NMR: δ 138.9 (CH=*C*H_2), 130.2 (*C*H=CH_2), 75.2 (*C*$_{cluster}$), 69.0 (*C*$_{cluster}$), 25.3 ($C_{cluster}$-*C*H_3). ^{29}Si{^{1}H} NMR: -19.29. FTIR (KBr), cm^{-1}: 3060 (ν(C_{vinyl}-H)), 2985-2950 (ν(C_{alkyl}-H)), 2584 (ν(B-H)). Anal. Calcd. for $C_9H_{22}B_{10}Si$: C, 40.57; H, 8.32. Found: C, ;41.0 H, 8.28.

Synthesis of 1-C_6H_5-2-[$Si(CH=CH_2)_3$]-1,2-$C_2B_{10}H_{10}$ (3). The procedure was the same as for compound **1** using 1.01 g (4.59 mmol) of 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ in Et_2O (7 mL) and toluene (14 mL), 3.0 mL (4.80 mmol) of 1.6 M solution of *n*-BuLi in hexane and 0.8 mL (4.59 mmol) of $(CH_2=CH)_3SiCl$. The reaction mixture was stirred for 10 min and filtered off through Celite. The solvent was removed *in vacuo* giving **3** as a white waxy solid. Yield: 1.20 g, 80.0 %. An Et_2O solution of **3** gave single crystals suitable for X-ray analysis. ^{1}H NMR: δ 7.64-7.30 (m, 5H, C_6H_5), 6.07 (dd, ^{3}J(H,H) = 14.2, ^{2}J(H,H) = 3.2, 3H, CH=C*H*$_2$), 5.77 (t, ^{3}J(H,H) = 19.9, 3H, C*H*=CH_2), 5.58 (dd, ^{3}J(H,H)

= 19.9, ^{2}J(H,H) = 3.2, 3H, CH=CH_2), 3.51-1.51 (br s, B-*H*). ^{1}H{^{11}B} NMR: δ 7.64-7.30 (m, 5H, C_6H_5), 6.07 (dd, ^{3}J(H,H) = 14.2, ^{2}J(H,H) = 3.2, 3H, CH=CH_2), 5.77 (t, ^{3}J(H,H) = 19.9, 3H, C*H*=CH_2), 5.58 (dd, ^{3}J(H,H) = 19.9, ^{2}J(H,H) = 4.1, ^{2}J(H,H) = 3.2, 3H, CH=CH_2), 3.11 (br s, B-*H*), 2.66 (br s, B-*H*), 2.19 (br s, B-*H*), 1.51 (br s, B-*H*). ^{11}B NMR: δ 1.5 (d, ^{1}J(B, H) = 142, 1B), -3.7 (d, ^{1}J(B, H) = 145, 1B), -8.0 (d, ^{1}J(B, H) = 156, 4B), -10.1 (2B), -11.4 (d, ^{1}J(B, H) = 151, 2B). ^{13}C{^{1}H} NMR: δ 138.0 (CH=*C*H_2), 132.3 (Ph-C_{ipso}), 131.5 (Ph-C_{meta}), 130.6 (*C*H=CH_2), 129.7 (Ph-C_{ortho}), 128.3 (Ph-C_{para}), 83.1 ($C_{cluster}$), 74.3 ($C_{cluster}$). ^{29}Si{^{1}H} NMR: -19.80. FTIR (KBr), cm^{-1}: 3060 (ν(C-H)), 2985-2950 (ν(C_{alkyl}-H)), 2574 (ν(B-H)). Anal. Calcd. for $C_{14}H_{24}B_{10}Si$: C, 51.18; H, 7.36. Found: C, 51.27; H 7.36.

Synthesis of 1,2-[Si(CH$_2$CH$_2$(CH$_3$)$_2$SiCl)$_3$]$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (4). In a Schlenk flask, **1** (0.20 g, 0.55 mmol), $(CH_3)_2$HSiCl (0.8 mL, 6.59 mmol) and Karstedt catalyst (10 µl, 0.02 mmol) were mixed and stirred for 43 h at room temperature. Evaporation of volatiles and the excess of $(CH_3)_2$HSiCl gave **4** as a transparent oil. Yield: 0.42 g, 80.3 %. ^{1}H NMR: δ 3.01-2.17 (br s, B-*H*), 0.94 (m, 12H, Si-CH_2), 0.80 (m, 12H, Si-CH_2), 0.46 (s, 36H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 2.50 (br s, B-*H*), 2.27 (br s, B-*H*), 2.17 (br s, B-*H*), 0.94 (m, 12H, Si-CH_2), 0.80 (m, 12H, Si-CH_2), 0.46 (s, 36H, Si-CH_3). ^{11}B NMR: δ 4.1 (br, 2B), -3.7 (br, 2B), -7.7 (br, 6B). ^{13}C{^{1}H} NMR: δ 74.5 ($C_{cluster}$), 11.8 (Si-*C*H_2), 6.0 (Si-*C*H_2), 1.1 (Si-*C*H_3). ^{29}Si{^{1}H} NMR: 32.43 (*Si*-Cl), 10.75 (*Si*-$C_{cluster}$).

Synthesis of 1-CH$_3$-2-[Si(CH$_2$CH$_2$(CH$_3$)$_2$SiCl)$_3$]-1,2-C$_2$B$_{10}$H$_{10}$ (5). The process was the same as for compound **4** using 0.21 g (0.79 mmol) of **2**, 0.6 mL (5.13 mmol) of $(CH_3)_2$HSiCl and 10 µl (0.02 mmol) of Karstedt catalyst. The mixture was stirred for 16 h at room temperature. Evaporation of the excess of $(CH_3)_2$HSiCl gave **5** as a brown oil.

Yield: 0.39 g, 90.7 %. ^{1}H NMR: δ 2.04 (s, 3H, $C_{cluster}$-C*H*$_3$), 0.91 (m, 6H, Si-C*H*$_2$), 0.81 (m, 6H, Si-C*H*$_2$), 0.46 (s, 18H, Si-C*H*$_3$). ^{1}H{^{11}B} NMR: 2.44 (br s, B-*H*), 2.36 (br s, B-*H*), 2.27 (br s, B-*H*), 2.12 (br s, B-*H*), 2.04 (s, 3H, $C_{cluster}$-C*H*$_3$), 0.91 (m, 6H, Si-C*H*$_2$), 0.81 (m, 6H, Si-C*H*$_2$), 0.46 (s, 18H, Si-C*H*$_3$). ^{11}B NMR: δ 2.6 (d, ^{1}J(B, H) = 106, 1B), -3.4 (d, ^{1}J(B, H) = 140, 1B), -6.4 (d, ^{1}J(B, H) = 106, 6B), -8.7 (br, 2B). ^{13}C{^{1}H} NMR: δ 75.9 (*C*$_{cluster}$), 70.8 (*C*$_{cluster}$), 26.2 ($C_{cluster}$-*C*H$_3$), 11.3 (Si-*C*H$_2$), 4.58 (Si-*C*H$_2$), 0.99 (Si-*C*H$_3$). ^{29}Si{^{1}H} NMR: 32.24 (*Si*-Cl), 9.45 (*Si*-$C_{cluster}$).

Synthesis of 1-C_6H_5-2-[Si($CH_2CH_2(CH_3)_2SiCl)_3$]-1,2-$C_2B_{10}H_{10}$ (6): The process was the same as for compound **4** using 0.21 g (0.64 mmol) of **3**, 0.5 mL (4.28 mmol) of $HSiMe_2Cl$ and 10 μl (0.02 mmol) of Karstedt catalyst. The mixture was stirred for 14 h at room temperature. Evaporation of the excess of $(CH_3)_2HSiCl$ gave **6** as a yellow waxy solid. Yield: 0.37 g, 94.9 %. ^{1}H NMR: δ 7.69-7.33 (m, 5H, C_6H_5), 0.60 (m, 6H, Si-C*H*$_2$), 0.49 (m, 6H, Si-C*H*$_2$), 0.39 (s, 18H, Si-C*H*$_3$). ^{1}H{^{11}B} NMR: δ 7.69-7.33 (m, 5H, C_6H_5), 2.94 (br s, B-*H*), 2.60 (br s, B-*H*), 2.40 (br s, B-*H*), 2.25 (br s, B-*H*), 0.60 (m, 6H, Si-C*H*$_2$), 0.49 (m, 6H, Si-C*H*$_2$), 0.39 (s, 18H, Si-C*H*$_3$). ^{11}B NMR: δ 3.6 (d, ^{1}J(B, H) = 113, 1B), -1.3 (d, ^{1}J(B, H) = 145, 1B), -6.3 (d, ^{1}J(B, H) = 147, 4B), -8.8 (br, 2B), -10.07 (br, 2B). ^{13}C{^{1}H} NMR: δ 132.8 (Ph-*C*$_{ipso}$), 131.3 (Ph-*C*$_{meta}$), 130.8 (Ph-*C*$_{ortho}$), 128.8 (Ph-*C*$_{para}$), 84.0 (*C*$_{cluster}$), 76.2 (*C*$_{cluster}$), 11.2 (Si-*C*H$_2$), 3.8 (Si-*C*H$_2$), 1.0 (Si-*C*H$_3$). ^{29}Si{^{1}H} NMR: 32.20 (*Si*-Cl), 10.28 (*Si*-$C_{cluster}$).

Synthesis of 1,2-[Si($CH_2CH_2(CH_3)_2SiH)_3$]$_2$-1,2-$C_2B_{10}H_{10}$ (7): To a solution of $LiAlH_4$ (64.1 mg, 1.69 mmol) in Et_2O (10 mL) at 0 ºC was added drop-wise a solution of **4** (0.52 g, 0.56 mmol) in Et_2O (10 mL). The mixture was stirred for 15 h at room temperature and filtered off through Celite twice. The solvent was removed *in vacuo* to

give **7** as a transparent oil. Yield: 0.24, 58.5%. ^{1}H NMR: δ 3.87 (sept, J(H, H) = 3.7, 6H, Si-*H*), 3.01-2.17 (br s, B-*H*), 0.83 (m, 12H, Si-C*H*$_2$), 0.57 (m, 12H, Si-C*H*$_2$), 0.12 (d, ^{1}J(H, H) = 3.7, 36H, Si-C*H*$_3$). ^{1}H{^{11}B} NMR: δ 3.87 (sept, ^{3}J(H, H) = 3.7, 6H, Si-*H*), 2.47 (br s, B-*H*), 2.31 (br s, B-*H*), 2.17 (br s, B-*H*), 0.83 (m, 12H, Si-C*H*$_2$), 0.57 (m, 12H, Si-C*H*$_2$), 0.12 (d, ^{3}J(H, H) = 3.7, 36H, Si-C*H*$_3$). ^{11}B NMR: δ 3.6 (br, 2B), -3.3 (br, 2B), -7.7 (br, 6B). ^{13}C{^{1}H} NMR: δ 74.5 (*C*$_{cluster}$), 7.18 (Si-*C*H$_2$), 6.59 (Si-*C*H$_2$), -4.50 (Si-*C*H$_3$). ^{29}Si{^{1}H} NMR: 9.60 (*Si*-C$_{cluster}$), -9.62 (*Si*-H). FTIR (NaCl), cm^{-1}: 2957-2900 (ν(C$_{alkyl}$-H)), 2584 (ν(B-H)), 2112 (ν(Si-H)), 1249 (δ(Si-CH$_3$)).

Synthesis of 1-CH$_3$-2-[Si(CH$_2$CH$_2$(CH$_3$)$_2$SiH)$_3$]-1,2-C$_2$B$_{10}$H$_{10}$ (8): The process was the same as for compound **7** using LiAlH (40.1 mg, 1.00 mmol) of in Et$_2$O (10 mL) and **5** (0.37 (0.67 mmol) in Et$_2$O (5 mL). The mixture was stirred for 15 h at room temperature and filtered off through Celite three times. The solvent was removed *in vacuo* to give **8** as a transparent oil. Yield: 0.18 g, 60.0%. ^{1}H NMR: δ 3.87 (sept, J(H, H) = 3.7, 3H, Si-*H*), 2.03 (s, C$_{cluster}$-C*H*$_3$), 0.84 (m, 6H, Si-C*H*$_2$), 0.58 (m, 6H, Si-C*H*$_2$), 0.13 (d, ^{1}J(H, H) = 3.7, 18H, Si-C*H*$_3$). ^{1}H{^{11}B} NMR: 3.87 (sept, ^{3}J(H, H) = 3.7, 3H, Si-*H*), 2.42 (br s, B-*H*), 2.36 (br s, B-*H*), 2.26 (br s, B-*H*), 2.16 (br s, B-*H*), 2.03 (s, C$_{cluster}$-C*H*$_3$), 0.84 (m, 6H, Si-C*H*$_2$), 0.58 (m, 6H, Si-C*H*$_2$), 0.13 (d, ^{3}J(H, H) = 3.7, 18H, Si-C*H*$_3$). ^{11}B NMR: δ 2.2 (d, ^{1}J(B, H) = 133, 1B), -3.4 (d, ^{1}J(B, H) = 158, 1B), -6.5 (d, ^{1}J(B, H) = 151, 6B), -8.5 (br, 2B). ^{13}C{^{1}H} NMR: 75.7 (*C*$_{cluster}$), 71.8 (*C*$_{cluster}$), 26.1 (C$_{cluster}$-*C*H$_3$), 6.6 (Si-*C*H$_2$), 6.1 (Si-*C*H$_2$), -4.9 (Si-*C*H$_3$). ^{29}Si{^{1}H} NMR: 9.30 (*Si*-C$_{cluster}$), -9.82 (*Si*-H). FTIR (NaCl), cm^{-1}: 2957-2900 (ν(C$_{alkyl}$-H)), 2584 (ν(B-H)), 2112 (ν(Si-H)), 1249 (δ(Si-CH$_3$)). MALDI-TOF-MS (m/z): calcd. 446.98 found. 445.31 [M-1]$^{-}$, 155.98 [M-(C$_{12}$H$_{33}$Si$_4$)]$^{-}$ or [C$_3$H$_{13}$B$_{10}$]$^{-}$.

Synthesis of 1-C_6H_5-2-[$Si(CH_2CH_2Si(CH_3)_2H)_3$]-1,2-$C_2B_{10}H_{10}$ (9): The process was the same as for compound **7** using LiAlH (22.0 mg, 5.51 mmol) in Et_2O (8 mL) and **6** (0.22 g, 0.36 mmol) in Et_2O (5 mL). The mixture was stirred for 16 h at room temperature and filtered off through Celite three times. The solvent was removed *in vacuo* giving **9** as a transparent oil. Yield: 0.15 g, 78.9%. ^{1}H NMR: δ 7.69-7.34 (m, 5H, C_6H_5), 3.77 (sept, ^{3}J(H, H) = 3.7, 3H, Si-*H*), 0.40 (s, 12H, Si-CH_2), 0.05 (d, ^{3}J(H, H) = 3.7, 18H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 7.69-7.34 (m, 5H, C_6H_5), 3.77 (sept, ^{3}J(H, H) = 3.7, 3H, Si-*H*), 2.93 (br s, B-*H*), 2.57 (br s, B-*H*), 2.38 (br s, B-*H*), 2.26 (br s, B-*H*), 0.40 (s, 12H, Si-CH_2), 0.05 (d, ^{3}J(H, H) = 3.7, 18H, Si-CH_3). ^{11}B NMR: δ 3.0 (d, ^{1}J(B, H) = 118, 1B), -1.5 (d, ^{1}J(B, H) = 144, 1B), -6.4 (d, ^{1}J(B, H) = 153, 4B), -8.5 (br, 2B), -10.2 (br, 2B). ^{13}C{^{1}H} NMR: δ 133.1 (Ph-C_{ipso}), 131.3 (Ph-C_{meta}), 130.5 (Ph-C_{ortho}), 128.5 (Ph-C_{para}), 83.9 ($C_{cluster}$), 76.1 ($C_{cluster}$), 6.4 (Si-CH_2), 5.3 (Si-CH_2), -4.9 (Si-CH_3). ^{29}Si{^{1}H} NMR: 10.27 (*Si*-$C_{cluster}$), -10.04 (*Si*-H). FTIR (NaCl), cm^{-1}: 3064 (ν(C_{aryl}-H)), 2957-2903 (ν(C_{alkyl}-H)), 2586 (ν(B-H)), 2110 (ν(Si-H)), 1249 (δ(Si-CH_3)). MALDI-TOF-MS (m/z): calcd. 509 found: 508.41 $[M-1]^-$, 218.07 $[C_8B_{10}H_{14}]^-$.

Synthesis of 1-CH_3-2-[$Si(CH_2CH_2Si(CH_3)_2CH_2CH_2C_6H_5)_3$]-1,2-$C_2B_{10}H_{10}$ (10): In a Schlenk flask, **8** (0.11 g, 0.24 mmol), $C_6H_5CH{=}CH_2$ (8.3 μL, 0.72 mmol) and Karstedt catalyst (5.0 μL, 0.01 mmol) were mixed and stirred overnight at room temperature. The volatiles were removed *in vacuo* giving **10** as a yellow oil. Yield: 0.18 g, ~99%. ^{1}H NMR: δ 7.33-7.21 (m, 5H, C_6H_5), 2.67 (t, ^{2}J(H, H) = 8.5, 6H, CH_2-C_6H_5), 2.01 (s, 3H, $C_{cluster}$-CH_3), 0.95 (t, ^{2}J(H, H) = 8.5, 6H, Si-CH_2), 0.74 (m, 6H, Si-CH_2), 0.47 (m, 6H, Si-CH_2), 0.06 (s, 18H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 7.33-7.21 (m, 5H, C_6H_5), 2.67 (t, ^{2}J(H, H) = 8.5, 6H, CH_2-C_6H_5), 2.49 (br, B-*H*), 2.35 (br s, B-*H*), 2.29 (br s, B-*H*), 2.19 (br s, B-*H*), 2.01 (s, 3H, $C_{cluster}$-CH_3), 0.95 (t, ^{2}J(H, H) = 8.5, 6H, Si-CH_2), 0.74 (m, 6H,

Si-CH_2), 0.47 (m, 6H, Si-CH_2), 0.06 (s, 18H, Si-CH_3). ^{11}B NMR: δ 2.2 (br, 1B), -3.4 (br,1B), -6.5 (br, 8B). ^{13}C{^{1}H} NMR: δ 144.8, 128.3, 127.7, 125.7 (C_6H_5), 75.7 ($C_{cluster}$), 72.1 ($C_{cluster}$), 30.0 (CH_2-C_6H_5), 26.2 ($C_{cluster}$-CH_3), 16.6 (Si-CH_2), 7.6 (Si-CH_2), 5.3 (Si-CH_2), -4.0 (Si-CH_3). ^{29}Si{^{1}H} NMR: 9.37 (*Si*-$C_{cluster}$), 4.73 (*Si*-CH_2). FTIR (NaCl), cm^{-1}: 3062 (ν(C_{aryl}-H)), 2921 (ν(C_{alkyl}-H)), 2582 (ν(B-H)), 1249 (δ(Si-CH_3)). MS-Electrospray (ESI) solution of $CHCl_3$/MeOH m/z calcd for $C_{39}H_{70}B_{10}Si_4$: 759.4; found: 782.5 $[M+Na]^+$.

Synthesis of 1-C_6H_5-2-[Si($CH_2CH_2(CH_3)_2SiCH_2CH_2C_6H_4CH_2Cl)_3$]-1,2-$C_2B_{10}H_{10}$ (11). In a Schlenk flask, **9** (0.15 g, 0.29 mmol), (CH=CH_2)$C_6H_4CH_2Cl$ (0.13 mL, 0.86 mmol) and Karstedt catalyst (5 μl, 0.01 mmol) were mixed and stirred overnight at room temperature. The volatiles were removed *in vacuo* to give **11** as a yellow oil. Yield: 0.28 g, ~99%. ^{1}H NMR: δ 7.69-7.34 (m, 5H, C_6H_5), 7.33-7.17 (m, 12H, C_6H_4), 4.59 (s, 6H, CH_2-Cl), 2.58 (t, ^{2}J(H, H) = 8.5, 6H, C_6H_4-CH_2), 0.83 (t, ^{2}J(H, H) = 8.5, 6H, Si-CH_2), 0.35 (s, 12H, Si-CH_2), -0.02 (s, 18H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 7.69-7.34 (m, 5H, C_6H_5), 7.33-7.17 (m, 12H, C_6H_4), 4.59 (s, 6H, CH_2-Cl), 2.58 (t, ^{2}J(H, H) = 8.5, 6H, C_6H_4-CH_2), 2.91 (br s, B-*H*), 2.38 (br s, B-*H*), 2.28 (br s, B-*H*), 0.83 (t, ^{2}J(H, H) = 8.5, 6H, Si-CH_2), 0.35 (s, 12H, Si-CH_2), -0.02 (s, 18H, Si-CH_3). ^{11}B NMR: δ 3.45 (br, 1B), -1.2 (br,1B), -6.2 (br, 8B). ^{13}C{^{1}H} NMR: δ 145.8, 134.9, 133.1, 130.6 (C_6H_5), 131.3, 128.7, 128.5, 128.2 (C_6H_4), 83.8 ($C_{cluster}$), 76.1 ($C_{cluster}$), 46.2 (CH_2-Cl), 29.7 (C_6H_4-CH_2), 16.5 (Si-CH_2), 7.4 (Si-CH_2), 4.6 (Si-CH_2), -4.0 (Si-CH_3). ^{29}Si{^{1}H} NMR: δ 10.38 (*Si*-$C_{cluster}$), 4.72 (*Si*-CH_2). FTIR (NaCl), cm^{-1}: 3053 (ν(C_{aryl}-H)), 2952-2923 (ν(C_{alkyl}-H)), 2586 (ν(B-H)), 1247 (δ(Si-CH_3)). MS-Electrospray (ESI) solution of $CHCl_3$/MeOH m/z calcd for $C_{47}H_{75}B_{10}Si_4Cl_3$: 966.9; found: 984.4 $[M+H_2O]^+$

Synthesis of 1-CH_3-2-[$Si(CH_2CH_2(CH_3)_2Si(1\text{-}CH_3\text{-}1,2\text{-}C_2B_{10}H_{10})_3]$-1,2-$C_2B_{10}H_{10}$ (12). To a solution of 1-CH_3-1,2-$C_2B_{10}H_{11}$ (0.33 g, 2.09 mmol) in Et_2O (3 mL) and toluene (6 mL) at 0ºC was added drop-wise a 1.6 M solution of *n*-BuLi in hexane (1.4 mL, 2.24 mmol). The mixture was stirred for 1 h at room temperature. After cooling it to 0ºC, a solution of **5** (0.38 g, 0.70 mmol) in toluene (6 mL) and Et_2O (3 mL) was added drop-wise with stirring. The suspension was stirred for 2 h at room temperature and was filtered off through Celite. The solvent was removed and the residue was treated with 5 mL of cold Et_2O to isolate **12** as a white solid. Yield: 0.13 g, 20.3%. ^1H NMR: δ 2.02 (s, 12H, $C_{cluster}$-C*H*$_3$), 0.82 (m, 12H, Si-C*H*$_2$), 0.38 (s, 18H, Si-C*H*$_3$). $^1H\{^{11}B\}$ NMR: δ 2.46 (br s, B-*H*), 2.27 (br s, B-*H*), 2.02 (s, 12H, $C_{cluster}$-C*H*$_3$), 0.82 (m, 12H, Si-C*H*$_2$), 0.38 (s, 18H, Si-C*H*$_3$). ^{11}B NMR: δ 2.4 (br, 1B), -3.3 (br, 1B), -6.5 (br, 4B), -7.5 (br, 2B), -11.2 (br, 2B). $^{13}C\{^1H\}$ NMR: δ 75.3 (*C*$_{cluster}$), 70.3 (*C*$_{cluster}$), 25.8 ($C_{cluster}$-*C*H$_3$), 9.5 (Si-*C*H$_2$), 5.5 (Si-*C*H$_2$), -2.2 (Si-*C*H$_3$). $^{29}Si\{^1H\}$ NMR: δ 9.00 (*Si*$_{periphery}$), 8.06 (Si$_{core}$). FTIR (KBr), cm^{-1}: 2951 (ν(C_{alkyl}-H)), 2582 (ν(B-H)), 1258 (δ(Si-CH_3)). Anal. Calcd. for $C_{24}H_{82}B_{40}Si_4$: C, 31.48; H, 9.03. Found: C, ; H,. MS-Electrospray (ESI) solution of $CHCl_3$/MeOH m/z calcd for $C_{24}H_{82}B_{40}Si_4$: 915.1; found, 938.8 $[M+Na]^+$

Synthesis of 1-C_6H_5-2-[$Si(CH_2CH_2Si(CH_3)_2(1\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_{10})_3]$-1,2-$C_2B_{10}H_{10}$ (13). The procedure was the same as for **12** using 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ (0.19 g, 0.87 mmol) and *n*-BuLi (0.59 mL, 0.94 mmol) in toluene (2 mL) and Et_2O (1 mL). After cooling at 0ºC, a solution of **6** (0.18 g, 0.29 mmol) in toluene (2mL) and Et_2O (1 mL) was added drop-wise with stirring. The suspension was stirred for 5 h at room temperature and filtered off through Celite. The solvent was removed to vacuum to give a brown oil, which was treated with hexane to obtain **13** as a brown oil. Yield: 0.08 g,

24.5%. ^{1}H NMR: δ 7.68-7.36 (m, 20H, C_6H_5), 0.21 (m, 12H, Si-CH_2), -0.19 (s, 18H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 7.68-7.36 (m, 20H, C_6H_5), 2.89 (br s, B-*H*), 2.62 (br s, B-*H*), 2.35 (br s, B-*H*), 0.21 (m, 12H, Si-CH_2), -0.19 (s, 18H, Si-CH_3). ^{11}B NMR: δ 3.3 (br, 1B), -1.0 (br, 1B), -6.4 (br, 4B), -9.3 (br, 4B). ^{13}C{^{1}H} NMR: δ 132.6-128.5 (C_6H_5), 83.5 ($C_{cluster}$), 75.4 ($C_{cluster}$), 8.5 (Si-*C*H_2), 4.3 (Si-*C*H_2), -3.4 (Si-*C*H_3). ^{29}Si{^{1}H} NMR: δ 10.32 ($Si_{periphery}$), 10.02 (Si_{core}). FTIR (KBr), cm^{-1}: 3074 (ν(C-H)), 2960-2926 (ν(C_{alkyl}-H)), 2583 (ν(B-H)), 1259 (δ(Si-CH_3)). MS-Electrospray (ESI) solution of $CHCl_3$/MeOH m/z calcd for $C_{44}H_{90}B_{40}Si_4$: 1164.0; found, 1187.0 $[M+Na]^+$

Synthesis of [N(Me)$_4$][7-Si(CH=CH$_2$)$_3$-μ-(9,10-CHSi(CH=CH$_2$)$_3$)-*nido*-CB$_{10}$H$_{10}$ (14). In a Schlenk flask were added Mg (1.25 g, 0.05 mmol), 1 mL of THF and a crystal of I_2. Then a solution of **1** (0.25 g, 0.69 mmol) in THF (5 mL) and dibromoethane (1.3 mL, 3.17 mmol) were added drop-wise at the same time to the flask. After the addition was completed, the reaction mixture was refluxed for 15 h and cooled at room temperature. The volatile compounds were removed *in vacuo* and the reaction residue washed with water (50 mL) and filtered. An excess of [N(CH_3)$_4$]Cl in water was added to precipitate a white solid. The solid was filtered off, washed with water and dried under vacuum to obtain **14**. Yield: 93 mg, 31 %. ^{1}H NMR [(CD_3)$_2$CO]: δ 6.34-5.79 (m, 18H, C*H*=CH_2), 3.80 (s, 1H, C-*H*), 3.45 (s, 12H, ([N(CH_3)$_4$]). ^{1}H{^{11}B} NMR [(CD_3)$_2$CO]: δ 6.34-5.787 (m, 18H, C*H*=CH_2), 4.22 (br s, 2H, B-*H*), 3.80 (s, 1H, Si-C-*H*), 3.78 (br s, 1H, B-*H*), 3.45 (s, 12H, ([N(CH_3)$_4$]), 3.05 (br s, 2H, B-*H*), 2.20 (br s, 2H, B-*H*), 1.67 (br s, 2H, B-*H*), 0.99 (br s, 2H, B-*H*). ^{11}B NMR [(CD_3)$_2$CO]: δ 20.3 (d, ^{1}J(B, H) = 139, 2B), 17.4 (d, ^{1}J(B, H) = 143, 1B), 4.7 (d, ^{1}J(B, H) = 142, 1B), -4.9 (d, ^{1}J(B, H) = 149, 2B), -12.6 (d, ^{1}J(B, H) = 136, 2B), -20. (d, ^{1}J(B, H) = 134, 2B). ^{13}C{^{1}H} NMR [(CD_3)$_2$CO]: δ 138.4-131.7 (*C*H=*C*H_2), 81.7 (*C*HSi), 55.2 ([N(CH_3)$_4$]). FTIR (KBr), cm^{-1}: 3051 (ν(C-H)),

2945 (ν(C_{alkyl}-H)), 2515 (ν(B-H)), 1404 (ν(N-H)). MALDI-TOF-MS (m/z): calcd. 361, found 360.

Synthesis of [N(Me)$_4$][7-Si(CH=CH$_2$)$_3$-μ-(9,10-CHCH$_3$)-*nido*-CB$_{10}$H$_{10}$] (15). The procedure was the same as for **14** using Mg (1.25 g, 0.05 mmol), a crystal of I_2 in THF (1 mL), a solution of **2** (0.23 g, 0.86 mmol) in THF (5 mL) and dibromoethane (1.3 mL, 3.17 mmol). After 15 h at reflux the compound **15** was obtained as a white solid by using the same work up as for **14**. Yield: 40.0 mg, 32%. ^{1}H NMR [$(CD_3)_2CO$]: δ 6.28 (dd, ^{3}J(H,H) = 20.2, ^{3}J(H,H) = 14.6, 3H, C*H*=CH$_2$), 6.03 (dd, ^{3}J(H,H) = 14.6, ^{2}J(H,H) = 4.4, 3H, CH=C*H*$_2$), 5.71 (dd, ^{3}J(H,H) = 20.2, ^{2}J(H,H) = 4.4, 3H, CH=C*H*$_2$), 3.68 (m, 1H, CH_3-C*H*), 3.45 (s, 12H, [N(C*H*$_3$)$_4$]), 1.30 (s, 3H, C*H*$_3$-CH). ^{1}H{^{11}B} NMR [$(CD_3)_2CO$]: δ 6.28 (dd, ^{3}J(H,H) = 20.2, ^{3}J(H,H) = 14.6, 3H, C*H*=CH$_2$), 6.03 (dd, ^{3}J(H,H) = 14.6, ^{2}J(H,H) = 4.4, 3H, CH=C*H*$_2$), 5.71 (dd, ^{3}J(H,H) = 20.2, ^{2}J(H,H) = 4.4, 3H, CH=C*H*$_2$), 3.83 (br s, 2H, B-*H*), 3.68 (m, 1H, CH_3-C*H*), 3.45 (s, 12H, [N(C*H*$_3$)$_4$]), 2.85 (br s, 1H, B-*H*), 2.70 (br s, 2H, B-*H*), 1.69 (br s, 2H, B-*H*), 1.30 (d, ^{3}J(H, H) = 6.2, 3H, C*H*$_3$-CH), 1.23 (br s, 2H, B-*H*). ^{11}B NMR [$(CD_3)_2CO$]: δ 18.0 (d, ^{1}J(B, H) = 143, 2B), 13.5 (d, ^{1}J(B, H) = 135, 1B), 1.1 (d, ^{1}J(B, H) = 130, 1B), -5.7 (d, ^{1}J(B, H) = 145, 2B), -10.3 (d, ^{1}J(B, H) = 132, 2B), -16.2. (d, ^{1}J(B, H) = 137, 2B). ^{13}C NMR [$(CD_3)_2CO$]: δ 136.4 (d, ^{1}J(C, H) = 136, *C*H=CH$_2$), 132.6 (t, ^{1}J(C,H) = 165, CH=*C*H$_2$), 91,1 (d, ^{1}J(C, H) = 168, CH_3-*C*H), 55.1 (q, ^{1}J(C, H) = 143, [N(C*H*$_3$)$_4$]), 32.1 (q, ^{1}J(C,H) = 136, CH*C*H$_3$). FTIR (KBr), cm^{-1}: 3049 (ν(C-H)), 2941 (ν(C_{alkyl}-H)), 2515 (ν(B-H)), 1400 (ν(N-H)). MALDI-TOF-MS (m/z): calcd. 266, found 266.

Synthesis of [N(Me)$_4$][7-Si(CH=CH$_2$)$_3$-μ-(9,10-CHC$_6$H$_5$)-*nido*-CB$_{10}$H$_{10}$ (16). The procedure was the same as for **14** using Mg (1.25 g, 0.05 mmol), a crystal of I_2 in THF

(1 mL), a solution of **3** (0.25 g, 0.76 mmol) in THF (5 mL) and dibromoethane (1.3 mL, 3.17 mmol). After 15 h at reflux **16** was obtained as a white solid by using the same work up as for **14**. Yield: 45.0 mg, 32.0%. ^{1}H NMR [$(CD_3)_2CO$]: δ 7.06 (m, 5H, C_6H_5), 6.39 (dd, ^{3}J(H,H) = 20.2, ^{3}J(H,H) = 14.6, 3H, C*H*=CH_2), 6.13 (dd, ^{3}J(H,H) = 14.6, ^{2}J(H,H) = 4.4, 3H, CH=C*H*$_2$), 5.81 (dd, ^{3}J(H,H) = 20.2, ^{2}J(H,H) = 4.4, 3H, CH=C*H*$_2$), 6.41-5.77 (m, 9H, C*H*=C*H*$_2$), 4.48 (s, 1H, C_6H_5-C*H*), 3.45 (s, 12H, [N(C*H*$_3$)$_4$]). ^{1}H{^{11}B} NMR [$(CD_3)_2CO$]: δ 7.06 (m, 5H, C_6H_5), 6.39 (dd, ^{3}J(H,H) = 20.2, ^{3}J(H,H) = 14.6, 3H, C*H*=CH_2), 6.13 (dd, ^{3}J(H,H) = 14.6, ^{2}J(H,H) = 4.4, 3H, CH=C*H*$_2$), 5.81 (dd, ^{3}J(H,H) = 20.2, ^{2}J(H,H) = 4.4, 3H, CH=C*H*$_2$), 4.48 (s, 1H, C_6H_5-C-*H*), 3.83 (br s, B-*H*), 3.45 (s, 12H, [N(C*H*$_3$)$_4$]), 2.77 (br s, B-*H*), 1.76 (br s, B-*H*), 1.56 (br s, B-*H*), 1.29 (br s, B-*H*). ^{11}B NMR [$(CD_3)_2CO$]: δ 20.0 (d, ^{1}J(B, H) = 146, 2B), 13.8 (d, ^{1}J(B, H) = 138, 1B), 2.2 (d, ^{1}J(B, H) = 133, 1B), -5.9 (d, ^{1}J(B, H) = 139, 2B), -10.0 (d, ^{1}J(B, H) = 128, 2B), -14.1. (d, ^{1}J(B, H) = 129, 2B). ^{13}C NMR [$(CD_3)_2CO$]: δ 136.2 (*C*H=CH_2), 133.0 (CH=*C*H$_2$), 128.1-124.6 (C_6H_5), 89.6 (*C*HC_6H_5), 55.1 (N(C*H*$_3$)$_4$). FTIR (KBr), cm^{-1}: 3051 (ν(C-H)), 2958 (ν(C_{alkyl}-H)), 2525 (ν(B-H)), 1431 (ν(N-H)). MALDI-TOF-MS (m/z): calcd. 328, found 327.

X-ray crystallography:

Single-crystal data collection for **1**-**3** were performed at –100ºC with an Enraf Nonius KappaCCD diffractometer using graphite monochromatized Mo K_α radiation (λ = 0.71073 Å). A total of 4252, 5982 and 7340 unique reflections were collected for **1**-**3,** respectively. The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[1] All non-hydrogen atoms were refined with anisotropic displacement parameters, but the hydrogen atoms were treated as riding atoms using the

SHELX97 default parameters. Crystallographic parameters for **1**-**3** are collected in Table 2.

Table 1.

Compound	H^a	H^b	H^c
10	6.27-6.17	6.27-6.17	5.84
11	6.22	6.34	5.92
12	5.77	6.07	5.58
13	6.34-5.79	6.34-5.79	6.34-5.79
14	6.28	6.03	5.71
15	6.39	6.13	5.81

Table 2.- Symmary of Crystallographic Data for 1-3 at 173(2) K

	1	**2**	**3**
empirical formula	$C_{14}H_{28}B_{10}Si_2$	$C_9H_{22}B_{10}Si$	$C_{14}H_{24}B_{10}Si$
formula weight	360.64	266.46	328.52
crystal habit, color	prism, colorless	block, colorless	prism, colorless
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/c$ (no. 14)	P-1 (no. 2)	$P2_1/c$ (no. 14)
a (Å)	15.8018(8)	7.7775(2)	16.7308(12)
b (Å)	10.5930(6)	14.1714(3)	13.0118(5)
c (Å)	13.4179(4)	15.9281(5)	19.7733(13)
α(deg)	90	96.034(2)	90
β (deg)	99.317(3)	103.042(2)	113.094(2)
γ (deg)	90	100.443(2)	90
V (V^3)	2216.37(18)	1662.30(8)	3959.6(4)
Z	4	4	8
ρ (g cm^{-3})	1.081	1.065	1.102
μ (cm^{-1})	1.56	1.19	1.12
no. measured reflns.	7421	10437	13072
R_{int}	0.0466	0.0262	0.0414
goodness-of-fit[a] on F^2	1.046	1.030	1.041
R[b] $[I > 2\sigma(I)]$	0.0460	0.0426	0.0535
R_w[c] $[I > 2\sigma(I)]$	0.1055	0.1070	0.1230

[a] $S = [\Sigma(w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$, [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, [c] $R_w = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

[1] Sheldrick, G. M. SHELX97. University of Göttingen, Germany, **1997.**

Modular Construction of Neutral and Anionic Carborane-Containing Carbosilane Dendrimers

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New carbosilane dendrimers containing peripheral carborane derivatives and propyl linkages between the $C_{cluster}$ and the Si atoms were synthesized. Regiospecific hydrosilylation of 1-allyl-2-Ph-1,2-$C_2B_{10}H_{10}$ (**1**) and 1-allyl-2-Me-1,2-$C_2B_{10}H_{10}$ (**2**) offers an efficient route to molecular precursors and dendrons that can provide both divergent and convergent strategies for dendritic growth. A modular construction of dendrimers containing four and eight *closo*-carboranes has been developed using different methodologies and precursors. First generations of neutral carborane-containing dendrimers were constructed by two approaches: a) a divergent approach via hydrosilylation of **1-2** with the first generation of carbosilane dendrimers containing peripheral Si-H, $Si[(CH_2)_2(CH_3)_2SiH]_4$, **1G-H**; and b) a pseudo-convergent strategy being initiated at the site that will became the periphery of the molecule, the carborane. In the latter, the hydrosilylation of the allyl group in **1**-**2** with Me_2HSiCl was carried out leading to the formation of 1-$(CH_2)_3$SiCl-2-R-$C_2B_{10}H_{10}$ (R = Ph (**3**), Me (**4**)), followed by reduction with $LiAlH_4$, and the resultant 1-$(CH_2)_3$SiH-2-R-$C_2B_{10}H_{10}$ (R= Ph (**5**), Me (**6**) was reacted with the tetravinylsilane or core molecule to yield the first generation dendrimers, **7** and **8,** with four carborane clusters. The next-generation dendrimers could be built up in a similar manner, by the hydrosilylation of the vinyl group of dendrons **9-10,** prepared from the alkylation of **3-4** with vinylmagnesium chloride, with **1G-H**. A second strategy to prepare the second generation consists in growing the carboranylsilane dendrons to a second generation and later assembling all to the core tetravinylsilane. Finally, another second generation dendrimers containing eight carborane clusters were prepared by hydrosilylation of the vinyl groups in the dendrimer $Si\{(CH_2)_2(CH_3)Si[(CHCH_2)_2\}_4]$ with carboranylsilane dendrons containing Si-H functions. Degradation reaction of the peripheral *closo*-carboranes in dendrimers **7** and **8** using KOH/EtOH led to the formation of the corresponding polianionic carbosilane dendrimers containing four peripheral *nido*-carborane clusters.

Introduction

Dendrimers are hyperbranched and mono-dispersed macromolecules, which emanate from a central core and are obtained by an iterative sequence of reactions steps.[1] Their well-defined size, molecular weight, internal connectivity and specific number of end groups give access to dendritic macromolecules having special properties and a variety of functions.[2] Nowadays, dendrimers are widely investigated as supports for functional groups and metal fragments, which can be localized in the core or at the periphery. The incorporation of metals in dendritic structures has attracted growing interest as it generates new metallodendrimers with interesting redox, magnetic, and photo-optical properties.[3] Transition metal catalysis based on functionalized dendrimers is another very promising application of dendrimers.[4,5] These have inspired many chemists to develop new materials and several applications have been explored, e.g. in industry as novel catalysts and materials for molecular electronic devices and light energy conversion, in medicine and in other fields. To medicine dendrimers are substances whose possible applications as diagnostic, or even as therapeutic agents in BNCT[6] have been discussed and studied.[7] The fast growing area of dendrimer chemistry is still young, and the first synthesis of dendritic macromolecules has been only 30 years ago.[8]

Although the field of carboranes chemistry and their applications has been developed for over 40 years,[9,10,11] few carborane-containing dendrimers have been reported.[12]

In view of the availability of carbosilane dendrimers[13] as inert scaffolds for attaching carborane derivatives on the periphery and the versatility of carborane cluster for synthesis and application, we have started using several strategies to functionalize the surface of star-shaped carbosilanes incorporating carboranes by Si-$C_{cluster}$ direct bonds.[14] To our opinion, these systems have provide an interesting example, from the scientific point of view, for testing the reactivity of the carborane derivatis towards

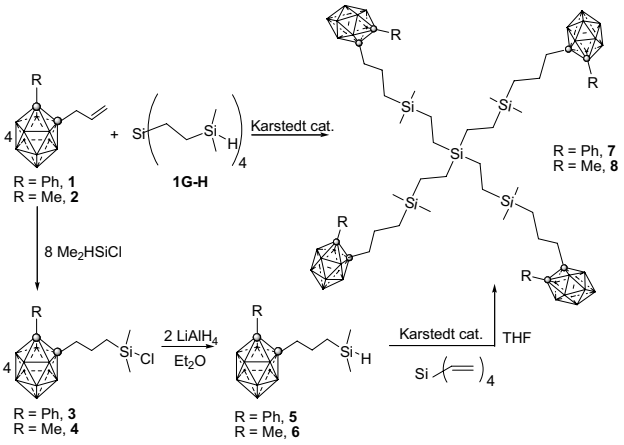
different organosilanes and for testing their reactivity as hydrosilylating agents. However, due to the sensibility of the C_c-Si bond to the nucleophilic attack, they also present a restraint for further reactions on the peripheral cluster.

Pursuing our work dealing with the preparation, functionalization and study of reactivity of carborane-containing carbosilane dendrimers, we have prepared a family of dendrimers, in which *o*-carborane derivatives are bonded to the Si atom through an alkyl spacer. For this purpose, we have used the *divergent* routine or alternatively a *pseudo-convergent* strategy, for which a set of carboranyl compounds have been synthesized to be used as branched subunits that are attached at the end to a core molecule. Thus, the new approach to functionalize carboranylsilane monodendrons described below could be adapted to assembly of other dendrimeric systems and uses as coupling point. Furthermore, the new carborane-containing dendrimeric compounds allow the modification and degradation of the cluster located at the periphery, leading to new polianionic species, which we expect endured a further metallation.

Results and Discussion

Preparation of First Generations of Carboranyl-Containing Carbosilane Dendrimers. Dendritic carbosilanes are generally prepared using the divergent approach by successive allylation (using alkylated agents) and hydrosilylation steps (using silanes as hydrosilylating agents),[13] although a convergent strategy has also been used to attach dendritic carbosilane fragment to core systems.[15] With this idea, we have developed carboranylsilane monodendrons in order to used as source in different synthetic paths for the construction of carboranyl-containing first and second generation of dendrimer synthesis. Thus, precursors **1-2** were prepared from the reaction of the monolithium salts of the corresponding carboranes; 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ and 1-CH_3-1,2-$C_2B_{10}H_{11}$ respectively, with the stoichiometric amount of ($CH_2CH{=}CH_2$)Br in a Et_2O/toluene solution at room temperature, to give crystalline air-stable solids in 82 and 88 % yield, respectively. The presence of the allyl function allows the platinum-catalyzed hydrosilylation with $(CH_3)_2HSiCl$, that is carried out in the absence of solvent at room temperature for four hours, to give chloroterminated carboranylsilane monodendrons **3** and **4**, respectively (Scheme 1). The ^1H NMR olefinic resonances were used to follow the complete hydrosilylation reaction by the disappearance of the double bonds protons. Subsequent reduction of the Si-Cl functions in carboranyl-chlorosilanes **3-4** was carried out with lithium tetrahydroaluminate, $Li[AlH_4]$, in Et_2O at room temperature overnight to give **5-6** in 93-72 % yield, as analytical and spectroscopically pure oils (Scheme 1). In order to obtain the first generation of carboranyl-containing carbosilane dendrimers, two different approaches have been used: a) hydrosililation reaction of precursors **1-2** with the previously prepared **1G-H**; b) hydrosililation of tetravinylsilane using **5-6** as hydrosilylating agents. For the first method, $Si[(CH_2)_2(CH_3)_2SiH]_4$, **1G-H**[13a] was synthesized according to literature procedures, the subsequent reaction of this with compounds **1-2** in the presence of Karstedt catalyst, at room temperature for 48 hours and after workup, gave dendrimers **7-8**, respectively (Scheme 1). Using the second way, **7-8** were also obtained in higher yield (99%), by platinum-catalyzed hydrosilylation of tetravinylsilane with **5-6** in toluene, at room temperature overnight. The second method is faster and cleaner and affords **7-8** in higher yield (Scheme 1).

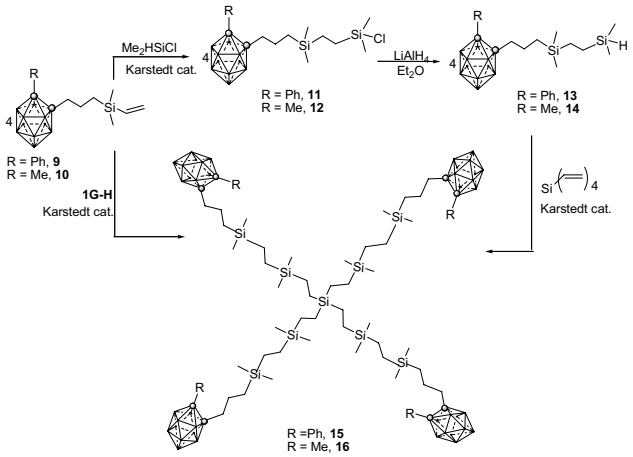
Scheme 1. Preparation of the Carboranyl-Containing First Generation Dendrimers **7** and **8** using two different approaches



Preparation of Second Generations of Carboranyl-Containing Carbosilane Dendrimers. To prepare second generation dendrimers we have used several approaches, in order to obtain dendrimers with four and eight clusters. In a first time, we have used a *pseudo-convergent* method which consists in growing the monodendrons **3-4** using a repetitive sequence of alquenilation, hydrosilylation an reduction reactions. Thus, he reaction of compounds **3-4** with vinylmagnesium chloride in THF, at room temperature overnight gave the corresponding vinyl-carborane derivatives **9-10** as yelow oils (Scheme 2). The subsequent hydrosilylation reaction of **9-10** with Me_2HSiCl in the presence of Karstedt catalyst, at room temperature for 12 and 2 hours, respectively, led to the formation of **11-12** in exceptional high yield (> 99%). The reduction of the Si-Cl function in **11-12** with $LiAlH_4$ in an ether solution gave after workup reaction the carboranyl-silane derivatives **13-14** (Scheme 2).

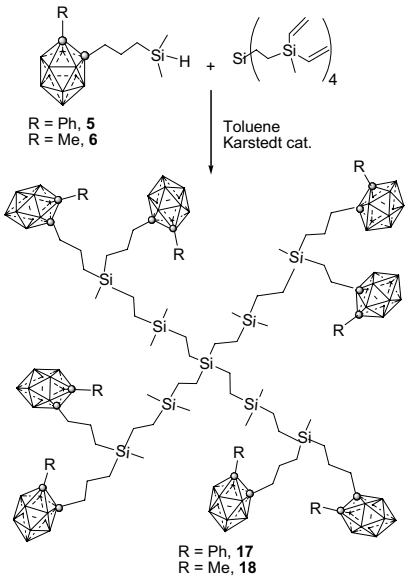
Finally, a solvent free platinum-catalyzed hydrosilylation reaction of tetravinylsilane with **13-14**, at room temperature overnight, led to the formation of the second generation dendrimer **15** and **16**, respectively as yellow oils (Scheme 2). A second method used to obtain dendrimers **15-16** consists in the reaction of vinyl-carborane derivatives **9** and **10** with a freshly prepared **1G-H** in the presence of Karstedt catalyst overnight. Both methods provide compounds **15-16** in very high yield.

Scheme 2. Preparation of Carboranyl-Containing Second Generation Dendrimers with Four Peripheral Clusters, **15-16**.



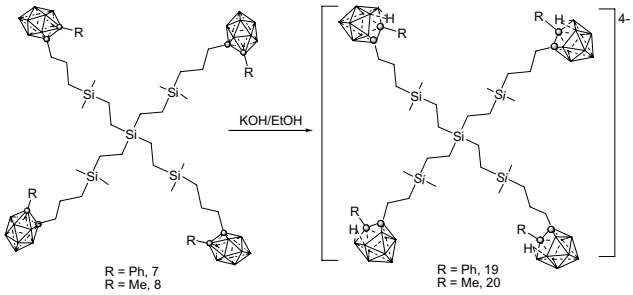
Two second generation dendrimers containing eight peripheral carborane clusters have been prepared from the reaction of compound **5** and **6** with the dendrimer **1G-(CH=CH$_2$)$_2$**,[13e] which contains two vinyl function in each branch. The hydrosilylation reaction of **5-6** on the dendrimer is carried out in toluene using Kartestd as catalyst, at room temperature overnight (Scheme 3). After workup, dendrimers **17** and **18**, respectively, were obtained as yellow oils in relative high yield.

Scheme 3. Preparation of Carboranyl-Containing Second Generation Dendrimers with Eight Peripheral Clusters, **17-18**.



Preparation of Carboranyl-Containing Polianionic Carbosilane Dendrimers. In this work we present the preliminary results in the preparation of polianionic dendrimers from carboranyl-containing carbosilane dendrimers. For this purpose, the degradation reaction of peripheral carboranes incorporated in dendrimers **7** and **8** was achieved, using KOH/EtOH at reflux for several hours (Scheme 4). The nucleofilic attack of the EtO$^-$ ion on the cluster caused its degradation obtaining the corresponding anionic *nido* species, without alteration of the dendrimeric structure. Thus, polianionic compounds **19-20** were isolated and purified as tetramethylammonium salts in very good yield. It is important to notice that the presence of the alkyl spacer between the $C_{cluster}$ and the Si atom allows to prove the reactivity of the cluster towards nucleophiles and open the way to the modification and metallation of the cluster in order to obtain metallodendrimers.

Scheme 4. Preparation of Carboranyl-Containing Polianionic Carbosilane Dendrimers, **19-20**.



Characterization of Precursors and Dendrimers. The structures of compounds **1-20** were established on the basis of elemental analysis, IR, ^{1}H, ^{13}C, ^{11}B, ^{29}Si NMR and mass spectroscopies and for 1-2 unequivocally confirmed by X-ray diffraction analysis. The IR spectra of **1-18** present typical υ(B-H) strong bands for *closo* clusters between 2570 and 2590 cm^{-1}, and intense bands near 1255 cm^{-1} corresponding to δ(Si-CH$_3$). For compounds **5**, **6**, **13** and **14** a characteristic band at 2110 cm^{-1} corresponding to υ(Si-H) was also observed. For anionic **19-20** the υ(B-H) appears around 2517 cm^{-1}, which is typical for *nido* clusters. The ^{1}H NMR spectra for **1-2** exhibit resonances for allyl protons in the region 5.80-4.75 ppm, while **9-10** present the vinyl protons in the region 6.15-5.58 ppm. The allyl and vinyl protons have been used to follow the complete hydrosililation and to check the formation of corresponding products. The ^{1}H NMR spectra of 3-18 exhibit resonances for Si-CH$_3$ protons in the region -0.15 to 0.45 ppm and methylene protons between 0.25 and 0.56 ppm, which has been unambiguously assigned to the corresponding protons, in the majority of cases. In these compounds the C_c-CH$_2$ protons appear at lower field due to the electron-withdrawing character of the *closo*-cluster. Contrarily, for anionic **19-20**, these protons are shifted to higher field, respect to the *closo*-precursors 7-8, due to the electro-donor character of the *nido*-cluster. Additionally, for compounds **5**, **6**, **13** and **14**, the presence of Si-H bonds in the molecule was confirmed by a multiplet displayed between 3.89 and 3.70 ppm. The ^{13}C{^{1}H} NMR spectra shows resonances for $C_{cluster}$ from 83.5 to 80.6 ppm for the Ph-carborane derivatives and between 78.2 and 74.4 ppm for the Me-carborane derivatives. The Si-*C*H$_3$ carbons appear in a wide range of the ^{13}C NMR spectrum, between -4.9 and 1.5 ppm, depending on the other substitutents at

the Si atom. Finally, the CH_2 carbons are exhibited in the region 39.0 (for C_c-*C*H_2) and 2.6 ppm (Si-*C*H_2). The position for C_c-*C*H_2 is very similar for monomers or dendrimers, however, the Si-*C*H_2 chemical shifts depend on the type of compounds and substituent at the Si atom.

The $^{11}B\{^1H\}$ NMR resonances for compounds **1-18** appear in the *closo* region,[16] from δ -3.8 to -10.52 ppm. Without exception, all compounds containing 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ present broad underhanded bands with the pattern 2:8, while derivative compounds of 1-CH_3-1,2-$C_2B_{10}H_{11}$ show the general patterns 1:1:8 or 1:1:3:5. Contrarily, the ^{11}B resonances of *nido*-compounds **19-20** appear in the typical region of *nido*-carboranes between -6.0 and -35.0 ppm with the pattern 1:1:1:4:1:1.

The $^{29}Si\{^1H\}$ NMR spectra of compounds **3-6** and **9-10** exhibit an unique signal whose chemical shift depended on the substituents on the Si atom. The resonances for Si-Cl appear around δ = 30.4 ppm, the Si-H resonances are observed at higher field, about δ = -14.0 ppm, and the Si-C=C are exhibited at -6.3 ppm. For first generation neutral dendrimers **7-8** the $^{29}Si\{^1H\}$ NMR spectra exhibit two signals, whereas for second generation dendrimers **15-18** three resonances are observed. All resonances are assigned on the basis of the chemical shifts and the peak intensities. For all dendrimers the Si_{core} appears in the region 7.26-9.05 ppm, whereas the $Si_{periphery}$ are exhibited in a close interval, between 3.32 and 3.56 ppm. Additionally, the spectra of **15-18** exhibit a third peak in the region 5.05-7.26 ppm corresponding to the branch Si-C. Finally, for anionic dendrimers **19-20**, the ^{29}Si NMR spectra show two signals corresponding to the $Si_{core,}$ at 8.54 and 9.47 ppm, respectively and to the $Si_{periphery}$ at 2.97 and 4.06 ppm.

X-ray Crystal Structures of 1 and 2. Precursors **1** and **2** were isolated as monocrystals suitable for X-ray structural determination from a solution of Et_2O. The molecular structures of **1** and **2** are presented in Figure 1.

Figure 1. Molecular structures of precursors **1** and **2**.

Conclusions

Carborane derivatives **1-2** that contain one *exo*-cluster allyl function have shown to be good precursors for a modular construction of carboranyl-containing carbosilane dendrons and dendrimers. Different synthetic strategies using divergent and convergent steps have been developed in order to obtain neutral first and second generation dendrimers, **7**, **8**, **15** and **16**, which contain four peripheral carborane clusters linked to the Si atoms though a propyl chain. Additionally, two neutral second deneration carbosilane dendrimers peripherally functionalized with eight carborane cluster, **17-18**, have also been prepared. The degradation of *closo*-carborane to the corresponding *nido*-species was performed using the EtO^- as nucleophiles, leading to the formation of polianionic carboranyl-containing carbosilane dendrimers. Thus the versatility of the carboranes have provide the development of several ways to prepared different king of carborane-containing carbosilane dendrimers.

Experimental Section

Instrumentation. Microanalyses were performed in the analytical laboratory using a Carlo Erba EA1108 microanalyser. 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 a ions trap analyzer. 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 22ºC. 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-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. $(CH_3)_2HSiCl$ and Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex, 2.1-2.4% platinum in vinyl terminated polydimethylsiloxane in xylene solution) were purchased from ABCR and used as received. The $[Si(CH{=}CH_2)_4]$ was purchased from Across. The n-BuLi solution (1.6M in hexanes) was purchased from Lancaster or Aldrich and CH_2=CHMgCl from Aldrich. Dendrimers $Si[(CH_2)_2(CH_3)_2SiH]_4$, **1G-H** and $Si\{(CH_2)_2(CH_3)Si[(CHCH_2)_2\}_4]$, **1G-(CH=CH$_2$)$_2$** were prepared according to the literature.[13a,e]

Synthesis of 1-C_6H_5-2-$CH_2CH{=}CH_2$-1,2-$C_2B_{10}H_{10}$ (1). To a solution of 1-C_6H_5-$C_2B_{10}H_{11}$ (0.50 g, 2.3 mmol) a mixture toluene (7 mL) and diethyl ether (3.5 mL) at 0 ºC, was added dropwise a solution of *n*-BuLi 1.6 M in hexane (1.5 mL, 2.4 mmol). The mixture was stirred for 1 h at room temperature, cooled again at 0 ºC, and (CH_2=CH-CH_2)Br (0.2 mL, 2.3 mmol) was added. The mixture was stirred for 2 h at room temperature and refluxed overnight. Next, the mixture was warmed at room temperature, quenched with 20 mL of water, transferred to a separatory

funnel and extracted with Et_2O (3 x 10 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuo to obtain compound **1** as a white solid. Yield: 0.52 g, 88 %. An Et_2O solution of **1** gave single crystals suitable for X-ray analysis. ^{1}H NMR: δ 7.68-7.36 (m, 5H, C_6H_5), 5.65 (ddt, ^{3}J(H,H) = 16.7, ^{3}J(H,H) = 10.0, ^{3}J(H,H) = 7.3, 1H, CH_2CH=CH_2), 5.05 (d, ^{3}J(H,H) = 10.0, 1H, CH_2CH=CH_2), 4.75 (d, ^{3}J(H,H) = 16.7, 1H, CH_2CH=CH_2), 2.57 (d, ^{3}J(H,H) = 7.32, 2H, CH_2CH=CH_2). ^{1}H{^{11}B} NMR: δ 7.68-7.36 (m, 5H, C_6H_5), 5.65 (ddt, ^{3}J(H,H) = 16.7, ^{3}J(H,H) = 10.0, ^{3}J(H,H) = 7.3, 1H, CH_2CH=CH_2), 5.05 (d, ^{3}J(H,H) = 10.0, 1H, CH_2CH=CH_2), 4.75 (d, ^{3}J(H,H) = 16.7, 1H, CH_2CH=CH_2), 2.76 (br s, B-*H*), 2.57 (d, ^{3}J(H,H) = 7.3, 2H, CH_2CH=CH_2), 2.38 (br s, B-*H*), 2.28 (br s, B-*H*). ^{11}B NMR: δ -3.8 (d, ^{1}J(B,H) = 147, 2B), -10.5 (8B). ^{13}C{^{1}H} NMR: δ 132.4 (CH_2CH=CH_2), 131.3 (Ph-C_{meta}), 130.7 (Ph-C_{ortho}), 130.5 (Ph-C_{ipso}), 128.8 (Ph-C_{para}), 119.3 (CH_2CH=CH_2), 83.2 (C_c), 80.6 (C_c), 39.2 (CH_2CH=CH_2). FTIR (KBr), cm^{-1}: 3084 (ν (C=H)), 2967, 2927 (ν (C_{alkyl}-H)), 2575 (ν (B-H)). Anal. Calcd. for $C_{11}H_{20}B_{10}$: C, 50.74; H, 7.74. Found: C, 50.36; H 7.61.

Synthesis of 1-CH_3-2-CH_2CH=CH_2-1,2-$C_2B_{10}H_{10}$ (2). The procedure was the same as for 1 using 1.00 g (6.32 mmol) of 1-CH_3-1,2-$C_2B_{10}H_{11}$ in toluene (14 mL) and Et_2O (7 mL), 4.1 mL (6.56 mmol) of 1.6 M solution of *n*-BuLi in hexane and 0.55 mL (6.33 mmol) of (CH_2=CH-CH_2)Br. The mixture was stirred for 2 hours at room temperature and refluxed overnight. The workup was the same as for 1 to give **2** as a yellow oil. Yield: 1.02 g, 82 %. An Et_2O solution of **2** gave single crystals suitable for X-ray analysis. ^{1}H NMR: δ 5.78 (ddt, ^{3}J(H,H) = 16.8, ^{3}J(H,H) = 10.0, ^{3}J(H,H) = 7.2, 1H, CH_2CH=CH_2), 5.21 (d, ^{3}J(H,H) = 10.0, 1H, CH_2CH=CH_2), 5.13 (d, ^{3}J(H,H) = 16.8, 1H, CH_2CH=CH_2), 2.97 (d, ^{3}J(H,H) = 7.2, 2H, CH_2CH=CH_2), 2.03 (s, 3H, C_c-CH_3). ^{1}H{^{11}B} NMR: δ 5.78 (ddt, ^{3}J(H,H) = 16.8, ^{3}J(H,H) = 10.0, ^{3}J(H,H) = 7.2, 1H, CH_2CH=CH_2), 5.21 (d, ^{3}J(H,H) = 10.0, 1H, CH_2CH=CH_2), 5.13 (d, ^{3}J(H,H) = 16.8, 1H, CH_2CH=CH_2), 2.97 (d, ^{3}J(H,H) = 7.2, 2H, CH_2CH=CH_2), 2.26 (br s, B-*H*), 2.21 (br s, B-*H*), 2.14 (br s, B-*H*), 2.03 (s, 3H, C_c-CH_3). ^{11}B NMR: δ -2.9 (d, ^{1}J(B,H) = 124, 1B), -4.1 (d, ^{1}J(B,H) = 135, 1B), -8.2 (br s, 3B), -9.1 (d, ^{1}J(B,H) = 143, 5B). ^{13}C{^{1}H} NMR: δ 132.5 (CH_2CH=CH_2), 119.5 (CH_2CH=CH_2), 78.1 (C_c), 74.4 (C_c), 39.6 (CH_2CH=CH_2), 23.0 (C_c-CH_3). FTIR (NaCl), cm^{-1}: 3086 (ν (C=H)), 2987, 2947 (ν (C_{alkyl}-H)), 2586 (ν (B-H)). Anal. Calcd. for $C_6H_{18}B_{10}$: C, 36.34; H, 9.15. Found: C, 36.42; H, 9.25.

Synthesis of 1-C_6H_5-2-[$CH_2CH_2CH_2(CH_3)_2SiCl$]-1,2-$C_2B_{10}H_{10}$ (3). In a Schlenk flask, 1 (0.32 g, 1.23 mmol), $(CH_3)_2HSiCl$ (0.3 mL, 2.56 mmol) and Karstedt catalyst (5 µl, 0.01 mmol) were mixed and stirred for 4 h at room temperature. Evaporation of volatiles and the excess of $(CH_3)_2HSiCl$ gave **3** as a yellow oil. Yield: 0.43 g, > 99 %. ^{1}H NMR: δ 7.67-7.41 (m, 5H, C_6H_5), 1.84 (t, ^{3}J(H,H) = 7.5, 2H, C_c-CH_2), 1.52 (m, 2H, $CH_2CH_2CH_2$), 0.60 (t, ^{3}J(H,H) = 8.1, 2H, Si-CH_2), 0.31 (s, 6H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 7.67-7.41 (m, 5H, C_6H_5), 2.73 (br s, 2H, B-*H*), 2.36 (br s, 6H, B-*H*), 2.27 (br s, 2H, B-*H*), 1.84 (t, ^{3}J(H,H) = 7.5, 2H, C_c-CH_2), 1.52 (m, 2H, $CH_2CH_2CH_2$), 0.60 (t, ^{3}J(H,H) = 8.1, 2H, Si-CH_2), 0.31 (s, 6H, Si-CH_3). ^{11}B NMR: δ -3.6 (d, ^{1}J(B,H) = 145, 2B), -10.5 (br s, 8B). ^{13}C{^{1}H} NMR: δ 131.1-128.9 (C_6H_5), 83.5 (C_c), 81.9 (C_c), 37.8 (C_c-CH_2), 23.1 ($CH_2CH_2CH_2$), 18.4 (SiCH_2), 1.5 (Si-CH_3). ^{29}Si{^{1}H} NMR: δ 30.42.

Synthesis of 1-CH_3-2-[$CH_2CH_2CH_2(CH_3)_2SiCl$]-1,2-$C_2B_{10}H_{10}$ (4). The procedure was the same as for compounds **3** using **2** (0.64 g, 3.21 mmol), $(CH_3)_2HSiCl$ (0.75 mL, 6.42 mmol) and Karstedt catalyst (10 µl, 0.02 mmol). The mixture was stirred under N_2 for 5 h at room temperature. Evaporation of volatiles gave **4** as a yellow oil. Yield: 0.94 g, > 99 %. ^{1}H NMR: δ 2.24 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 2.03 (s, 3H, C_c-CH_3), 1.70 (quint., ^{3}J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.85 (t, ^{3}J(H,H) = 8.1, 2H, Si-CH_2), 0.45 (s, 6H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 2.26 (br s, B-*H*), 2.20 (br s, B-*H*), 2.17 (br s, B-*H*), 1.70 (quint., ^{3}J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.85 (t, ^{3}J(H,H) = 8.13, 2H, Si-CH_2), 0.45 (s, 6H, Si-CH_3). ^{11}B NMR: δ -2.9 (d, ^{1}J(B,H) = 132, 1B), -4.2 (d, ^{1}J(B,H) = 144, 1B), -9.1 (d, ^{1}J(B,H) = 139, 8B). ^{13}C{^{1}H} NMR: δ 77.7 (C_c), 74.6 (C_c), 38.1 (C_c-CH_2), 23.3 ($CH_2CH_2CH_2$), 23.2 (C_c-CH_3), 18.6 (CH_2-Si), 1.6 (Si-CH_3). ^{29}Si{^{1}H} NMR: δ 30.45.

Synthesis of 1-C_6H_5-2-[$CH_2CH_2CH_2(CH_3)_2SiH$]-1,2-$C_2B_{10}H_{10}$ (5). To a solution of $LiAlH_4$ (38.0 mg, 1.00 mmol) in Et_2O (16 mL) at 0 ºC was added dropwise a solution of **3** (0.70 g, 1.98 mmol) in Et_2O (8 mL). The mixture was stirred for 15 h at room temperature and filtered off through Celite twice. The solvent was removed *in vacuo* to give **5** as a transparent oil. Yield: 0.59 g, 93 %. ^{1}H NMR: δ 7.65-7.39 (m, 5H, C_6H_5), 3.70 (m, 1H, Si-*H*), 1.81 (t, ^{3}J(H,H) = 8.5, 2H, C_c-CH_2), 1.45 (tt, ^{3}J(H,H) = 8.5, ^{3}J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.37 (td, ^{3}J(H,H) = 8.1, ^{3}J(H,H) = 3.2, 2H, Si-CH_2), -0.02 (d, ^{3}J(H,H) = 3.7, 6H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 7.65-7.39 (m, 5H, C_6H_5), 3.70 (m, 1H, Si-*H*), 2.73 (br s, 2H, B-*H*), 2.36 (br s, 6H, B-*H*), 2.25 (br s, 2H, B-*H*), 1.81 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 1.45 (tt, ^{3}J(H,H) = 8.5, ^{3}J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.37 (td, ^{3}J(H,H) = 8.1, ^{3}J(H,H) = 3.2, 2H, Si-CH_2), -0.02 (d, ^{3}J(H,H) = 3.7, 6H, Si-CH_3). ^{11}B NMR: δ -2.3 (d, ^{1}J(B,H) = 146, 2B), -9.1 (d, ^{1}J(B,H) = 121, 8B). ^{13}C{^{1}H} NMR: δ 131.1-128.9 (C_6H_5), 83.5 (C_c), 82.4 (C_c), 38.1 (C_c-CH_2), 24.5 (CH_2), 13.8 (Si-CH_2), -4.7 (Si-CH_3). ^{29}Si{^{1}H} NMR: δ -14.10. FTIR (NaCl), cm^{-1}: 3065 (ν (C_{aryl}-H)), 2957 (ν (C_{alkyl}-H)), 2590 (ν (B-H)), 2114 (ν (Si-H)), 1252 (δ (Si-CH_3)).

Synthesis of 1-CH_3-2-[$CH_2CH_2CH_2(CH_3)_2SiH$]-1,2-$C_2B_{10}H_{10}$ (6). The process was the same as for compound **5** using $LiAlH_4$ (25.5 mg, 0.61 mmol) in Et_2O (8 mL) and **4** (0.36 g, 1.22 mmol) in Et_2O (2 mL). The mixture was stirred for 15 h at room temperature and filtered off through Celite three times. The solvent was removed *in vacuo* to give **6** as a transparent oil. Yield: 0.23 g, 72 %. ^{1}H NMR: δ 3.89 (m, 1H, Si-*H*), 2.20 (t, ^{3}J(H,H) = 8.5, 2H, C_c-CH_2), 2.02 (s, 3H, C_c-CH_3), 1.62 (tt, ^{3}J(H,H) = 8.5, ^{3}J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.61 (td, ^{3}J(H,H) = 8.1 ^{3}J(H,H) = 3.2, 2H, Si-CH_2), 0.11 (d, ^{3}J(H,H) = 3.7, 6H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 3.89 (m, 1H, Si-*H*), 2.25 (br s, B-*H*), 2.20 (t, ^{3}J(H,H) = 8.5, 2H, C_c-CH_2), 2.10 (br s, B-*H*), 2.02 (s, 3H, C_c-CH_3), 1.62 (tt, ^{3}J(H,H) = 8.5, ^{3}J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.61 (td, ^{3}J(H,H) = 8.1 ^{3}J(H,H) = 3.2, 2H, Si-CH_2), 0.11 (d, ^{3}J(H,H) = 3.7, 6H, Si-CH_3). ^{11}B NMR: δ -2.9 (d, ^{1}J(B,H) = 130, 1B), -4.2 (d, ^{1}J(B,H) = 140, 1B), -8.3 (br s, 3B), -9.1 (d, ^{1}J(B,H) = 145, 5B).

$^{13}C\{^1H\}$ NMR: δ 78.1 (C_c), 74.7 (C_c), 38.4 (C_c-CH_2), 24.8 ($CH_2CH_2CH_2$), 23.1 (C_c-CH_3), 14.0 (Si-CH_2), -4.5 (Si-CH_3). $^{29}Si\{^1H\}$ NMR: δ -14.07. FTIR (NaCl), cm^{-1}: 2957-2901 (ν (C_{alkyl}-H)), 2588 (ν (B-H)), 2114 (ν (Si-H)), 1252 (δ (Si-CH_3)).

Synthesis of 1G-$CH_2CH_2CH_2$-Phenyl-*o*-carborane (7). *Method A*: In a Schlenk flask, **1** (0.55 g, 2.12 mmol), **1G-H** (0.20 g, 0.53 mmol) and one drop of Karstedt catalyst were mixed and stirred for 1 h. Next, THF (0.5 mL) was added to the mixture and stirred for 48 h at room temperature. The volatiles were evaporated in the vacuum line to obtain a yellowish oil, which was treated with petroleum ether. An insoluble oily product was formed, separated from the solution and treated with acetonitrile. The insoluble part was separated, and the solution was evaporated to give **7** as a yellowish oil. Yield: 0.27 g, 36 %. *Method B*: In a Schlenk flask, **5** (0.11 g, 0.36 mmol), $Si(CH=CH_2)_4$ (16 μL, 0.09 mmol), one drop of Karstedt catalyst and 0.1 mL of THF. The mixture was stirred overnight, and solvent removal afforded the product **7** as a yellowish oil. Yield: 0.13 g, 99 %. ^1H NMR: δ 7.66-7.40 (m, 20H, C_6H_5), 1.78 (t, $^3J(H,H)$ = 8.1, 8H, C_c-CH_2), 1.39 (m, 8H, $CH_2CH_2CH_2$), 0.29 (m, 24H, $SiCH_2CH_2SiCH_2$), -0.12 (s, 24H, Si-CH_3). $^1H\{^{11}B\}$ NMR: δ 7.66-7.40 (m, 20H, C_6H_5), 2.72 (br s, 8H, B-*H*), 2.37 (br s, 24H, B-*H*), 2.25 (br s, 8H, B-*H*), 1.78 (t, $^3J(H,H)$ = 8.1, 8H, C_c-CH_2), 1.39 (m, 8H, $CH_2CH_2CH_2$), 0.29 (m, 24H, $SiCH_2CH_2SiCH_2$), -0.12 (s, 24, Si-CH_3). ^{11}B NMR: δ -2.1 (d, $^1J(B,H)$ = 136, 8B), -8.9 (d, $^1J(B,H)$ = 121, 32B). $^{13}C\{^1H\}$ NMR: δ 131.1-129.9 (C_6H_5), 83.4 (C_c), 82.4 (C_c), 38.6 (C_c-CH_2), 24.2 ($CH_2CH_2CH_2$), 14.5 (Si-CH_2), 7.1 (Si-CH_2CH_2-Si), 2.6 (Si-CH_2CH_2-Si), -4.0 (Si-CH_3). $^{29}Si\{^1H\}$ NMR: δ 9.05 (Si_{core}), 3.32 ($Si_{periphery}$). FTIR (NaCl), cm^{-1}: 3063 (ν (C_{aryl}-H)), 2957-2901 (ν (C_{alkyl}-H)), 2585 (ν (B-H)), 1252 (δ (Si-CH_3)). MS-electrospray (ESI), solution of $CHCl_3/CH_3OH$ (1:1) *m/z*: calcd for $C_{60}H_{124}B_{40}Si_5$, 1418.5; found, 1454.2 $[(M + 2H_2O)^-$, 100%].

Synthesis of 1G-$CH_2CH_2CH_2$-Methyl-*o*-carborane (8). *Method A*: In a Schlenk flask, **2** (0.13 g, 0.64 mmol), **1G-H** (60.2 mg, 0.16 mmol) and one drop of Karstedt catalyst were mixed and stirred for 48 h. The volatiles were evaporated in the vacuum line to obtain a yellowish oil, which was treated with acetonitrile. An insoluble oily product was formed and separated from the solution. Solvent removal afforded the product **8** as a yellow oil. Yield: 51.4 mg, > 37 %. *Method B*: The procedure was the same as for **7** using **6** (0.25 g, 0.97 mmol), $Si(CH=CH_2)_4$ (40 μL, 0.24 mmol), one drop of Karstedt catalyst. The mixture was stirred for 5 min, then THF (1 mL) was added. The mixture was stirred for 5 h, and solvent removal afforded the product **8** as a yellowish oil. Yield: 1.13 g, 99 %. ^1H NMR: δ 2.21 (t, $^3J(H,H)$ = 8.1, 8H, C_c-CH_2), 2.01 (s, 12H, C_c-CH_3), 1.56 (m, 8H, $CH_2CH_2CH_2$), 0.54 (t, $^3J(H,H)$ = 8.5, 8H, Si-CH_2), 0.39 (m, 16H, $SiCH_2CH_2Si$), 0.02 (s, 24H, Si-CH_3). $^1H\{^{11}B\}$ NMR: δ 2.24 (br s, B-*H*), δ 2.21 (t, $^3J(H,H)$ = 8.1, 8H, C_c-CH_2), 2.01 (s, 12H, C_c-CH_3), 1.56 (m, 8H, $CH_2CH_2CH_2$), 0.54 (t, $^3J(H,H)$ = 8.5, 8H, Si-CH_2), 0.39 (m, 16H, $SiCH_2CH_2Si$), 0.02 (s, 24H, Si-CH_3). ^{11}B NMR: -3.0 (4B), -4.7 (d, $^1J(B,H)$ = 145, 8B), -9.1 (d, $^1J(B,H)$ = 137, 32B). $^{13}C\{^1H\}$ NMR: 78.1 (C_c), 74.6 (C_c), 38.9 (C_c-CH_2), 24.4 ($CH_2CH_2CH_2$), 23.1 (C_c-CH_3), 14.7 (Si-CH_2), 7.2 (Si-CH_2CH_2-Si), 2.7 (Si-CH_2CH_2-Si), -3.9 (Si-CH_3). $^{29}Si\{^1H\}$ NMR: 8.54 (Si_{core}), 3.58 ($Si_{periphery}$). FTIR (NaCl), cm^{-1}: 2953,2903 (ν (C_{alkyl}-H)), 2588 (ν (B-H)), 1250 (δ (Si-CH_3)). MALDI-TOF-MS (m/z): calcd for $C_{40}H_{116}B_{40}Si_5$: 1170.3; found, 1168.9 $[M-1]^-$, 910.75 $[M-Si(CH_3)_2CH_2CH_2CH_2(C_3B_{10}H_{13})]^-$, 527.5 $[M-CH_2CH_2Si(CH_3)_2CH_2CH_2CH_2(C_3B_{10}H_{13})]^-$, 194.0 $[CH_2CH_2CH_2(C_3B_{10}H_{13})]^-$, 169.0 $[CH_2(C_3B_{10}H_{13})]^-$, 156 $[C_3B_{10}H_{13}]^-$.

Synthesis of 1-C_6H_5-2-[$CH_2CH_2CH_2(CH_3)_2SiCH=CH_2$]-1,2-$C_2B_{10}H_{10}$ (9). A solution of **3** (0.21 g, 0.80 mmol) in 6 mL of THF was dropwisely added into a solution of vinyl magnesium chloride (0.5 mL, 0.81 mmol). The mixture was refluxed overnight. Next, the solvent was removed *in vacuo* and dry hexane (6 mL) was added. The suspension was filtered off through Celite and the solvent was removed to give **9** as a yellow oil. Yield: 0.22 mg, 81 %. ^1H NMR: δ 7.66-7.38 (m, 5H, C_6H_5), 6.05-5.87 (m, 2H), 5.58 (m, 1H), 1.79 (t, $^3J(H,H)$ = 8.1, 2H, C_c-CH_2), 1.41 (tt, $^3J(H,H)$ = 8.1, 2H, $CH_2CH_2CH_2$), 0.34 (t, $^3J(H,H)$ = 8.1, 2H, Si-CH_2), -0.03 (s, 6H, Si-CH_3). $^1H\{^{11}B\}$ NMR: δ 7.66-7.38 (m, 5H, C_6H_5), 6.05-5.87 (m, 2H), 5.58 (m, 1H), 2.72 (br s, 2H, B-*H*), 2.36 (br s, 6H, B-*H*), 2.40 (br s, 2H, B-*H*), 1.79 (t, $^3J(H,H)$ = 8.1, 2H, C_c-CH_2), 1.41 (tt, $^3J(H,H)$ = 8.1, 2H, $CH_2CH_2CH_2$), 0.34 (t, $^3J(H,H)$ = 8.1, 2H, Si-CH_2), -0.03 (s, 6H, Si-CH_3). ^{11}B NMR: δ -2.2 (d, $^1J(B,H)$ = 146, 2B), -9.0 (d, $^1J(B,H)$ = 127, 8B). $^{29}Si\{^1H\}$ NMR: δ -6.30.

Synthesis of 1-CH_3-2-[$CH_2CH_2CH_2(CH_3)_2SiCH=CH_2$]-1,2-$C_2B_{10}H_{10}$ (10). The process was the same as for compound **9** using 0.5 mL (0.84 mmol) of vinyl magnesium chloride and 0.22 g (0.75 mmol) of **4** in 6 mL of THF. The mixture was refluxed overnight. The solvent was removed *in vacuo,* then dry hexane (6 mL) was added, and the suspension was filtered off through Celite. The solvent was removed to give **10** as a yellow oil. Yield: 0.17 g, 78 %. ^1H NMR: δ 6.15-5.98 (m, 2H), 5.70 (m, 1H), 2.19 (t, $^3J(H,H)$ = 8.1, 2H, C_c-CH_2), 2.01 (s, 3H, C_c-CH_3), 1.62 (m, 2H, $CH_2CH_2CH_2$), 0.61 (t, $^3J(H,H)$ = 8.5, 2H, Si-CH_2), 0.10 (s, 6H, Si-CH_3). $^1H\{^{11}B\}$ NMR: δ 6.15-5.98 (m, 2H), 5.70 (m, 1H), 2.25 (br, B-*H*), 2.04 (br, B-*H*), 2.01 (s, 3H, C_c-CH_3), 1.62 (m, 2H, $CH_2CH_2CH_2$), 0.61 (t, $^3J(H,H)$ = 8.5, 2H, Si-CH_2), 0.10 (s, 6H, Si-CH_3). ^{11}B NMR: δ -2.9 (d, $^1J(B,H)$ = 122, 1B), -4.1 (d, $^1J(B,H)$ = 141, 1B), -9.1 (d, $^1J(B,H)$ = 141, 8B). $^{13}C\{^1H\}$ NMR: δ 138.2 ($CH=CH_2$), 132.2 ($CH=CH_2$), 78.2 (C_c), 74.7 (C_c), 38.7 (C_c-CH_2), 24.3 (CH_2), 23.1 (C_c-CH_3), 15.3 (Si-CH_2), -3.4 (Si-CH_3). $^{29}Si\{^1H\}$ NMR: δ -6.27.

Synthesis of 1-C_6H_5-2-[$CH_2CH_2CH_2(CH_3)_2SiCH_2CH_2(CH_3)_2SiCl$]-1,2-$C_2B_{10}H_{10}$ (11). In a Schlenk flask, **9** (0.22 g, 0.64 mmol), $(CH_3)_2HSiCl$ (0.15 mL, 1.28 mmol) and one drop of Karstedt catalyst were mixed and stirred for 12 h at room temperature. Evaporation of volatiles and the excess of $(CH_3)_2HSiCl$ gave **11** as a yellow oil. Yield: 0.28 g, > 99 %. ^1H NMR: δ 7.67-7.41 (m, 5H, C_6H_5), 1.80 (t, $^3J(H,H)$ = 8.1, 2H, C_c-CH_2), 1.39 (m, 2H, $CH_2CH_2CH_2$), 0.61 (m, 2H, CH_2), 0.39 (m, 8H, Si_{core}-CH_2, $Si_{periphery}$-CH_3), 0.30 (m, 2H, CH_2), -0.11 (s, 6H, Si_{core}-CH_3). $^1H\{^{11}B\}$ NMR: δ 7.67-7.41 (m, 5H, C_6H_5), 2.73 (br s, 2B, B-*H*), 2.36 (br s, 8B, B-*H*), 1.80 (t, $^3J(H,H)$ = 8.1, 2H, C_c-CH_2),

1.39 (m, 2H, $CH_2CH_2CH_2$), 0.61 (m, 2H, CH_2), 0.39 (m, 8H, Si_{core}-CH_2, $Si_{periphery}$-CH_3), 0.30 (m, 2H, CH_2), -0.11 (s, 6H, Si_{core}-CH_3). ^{11}B NMR: δ -2.2 (d, ^{1}J(B,H) = 144, 2B), -8.9 (d, ^{1}J(B,H) = 130, 8B). ^{13}C{^{1}H} NMR: δ 131.1-128.9 (C_6H_5), 83.3 (C_c), 82.3 (C_c), 38.6 (C_c-CH_2), 24.0 (CH_2), 14.4 (CH_2), 11.3 (CH_2), 6.3 (CH_2), 0.9 (CH_3-$Si_{periphery}$), -4.1 (CH_3-Si_{core}).

Synthesis of 1-CH_3-2-[$CH_2CH_2CH_2(CH_3)_2SiCH_2CH_2(CH_3)_2SiCl$]-1,2-$C_2B_{10}H_{10}$ (12). The procedure was the same as for compound **11** using, **10** (0.12 g, 0.43 mmol), $(CH_3)_2HSiCl$ (0.1, 0.86 mmol) and one drop of Karstedt catalyst. The mixture was for 2 h at room temperature. Evaporation of volatiles and the excess of $(CH_3)_2HSiCl$ gave **12** as a yellow oil. Yield: 0.16 g, > 99 %. ^{1}H NMR: δ. 2.19 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 2.01 (s, 3H, C_c-CH_3), 1.57 (m, 2H, $CH_2CH_2CH_2$), 0.54 (m, 12H), 0.03 (s, 6H, Si-CH_3). ^{1}H{^{11}B} NMR: 2.20 (m, C_c-CH_2, B-*H*), 2.01 (s, 3H, C_c-CH_3), 1.57 (m, 2H, $CH_2CH_2CH_2$), 0.54 (m, 12H), 0.03 (s, 6H, Si-CH_3). ^{11}B NMR: δ -2.1 (d, ^{1}J(B,H) = 122, 1B), -3.3 (d, ^{1}J(B,H) = 141, 1B), -8.3 (d, ^{1}J(B,H) = 141, 8B).^{13}C{^{1}H} NMR: δ 78.1 (C_c), 74.5 (C_c), 39.0 (C_c-CH_2), 24.2 (CH_2), 23.1 (C_c-CH_3), 14.7 (CH_2), 11.4 (CH_2), 6.4 (CH_2), 0.9 ($Si_{periphery}$-CH_3), -4.0 (Si_{core}-CH_3).

Synthesis of 1-C_6H_5-2-[$CH_2CH_2CH_2(CH_3)_2SiCH_2CH_2(CH_3)_2SiH$]-1,2-$C_2B_{10}H_{10}$ (13). To a solution of $LiAlH_4$ (12.9 mg, 0. 32 mmol) in Et_2O (10 mL) at 0 ºC was added dropwise a solution of **11** (0.28 g, 0.64 mmol) in Et_2O (2 mL). The mixture was stirred for 12 h at room temperature and filtered off through Celite twice. The solvent was removed *in vacuo* to give **13** as a transparent oil. Yield: 0.16 g, 60 %. ^{1}H NMR: δ 7.66-7.40 (m, 5H, C_6H_5), 3.81 (m, 1H, Si-*H*), 1.78 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 1.39 (m, 2H, $CH_2CH_2CH_2$), 0.36 (m, 4H, CH_2), 0.27 (m, 2H, CH_2), 0.04 (d, J^3(H,H) = 3.7, 6H, $Si_{periphery}$-CH_3), -0.14 (s, 6H, Si_{core}-CH_3). ^{1}H{^{11}B} NMR: δ 7.66-7.40 (m, 5H, C_6H_5), 3.81 (m, 1H, Si-*H*), 2.7 (br s, 2H, B-*H*), 2.37 (br s, 6H, B-*H*), 2.25 (br s, 2H, B-*H*), 1.78 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 1.39 (m, 2H, $CH_2CH_2CH_2$), 0.36 (m, 4H, CH_2), 0.27 (m, 2H, CH_2), 0.04 (d, J^3(H,H) = 3.7, 6H, $Si_{periphery}$-CH_3), -0.14 (s, 6H, Si_{core}-CH_3). ^{11}B NMR: -1.2 (d, ^{1}J(B,H) = 144, 2B), -8.0 (d, ^{1}J(B,H) = 132, 8B). ^{13}C{^{1}H} NMR: 131.1-128.8 (C_6H_5), 83.3 (C_c), 82.4 (C_c), 38.7 (C_c-CH_2), 24.1 (CH_2), 14.5 (CH_2), 7.7 (CH_2), 6.3 (CH_2), -4.0 (CH_3-Si), -4.9 (CH_3-Si). FTIR (NaCl), cm^{-1}: 3065 (ν (C_{aryl}-H)), 2954 (ν (C_{alkyl}-H)), 2590 (ν (B-H)), 2110 (ν (Si-H)), 1250 (δ (Si-CH_3)).

Synthesis of 1-CH_3-2-[$CH_2CH_2CH_2(CH_3)_2SiCH_2CH_2(CH_3)_2SiH$]-1,2-$C_2B_{10}H_{10}$ (14). The process was the same as for compound *13* using $LiAlH_4$ (8.5 mg, 0.21 mmol) in Et_2O (8 mL) and **12** (0.16 g, 0.43 mmol) in Et_2O (2 mL). The mixture was stirred for 12 h at room temperature and filtered off through Celite three times. The solvent was removed *in vacuo* to give **14** as a transparent oil. Yield: 90 mg, 61 %. ^{1}H NMR: δ 3.85 (m, 1H, Si-*H*), 2.19 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 2.02 (s, 3H, C_c-CH_3), 1.55 (m, 2H, $CH_2CH_2CH_2$), 0.47 (m, 6H), 0.08 (d, ^{3}J(H,H) = 3.7, 6H, $Si_{periphery}$-CH_3), 0.005 (s, 6H, Si_{core}-CH_3). ^{1}H{^{11}B} NMR: δ 3.85 (m, 1H, Si-*H*), 2.15 (m, C_c-CH_2, B-*H*), 2.02 (s, 3H, C_c-CH_3), 1.55 (m, 2H, $CH_2CH_2CH_2$), 0.47 (m, 6H), 0.08 (d, ^{3}J(H,H) = 3.7, 6H, $Si_{periphery}$-CH_3), 0.005 (s, 6H, Si_{core}-CH_3). ^{11}B NMR: δ -2.1 (d, ^{1}J(B,H) = 122, 1B), -3.3 (d, ^{1}J(B,H) = 141, 1B), -8.3 (d, ^{1}J(B,H) = 141, 8B). ^{13}C{^{1}H} NMR: δ 78.1 (C_c), 74.6 (C_c), 39.0 (C_c-CH_2), 24.3 (CH_2), 23.1 (C_c-CH_3), 14.8 (CH_2), 7.8 (CH_2), 6.3 (CH_2), -3.9 (CH_3-Si), -4.9 (CH_3-Si). FTIR (NaCl), cm^{-1}: 2955-2905 (ν (C_{alkyl}-H)), 2589 (ν (B-H)), 2110 (ν (Si-H)), 1252 (δ (Si-CH_3)).

Synthesis of 2G-$CH_2CH_2CH_2$-Phenyl-*o*-carborane (15). *Method A*: In a Schlenk flask, **9** (83.9 mg, 0.24 mmol), **1G-H** (22.8 mg, 0.06 mmol) and one drop of Karstedt catalyst were mixed and stirred overnight. The volatiles were removed *in vacuo* to give a yellowish oil, which was treated with acetonitrile. An insoluble oil was formed and separated from the solution. This oily product was washed with petroleum ether and finally, the solvent removal afforded the product **15** as a yellow oil. Yield: 42.3 mg, 40 %. *Method B*: In a Schlenk flask, **13** (0.16 g, 0.38 mmol), Si(CH=CH_2) (17 µL, 0.10 mmol) and one drop of Karstedt catalyst were mixed and stirred overnight. The volatiles were evaporated in the vacuum line to obtain a yellowish oil, which was treated with acetonitrile. An insoluble oily product was formed and separated from the solution. Solvent removal afforded the product **15** as a yellow oil. Yield: 98 mg, 58 %. ^{1}H NMR: δ 7.66-7.40 (m, 20H, C_6H_5), 1.78 (t, ^{3}J(H,H) = 8.5, 8H, C_c-CH_2), 1.39 (m, 8H, $CH_2CH_2CH_2$), 0.33 (m, 40H, Si(1)CH_2CH_2Si(2)CH_2CH_2Si(3)CH_2), -0.05 (s, 24H, Si-CH_3), -0.15 (s, 24H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 7.66-7.40 (m, 20H, C_6H_5), 2.72 (br s, 8B, B-*H*), 2.35 (br s, 24B, B-*H*), 2.24 (br s, 8B, B-*H*), 1.78 (t, ^{3}J(H,H) = 8.5, 8H, C_c-CH_2), 1.39 (m, 8H, $CH_2CH_2CH_2$), 0.33 (m, 40H, Si(1)CH_2CH_2Si(2)CH_2CH_2Si(3)CH_2), -0.05 (s, 24H, Si-CH_3), -0.15 (s, 24H, Si-CH_3). ^{11}B NMR: δ -2.3 (d, ^{1}J(B,H) = 141, 8B), -9.0 (d, ^{1}J(B,H) = 127, 32B). ^{13}C{^{1}H} NMR: δ 131.1-128.9 (C_6H_5), 83.4 (C_c), 82.4 (C_c), 38.7 (C_c-CH_2), 24.1 ($CH_2CH_2CH_2$), 14.4 ($SiCH_2CH_2CH_2$), 7.1-6.5 ($SiCH_2CH_2SiCH_2CH_2Si$), -4.0 (Si-CH_3), -4.4 (Si-CH_3). ^{29}Si{^{1}H} NMR: δ 8.92 (*Si*(1)), 5.05 (*Si*(2)), 3.36 (*Si*(3)). FTIR (NaCl), cm^{-1}: 3063 (ν (C_{aryl}-H)) 2955-2901 (ν (C_{alkyl}-H)), 2584 (ν (B-H)), 1250 (δ (Si-CH_3)).

Synthesis of 2G-$CH_2CH_2CH_2$-Methyl-*o*-carborane (16). *Method A*: The procedure was the same as for compound **15** using **10** (0.17 g, 0.59 mmol), **1G-H** (55.2 mg, 0.15 mmol) and one drop of Karstedt catalyst. The mixture was stirred overnight, and the volatiles evaporated in the vacuum line to obtain a yellowish oil, which was treated with acetronitrile. An insoluble oily product was formed and separated from the solution. The oil was washed with petroleum ether and finally solvent removal afforded the product **16** as yellow oil. Yield: 0.10, 45 %. *Method B*: In a Schlenk flask, **14** (58.3 mg, 0.17 mmol), Si(CH=CH_2) (7.6 µL, 0.04 mmol) and one drop of Karstedt catalyst were mixed and stirred overnight. The volatiles were evaporated in vacuo to obtain a yellowish oil, which was treated with acetonitrile. an insoluble oily product was formed and separated from the solution. Solvent removal afforded the product **16** as a yellow oil. Yield: 38.8 g, 61 %. ^{1}H NMR: δ 2.18 (t, ^{3}J(H,H) = 8.5, 8H, C_c-CH_2), 2.01 (s, 12H, C_c-CH_3), 1.56 (m, 8H, $CH_2CH_2CH_2$), 0.52-0.39 (m, 40H, $SiCH_2CH_2SiCH_2CH_2SiCH_2$), -0.005 (s, 24H, Si-$CH_3$), -0.03 (s, 24H, Si-$CH_3$). ^{1}H{^{11}B} NMR: δ 2.19 (m, B-*H*, C_c-

CH_2), 1.56 (m, 8H, $CH_2CH_2CH_2$), 0.52-0.39 (m, 40H, $SiCH_2CH_2SiCH_2CH_2SiCH_2$), -0.005 (s, 24H, Si-$CH_3$), -0.03 (s, 24H, Si-$CH_3$). ^{11}B NMR: δ -3.0 (d, ^{1}J(B,H) = 117, 4B), -4.3 (d, ^{1}J(B,H) = 143, 4B), -9.2 (d, ^{1}J(B,H) = 140, 32B). ^{13}C{^{1}H} NMR: δ 78.1 (C_c), 74.5 (C_c), 39.0 (C_c-CH_2), 24.4 ($CH_2CH_2CH_2$), 23.1 (C_c-CH_3), 14.8 ($SiCH_2CH_2CH_2$), 7.2, 6.7 ($SiCH_2CH_2SiCH_2CH_2Si$), -3.9 (Si(3)-CH_3), -4.5 (Si(2)-CH_3). ^{29}Si{^{1}H} NMR: δ 7.26 (*Si*(1)), 5.21 (*Si*(2)), 3.52 (*Si*(3)). FTIR (NaCl), cm^{-1}: 2955-2901 (ν (C_{alkyl}-H)), 2578 (ν (B-H)), 1250 (δ (Si-CH_3)). MS-electrospray (ESI), solution of $CHCl_3$/CH_3OH (1:2) *m/z*: calcd for $C_{56}H_{156}B_{40}Si_9$, 1515.1; found, 1551.5 [(M + $2H_2O$)$^-$].

Synthesis of 2G-[$CH_2CH_2CH_2$-Phenyl-*o*-carborane]$_2$ (17). In a Schlenk flask, **5** (0.13 g, 0.41 mmol), **1G-(CH=CH_2)$_2$** (27.0 mg, 51 μmol), 0.4 mL of toluene and Karstedt catalyst were mixed and stirred during 48 hours. The volatiles were evaporated in the vacuum line to obtain a yellowish oil, which was treated with hexane. An insoluble oily product was formed and separated from the solution. Solvent removal afforded the product **17** as a yellow oil. Yield: 94.9 mg, 60%. ^{1}H NMR: δ 7.64-7.38 (m, 40H, C_6H_5), 1.77 (t, ^{3}J(H,H) = 8.1, 16H, C_c-CH_2), 1.38 (m, 16H, $CH_2CH_2CH_2$), 0.27 (br s, 64H, $SiCH_2CH_2Si(CH_2CH_2SiCH_2)_2$), -0.16 (br s, 60H, Si-$CH_3$). ^{1}H{^{11}B} NMR: δ 7.64-7.38 (m, 40H, C_6H_5), 2.72 (br s, 16H, B-*H*), 2.37 (br s, 48H, B-*H*), 2.25 (br s, 16H, B-*H*), 1.77 (t, ^{3}J(H,H) = 8.1, 16H, C_c-CH_2), 1.38 (m, 16H, $CH_2CH_2CH_2$), 0.27 (br s, 64H, $SiCH_2CH_2Si(CH_2CH_2SiCH_2)_2$), -0.16 (br s, 60H, Si-$CH_3$). ^{11}B NMR: δ -2.1 (d, ^{1}J(B,H) = 122, 16B), -8.8 (brs, 64B).

Synthesis of 2G-[$CH_2CH_2CH_2$-Methyl-*o*-carborane]$_2$ (18). In a Schlenk flask, **6** (0.17 g, 0.67 mmol), **1G-(CH=CH_2)$_2$** (44.1 mg, 84 μmol), 0.4 mL of toluene and Karstedt catalyst were mixed and stirred during 24 hours. The volatiles were evaporated in the vacuum line to obtain a yellowish oil, which was treated with petroleum ether. An insoluble oily product was formed and separated from the solution. Solvent removal afforded the product **18** as a yellowish waxy solid. Yield: 0.13 g, 58 %. ^{1}H NMR: δ 2.18 (t, ^{3}J(H,H) = 8.1, 16H, C_c-CH_2), 2.01 (s, 24H, C_c-CH_3), 1.55 (m, 16H, $CH_2CH_2CH_2$), 0.53 (t, ^{3}J(H,H) = 8.5, 16H, $CH_2CH_2CH_2$), 0.40 (br s, 48H, Si-CH_2CH_2-Si), 0.004 (s, 48H, Si(3)-CH_3), -0.04 (s, 12H, Si(2)-CH_3). ^{1}H{^{11}B} NMR: δ 2.25 (br s, B-*H*), 2.18 (t, ^{3}J(H,H) = 8.1, 16H, C_c-CH_2), 2.10 (br s, B-*H*), 2.01 (s, 24H, C_c-CH_3), 1.55 (m, 16H, $CH_2CH_2CH_2$), 0.53 (t, ^{3}J(H,H) = 8.5, 16H, $CH_2CH_2CH_2$), 0.40 (br s, 48H, Si-CH_2CH_2-Si), 0.004 (s, 48H, Si(3)-CH_3), -0.04 (s, 12H, Si(2)-CH_3). ^{11}B NMR: δ -3.1 (8B), -4.2 (d, ^{1}J(B,H) = 144, 8B), -9.1 (d, ^{1}J(B,H) = 136, 64B). ^{13}C{^{1}H} NMR: δ 78.1 (C_c), 74.7 (C_c), 39.0 (C_c-CH_2), 24.4 ($CH_2CH_2CH_2$), 23.1 (C_c-CH_3), 14.8 ($SiCH_2CH_2CH_2$), 7.3-4.5 ($SiCH_2CH_2SiCH_2CH_2Si$), -3.8 (Si-CH_3), -6.5 (Si-CH_3). ^{29}Si{^{1}H} NMR: δ 8.99 *Si*(1), 7.26 *Si*(2), 3.42 *Si*(3). FTIR (NaCl), cm^{-1}: 2955-2901 (ν (C_{alkyl}-H)), 2584 (ν (B-H)), 1250 (δ (Si-CH_3)). MS-electrospray (ESI), solution of $CHCl_3$/CH_3OH (1:2) *m/z*: calcd for $C_{92}H_{260}B_{80}Si_{13}$, 2597.1; found, 2661.8 [(M + $2CH_3OH$)$^-$].

Synthesis of 1G-$CH_2CH_2CH_2$-Phenyl-*nido*-carborane (19). To a two necked round bottom flask containing a solution of KOH (0.12g, 1.80 mmol) in deoxygenated ethanol (4 mL) was added a solution of **7** (0.13 g, 0.09 mmol) in 2 mL of THF. The mixture was refluxed during 10 hours. Then, the volatiles were evaporated in the vacuum and an excess of tetrabutylamonium chloride in water was added to obtain a white solid. This was filtered off, washed with water (3 x 15 mL), diethyl ether (3 x 10 mL), toluene (3 x 10 mL) and dried under vacuum to obtain **19** as a white solid. Yield: 0.13 g, 89 %. ^{1}H NMR (CD_3OCD_3): δ 7.36-7.12 (m, 20H, C_6H_5), 3.42 (s, 48H, $[NCH_3]_4$), 1.30 (m, 16H, C_c-CH_2CH_2), 0.35 (m, 24H, Si_{core}-CH_2CH_2-$Si_{periphery}CH_2$), -0.17 (s, 24H, Si-CH_3), -2.13 (br s, 4H, B*H*B). ^{1}H{^{11}B} NMR: δ 7.36-7.12 (m, 20H, C_6H_5), 1.57 (br s, B-*H*), 1.31 (br, B-*H*), 0.35 (m, 24H, Si_{core}-CH_2CH_2-$Si_{periphery}CH_2$), -0.17 (s, 24H, Si-CH_3), -2.13 (br s, 4H, B*H*B). ^{11}B NMR: δ -6.1 (4B), -8.2 (d, ^{1}J(B,H) = 140, 4B), -11.2 (d, ^{1}J(B,H) = 161, 4B), -15.6 (d, ^{1}J(B,H) = 128, 16B), -31.3 (dd, ^{1}J(B,H) = 119, ^{1}J(B,H) = 31, 4B), -34.1 (d, ^{1}J(B,H) = 135, 4B). ^{13}C{^{1}H} NMR: δ 143.0, 131.9, 129.2, 126.7 (C_6H_5), 67.0 (C_c), 63.3 (C_c), 55.2 (NCH_3), 40.7 (CH_2), 24.6 (CH_2), 15.1 (CH_2), 7.2 (CH_2), 2.4 (CH_2), -4.5 (CH_3). ^{29}Si{^{1}H} NMR: δ 8.54 (Si_{core}), 2.97 ($Si_{periphery}$). FTIR (KBr), cm^{-1}: 3032 (ν (C_{aryl}-H)), 2943-2904 (ν (C_{alkyl}-H)), 2517 (ν (B-H)), 1483 (ν (C-N)), 1246 (δ (Si-CH_3)). MS-electrospray (ESI), solution of $CHCl_3$/CH_3OH (1:2) *m/z*: calcd for $C_{76}H_{172}B_{36}Si_5$, 1671.8; found, 1597.5 [(M - $N(CH_3)_4$)$^-$.

Synthesis of 1G-$CH_2CH_2CH_2$-Methyl-*nido*-carborane (20). To a two necked round bottom flask containing a solution of KOH (0.10g, 1.80 mmol) in deoxygenated ethanol (5 mL) was added a solution of **8** (0.09 g, 0.08 mmol) in 1 mL of THF. The mixture was refluxed during 6 hours. Then, the volatiles were evaporated in the vacuum and an excess of tetrabutylamonium chloride in water was added to obtain a white solid. This was filtered off, washed with water (3 x 15 mL) and dried under vacuum to obtain **20** as a white solid. Yield: 0.08 g, 70 %. ^{1}H NMR (CD_3OCD_3): δ 3.44 (s, 48H, $[NCH_3]_4$), 1.62 (m, 16H, C_c-CH_2CH_2), 1.42 (s, 12H, C_c-CH_3), 0.46 (m, 24H, $SiCH_2CH_2SiCH_2$), -0.01 (s, 24H, Si-CH_3). ^{1}H{^{11}B} NMR: δ 3.44 (s, 48H, $[NCH_3]_4$), 1.62 (m, 16H, C_c-CH_2CH_2), 1.42 (s, 12H, C_c-CH_3), 0.46 (m, 24H, $SiCH_2CH_2SiCH_2$), -0.01 (s, 24H, Si-CH_3), -2.58 (br s, 4H, B*H*B). ^{11}B NMR: δ -6.0 (d, ^{1}J(B,H) = 158, 4B), -7.8 (d, ^{1}J(B,H) = 153, 8B), -15.1 (d, ^{1}J(B,H) = 112, 16B), -31.6 (dd, ^{1}J(B,H) = 133, ^{1}J(B,H) = 45, 4B), -34.1 (d, ^{1}J(B,H) = 140, 4B). ^{13}C{^{1}H} NMR: δ 55.2 (NCH_3), 40.3 (CH_2), 25.1 (CH_2), 21.6 (C_c-CH_3), 15.1 (CH_2), 7.3 (CH_2), 2.5 (CH_2), -4.3 (CH_3). ^{29}Si{^{1}H} NMR: δ 9.47 (Si_{core}), 4.06 ($Si_{periphery}$). FTIR (KBr), cm^{-1}: 2932 (ν (C_{alkyl}-H)), 2515 (ν (B-H)), 1481 (ν (C-N)), 1227 (δ (Si-CH_3)).

X-ray structure determinations of 1 and 2. Supporting Information: crystallographic data (CIF) for **1** and **2** are available free of charges via the Internet http://pubs.acs.org.

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Supporting Information Available. Crystallographic data (CIF) for **1** and **2** are available free of charge via the Internet http://pubs.acs.org

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Synthesis, Characterization and Reactivity of Carboranylsilsesquioxanes.

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Introduction

Polyhedral oligomeric soluble silsesquioxanes (POSS) are one type of hybrid inorganic-organic materials of the form $(RSiO_{1.5})n$, where organic substituents are attached to a silicon-oxygen cage.[1] The most known POSS cage is the octasilsesquioxane T8 (Si_8O_{12}), a cubic molecule of silicon atoms at the vertices of the cube, bringing by oxygen atoms. One of the major potential applications of POSS materials is as nanosized building blocks for organic/inorganic hybrids due to the control of the organic architecture between the rigid silica cores. The interest of these compounds is the possibility of the choice of functional group chemical reactivity associated with organic chemistry.In the literature exist several examples of carbosilane dendrimer-POSS compounds prepared from Si_8O_{12} silsesquioxane cores using sequential hydrosililation and alkenylation steps followed by surface functionalization.[2] In fact, POSS cages have been generally used as core units, from which a wide variety of functional groups have been attached, leading to its use in a variety of different applications.[3] Recently, POSS have been used for preparing a new generation of silica nanocomposites with particular use in cardiovascular interventional devices,[4] or to functionalized metal oxide nanoparticles.[5] Incorporation of POSS into organic polymers,[6] and surface dendrimers[7] have also offered the possibility for developing new materials. These inorganic-organic hybrids offer a unique set of physical, chemical and size-dependent properties that could not be realized from just ceramics or organic polymers alone. There are different strategies to prepare functionalized three-dimensional silsesquioxane cages, functionalizing the commercial octasilsesquioxanes or by controlled hydrolitic condensation of silanols, trialkoxy- or trichlorosilanes.[1b8] The 1-2-dicarba-*closo*-dodecaborane and derivatives present exceptional characteristics,[9,10] such as low nucleophilicity, chemical inertness, thermal stability,[11] electron-withdrawing properties,[12] and a highly polarizable σ-aromatic character, that have stimulated the development of a wide range of potential applications.[13] Their rigid geometry and the relative easiness of derivatization specially at the carbon atoms have allowed the preparation of a wide number of compounds.[14] Recently, we become interested in the synthesis of carborane-containing star-shaped molecules in which a carbosilane core is used as scaffold.[15] In view of the importance of POSS for the development of a wide range of novel materials, we are interested in the use of these as

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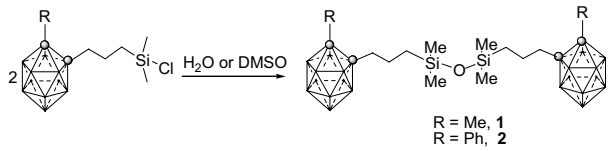
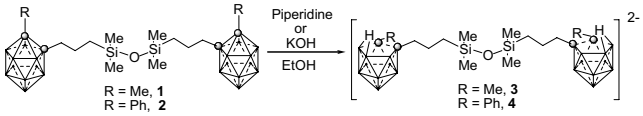
scaffold for the preparation of carboranyl-functionalized cages in order to study their properties and reactivity.

Results and Discussion

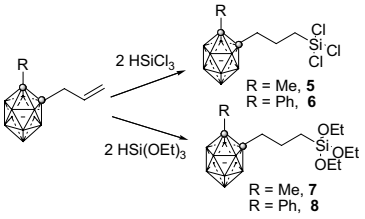
Scheme 1. Preparation of Carboranylsiloxane Dimers **1** and **2** using two different approaches



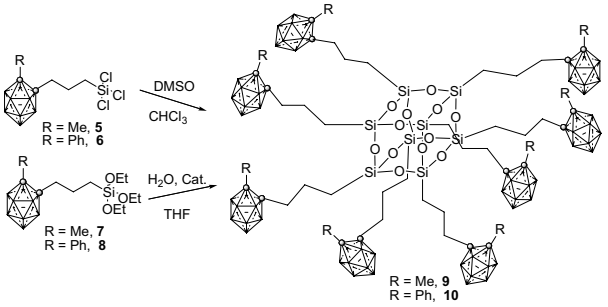
Scheme 2. Preparation of Carboranyl-Containing Polianionic Dimers, **3** and **4**.



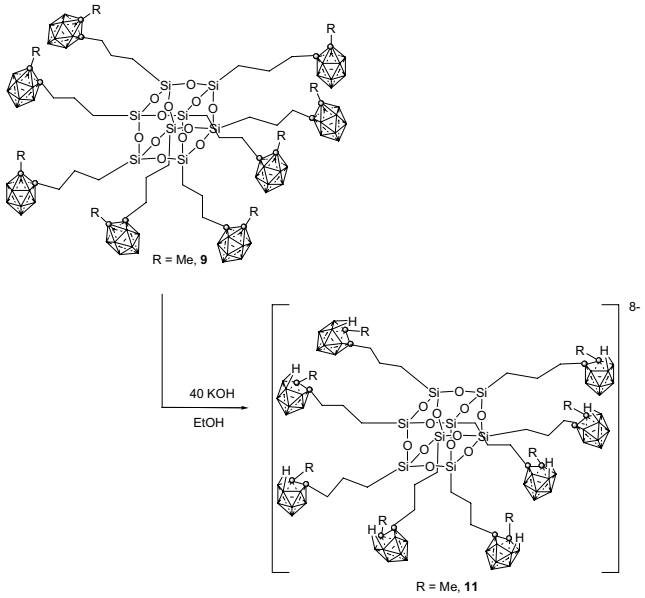
Scheme 3. Preparation of precursors **5-8**.



Scheme 4. Preparation of Carboranyl-Containing Silsesquioxanes, **9** and **10**.



Scheme 5. Preparation of Carboranyl-Containing Polianionic Silsesquioxane, **11**.



Experimental Section

Instrumentation. Microanalyses were performed in the analytical laboratory using a Carlo Erba EA1108 microanalyser. 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 a ions trap analyzer. The ^{1}H, $^{1}H\{^{11}B\}$ NMR (300.13 MHz), ^{11}B, $^{11}B\{^{1}H\}$ NMR (96.29 MHz), $^{13}C\{^{1}H\}$ 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. ^{29}Si CP MAS NMR (at 79.49 MHz) spectra were obtained on a Bruker Advance ASX400 using a CP MAS sequence. All NMR spectra were recorded in $CDCl_3$ and CD_3COCD_3 solutions at 22ºC. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$, and those for ^{1}H, $^{1}H\{^{11}B\}$, $^{13}C\{^{1}H\}$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-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. $HSiCl_3$, $His(OEt)_3$ and Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex, 2.1-2.4% platinum in vinyl terminated polydimethylsiloxane in xylene solution) were purchased from ABCR and used as

received. The [Si(CH=CH$_2$)$_4$] was purchased from Across. The n-BuLi solution (1.6M in hexanes) was purchased from Lancaster or Aldrich. **1-C$_6$H$_5$-2-CH$_2$CH=CH$_2$-1,2-C$_2$B$_{10}$H$_{10}$**, **1-CH$_3$-2-CH$_2$CH=CH$_2$-1,2-C$_2$B$_{10}$H$_{10}$**, **1-C$_6$H$_5$-2-[CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCl]-1,2-C$_2$B$_{10}$H$_{10}$** and **1-CH$_3$-2-[CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCl]-1,2-C$_2$B$_{10}$H$_{10}$** were prepared according to the literature.

Synthesis of [1-CH$_3$-2-CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$Si-1,2-closo-C$_2$B$_{10}$H$_{10}$]$_2$O (1). *Method A*: To a round bottom flask containing **1-CH$_3$-2-CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCl-1,2-C$_2$B$_{10}$H$_{10}$** (0.28 g, 0.95 mmol), 0.05 mL (2.7 mmol) of water and 5 mL of diethyl ether were added. The mixture was transferred to a separatory funnel and was extracted. The organic layer was dried over MgSO4 and concentrated in vacuum to obtain compound **1** as a white waxy solid. Yield: 0.18 g, 72 %. *Method B:* In a Schlenk flask, **1-CH$_3$-2-CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCl-1,2-C$_2$B$_{10}$H$_{10}$** (0.28 g, 0.95 mmol), DMSO (0.3 mL, 4.22 mmol) and 4 mL of $CHCl_3$ were mixed and stirred overnight. Then, the mixture was quenched with 8 mL of water, transferred to a separatory funnel and the organic layer was washed with water (2 x 8 mL), was dried over MgSO4 and concentrated in vacuum to obtain compound **1** as a white waxy solid. Yield: 0.10 g, 40 %. Hexane vapour diffusion into $CHCl_3$ solution of **1** gave single crystals suitable for X-ray analysis. ^{1}H-NMR: δ 2.20 (t, ^{3}J(H,H) = 8.5, 4H, C$_c$-C*H*$_2$), 2.02 (s, 6H, C$_c$-C*H*$_3$), 1.59 (m. 4H, CH$_2$C*H*$_2$CH$_2$), 0.54 (t, ^{3}J(H,H) = 8.5, 4H, CH$_2$CH$_2$C*H*$_2$), 0.10 (s, 12H, Si-C*H*$_3$). ^{1}H{^{11}B} NMR: δ 2.25, 2.21, 2.15, 2.11 (br s, B-*H*), 2.02 (s, 6H, C$_c$-C*H*$_3$), 1.59 (m, 4H, CH$_2$C*H*$_2$CH$_2$), 0.54 (t, 3J(H,H) = 8.5, 4H, CH$_2$CH$_2$C*H*$_2$), 0.10 (s, 12H, Si-C*H*$_3$). ^{11}B NMR: δ -3.9 (d, 1J(B,H) = 123, 2B), -5.0 (d, 1J(B,H) = 141, 2B), -9.9 (d, 1J(B,H) = 132, 16B). ^{13}C{^{1}H} NMR: δ 78.0 (*C*c), 74.6 (*C*$_c$), 38.7 (*C*H$_2$), 23.7 (*C*H$_2$), 23.1 (C$_c$-*C*H$_3$), 18.2 (Si-*C*H$_2$), 0.4 (Si-*C*H$_3$). ^{29}Si{^{1}H} NMR: δ 6.9. FTIR (KBr), cm^{-1}: 2954-2878 (ν (C$_{alkyl}$-H)), 2584 (ν (B-H)), 1256 (ν (Si-CH$_3$)), 1076 (ν (Si-O)). Anal. Calcd. for C$_{16}$H$_{50}$B$_{20}$Si$_2$O: C, 36.19; H, 9.49. Found: C, 36.27; H 9.58. MALDI-TOF-MS (m/z): cald. 530.97 found. 529.68 [M-1]$^-$.

Synthesis of [1-C$_6$H$_5$-2-CH$_2$CHCH$_2$(CH$_3$)$_2$Si-1,2-*closo*-C$_2$B$_{10}$H$_{10}$]$_2$O (2). To a round bottom flask containing **1-C$_6$H$_5$-2-CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCl-1,2-C$_2$B$_{10}$H$_{10}$** (0.28 g, 0.80 mmol), 3 mL of diethyl ether and 13 µL (0.81 mmol) of water were added. The mixture was stirred during 10 min. and transferred to a separatory funnel. The organic layer was washed with water (2 x 5 mL) and the aqueous layer with diethyl ether (3 x 5 mL). Then, the organic layer was dried over $MgSO_4$ and concentrated in vacuum to obtain compound **2** as a yellowish oil. Yield: 0.21, 81 %. ^{1}H NMR: δ 7.66-7.40 (m, 10H, C$_6$*H*$_5$), 1.77 t, ^{3}J(H,H) = 8.1, 4H, C$_c$-C*H*$_2$), 1.38 (m, 4H, CH$_2$C*H*$_2$CH$_2$), 0.24 (t, ^{3}J(H,H) = 8.5, 4H, CH$_2$CH$_2$C*H*$_2$), -0.08 (s, 12H, Si-C*H*$_3$). ^{1}H{^{11}B} NMR: δ 7.66-7.40 (m, 10H, C$_6$*H*$_5$), 2.73 (br s, 4B, B-*H*), 2.37 (br s, 12B, B-*H*), 2.27 (br s, 4B, B-*H*), 1.77 t, ^{3}J(H,H) = 8.1, 4H, C$_c$-C*H*$_2$), 1.38 (m, 4H, CH$_2$C*H*$_2$CH$_2$), 0.24 (t, ^{3}J(H,H) = 8.5, 4H, CH$_2$CH$_2$C*H*$_2$), -0.08 (s, 12H, Si-C*H*$_3$). ^{11}B NMR: δ -2.7 (d, ^{1}J(B,H) = 133, 4B), -9.5 (br s, 16B). ^{13}C{^{1}H} NMR: δ 131.1, 130.8, 130.6, 128.9 (*C*$_6$H$_5$), 83.4 (*C*$_c$), 82.3 (*C*$_c$), 38.3 (*C*H$_2$), 23.5 (*C*H$_2$), 17.9 (*C*H$_2$), 0.19 (Si-*C*H$_3$). ^{29}Si{^{1}H} NMR: δ 6.6. FTIR (NaCl), cm^{-1}: 3063 (ν (C$_{aryl}$-H)), 2955-2893 (ν (C$_{alkyl}$-H)), 2584 (ν (B-H)), 1257 (δ (Si-CH$_3$)), 1065 (ν (Si-O)). MALDI-TOF-MS (m/z): cald. 655.12 found. 654.42 [M-1]$^-$.

Synthesis of [NMe$_4$]$_2$[(7-CH$_3$-8-CH$_2$CHCH$_2$(CH$_3$)$_2$Si-7,8-*nido*-C$_2$B$_9$H$_{10}$)$_2$O] (3). *Method A*: To a two necked round bottom flask containing a solution of **1** (42.6 mg, 0.08 mmol) in deoxygenated ethanol (4 mL) was added an excess of piperidine (0.08 mL, 0.80 mmol). The mixture was stirred and refluxed during 20 hours. After this time, the solvent was removed and an a white solid was isolated by precipitation after addition of saturated aqueous [NMe$_4$]Cl solution. The solid is filtered off, washed with water (3 x 10 mL) and dried under vacuum to obtain **3** as a white solid. Yield: 21.0 mg, 40 % *Method B*: To a two necked round bottom flask containing a solution of KOH (0.13 g, 1.98 mmol) in deoxygenated ethanol (5 mL) was added **1** (0.10 g, 0.19 mmol). The mixture was stirred and refluxed during 6 hours. After this time, the solvent was removed and an a white solid was isolated by precipitation after addition of saturated aqueous [NMe$_4$]Cl solution. The solid is filtered off, washed with water (3 x 10 mL) and dried under vacuum to obtain **3**. Yield: 55.3 mg, 44 %. ^{1}H NMR (CD_3OCD_3): δ 3.43 (s, 24H, N(C*H*$_3$)$_4$), 1.64 (m, 8H, C$_c$-C*H*$_2$C*H*$_2$), 1.39 (br s, 6H, C$_c$-C*H*$_3$), 0.46 (t, ^{3}J(H,H) = 8.4, 4H, CH$_2$CH$_2$C*H*$_2$), 0.07 (s, 6H, Si-C*H*$_3$), 0.04 (s, 6H, Si-C*H*$_3$). ^{1}H{^{11}B} NMR: δ 3.43 (s, 24H, N(C*H*$_3$)$_4$), 1.64 (m, 8H, C$_c$-C*H*$_2$C*H*$_2$), 1.39 (br s, 6H, C$_c$-C*H*$_3$), 0.46 (t, ^{3}J(H,H) = 8.4, 4H, CH$_2$CH$_2$C*H*$_2$), 0.07 (s, 6H, Si-C*H*$_3$), 0.039 (s, 6H, Si-C*H*$_3$), -2.60 (br s, 2H, B*H*B). ^{11}B NMR: δ -8.2 (d, ^{1}J(B,H) = 157, 2B), -10.0 (^{1}J(B,H) = 151, 4B), -17.3 (^{1}J(B,H) = 122, 8B), -33.8 (dd, ^{1}J(B,H) = 126, ^{1}J(B,H) = 45, 2B), -36.3 (^{1}J(B,H) = 138, 2B). ^{13}C{^{1}H} NMR: δ 55.2 (N(*C*H$_3$)$_4$). 40.2, 40.0 (*C*H$_2$), 24.4 (*C*H$_2$), 21.5 (C$_c$-*C*H$_3$), 18.9, 18.7 (*C*H$_2$), -0.1, -0.7 (Si-*C*H$_3$). FTIR (KBr), cm^{-1}: 2932-2870 (ν (C$_{alkyl}$-H)), 2515 (ν (B-H)), 1481 (ν (C-N)), 1250 (δ (Si-CH$_3$)), 1034 (ν (Si-O)).

Synthesis of [NMe$_4$]$_2$[(7-C$_6$H$_5$-8-CH$_2$CHCH$_2$(CH$_3$)$_2$Si-7,8-*nido*-C$_2$B$_9$H$_{10}$)$_2$O] (4). To a two necked round bottom flask containing a solution of KOH (0.12 g, 1.78 mmol) in deoxygenated ethanol (10 mL) was added **2** (0.12 g, 0.18 mmol). The mixture was stirred and refluxed during 14 hours. After this time, the solvent was removed and an a white solid was isolated by precipitation after addition of saturated aqueous [NMe$_4$]Cl solution. The solid is filtered off, washed with water (3 x 15 mL) and dried under vacuum to obtain **4**. Yield: 0.55 g, 40 %. ^{1}H NMR (CD_3OCD_3): δ 7.30-7.03 (m, 10H, C$_6$*H*$_5$), 3.38 (s, 24H, N(C*H*$_3$)$_4$), 1.24 (m, 8H, C$_c$-CH$_2$CH$_2$), -0.04 (m, 4H, CH$_2$), -0.18, (s, 12H, Si-CH$_3$). ^{1}H{^{11}B} NMR: δ 7.30-7.03 (m, 10H, C$_6$*H*$_5$), 3.38 (s, 24H, N(C*H*$_3$)$_4$), 1.50 (br s, B-*H*), 1.24 (m, 8H, C$_c$-CH$_2$CH$_2$), 0.62 (br s, B-*H*), 0.18 (br s, B-*H*), -0.04 (m, 4H, CH$_2$), -0.18 (s, 12H, Si-CH$_3$), -2.19 (br s, 2H, B*H*B). ^{11}B NMR: δ -5.9 (d, ^{1}J(B,H) = 145, 2B), -8.1 (d, ^{1}J(B,H) = 141, 2B), -10.9 (2B), -14.0 (d, ^{1}J(B,H) = 156, 2B), -15.3 (d, ^{1}J(B,H) =127, 4B), -16.4 (2B), -30.8 (d, ^{1}J(B,H) = 131, 2B), -33.8 (d, ^{1}J(B,H) = 144, 2B).

Synthesis of 1-CH$_3$-2-CH$_2$CH$_2$CH$_2$SiCl$_3$-1,2-C$_2$B$_{10}$H$_{10}$ (5). In a Schlenk flask 1-CH$_3$-2-CH$_2$CHCH$_2$-C$_2$B$_{10}$H$_{10}$ (0.21 g, 1.05 mmol), $HSiCl_3$ (0.21 mL, 2.10 mmol) and Karstedt catalyst (5 µl, 0.01 mmol) were mixed and stirred

under N_2 for 5 h at room temperature. Evaporation of volatiles and the excess of $HSiCl_3$ gave **5** as a yellow oil. Yield: 0.42 g, >99 %. ^{1}H NMR: δ 2.29 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 2.02 (s, 3H, C_c-CH_3), 1.88 (m, 2H, $CH_2CH_2CH_2$), 1.45 (t, ^{3}J(H,H) = 8.1, 2H, Si-CH_2). ^{1}H{^{11}B} NMR: δ 2.26 (br s, B-*H*), 2.18 (br s, B-*H*), 2.02 (s, 3H, C_c-CH_3), 1.88 (m, 2H, $CH_2CH_2CH_2$), 1.45 (t, ^{3}J(H,H) = 8.1, 2H, Si-CH_2). ^{11}B NMR: δ -3.2 (d, ^{1}J(B,H) = 141, 1B), -4.6 (d, ^{1}J(B,H) = 146, 1B), -9.0 (8B). ^{13}C{^{1}H} NMR: δ 76.8 (C_c), 74.7 (C_c), 36.8 (CH_2), 23.7 (CH_2), 23.2 (C_c-CH_3), 22.6 (Si-CH_2). ^{29}Si{^{1}H} NMR: δ 11.5.

Synthesis of 1-C_6H_5-2-$CH_2CH_2CH_2SiCl_3$-1,2-$C_2B_{10}H_{10}$ (6). In a Schlenk flask 1-C_6H_5-2-CH_2CHCH_2-$C_2B_{10}H_{10}$ (0.21 g, 0.81 mmol), $HSiCl_3$ (0.17 mL, 1.60 mmol) and Karstedt catalyst (5 µl, 0.01 mmol) were mixed and stirred under N_2 for 5 h at room temperature. Evaporation of volatiles and the excess of $HSiCl_3$ gave **6** as a yellow oil. Yield: 0.32 g, >99 %. ^{1}H NMR: δ 7.67-7.42 (m, 5H, C_6H_5), 1.91(t, ^{3}J(H,H) = 8.2, 2H, C_c-CH_2), 1.70 (m, 2H, $CH_2CH_2CH_2$), 1.21 (t, ^{3}J(H,H) = 8.1, 2H, Si-CH_2). ^{1}H{^{11}B} NMR: δ 7.67-7.42 (m, 5H, C_6H_5), 2.74 (br s, 2H, B-*H*), 2.39 (br s, 6H, B-*H*), 2.28 (br s, 2H, B-*H*), 1.91(t, ^{3}J(H,H) = 8.2, 2H, C_c-CH_2), 1.70 (m, 2H, $CH_2CH_2CH_2$), 1.21 (t, ^{3}J(H,H) = 8.1, 2H, Si-CH_2). ^{11}B NMR: δ -2.6, (d, ^{1}J(B,H) = 145, 2B), -9.4 (8B). ^{13}C{^{1}H} NMR: δ 131.1, 130.8,130.5, 129.0 (C_6H_5), 83.6 (C_c), 81.1 (C_c), 36.5 (CH_2), 23.5 (CH_2), 22.3 (Si-CH_2). ^{29}Si{^{1}H} NMR: 11.3.

Synthesis of 1-CH_3-2-$CH_2CH_2CH_2Si(OEt)_3$-1,2-$C_2B_{10}H_{10}$ (7). In a Schlenk flask 1-CH_3-2-CH_2CHCH_2-$C_2B_{10}H_{10}$ (0.80 g, 4.0 mmol), $HSi(OEt)_3$ (1.53 mL, 8.04 mmol) and Karstedt catalyst (10 µl, 0.02 mmol) were mixed and stirred under N_2 for 5 h at room temperature. Evaporation of volatiles and the excess of $HSi(OEt)_3$ at 50 ºC gave **7** as a brown oil. Yield: 1.46 g, >99 %. ^{1}H NMR: δ 3.83 (q, ^{3}J(H,H) = 6.9, 6H, O-CH_2), 2.20 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 2.01 (s, 3H, C_c-CH_3), 1.68 (quint., ^{3}J(H,H) = 8.1, 6H, $CH_2CH_2CH_2$), 1.23 (t, ^{3}J(H,H) = 6.9, 9H, CH_2-CH_3), 0.63 (t, ^{3}J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$). ^{1}H{^{11}B} NMR: δ 3.83 (q, ^{3}J(H,H) = 6.9, 6H, O-CH_2), 2.26 (br s, B-*H*), 2.18 (br s, B-*H*), 2.01 (s, 3H, C_c-CH_3), 1.68 (quint., ^{3}J(H,H) = 8.1, 6H, $CH_2CH_2CH_2$), 1.23 (t, ^{3}J(H,H) = 6.9, 9H, CH_2-CH_3), 0.63 (t, ^{3}J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$). ^{1}B NMR: δ -3.2 (d, ^{1}J(B,H) = 122, 1B), -4.63 (d, ^{1}J(B,H) = 141, 1B), -9.2 (d, ^{1}J(B,H) = 145, 8B). ^{13}C{^{1}H} NMR: δ 78.7 (C_c), 75.0 (C_c). 58.9 (O-CH_2), 38.2 (CH_2), 23.7 (CH_2), 23.5 (C_c-CH_3), 18.5 (CH_2CH_3), 10.6 (Si-CH_2). ^{29}Si{^{1}H} NMR: δ -46.6.

Synthesis of 1-C_6H_5-2-$CH_2CH_2CH_2Si(OEt)_3$-1,2-$C_2B_{10}H_{10}$ (8). In a Schlenk flask **1-C_6H_5-2-CH_2CHCH_2-$C_2B_{10}H_{10}$** (0.16 g, 0.60 mmol), $HSi(OEt)_3$ (0.24 mL, 1.23 mmol) and Karstedt catalyst (5 µl, 0.01 mmol) were mixed and stirred under N_2 for 14 h at room temperature. Evaporation of volatiles and the excess of $HSi(OEt)_3$ at 50 ºC gave **8** as a brown oil. Yield: 0.26 g, >99 %. ^{1}H NMR: δ 7.62-7.39 (m, 5H, C_6H_5), 3.37 (q, ^{3}J(H,H) = 6.9, 6H, O-CH_2), 1.83 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 1.53 (m, 2H, $CH_2CH_2CH_2$), 1.20 (t, ^{3}J(H,H) = 6.9, 9H, CH_2-CH_3), 0,40 (t, ^{3}J(H,H) = 8.1, 2H, Si-CH_2). ^{1}H{^{11}B} NMR: δ 7.62-7.39 (m, 5H, C_6H_5), 3.37 (q, ^{3}J(H,H) = 6.9, 6H, O-CH_2), 2.73 (br s, 2H, B-*H*), 2.36 (br s, 6H, B-*H*), 2.25 (br s, 2H, B-*H*), 1.83 (t, ^{3}J(H,H) = 8.1, 2H, C_c-CH_2), 1.53 (m, 2H, $CH_2CH_2CH_2$), 1.20 (t, ^{3}J(H,H) = 6.9, 9H, CH_2-CH_3), 0,40 (t, ^{3}J(H,H) = 8.1, 2H, Si-CH_2). ^{11}B NMR: δ -2.6 (d, ^{1}J(B,H) = 143, 2B), -9.4 (d, ^{1}J(B,H) = 134, 8B). ^{13}C{^{1}H} NMR: δ 131.1, 130.8, 130.5, 128.8 (C_6H_5), 83.4 (C_c), 82.4 (C_c), 58.3 (O-CH_2), 37.8 (CH_2), 23.1 (CH_2), 18.1 (CH_2-CH_3), 10.2 (Si-CH_2). ^{29}Si{^{1}H} NMR: -46.4

Synthesis of (1-CH_3-2-$CH_2CH_2CH_2$-1,2-$C_2B_{10}H_{10}$)silsesquioxane (9). *Method A*: In a Schlenk flask **5** (0.42 g, 1.05 mmol), 0.2 mL of $CHCl_3$ and DMSO (0.23 mL, 3.24 mmols) were mixed and stirred under N_2 for 48 hours at room temperature. Then, the mixture was washed with water (3 x 10 mL), dried with $MgSO_4$ and evaporation of the solvent under reduced pressure gave an oily product. This residue was treated with EtOH to isolate **9** as a white solid. Yield: 60 mg, 23 %. *Method B*: In a tube, 0.72 g (1.99 mmol) of **7** was dissolved in 993 µL of dried THF. After, 993 µL of a solution containing 19 µL (19 µmol) of TBAF (1M in THF), 54 µL (2.98 mmol) of H_2O and 920 µL of dried THF were added. Then the suspension was stirred for 10 seconds. After 133 days, evaporation of volatiles gave a yellowish solid. This solid was washed with ethanol to isolate **9** as a white solid. Yield: 0.35 g, 70 %. *Method C*: In a tube, 0.53 g (1.46 mmol) of **7** was dissolved in 731 µL of dried THF. After, 731 µL of a solution containing 0.58 mg (0.015 mmol) of NaOH, 40 µL (3.95 mmol) of H_2O and 691 µL of dried THF were added. Then the suspension was stirred for 10 seconds. After 180 days, evaporation of volatiles gave a yellowish solid. This solid was washed with ethanol to isolate **9** as a white solid. Yield: 0.20 g, 55 %. ^{1}H NMR: δ 2.23 (br s, 16H, C_c-CH_2), 2.03 (br s, 24H, C_c-CH_3), 1.70 (br s, 16H, $CH_2CH_2CH_2$), 0.74 (br s, 16H, $CH_2CH_2CH_2$). ^{1}H{^{11}B} NMR: δ 2.23 (br s, B-*H*, C_c-CH_2), 2.03 (br s, 24H, C_c-CH_3), 1.70 (br s, 16H, $CH_2CH_2CH_2$), 0.74 (br s, 16H, $CH_2CH_2CH_2$). ^{11}B NMR: δ -4.2 (16B), -8.9 (64B). ^{13}C{^{1}H} NMR: δ 75.1 (C_c), 37.9 (CH_2), 23.2 (CH_2, C_c-CH_3), 12.6 (Si-CH_2). ^{29}Si CP MAS NMR: δ -66.1. FTIR (KBr), cm^{-1}: 2939-2893 (ν (C_{alkyl}-H)), 2592 (ν (B-H)), 1119 (ν (Si-O)). Anal. Calcd. for $C_{48}H_{152}B_{80}O_{12}Si_8$: C, 28.66; H, 7.62, Found: C, 28.77; H, 7.52.

Synthesis of (1-C_6H_5-2-$CH_2CH_2CH_2$-1,2-$C_2B_{10}H_{10}$)silsesquioxane (10). The procedure was the same as for **9** using **6** (0.31 g, 0.78 mmol), 0.2 mL of $CHCl_3$ and DMSO (0.17 mL, 2.39 mmol). The mixture were stirred under N_2 for 48 hours at room temperature and was washed with water (3 x 10 mL), dried with $MgSO_4$ and evaporation of the solvent under reduced pressure gave an oily product. This residue was treated with EtOH to isolate **9** as a white solid. Yield: 51.6 mg, 21 %. ^{1}H NMR: δ 7.64-7.39 (m, 40H, C_6H_5), 1.75 (br s, 16H, C_c-CH_2), 1.43 (br s, 16H, $CH_2CH_2CH_2$), 0.36 (br s, 16H, $CH_2CH_2CH_2$). ^{1}H{^{11}B} NMR: δ 7.64-7.39 (m, 40H, C_6H_5), 2.40 (br s, B-*H*), 2.27 (br s, B-*H*), 1.75 (br s, 16H, C_c-CH_2), 1.43 (br s, 16H, $CH_2CH_2CH_2$), 0.36 (br s, 16H, $CH_2CH_2CH_2$). ^{11}B NMR: δ -2.0 (16B), -8.6 (64B). FTIR (KBr), cm^{-1}: 3063 (ν (C_{aryl}-H)), 2939-2893 (ν (C_{alkyl}-H)), 2584 (ν (B-H)), 1103 (ν (Si-O)).

Synthesis of $[NMe_4]_8$(7-CH_3-2-$CH_2CH_2CH_2$-7,8-*nido*-$C_2B_9H_{10}$)silsesquioxane (11). To a two necked round bottom flask containing a solution of KOH (0.13 g, 2.00

mmol) in deoxygenated ethanol (10 mL) was added a solution of **9** (0.10 g, 0.05 mmol) in 1 ml of THF. The mixture was refluxed during 6 hours. Then, the volatiles were evaporated in the vacuum and an excess of tetrabutylamonium chloride in water was added to obtain a white solid. This was filtered off, washed with water (3 x 10 mL) and dried under vacuum to obtain **11** as a white solid. Yield: 52.6 mg, 42 %. ^{1}H NMR (CD_3OCD_3): δ 3.43 (s, 96H, $[NCH_3]_4$), 1.68 (br s, 32H, C_c-$CH_2CH_2CH_2$), 1.47 (br s, 24H, C_c-CH_3), 0.63 (br s, 16H, $CH_2CH_2CH_2$). ^{1}H{^{11}B} NMR: δ .43 (s, 96H, $[NCH_3]_4$), 1.68 (br s, 32H, C_c-$CH_2CH_2CH_2$), 1.47 (br s, 24H, C_c-CH_3), 0.63 (br s, 16H, $CH_2CH_2CH_2$), 0.50 (br s, B-*H*), 0.05 (br s, B-*H*), -2.57 (br s, 8H, B*H*B). ^{11}B NMR: δ -6.8 (8B) -8.3 (16B), -16.3 (32B), -32.2 (dd, $^{1}J(B,H)$ = 115, $^{1}J(B,H)$ = 43, 8B), -34.6 (d, $^{1}J(B,H)$ = 138, 8B). ^{13}C{^{1}H} NMR: δ 61.6 (C_c), 55.4 ($[NCH_3]_4$), 39.4 (CH_2), 23.8 (CH_2) 21.8 C_c-CH_3), 13.3 (Si-CH_2). FTIR (KBr), cm^{-1}: 2932-2893 (ν (C_{alkyl}-H)), 2515 (ν (B-H)), 1489 (ν (C-N)) 1111 (ν (Si-O)).

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ANNEX III - RECONEIXEMENT CIENTÍFIC

La Societat Catalana de Química, ha atorgat un accèssit al

Premi de la Societat Catalana de Química

corresponent al LXXIII Cartell de premis i de borses d'estudi

a la senyora

Arántzazu González Campo

pel treball titulat

Els clústers de bor com a integrants d'estructures dendrimèriques

Antoni Riera
Secretari

Vist i plau,

Àngel M[illegible]eguer
President

Barcelona, 22 d'abril de 2004

Institvt d'Estvdis Catalans

I'EC

CONCENTRATES

Carborane carbosilanes prepared

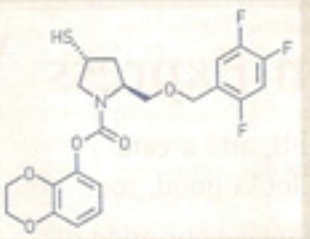
Synthetic methods to incorporate carborane moieties into organosilicon scaffolds to make dendrimers have been reported for the first time by Rosario Núñez and Francesc Teixidor of the Barcelona Institute of Materials Science, in Spain, and their colleagues [*Org. Lett.*, 7, 231 (2005)]. Carboranes are carbon-boron polyhedral clusters, such as $C_2B_{10}H_{12}$, that are readily derivatized. Their applications include boron neutron-capture cancer therapy, selective extraction of radionuclides, and catalysis. The research team used two approaches to make the first-generation dendrimer shown (Si = purple, C = blue, B = orange, H = white). One method involves reacting a carbosilane, $Si[CH_2CH_2Si(CH_3)_2Cl]_4$, with four equivalents of the lithium salt of a phenyl-substituted C_2B_{10} carborane; the carbosilane becomes the core of the dendrimer structure. The second method involves forming a silyl-substituted carborane followed by its reaction with tetravinylsilane, $Si(CH{=}CH_2)_4$.

Flame retardants in household dust

Household dust may be a significant source of polybrominated diphenyl ethers (PBDEs) for humans, according to a study released by NIST and EPA [*Environ. Sci. Technol.*, published online Dec. 29, 2004, http://dx.doi.org/10.1021/es0486824]. Levels of PBDEs, used widely as flame retardants, have increased in human blood and breast milk over the past 25 years. Yet scientists haven't been able to pin down PBDE sources. Earlier work found the chemicals in groceries, which suggested dietary ingestion. However, because PBDEs are used in many household products, including computers, TVs, and couches, NIST's Heather M. Stapleton and her colleagues tested household dust and clothes dryer lint from 17 homes in the southern U.S. They found surprisingly high levels of the compounds, ranging from 700 to 30,100 ng of PBDE per g of dust. Outdoor dirt samples usually average around 100 ng per g.

Anticancer route targets ECE-1

Swiss researchers have shown that thiol inhibitors of endothelin-converting enzyme 1 (ECE-1) represent a promising new type of anticancer agent. The endogenous peptide endothelin-1 (ET-1) is known to promote human tumors by inducing mitosis and preventing apoptosis of cancer cells. Antagonists to ET-1—compounds that prevent it from activating its receptors—are being studied as possible cancer treatments. ET-1 might also be blocked by inhibiting ECE-1, which catalyzes production of ET-1 from an inactive precursor peptide. ECE-1 inhibitors have been identified before, but they've only been studied as potential treatments for cardiovascular or pulmonary disorders. Now, thiol-containing ECE-1 inhibitors (such as the structure shown and a thioacetyl prodrug version) have been synthesized and evaluated for anticancer activity by Johannes D. Aebi of Hoffmann-La Roche, Basel; Lucienne Juillerat-Jeanneret of the University of Lausanne; and coworkers [*J. Med. Chem.*, published online Dec. 31, 2004, http://dx.doi.org/10.1021/jm040857x]. Their experiments show that the compounds inhibit glioblastoma cell growth at low concentrations. Glioblastomas are malignant brain tumors that are currently difficult to treat, and ECE-1 inhibitors may provide a new way to fight such cancers.



Proteomics reveals dynamics of nucleolus

A team at the University of Southern Denmark and the University of Dundee, in Scotland, has used proteomic techniques to study the flux of 489 proteins in the human nucleolus, the structure in the cell nucleus that coordinates the synthesis and assembly of ribosomal subunits, showing that proteomics can measure both dynamic and static situations. Using mass spectrometry and stable-isotope labeling, team leaders Matthias Mann, Angus I. Lamond, and coworkers analyze changes over time in the protein composition of the nucleolus in response to drugs that inhibit transcription or protein degradation [*Nature*, 433, 77 (2005)]. Different nucleolar components show major differences in their kinetics. For example, members of the DEAD box helicase family of proteins respond with a range of kinetics, whereas the subunits of RNA polymerase I leave the nucleolus at almost identical rates. Although many nucleolus components accumulate only in the presence of ribosomal RNA, other protein levels remain steady or even increase in response to transcription inhibition, suggesting that the nucleolus is not a transient structure that breaks down in the absence of transcription.

New microbes thrive in brine

Further evidence has surfaced that microbes can thrive in seemingly inhospitable, salty environments. An international team led by microbial ecologist Paul W. J. J. van der Wielen at the University of Groningen in Haren, the Netherlands, found a thriving ecosystem of microorganisms, including a new order of the saline-loving *Euryarchaeota*, in thousand-year-old anoxic, sequestered salt basins far beneath the eastern Mediterranean Sea [*Science*, 307, 121 (2005)]. Of particular note is the discovery of a unique prokaryotic system in the Discovery Basin, which is almost saturated with magnesium chloride and is one of the most extreme saline environments known on Earth. These prokaryotes contribute to a biogeochemical cycle that includes sulfate reduction and methane production. The work "widens the picture of microbial adaptation to salinity," the authors write, and should increase interest in saline environments elsewhere in the solar system, such as that believed to exist below the icy surface of Jupiter's moon Europa.

NOTICIAS CIENTÍFICAS RELEVANTES

"BUCKYFOLIOS" A PARTIR DE NANOTUBOS DE DOBLE PARED

Aunque los nanotubos de pared sencilla casi siempre eclipsan a sus análogos de doble pared (DWNTs), se prevé que estos últimos tengan mejores propiedades mecánicas, conductividad térmica y estabilidad estructural. Su principal inconveniente es la dificultad de obtener DWNTS en su forma cristalina y pura que permita estudiar sus propiedades a fondo. Muy recientemente, el grupo de M. Endo, profesor de Ingeniería de la Universidad de Shinshu en Nagano, Japón, ha conseguido desarrollar un proceso de obtención de DWNTs de alta pureza [*Nature* **2005**, *433*, 476]. El grupo de M. Endo ha conseguido aislar DWNTs en forma de láminas, como si fuesen "buckyfolios", con una flexibilidad suficiente como para preparar un diminuto avión de papel. EL grupo del Prof. Endo, considera que en un futuro se podrán conseguir aplicaciones reales de este material en el campo de los bi-cables y los dispositivos electrónicos.

El método de purificación de los DWNTs desarrollado por Endo consiste en un procedimiento estándar de deposición en fase de vapor. Para ello se ha utilizado un catalizador de molibdeno que favorece la formación preferencial de nanotubos de doble pared en lugar de nanotubos de pared sencilla. Una posterior purificación de estos "buckyfolios" se consigue mediante un lavado con HCl y posterior oxidación con aire. Este método ha permitido obtener nanotubos de diámetro uniforme y sin la presencia de impurezas tales como nanotubos de pared sencilla, carbono amorfo, catalizador metálico, etc.

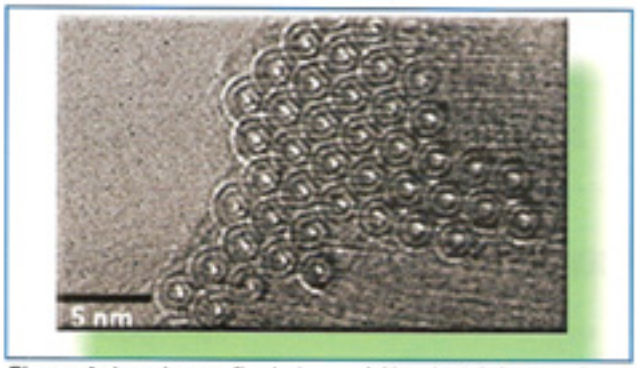


Figura 1. *La micrografía de transmisión electrónica revela un empaquetamiento hexagonal perfecto de los DWNTs.*

LOS ANTIBIÓTICOS PROTEGEN LAS NEURONAS

Recientemente se ha descubierto que las β-lactamas tienen otras aplicaciones distintas de su conocida habilidad para destruir bacterias. Así, se ha visto que estos medicamentos podrían ser la base de los tratamientos de algunas enfermedades neurológicas, incluyendo la esclerosis lateral amiotrópica (ALS). Los investigadores han descubierto esta capacidad de los antibióticos β-lactámicos al comprobar 1040 fármacos aprobados por la FDA. El neurólogo J.D. Rothstein, de la Hopkins University ha investigado compuestos capaces de estimular la producción de transportador de glutamato GLT1. Este glutamato es un neurotransmisor liberado por las neuronas para trasmitir la señal nerviosa a otras neuronas. Pero este componente no tiene un carácter benigno. Si se acumula demasiado glutamato entre las conexiones sinápticas de las neuronas, el sobreestímulo puede provocar la muerte de estas células, favoreciendo la aparición de la ALS. Para evitar estos daños, otras células neuronales, las astroglia, elimina este exceso acumulando el glutamato es su pared celular, evitando así la destrucción de las neuronas. Durante el proceso de *screening* de esos 1040 fármacos, Rothstein y sus colegas descubrieron que las β-lactamas y algunos de sus derivados triplican el efecto neuroprotector [*Nature* **2005**, *433*, 73]. En ratones, el tratamiento con la b-lactama ceftriaxona ralentiza notablemente el avance de la ALS. Estos hallazgos han permitido asegurar a Rothstein que "los fármacos, que no se hayan diseñado genéticamente, pueden aumentar el número de transportadores en las células del cerebro".

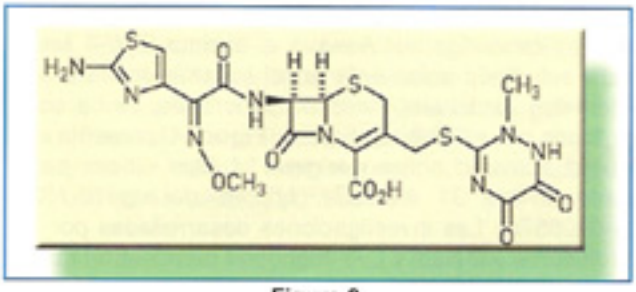


Figura 2.

SÍNTESIS DE CARBORANOS-CARBOSILANOS

Los primeros métodos sintéticos para incorporar fragmentos de carborano en derivados de silicio dirigidos a la preparación de dendrímeros se han descrito en Barcelona, por el grupo de investigación de R. Núñez y F. Teixidor, del Instituto de Ciencia de Materiales [*Org. Lett.* **2005**, *7*, 231]. Los carboranos son clusters poliédricos de carbono y boro, como por ejemplo $C_2B_{10}H_{12}$, que se pueden funcionalizar fácilmente. Entre sus aplicaciones destaca la terapia anticancerígena de captura de boro neutro, la extracción selectiva de radionucleótidos y la catálisis. Estos investigadores han utilizado dos aproximaciones diferentes para obtener el dendrímero

de primera generación mostrado en la **Figura 3** (Si = púrpura, C = azul, B = naranja, H = blanco). Uno de estos métodos consiste en hacer reaccionar un carbosilano, $Si[CH_2CH_2Si(CH_3)_2Cl]_4$, con cuatro equivalentes de la sal de litio de un carborano C_2B_{10} con un sustituyente fenilo, de tal forma que el carbosilano constituye el core central de la estructura dendrimérica. El segundo método sintético consiste en formar un carborano silil-sustituido, seguido de su reacción con tetravinilsilano, $Si(CH=CH_2)_4$.

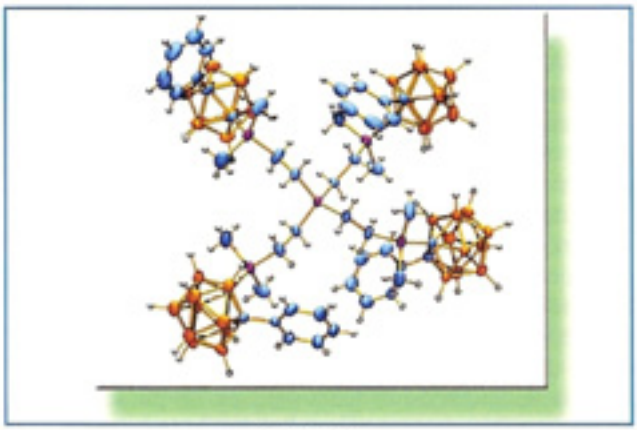


Figura 3.

AGENTES ANTICANCERÍGENOS PORTADORES DE GRUPOS TIOL

Un grupo de investigadores de la Universidad de Lausanne, Suiza, ha comprobado que el enzima ECE-1, portadora de un grupo tiol, representa un prometedor agente anticancerígeno. Es conocido que el péptido endotelina-1 (ET-1) es capaz de generar tumores en humanos al inducir la mitosis y evitar la apoptosis de las células cancerígenas. Aunque el enzima ECE-1 había sido estudiado solamente en el tratamiento de enfermedades cardiovasculares o pulmonares, se ha comprobado que el inhibidor ECE-1 (**Figura 4**) presenta una buena actividad anticancerígena [*J. Med. Chem. publicado on-line 31 /12/2004, http://dx.doi.org//10.1021/jm040857x*]. Las investigaciones desarrolladas por los profesores J.D Aebi y L.-J Jeanneret demuestran que el enzima ECE-1 inhibe el crecimiento de las células de glioblastoma, las cuales dan lugar a tumores malignos cerebrales de difícil tratamiento, constituyendo un importante arma para la lucha contra este tipo de cánceres.

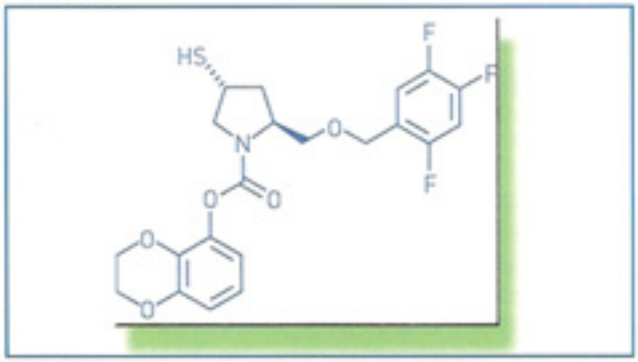


Figura 4.

RELLENANDO FULLERENOS

Mediante el uso de la síntesis orgánica como bisturí y como puntos de sutura, el grupo de Komatsu, en la Universidad de Kyoto, Japón, ha desarrollado una *cirugía molecular* en un fullereno. Este grupo de investigación ha conseguido abrir un orificio en la jaula de carbono del fullereno, introducir H_2 en su interior y, en cuatro pasos de síntesis, cerrar el armazón de C_{60} para obtener un fullereno endohédrico $H_2@C_{60}$ [*Science* **2005**, *307*, 238]. El punto clave de este trabajo, es que "por primera vez, se muestra el gran potencial de la síntesis orgánica en la producción de fullerenos endohédricos, cuya producción actual se basaba en métodos físicos de difícil control y en condiciones extremas", según palabras del propio Komatsu.

Previamente, el grupo del profesor Komatsu había descrito la síntesis de un nanocontenedor derivado de C_{60} con un orificio correspondiente a un anillo de 13 miembros el cual se ha rellenado con H_2 (*C&EN, 16 Junio 2003, p.5*). Según palabras de Komatsu, "su éxito depende de la presencia de un átomo de azufre, fácilmente eliminable, en el borde del orificio. Una vez que el hidrógeno queda atrapado dentro del fullereno, el átomo de azufre se oxida pasando a un grupo sulfóxido, el cual se elimina fotoquímicamente, disminuyendo así el tamaño del orificio. El acoplamiento de los carbonos carbonílicos catalizado por titanio disminuye aún más el tamaño de dicho orificio, de tal forma, que ahora es tan pequeño que es posible calentar el compuesto si perder el H_2. El derivado de fullereno sufre una transposición, se cree que una electrociclación térmicamente permitida, para restablecer el fullereno.

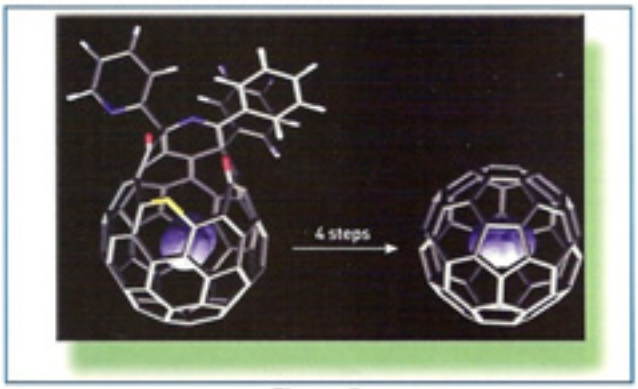


Figura 5.

NUEVA RUTA SINTÉTICA DE AMINOÁCIDOS ALÍLICOS

La síntesis de compuestos con interés biológico puede haber experimentado un notable avance gracias a la nueva ruta sintética de aminoácidos alílicos descrita por J. Sweeney, de la Universidad de Reading (Inglaterra). El grupo de Sweeney ha comprobado que los iluros de amonio acíclicos y alílicos se pueden reconvertir en una amplia gama de aminoácidos análogos con buenos rendimientos y con elevadas estereo- y enantioselectividades. El método permite obtener de forma rápida y eficaz (*R*)-alilglicina (**Figura 6**) en un 86 % de