Carboranyl Substituted Siloxanes and Octasilsesquioxanes: Synthesis, Characterization, and Reactivity

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ABSTRACT: Carboranyl-containing disiloxane, cyclic-siloxane and cage-like silsesquioxane have been prepared in high yields. Two routes are compared for their preparation, a classical hydrolytic process based on hydrolysis and condensation of the freshly prepared carboranylalkylchlorosilane and ethoxysilane precursors and a nonhydrolytic route based on the specific reactivity of chorosilane toward DMSO. Based on the typical reactivity of the carboranyl group toward nucleophiles, dianionic disiloxanes and octaanionic silsesquioxanes were obtained without modification of the siloxane bond. Products are fully characterized by FTIR, NMR and MALDI-TOF methods.

Introduction

The 1,2-dicarba-*closo*-dodecaborane and derivatives present exceptional characteristics,[1,2] such as low nucleophilicity, chemical inertness, thermal stability,[3] electron-withdrawing properties,[4] and stability and low toxicity in biological systems,[5] which have stimulated the development of a wide range of potential applications based on a molecular approach of the synthesis of material.[6,7] Moreover, the rigid geometry and the relative easiness of derivatization of the carborane allows the preparation of a wide number of compounds in view of the preparation of precursors of materials.[8] Indeed, we have reported the synthesis of carboranyl-containing star-shaped molecules and dendrimers in which carbosilane cores are used as scaffold.[9] Due to the specificity and the versatility of carboranes to be chemically modified,[10] they have been an ideal stable and suitable group whose partial degradation allows a unique route to very large carboranyl-containing polyanionic dendrimers.[9c] On the other hand, as a part of our ongoing studies, hybrid organic−inorganic silicon-based material have been prepared by Sol−Gel chemistry.[11] The resulting insoluble organo-carboranyl bridged polysilsesquioxanes have been prepared and have shown to be a versatile class of materials in which the presence of carborane units provides mesostructuration and a high thermal and chemical stability.[3b,11]

Following with our interest on the functionalization of carborane clusters-containing dendrimers and macromolecules, we thought that the preparation of a new family of siloxane compounds was an important field to explore. In this paper, we report on the association of the cage structure of carborane with siloxane and silsesquioxane cage-like structure. Such polyhedral oligomeric silsesquioxanes [POSS; $(RSiO_{1.5})_n$; $n = 8$] are nanosized building blocks for organic/inorganic hybrid materials; their high potential for applications is based on the possibility to control and balance the inorganic and organic moieties in their architecture.[12] Therefore, they can be tuned for very different applications in accordance with the nature of the organic functionality, as demonstrated by some recent examples: in biomaterial systems, POSS have been used for preparing a new generation of silica nanocomposites with particular use in cardiovascular interventional devices,[13] and in material chemistry, they are used as coupling agents of metal oxide nanoparticles,[14] cross-linking agents into organic polymers,[15] and as octa-arms dendrimers-core.[12f,16,17]

Our aim is to obtain new carboranyl-containing molecules and macromolecules in which the clusters are attached to linear, cyclic, or cage structures like in siloxanes and silsesquioxanes as cores, respectively. Such silicon-containing structures are usually prepared by hydrolysis and condensation of alkylchlorosilanes but this approach is limited due to the formation of linear siloxanes or resins and a large variety of cages as byproduct. Nevertheless, their formation can be controlled using a water-free approach such as employing DMSO as oxygen source[18] or the condensation between Si−H and Si−OMe.[19] This former method has recently been used to prepare hexasilsesquioxanes (T_6),[18a] silicones,[18b] cyclodisiloxanes,[18c,d] and silsesquioxanes particles,[18e] providing a well controlled way to obtain Si−O bonds using soft conditions.

The controlled chemical modification of the carborane moieties in such siloxane structure is, *a priori*, achievable according to the known literature procedure, by elimination of one vertex BH from the *closo* clusters using nucleophiles, such as alkoxides,[20] amines,[21] fluorides,[22] or phosphanes.[23] One important point was to clarify if this chemical modification of the carborane part could be compatible with the siloxane linkage in the present compounds. It is well-known that the Si−O−Si bond presents a great thermal, hydrolytic, and photostability; however, at high temperatures and in the presence of acids or bases, the Si−O bond in silicones can undergo hydrolytic scission.[24]

Although the disiloxyl link is formally analogous to an ether link, it is considerably more polar so that it is both more hydrophilic and more susceptible to hydrolysis.

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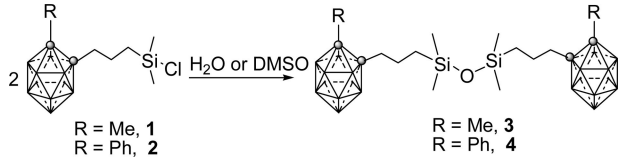
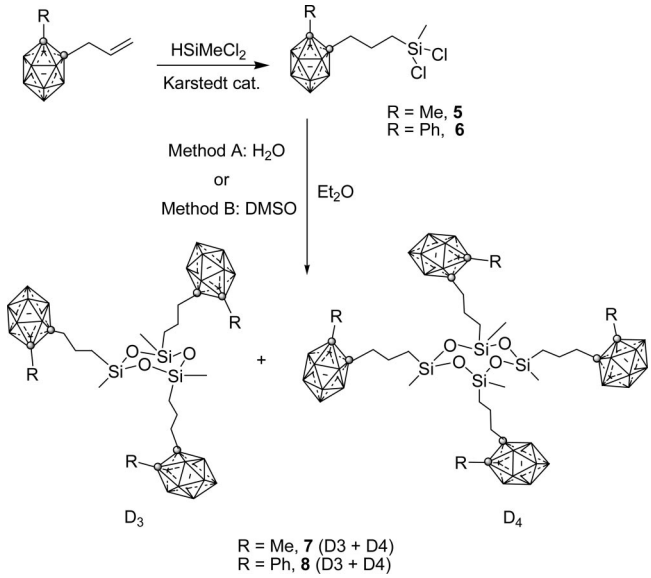
Scheme 1. Preparation of Carboranyldisiloxane Dimers 3 and 4 Using Either Water or Dimethylsulfoxyde as an Oxygen Donor



Scheme 2. Preparation of 7 and 8 as a Mixture of D_3 and D_4 Cyclosiloxanes via the Hydrolysis of Dichlorosilanes 5 and 6



Results and Discussion

Preparation of Disiloxanes, Cyclosiloxanes, and Octasilsesquioxanes. Recently, we have reported the synthesis of 1-CH_3-2-[$CH_2CH_2CH_2(CH_3)_2SiCl$]-1,2-*closo*-$C_2B_{10}H_{10}$ (**1**) and 1-C_6H_5-2-[$CH_2CH_2CH_2(CH_3)_2SiCl$]-1,2-*closo*-$C_2B_{10}H_{10}$ (**2**) by hydrosilylation of the corresponding allylic precursor.[9c]

Here, monomers **1** and **2** displayed the typical reactivity of silylchloride in the presence of water leading, respectively, to the disiloxane [1-CH_3-2-$CH_2CH_2CH_2(CH_3)_2$Si-1,2-*closo*-$C_2B_{10}H_{10}]_2O$, (**3**) and [1-C_6H_5-2-$CH_2CH_2CH_2(C_6H_5)_2$Si-1,2-*closo*-$C_2B_{10}H_{10}]_2O$ (**4**; Scheme 1), without any other byproduct and in high yield. The HCl released by the hydrolysis of the Si−Cl bond acts as a catalyst for the condensation of the silanol without hydrolysis of the Si−O bonds that is sometime observed.[24]

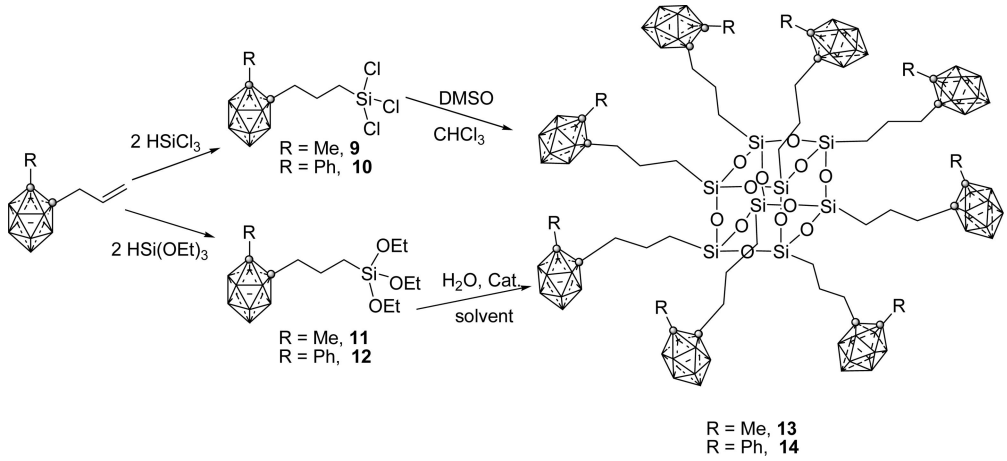
Likewise, a "non-aqueous" approach using DMSO as oxygen source[18b] has also been used to form the carboranyl-containing disiloxanes **3** and **4**. The reaction of **1** and **2** with DMSO in $CHCl_3$ at room temperature overnight led to the formation of the corresponding siloxane, although the yield is lower than that of the hydrolytic route.

Following the same general approaches, we intended the preparation of cyclic siloxanes from dichlorosilanes via hydrolytic or DMSO route. In a first step, compounds 1-CH_3-2-[$CH_2CH_2CH_2(CH_3)SiCl_2$]-1,2-*closo*-$C_2B_{10}H_{10}$ (**5**) and 1-C_6H_5-2-[$CH_2CH_2CH_2(CH_3)SiCl_2$]-1,2-*closo*-$C_2B_{10}H_{10}$ (**6**) were prepared by hydrosilylation of the corresponding allylic compound with $H(CH_3)SiCl_2$ in the presence of Karstedt catalyst (Scheme 2). Reaction of compounds **5** and **6** in Et_2O with the stoichiometric amount of DMSO for 30 min at room temperature (Method B) or an excess of H_2O (Method A) for 2 h give compounds **7** and **8**, respectively (Scheme 2). According to the NMR and the MALDI-TOF data (see results below) **7** and **8** are a mixture of cyclic siloxanes: D_3 (cyclotrisiloxane), D_4 (cyclotetrasiloxane), along with different quantities of linear polysiloxanes (L). After chromatography of the crude over a silica column (hexane/Et_2O (1:1)) the following mixture was identified: the DMSO method leads to mostly a D_3/D_4/L (50:50:0) mixture for **7**, and a D_3/D_4/L (50:44:6) mixture for **8**; whereas, the hydrolytic approach leads to a D_3/D_4/L (33:40:27) mixture for **7** and a D_3/D_4/L (22:12:66) mixture for **8**. As previously reported,[18c] when DMSO was used as oxygen source, the percentage of D_3 was slightly higher compared to D_4. In addition, minor amounts of linear siloxanes were produced by this route, whereas in the hydrolytic method an elevated concentration of linear polysiloxane was obtained.

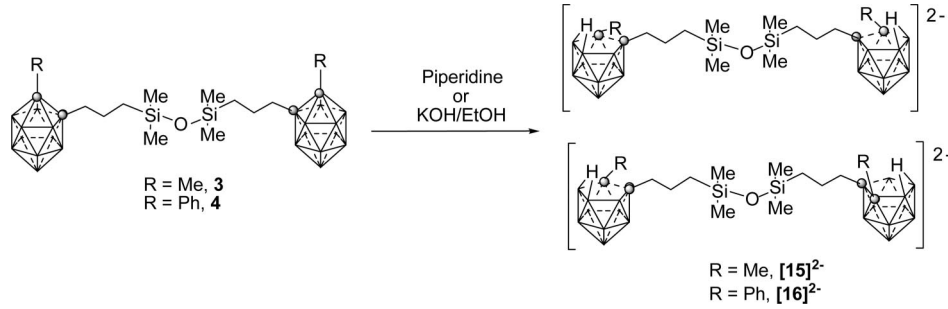
The next step was to prepare the T_8 structures[12b] either by the "anhydrous" DMSO methods or the hydrolytic one. The required precursors were prepared by hydrosilylation of 1-CH_3-2-$CH_2CH{=}CH_2$-1,2-$C_2B_{10}H_{10}$ and 1-C_6H_5-2-$CH_2CH{=}CH_2$-1,2-$C_2B_{10}H_{10}$ with $HSiCl_3$ and $HSi(OCH_2CH_3)_3$, respectively. Compounds **9**−**12** were obtained quantitatively, and remarkably, only the α adduct is formed (Scheme 3). Preparation of POSS by the nonhydrolytic method from trichlorosilanes **9** and **10** was carried out in DMSO/$CHCl_3$ mixture (2:1) or (3:1) at room temperature leading to T_8 cages **13** and **14** in 23 and 21% yields, respectively (Scheme 3). Remarkably, only one signal at −66 ppm was observed by ^{29}Si NMR spectroscopy. This is in accordance with the chemical shifts for Si atoms in T_8 cages (from −65 to −67 ppm),[25] and this is clearly different from the chemical shifts measured for T_6 cage (usually between −54 to −57 ppm) reported by Taylor and Bassindale who prepared them by the DMSO route.[18a] POSS **13** and **14** were also obtained by the hydrolysis of **11** and **12**, respectively, using different reaction conditions for each case. POSS **13** was obtained in 70% yield by adding the stoichiometric amount of water to a solution of **11** in THF using TBAF as catalyst at room temperature for a long reaction time (133 days). When the NaOH was used as catalyst, a longer reaction time was necessary (180 days), however, a lower yield was obtained (55%). On the other hand, POSS **14** was also obtained in only 28% yield by addition of water to a solution of **12** in $CHCl_3$ using TBAF at room temperature for 24 h. The TBAF was a better catalyst, however, attempts to decrease the reaction time led to lower yields and increasing the amounts of TBAF or NaOH were unsuccessful because they gave rise to the *closo* cluster degradation and formation of *nido* compounds.

Controlled Chemical Transformation of Disiloxanes and Octasilsesquioxanes. Partial degradation of the carborane moiety in **3** and **4** was achieved in a first approach by the deboronation reaction using soft conditions such as piperidine in ethanol at reflux with a carborane/piperidine ratio of 1:5.[26] This method was developed by our group to avoid the $C_{cluster}$−P (C_c-P) cleavage by the nucleophilic attack in the degradation of *closo*-carboranylphosphines and have been recently used for the degradation of *closo*-carboranyldisulfides.[27] In this method, the nucleophile, the ion EtO^-, is smoothly generated by reaction of the ethanol with piperidine. In the present work, the dianionic disiloxanes {[1-CH_3-2-$CH_2CH_2CH_2(CH_3)_2$Si-1,2-*nido*-$C_2B_9H_{10}]_2O\}^{2-}$, $[\mathbf{15}]^{2-}$, and {[1-C_6H_5-2-$CH_2CH_2CH_2(CH_3)_2$Si-1,2-*nido*-$C_2B_9H_{10}]_2O\}^{2-}$, $[\mathbf{16}]^{2-}$ were isolated in high yield (Scheme 4). The modification of the carboranyldisiloxanes **3** and **4** was also performed by the classical reaction of KOH in ethanol at reflux, with a carborane/KOH ratio of 1:5, leading again to the formation of the dianionic compounds $[\mathbf{15}]^{2-}$ and $[\mathbf{16}]^{2-}$. Contrarily, to the *closo*-carboranyldisulfides, (1-*S*-2-*R*-1,2-*closo*-$C_2B_{10}H_{10})_2$,[27] in which the disulfide bridge S−S was split to give the anionic thiolate fragment [1-*S*-2-*R*-1,2-*closo*-$C_2B_{10}H_{10}]^-$, in our case, the EtO^- act as nucleophile, removing the B(3) or B(6) from the *closo* cluster and keeping the Si−O−Si bond unaltered. In addition, both clusters were

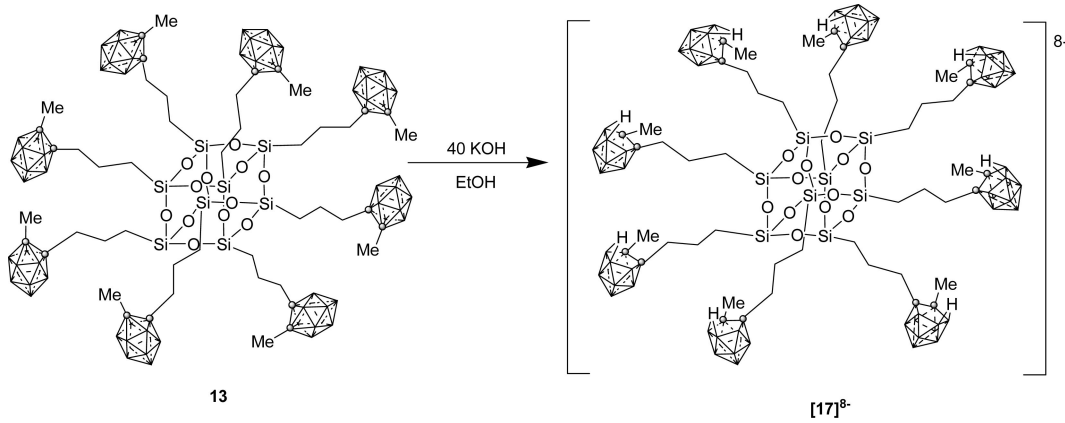
Scheme 3. Preparation of Precursors 9−12 by Hydrosilylation of 1-*R*-$CH_2CH{=}CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$ and the Preparation of Carboranyl-Containing Silsesquioxanes 13 and 14 by the Hydrolytic and the Nonhydrolytic Methods



Scheme 4. Chemical Transformation of Carboranyldisiloxanes 3 and 4 Leading to Dianionic Species $[15]^{2-}$ and $[16]^{2-}$



Scheme 5. Chemical Transformation of *closo*-Carboranylsilsesquioxane 13 Leading to the Octaanionic Species $[17]^{8-}$



deboronated to obtain the dianionic species, quite the opposite than for dicarboranylthioether (2-CH_3-1,2-*closo*-$C_2B_{10}H_{10})_2S$ in which the monoanionic sulfur bridge anion [(2-CH_3-1,2-*closo*-$C_2B_{10}H_{10})S$(8-CH_3-7,8-*nido*-$C_2B_9H_{10})]^-$ was formed. Dianions $[\mathbf{15}]^{2-}$ and $[\mathbf{16}]^{2-}$ were isolated as $[N(CH_3)_4]^+$ salts by precipitation with a solution of $[N(CH_3)_4]Cl$.

Likewise, the chemical modification of T_8 cage **13**, using EtO^- as nucleophile, was also achieved using KOH with the same carboranyl/KOH ratio as used for the carboranyldisiloxanes, getting the octaanionic species $[\mathbf{17}]^{8-}$ (Scheme 5).

Characterization of Compounds. The structures of compounds **3**−$[\mathbf{17}]^{8-}$ were established on the basis of FT-IR, ^1H, ^{11}B, ^{13}C, and ^{29}Si NMR spectroscopy, MALDI-TOF and ESI mass spectrometry in some cases and the structure of **3** was also confirmed by X-ray diffraction analysis. The IR spectra of compounds containing *closo* clusters present the typical ν(B−H) strong bands around 2584 cm^{-1}, whereas for anionic species the ν(B−H) appears at 2515 cm^{-1}, due to the presence of *nido* clusters. In compounds **3**, **4**, **7**, and **8**, bands near 1256 cm^{-1} corresponding to $\delta(Si-CH_3)$ and characteristic bands between 1065 and 1072 cm^{-1} due to the vibration frequency of the Si−O bond are presented. In octasilsesquioxanes **13** and **14**, the absorption on this vibration is shifted to 1103−1119 cm^{-1}. The ^1H NMR spectra of the methyl-carborane exhibit resonances around 2.02 ppm attributed to the C_c-CH_3 protons, whereas the phenyl-carborane derivatives show signals in the 7.68−7.36 ppm due to phenyl protons. Resonances for protons of the propyl chain -$(CH_2)_3$-, in the region 2.23−0.24 ppm, have been unambiguously assigned in most cases. As can be appreciated, in the phenyl-carborane derivatives, -$(CH_2)_3$- proton resonances are shifted to a higher field with respect to methyl-carborane derivatives, probably due to the electronic ring effect caused

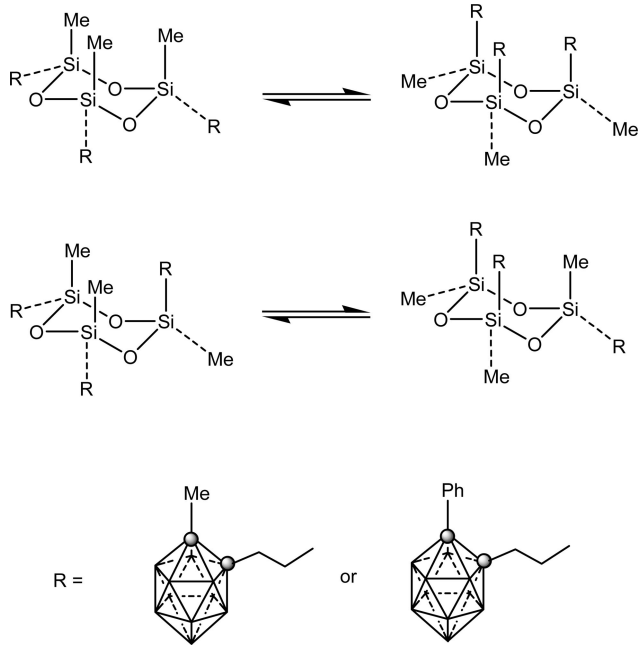


Figure 1. Different isomers for cyclotrisiloxanes D3.

by the phenyl group.[28] It has been reported that in carboranyl derivatives, when hydrogen atoms are placed on the top of the phenyl ring, a displacement to a high field is observed in the ^{1}H NMR spectrum.[9a,28b] The same effect was observed in anionic species, in which methylene protons appear in the region 1.68 to 0.46 ppm for [**15**]$^{2-}$ and [**17**]$^{8-}$, whereas [**16**]$^{2-}$ appears between 1.24 and −0.04 ppm. Another important point of the ^{1}H NMR spectra of compounds **3**−**8** is the resonances for Si−CH_3 protons from 0.07 to −0.18 ppm. For the mixture, the signals are difficult to assign due to the presence of chains and isomers of cycles D_3 and D_4, in which the methyl groups can be distributed in axial or equatorial positions, such as shown in Figure 1 for D_3. Indeed, for D_3 and D_4, the Si−CH_3 signals in the ^{1}H NMR appear as a set of three resonances. A tentative attribution is given in the experimental part and is based on the ^{1}H NMR integration supported by the MALDI-TOF data. For anionic compounds, the signal of the B−H−B bridge was unambiguously characterized by ^{1}H{^{11}B} NMR spectra, which appears between −2.60 and −2.19 ppm. The ^{13}C{^{1}H} NMR spectra for phenyl-*o*-carborane derivatives show resonances around 83.0 and 81.1 ppm attributed to the C_c atoms and additional resonances between 131 and 127 ppm due to phenyl carbon atoms. For methyl-*o*-carborane derivatives, the resonances attributed to the C_c atoms appear at higher fields, between 78.7 and 74.6 ppm, and CH_3 groups bonded to the cluster at 22−23 ppm. The Si-CH_3 carbon resonances appear at 0.4 and 0.2 ppm in the ^{13}C{^{1}H} NMR spectra. The ^{11}B{^{1}H} NMR resonances for **3**, **4**, **7**, **8**, **9**, and **10** appear in the *closo* region,[29] from δ −2.6 to −9.9 ppm, signals appearing in these cases with the following patterns 1:1:8 and 2:8, in general. Conversely, the ^{11}B resonances of anionic compounds appear between −5.9 and −36.3 ppm due to the presence of *nido*-carboranes with patterns 1:2:4:1:1 or 1:1:1:2:1:1:1 (see Figure 2).

The ^{29}Si{^{1}H} NMR spectra of both disiloxanes **3** and **4** exhibit a single signal around 6.7 ppm. In agreement with the previous literature, the trichlorosilanes precursors **9** and **10** show resonances at 11.5 and 11.3 ppm, respectively, whereas the triethoxysilanes precursors **11** and **12** show resonances at higher fields, around −46.5 ppm. The ^{29}Si CP MAS spectrum for **13** and **14** show a resonance at −66.0 ppm, which confirmed the formation of T_8 cages. The presence of *nido* carborane clusters in compounds [**15**]$^{2-}$, [**16**]$^{2-}$, and [**17**]$^{8-}$ did not affect the ^{29}Si

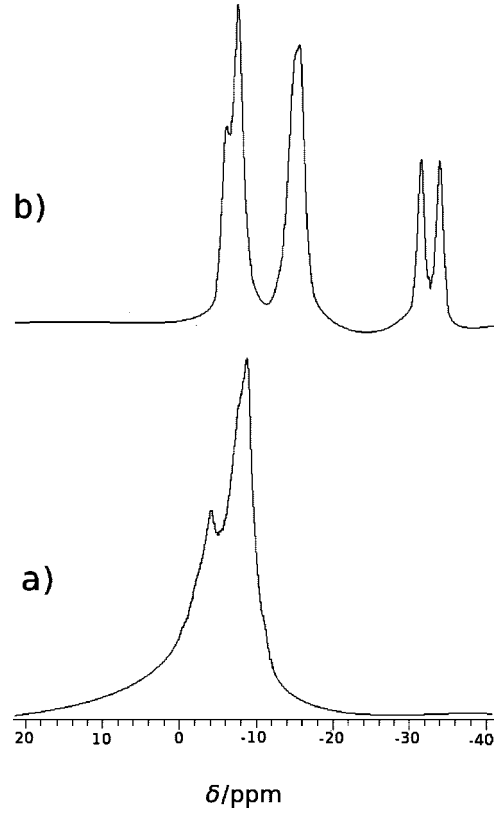


Figure 2. ^{11}B NMR spectra for (a) **13** and (b) [**17**]$^{8-}$.

NMR chemical shifts with respect to their respective precursors **3**, **4**, and **13**. No influence on the ^{29}Si{^{1}H} NMR chemical shifts for related *closo* and *nido* compounds (**3** and [**15**]$^{2-}$; **4** and [**16**]$^{2-}$; **13** and [**17**$^{8-}$) was observed. Finally, as was remarked previously, for T_8 cages, only one signal was observed at −66 ppm, in agreement with the range for common octasilsesquioxanes.[25]

The molecular formula of disiloxanes and cyclosiloxanes was confirmed by using the MALDI-TOF mass spectrometry in the negative-ion mode without matrix. For all cases, a full agreement between the experimental and calculated patterns was also obtained for the molecular ion peaks. The MALDI-TOF mass spectrum of **3** indicated that the molecular ion peak appears at m/z = 529.68, with a perfect concordance with the calculated pattern. For **7**, two molecular ion peaks at m/z = 776.34 and 1034.81, corresponding to the respective D_3 and D_4, indicated the presence of both cyclosiloxanes in the solid. In addition, an elevated number of molecular peaks corresponding to different fragments were also found, which was higher when the hydrolytic process was used.

Crystal Structure of 3. The molecular structure of **3** is shown in Figure 3. Molecule **3** is located around a crystallographic inversion center, which means that the oxygen atom (O1) is disordered in two positions in the vicinity of the inversion center, and also, each Si, C17, and C18 atom occupies two neighboring positions (a and b) leading to nonlinear Si−O−Si angles of about 166° (see Figure 3, only the a form is shown). If the structure was more ordered, the central oxygen atom would occupy the center of inversion thus leading to a linear Si−O−Si angle.

The Si−O−Si angle of 166° that is measured here is in the range of that recently reported for 40 acyclic disiloxanes varying from 140 to 180°, with no clear reason for this variation.[30]

The quality of the crystal and the structural disorder that results does not allow for deeper discussion of the bonding

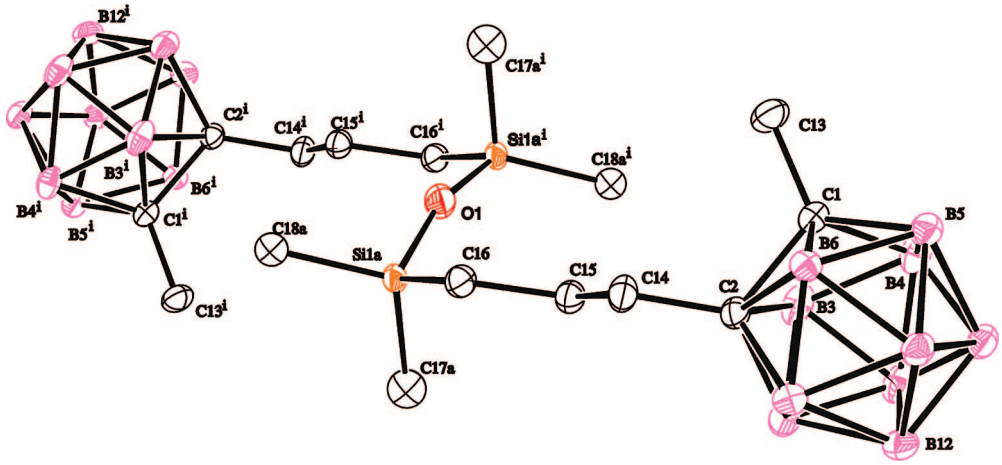


Figure 3. Molecular structure of [1-CH_3-2-$CH_2CH_2CH_2(CH_3)_2$Si-1,2-*closo*-$C_2B_{10}H_{10}]_2O$ (**3**).

parameters. However, the bonding parameters in the boron cage are quite usual. This is exemplified by the C1−C2 bond of 1.664(7) Å, which is quite a normal C−C bond in this type of the boron cages.

Conclusions

The present results have demonstrated the possibility to combine easily in the same molecule a carboranyl substructure with the Si−O−Si linkage of either a cyclic siloxane or a cage-like structure of polysilsesquioxane. Moreover, we point out the efficiency of the nonhydrolytic route with DMSO, which is particularly attractive for limiting the formation of linear oligo-polysiloxane. Finally, in all the cases, the Si−O−Si bond is chemically stable enough to allow the specific and clean partial degradation of the carboranyl group. The polyanionic species that results from this transformation could be further tested for silicon or ionic liquid applications.

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 an ions 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 pulses); voltage ion source 20.00 kV (Uis1) and 17.50 kV (Uis2)]. 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. ^{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 $CDCl_3$ or CD_3COCD_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 at room temperature otherwise it is mentioned. Solvents were reagent grade and were purified by distillation from appropriate drying agents before using. 1-CH_3-1,2-*closo*-$C_2B_{10}H_{11}$ and 1-C_6H_5-1,2-*closo*-$C_2B_{10}H_{11}$ were supplied by Katchem Ltd. (Prague) and used as received. Karstedt's catalyst (platinum−divinyltetramethyldisiloxane complex, 2.1−2.4% platinum in vinyl-terminated polydimethylsiloxane in xylene solution), $HSiCl_3$, and $HSi(OCH_2CH_3)_3$ were purchased from ABCR and used as received. Compound $[Si(CH{=}CH_2)_4]$ was purchased from Acros. The *n*-BuLi solution (1.6 M in hexanes) and $H(CH_3)SiCl_2$ were purchased from Aldrich. The TBAF solution (1 M in THF) and NaOH were purchased from Aldrich and used as received. 1-(C_6H_5)-2-$CH_2CH{=}CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$, 1-(CH_3)-2-$CH_2CH{=}CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$,1-(C_6H_5)-2-$[CH_2CH_2CH_2(CH_3)_2SiCl]$-1,2-*closo*-$C_2B_{10}H_{10}$ and 1-(CH_3)-2-$[CH_2CH_2CH_2Si(CH_3)_2Cl]$-1,2-*closo*-$C_2B_{10}H_{10}$ were prepared according to the literature.[9c] Silica SDS 60 with 35−70 μm and 550 m^2g^{-1} was used for column chromatography.

Preparation of [1-CH_3-2-$CH_2CH_2CH_2(CH_3)_2$Si-1,2-*closo*-$C_2B_{10}H_{10}]_2O$ (3). *Method A.* To a round-bottom flask containing 1-(CH_3)-2-$CH_2CH_2CH_2(CH_3)_2$SiCl-1,2-*closo*-$C_2B_{10}H_{10}$ (0.28 g, 0.95 mmol), 0.05 mL (2.7 mmol) of H_2O, and 5 mL of dried Et_2O were added. The mixture was stirred over a period of 10 min, transferred to a separatory funnel, and extracted. The organic layer was dried over $MgSO_4$ and concentrated in vacuum to obtain **3** as a white waxy solid. Yield: 0.18 g, 72%.

Method B. In a Schlenk flask, 1-(CH_3)-2-$CH_2CH_2CH_2((CH_3))_2$SiCl-1,2-*closo*-$C_2B_{10}H_{10}$ (0.28 g, 0.95 mmol), $(CH_3)_2SO$ (0.3 mL, 4.22 mmol), and 4 mL of $CHCl_3$ were mixed and stirred overnight. The mixture was then quenched with 8 mL of H_2O and transferred to a separatory funnel. The organic layer was washed with water (2 × 8 mL), dried over $MgSO_4$, and concentrated in vacuum to obtain **3** as a white waxy solid. Yield: 0.10 g, 40%. Hexane vapor diffusion into $CHCl_3$ solution of **3** gave single crystals for X-ray analysis. ^1H NMR δ 2.20 (t, $^3J_{(H,H)}$ = 8.5, 4H, C_c-CH_2), 2.02 (s, 6H, C_c-CH_3), 1.59 (m. 4H, $CH_2CH_2CH_2$), 0.54 (t, $^3J_{(H,H)}$ = 8.5, 4H, CH_2-Si), 0.10 (s, 12H, Si−CH_3). $^1H\{^{11}B\}$ NMR δ 2.20 (t, $^3J_{(H,H)}$ = 8.5, 4H, C_c-CH_2), 2.25, 2.21, 2.15, 2.11 (br s, B-*H*), 2.02 (s, 6H, C_c-CH_3), 1.59 (m, 4H, $CH_2CH_2CH_2$), 0.54 (t, $^3J_{(H,H)}$ = 8.5, 4H, CH_2-Si), 0.10 (s, 12H, Si−CH_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). $^{13}C\{^1H\}$ NMR δ 78.0 (C_c), 74.6 (C_c), 38.7 (CH_2), 23.7 CH_2 or C_c-CH_3), 23.1 (CH_2 or C_c-CH_3), 18.2 (Si-CH_2), 0.4 (Si-CH_3). $^{29}Si\{^1H\}$ 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 $C_{16}H_{50}B_{20}Si_2O$: C, 36.19; H, 9.49. Found: C, 36.27; H 9.58. MALDI-TOF-MS (*m*/*z*): calcd, 530.97; found, 529.68 [M − 1]$^-$.

Preparation of [1-C_6H_5-2-$CH_2CH_2CH_2(CH_3)_2$Si-1,2-*closo*-$C_2B_{10}H_{10}]_2O$ (4). To a round-bottom flask containing 1-(C_6H_5)-2-$CH_2CH_2CH_2(CH_3)_2$SiCl-1,2-*closo*-$C_2B_{10}H_{10}$ (0.28 g, 0.80 mmol), 3 mL of dried Et_2O, and 13 μL (0.81 mmol) of H_2O were added. The mixture was stirred over a period of 10 min and transferred to a separatory funnel. The organic layer was washed with H_2O (2 × 5 mL) and the aqueous layer was washed with Et_2O (3 × 5 mL). Then the organic layer was dried over $MgSO_4$ and concentrated in vacuum to obtain compound **4** as a yellowish oil. Yield: 0.21 g, 81%. ^1H NMR δ 7.66−7.40 (m, 10H, C_6H_5), 1.77 (t, $^3J_{(H,H)}$ = 8.1,

4H, C_c-CH_2), 1.38 (m, 4H, $CH_2CH_2CH_2$), 0.24 (t, $^3J_{(H,H)}$ = 8.5, 4H, CH_2-Si), −0.08 (s, 12H, Si−CH_3). ^{1}H{^{11}B} NMR δ 7.66−7.40 (m, 10H, C_6H_5), 2.73 (br s, 4H, B-*H*), 2.37 (br s, 12H, B-*H*), 2.27 (br s, 4H, B-*H*), 1.77 t, $^3J_{(H,H)}$ = 8.1, 4H, C_c-CH_2), 1.38 (m, 4H, $CH_2CH_2CH_2$), 0.24 (t, $^3J_{(H,H)}$ = 8.5, 4H, CH_2-Si), −0.08 (s, 12H, Si−CH_3). ^{11}B NMR δ −2.7 (d, $^1J_{(B,H)}$ = 133, 4B), −9.5 (br s, 16B). ^{13}C{^{1}H} NMR δ 131.1, 130.8, 130.6, 128.9 (C_6H_5), 83.4 (C_c), 82.3 (C_c), 38.3 (CH_2), 23.5 (CH_2), 17.9 (CH_2), 0.19 (Si-CH_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*) calcd, 655.12; found, 654.42 [M − 1]$^-$.

Preparation of 1-CH_3-2-$CH_2CH_2CH_2(CH_3)SiCl_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (5). In a Schlenk flask, 1-(CH_3)-2-CH_2CH=CH_2-1,2-*closo*-$C_2B_{10}H_{10}$ (0.21 g, 1.03 mmol), Karstedt catalyst (5 μL, 0.01 mmol), and H(CH_3)$SiCl_2$ (0.13 mL, 1.25 mmol) were mixed and stirred under dinitrogen for 5 h at room temperature. Evaporation of the excess of H(CH_3)$SiCl_2$ gave **5** as a yellow oil. Yield: 0.32 g, >90%. ^{1}H NMR δ 2.26 (t, $^3J_{(H,H)}$ = 8.7, 2H, C_c-CH_2), 2.02 (s, 3H, C_c-CH_3), 1.87 (m, 2H, $CH_2CH_2CH_2$), 1.39 (t, $^3J_{(H,H)}$ = 8.1, 2H, Si−CH_2), 0.81 (s, 3H, Si−CH_3). ^{1}H{^{11}B} NMR δ 2.26 (t, $^3J_{(H,H)}$ = 8.7, 2H, C_c-CH_2), 2.26, 2.18, 2.11 (br s, B-*H*), 2.02 (s, 3H, C_c-CH_3), 1.87 (m, 2H, $CH_2CH_2CH_2$), 1.39 (t, $^3J_{(H,H)}$ = 8.1, 2H, Si−CH_2), 0.81 (s, 3H, Si−CH_3). ^{11}B NMR δ −4.1 (d, $^1J_{(B,H)}$ = 140, 1B), −5.6 (d, $^1J_{(B,H)}$ = 143, 1B), −10.6 (d, $^1J_{(B,H)}$ = 135, 8B). ^{13}C{^{1}H} NMR δ 77.4 (C_c), 74.8 (C_c), 37.2 (CH_2), 23.1 (CH_2), 22.7 (C_c-CH_3), 20.9 (Si-CH_2), 5.1 (Si-CH_3). ^{29}Si{^{1}H} NMR δ 31.6.

Preparation of 1-C_6H_5-2-$CH_2CH_2CH_2(CH_3)SiCl_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (6). In a Schlenk flask, 1-(C_6H_5)-2-CH_2CH=CH_2-1,2-$C_2B_{10}H_{10}$ (0.25 g, 0.95 mmol), H(CH_3)$SiCl_2$ (0.12 mL, 1.14 mmol), and Karstedt catalyst (5 μL, 0.01 mmol) were mixed and stirred under dinitrogen for 5 h at room temperature. Evaporation of the excess of H(CH_3)$SiCl_2$ gave **6** as a yellow oil. Yield: 0.34 g, >90%. ^{1}H NMR δ 7.68−7.36 (m, 5H, C_6H_5), 1.90 (t, $^3J_{(H,H)}$ = 7.2, 2H, C_c-CH_2), 1.65 (m, 2H, $CH_2CH_2CH_2$), 0.93 (t, $^3J_{(H,H)}$ = 8.1, 2H, Si−CH_2), 0.70 (s, 3H, Si−CH_3). ^{1}H{^{11}B} NMR δ 7.68−7.36 (m, 5H, C_6H_5), 2.78 (br s, 2H, B-*H*), 2.38 (br s, 6H, B-*H*), 2.32 (br s, 2H, B-*H*), 1.90 (t, $^3J_{(H,H)}$ = 7.2, 2H, C_c-CH_2), 1.65 (m, 2H, $CH_2CH_2CH_2$), 0.93 (t, $^3J_{(H,H)}$ = 8.1, 2H, Si−CH_2), 0.70 (s, 3H, Si−CH_3). ^{11}B NMR δ −3.5, (d, $^1J_{(B,H)}$ = 135, 2B), −10.3 (8B). ^{13}C{^{1}H} NMR δ 129.9, 129.0, 128.9, 127.5 (C_6H_5), 83.7 (C_c), 81.7 (C_c), 37.2 (CH_2), 22.6 (CH_2), 20.9 (Si-CH_2), 5.1 (Si-CH_3). ^{29}Si{^{1}H} NMR δ 31.4.

Preparation of [1-CH_3-2-$CH_2CH_2CH_2(CH_3)$Si-1,2-*closo*-$C_2B_{10}H_{10}$]O)$_n$ (n = 3−4) (7). *Method A.* To a round-bottom flask containing a solution of 1-(CH_3)-2-$CH_2CH_2CH_2(CH_3)SiCl_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (0.32 g, 1.03 mmol) in 2.5 mL of dried Et_2O, 2.5 mL of H_2O were added dropwise with continuous vigorous stirring. After 30 min of reaction at room temperature, the mixture was transferred to a separatory funnel and the organic phase was extracted with H_2O (2 × 10 mL). The organic layer was dried over $MgSO_4$ and concentrated in vacuum to obtain a clear yellow oil. This oily residue was purified in a SiO_2 column chromatography of 15 cm length and 1.5 cm diameter. First, the oil was eluted with 250 mL of C_6H_{14} to remove Karstedt catalyst and minor impurities. After this, 250 mL of a mixture of C_6H_{14}/Et_2O (1:1) was used as eluent. The solvents were removed under reduced pressure to obtain 32 mg of **7** as a colorless oil.

Method B. To a Schlenk flask containing a vigorous stirring solution of 1-(CH_3)-2-$CH_2CH_2CH_2(CH_3)SiCl_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (0.32 g, 1.03 mmol) in 2.5 mL of dried Et_2O, 0.1 mL (1.41 mmol) of dried $(CH_3)_2SO$ was added dropwise. The mixture was stirred over 2 h at room temperature. Then, the mixture was quenched with 10 mL of H_2O, transferred to a separatory funnel and the organic layer was washed with brine (2 × 10 mL). The organic phase was dried over $MgSO_4$ and concentrated in vacuum to obtain a yellow oil. After that, the purification workup was the same than in Method A to give 45 mg of **7** as a colorless oil. ^{1}H NMR (from Method A) δ 2.19 (t, $^3J_{(H,H)}$ = 8.5, 2H, C_c-CH_2), 2.01 (s, 3H, C_c-CH_3), 1.62 (m. 2H, $CH_2CH_2CH_2$), 0.60 (m, 2H, CH_2-Si), 0.21 (m, 1H, Si−CH_3, D3), 0.17 (s, 0.8H, Si−CH_3, linear siloxanes L), 0.14 (m, 1.2H, Si−CH_3, D4). ^{1}H{^{11}B} NMR (from Method A) δ 2.32, 2.25, 2.17, 2.10 (br s, B-*H*), 2.19 (t, $^3J_{(H,H)}$ = 8.5, 2H, C_c-CH_2), 2.01 (s, 3H, C_c-CH_3), 1.62 (m. 2H, $CH_2CH_2CH_2$), 0.60 (m, 2H, CH_2-Si), 0.21 (m, 1H, Si−CH_3, D3), 0.17 (s, 0.8H, Si−CH_3, linear siloxanes L), 0.14 (m, 1.2H, Si−CH_3, D4). ^{1}H NMR (from Method B) δ 2.19 (t, $^3J_{(H,H)}$ = 8.5, 2H, C_c-CH_2), 2.01 (s, 3H, C_c-CH_3), 1.63 (m. 2H, $CH_2CH_2CH_2$), 0.60 (m, 2H, CH_2-Si), 0.21 (m, 1.5H, Si−CH_3, D3), 0.14 (m, 1.5H, Si−CH_3, D4). ^{1}H{^{11}B} NMR (from Method B) δ 2.32, 2.25, 2.17, 2.10 (br s, B-*H*), 2.19 (t, $^3J_{(H,H)}$ = 8.5, 2H, C_c-CH_2), 2.01 (s, 3H, C_c-CH_3), 1.63 (m. 2H, $CH_2CH_2CH_2$), 0.60 (m, 2H, CH_2-Si), 0.21 (m, 1.5H, Si−CH_3, D3), 0.14 (m, 1.5H, Si−CH_3, D4). ^{11}B NMR δ −4.4 (d, $^1J_{(B,H)}$ = 111, 2B), −5.7 (d, $^1J_{(B,H)}$ = 145, 2B), −10.6 (d, $^1J_{(B,H)}$ = 133, 16B). ^{13}C{^{1}H} NMR δ 77.85 (C_c), 74.8 (C_c), 38.5 (CH_2), 29.65 (CH_2), 26.52 (CH_2), 23.1 (C_c-CH_3), 16.9 (Si-CH_2), −0.5 (Si-CH_3). FTIR (NaCl, cm^{-1}) 2957−2878 (ν (C_{alkyl}-H)), 2590 (ν (B−H)), 1261 (ν (Si-CH_3)), 1072 (ν (Si−O)). MALDI-TOF-MS (*m*/*z*) calcd, 775.73 [D3]; found, 776.34 [D3]$^-$; calcd [D4], 1034.01; found, 1034.81 [D4]$^-$.

Synthesis of [1-(C_6H_5)-2-$CH_2CH_2CH_2(CH_3)$Si-1,2-*closo*-$C_2B_{10}H_{10}$]O)$_n$ (n = 3−4) (8). *Method A.* To Schlenk flask containing a vigorous stirring solution of 1-(C_6H_5)-2-$CH_2CH_2CH_2(CH_3)SiCl_2$-1,2-closo-$C_2B_{10}H_{10}$ (0.31 g, 0.84 mmol) in 2.0 mL of dried diethyl ether, 2.0 mL of water was added drop by drop. The procedure was the same as for **7** using Method A to give 35 mg of **8** as a colorless oil.

Method B. To a Schlenk flask containing a vigorous stirring solution of 1-C_6H_5-2-$CH_2CH_2CH_2(CH_3)SiCl_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (353 mg, 0.94 mmol) in 2.5 mL of dried diethyl ether, 0.1 mL (1.41 mmol) of dry DMSO was added dropwise. The mixture was stirred over 2 h at room temperature. The procedure was the same as for **7** using the Method B to obtain 33 mg of **8** as a colorless oil. ^{1}H NMR (from Method A) δ 7.63−7.37 (m, 5H, C_6H_5), 1.77 (t, $^3J_{(H,H)}$ = 8.4, 2H, C_c-CH_2), 1.43 (m, 2H, $CH_2CH_2CH_2$), 0.31 (t, $^3J_{(H,H)}$ = 8.4, 2H, CH_2-Si), 0.06 (m, 2H, Si−CH_3, linear siloxanes L), −0.04 (m, 0.6H, Si−CH_3, D3), −0.08 (m, 0.4H, Si−CH_3, D4). ^{1}H{^{11}B} NMR (from Method A) δ 7.63−7.37 (m, 5H, C_6H_5), 2.70, 2.37, 2.32, 2.24 (br s, B-*H*), 1.77 (t, $^3J_{(H,H)}$ = 8.4, 2H, C_c-CH_2), 1.43 (m, 2H, $CH_2CH_2CH_2$), 0.31 (t, $^3J_{(H,H)}$ = 8.4, 2H, CH_2-Si), 0.06 (m, 2H, Si−CH_3, linear siloxanes L), −0.04 (m, 0.6H, Si−CH_3, D3), −0.08 (m, 0.4H, Si−CH_3, D4). ^{1}H NMR (from Method B) δ 7.63−7.37 (m, 5H, C_6H_5), 1.77 (t, $^3J_{(H,H)}$ = 8.4, 2H, C_c-CH_2), 1.43 (m, 2H, $CH_2CH_2CH_2$), 0.31 (t, $^3J_{(H,H)}$ = 8.4, 2H, CH_2-Si), 0.06 (m, 0.2H, Si−CH_3, linear siloxanes L), −0.04 (m, 1.5H, Si−CH_3, D3), −0.08 (m, 1.3H, Si−CH_3, D4). ^{1}H{^{11}B} NMR (from Method B) δ 7.63−7.37 (m, 5H, C_6H_5), 2.70, 2.37, 2.32, 2.24 (br s, B-*H*), 1.77 (t, $^3J_{(H,H)}$ = 8.4, 2H, C_c-CH_2), 1.43 (m, 2H, $CH_2CH_2CH_2$), 0.31 (t, $^3J_{(H,H)}$ = 8.4, 2H, $CH_2CH_2CH_2$), 0.06 (m, 0.2H, Si−CH_3, linear siloxanes L), −0.04 (m, 1.5H, Si−CH_3, D3), −0.08 (m, 1.3H, Si−CH_3, D4). ^{11}B NMR δ −3.5 (d, $^1J_{(B,H)}$ = 138, 4B), −10.2 (d, $^1J_{(B,H)}$ = 123, 16B). ^{13}C{^{1}H} NMR δ 131.1, 130.7, 130.6, 128.9 (C_6H_5), 83.5 (C_c), 82.1 (C_c), 38.0 (CH_2), 22.8 (CH_2), 16.8 (CH_2), 14.1 (CH_2), −0.7 (Si-CH_3). FTIR (NaCl, cm^{-1}) 3067 (ν (C_{aryl}-H)), 2957−2872 (ν (C_{alkyl}-H)), 2582 (ν (B−H)), 1261 (δ (Si-CH_3)), 1080 (ν (Si−O)). MALDI-TOF-MS (*m*/*z*) calcd, 961.86 [D3]; found, 962.8 [D3]$^-$; calcd, 1282.1 [D4]; found, 1016.45 [D4-{1-C_6H_5-2-$CH_2CH_2CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$}]$^-$.

Synthesis of 1-(CH_3)-2-$CH_2CH_2CH_2SiCl_3$-1,2-*closo*-$C_2B_{10}H_{10}$ (9). In a Schlenk flask, 1-(CH_3)-2-CH_2CH=CH_2-1,2-*closo*-$C_2B_{10}H_{10}$ (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 dinitrogen for 5 h at room temperature. Evaporation of the excess of $HSiCl_3$ gave **9** as a yellow oil. Yield: 0.42 g, >99%. ^{1}H NMR δ 2.29 (t, $^3J_{(H,H)}$ = 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, $^3J_{(H,H)}$ = 8.1, 2H, Si−CH_2). ^{1}H{^{11}B} NMR δ 2.26, 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, $^3J_{(H,H)}$ = 8.1, 2H, Si−CH_2). ^{11}B NMR δ −3.2 (d, $^1J_{(B,H)}$ = 141, 1B), −4.6 (d, $^1J_{(B,H)}$ = 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-*closo*-$C_2B_{10}H_{10}$ (10). In a Schlenk flask, 1-(C_6H_5)-2-CH_2CH=CH_2-1,2-*closo*-$C_2B_{10}H_{10}$ (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 dinitrogen for 5 h at room temperature. Evaporation of the excess of $HSiCl_3$ gave **10** 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, $^3J_{(H,H)}$ = 8.2, 2H, C_c-CH_2), 1.70 (m, 2H, $CH_2CH_2CH_2$), 1.21 (t, $^3J_{(H,H)}$ = 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, $^3J_{(H,H)}$ = 8.2, 2H, C_c-CH_2), 1.70 (m, 2H, $CH_2CH_2CH_2$), 1.21 (t, $^3J_{(H,H)}$ = 8.1, 2H, Si−CH_2). ^{11}B NMR δ −2.6, (d, $^1J_{(B,H)}$ = 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-$CH_2CH_2CH_2Si(OCH_2$-$CH_3)_3$-1,2-*closo*-$C_2B_{10}H_{10}$ (11). In a Schlenk flask, 1-(CH_3)-2-CH_2CH=CH_2-1,2-*closo*-$C_2B_{10}H_{10}$ (0.80 g, 4.0 mmol), $HSi(OCH_2CH_3)_3$ (1.53 mL, 8.04 mmol), and Karstedt catalyst (10 μL, 0.02 mmol) were mixed and stirred under dinitrogen for 5 h at room temperature. Evaporation of the excess of $HSi(OCH_2CH_3)_3$ at 50 °C gave **11** as a brown oil. Yield: 1.46 g, >99%. ^{1}H NMR δ 3.83 (q, $^3J_{(H,H)}$ = 6.9, 6H, O−CH_2), 2.20 (t, $^3J_{(H,H)}$ = 8.1, 2H, C_c-CH_2), 2.01 (s, 3H, C_c-CH_3), 1.68 (quint, $^3J_{(H,H)}$ = 8.1, 6H, $CH_2CH_2CH_2$), 1.23 (t, $^3J_{(H,H)}$ = 6.9, 9H, CH_2−CH_3), 0.63 (t, $^3J_{(H,H)}$ = 8.1, 2H, $CH_2CH_2CH_2$). ^{1}H{^{11}B} NMR δ 3.83 (q, $^3J_{(H,H)}$ = 6.9, 6H, O−CH_2), 2.26, 2.18 (br s, B-*H*), 2.01 (s, 3H, C_c-CH_3), 1.68 (quint, $^3J_{(H,H)}$ = 8.1, 6H, $CH_2CH_2CH_2$), 1.23 (t, $^3J_{(H,H)}$ = 6.9, 9H, CH_2−CH_3), 0.63 (t, $^3J_{(H,H)}$ = 8.1, 2H, $CH_2CH_2CH_2$). ^{11}B NMR δ −3.2 (d, $^1J_{(B,H)}$ = 122, 1B), −4.63 (d, $^1J_{(B,H)}$ = 141, 1B), −9.2 (d, $^1J_{(B,H)}$ = 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-$CH_2CH_2CH_2Si(OCH_2$-$CH_3)_3$-1,2-$C_2B_{10}H_{10}$ (12). In a Schlenk flask, 1-(C_6H_5)-2-CH_2CH=CH_2-1,2-*closo*-$C_2B_{10}H_{10}$ (0.16 g, 0.60 mmol), $HSi(OCH_2CH_3)_3$ (0.24 mL, 1.23 mmol), and Karstedt catalyst (5 μL, 0.01 mmol) were mixed and stirred under dinitrogen for 14 h at room temperature. Evaporation of the excess of $HSi(OCH_2CH_3)_3$ at 50 °C gave **12** 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, $^3J_{(H,H)}$ = 6.9, 6H, O−CH_2), 1.83 (t, $^3J_{(H,H)}$ = 8.1, 2H, C_c-CH_2), 1.53 (m, 2H, $CH_2CH_2CH_2$), 1.20 (t, $^3J_{(H,H)}$ = 6.9, 9H, CH_2-CH_3), 0.40 (t, $^3J_{(H,H)}$ = 8.1, 2H, Si-CH_2). ^{1}H{^{11}B} NMR δ 7.62−7.39 (m, 5H, C_6H_5), 3.37 (q, $^3J_{(H,H)}$ = 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, $^3J_{(H,H)}$ = 8.1, 2H, C_c-CH_2), 1.53 (m, 2H, $CH_2CH_2CH_2$), 1.20 (t, $^3J_{(H,H)}$ = 6.9, 9H, CH_2-CH_3), 0.40 (t, $^3J_{(H,H)}$ = 8.1, 2H, Si-CH_2). ^{11}B NMR δ −2.6 (d, $^1J_{(B,H)}$ = 143, 2B), −9.4 (d, $^1J_{(B,H)}$ = 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 −46.2.

Synthesis of (1-(CH_3)-2-$CH_2CH_2CH_2SiO_{1.5}$-1,2-*closo*-$C_2B_{10}H_{10})_8$ (13). *Method A.* In a Schlenk flask, **9** (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 dinitrogen for 48 h at room temperature. Then the mixture was washed with water (3 × 10 mL) and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure gave an oily product. The addition of EtOH to the residue gave **13** as a white solid. Yield: 60 mg, 23%.

Method B. In a tube, 0.72 g (1.99 mmol) of **11** was dissolved in 993 μL of dried THF. After, 993 μL of a solution containing 19 μL (19 μmol) of TBAF (1 M in THF), 54 μL (2.98 mmol) of H_2O, and 920 μL of dried THF were added. The suspension was stirred for 10 s. After 133 days at room temperature, evaporation of volatiles gave a yellowish solid. This solid was washed with ethanol to isolate **11** as a white solid. Yield: 0.35 g, 70%.

Method C. In a tube, 0.53 g (1.46 mmol) of **11** 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 s. After 180 days, evaporation of volatiles gave a yellowish solid. This solid was washed with ethanol to isolate **13** 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, $CH_2CH_2CH_2$). ^{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. ESI-MS (*m*/*z*) calcd, 2033.0 (**13**)Na$^+$; found, 2033.8.

Synthesis of (1-(C_6H_5)-2-$CH_2CH_2CH_2SiO_{1.5}$-1,2-*closo*-$C_2B_{10}H_{10})_8$ (14). *Method A.* The procedure was the same as for **13** using **10** (0.31 g, 0.78 mmol), 0.2 mL of $CHCl_3$, and DMSO (0.17 mL, 2.39 mmol). The mixture was stirred under dinitrogren for 48 h at room temperature, washed with water (3 × 10 mL), and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure gave an oily product. The addition of EtOH to the residue gave **14** as a white solid. Yield: 51.6 mg, 21%.

Method B. To a solution of **12** (0.26 g, 0.60 mmol) in $CHCl_3$ (10 mL) was added TBAF (0.3 mL, 0.30 mmol) and the mixture was stirred for 24 h. The mixture was transferred to a separatory funnel and the organic phase was extracted with H_2O (3 × 10 mL) for three days consecutively. The organic layer was dried over $MgSO_4$ and concentrated in vacuum to obtain **14** as a white solid. Yield: 53.7 mg, 28%. ^{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). ^{13}C{^{1}H} NMR δ 131.1, 130.8,130.5, 129.0 (C_6H_5), 82.6 (C_c), 37.5 (CH_2), 23.5 (CH_2), 12.3 (Si-CH_2). ^{29}Si CP MAS NMR δ −66.0. FTIR (KBr, cm^{-1}) 3063 (ν (C_{aryl}-H)), 2939−2893 (ν (C_{alkyl}-H)), 2584 (ν (B−H)), 1103 (ν (Si−O)). Anal. Calcd for $C_{88}H_{168}B_{80}O_{12}Si_8$: C, 42.15; H, 6.75. Found: C, 41.76; H, 7.05.

Synthesis of $[N(CH_3)_4]_2$[(7-(CH_3)-8-$CH_2CH_2CH_2(CH_3)_2$Si-7,8-*nido*-$C_2B_9H_{10})_2O]$ $[N(CH_3)_4]_2$[15]. *Method A.* To a two-necked round-bottom flask containing a solution of **3** (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 h. After this time, the solvent was removed and a white solid was isolated by precipitation after addition of saturated aqueous solution of $[N(CH_3)_4]$Cl. The solid is filtered off, washed with H_2O (3 × 10 mL), and dried under vacuum to obtain **15** 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 EtOH (5 mL) was added **3** (0.10 g, 0.19 mmol). The mixture was stirred and refluxed during 6 h. After this time, the solvent was removed and a white solid was isolated by precipitation after addition of saturated aqueous $[N(CH_3)_4]$Cl solution. The solid is filtered off, washed with H_2O (3 × 10 mL) and dried under vacuum to obtain $[N(CH_3)_4]_2$[**15**]. Yield: 55.3 mg, 44%. ^{1}H NMR (CD_3OCD_3) δ 3.43 (s, 24H, $N(CH_3)_4$), 1.64 (m, 8H, C_c-CH_2CH_2), 1.39 (br s, 6H, C_c-CH_3), 0.46 (t, $^3J_{(H,H)}$ = 8.4, 4H, $CH_2CH_2CH_2$), 0.07 (s, 6H, Si−CH_3), 0.04 (s, 6H, Si−CH_3), −2.60 (br s, 2H, B*H*B). ^{1}H{^{11}B} NMR δ 3.43 (s, 24H, $N(CH_3)_4$), 1.64 (m, 8H, C_c-CH_2CH_2), 1.39 (br s, 6H, C_c-CH_3), 0.46 (t, $^3J_{(H,H)}$ = 8.4, 4H, $CH_2CH_2CH_2$), 0.07 (s, 6H, Si−CH_3), 0.04 (s, 6H, Si−CH_3), −2.60 (br s, 2H, B*H*B). ^{11}B NMR δ −8.2 (d, $^1J_{(B,H)}$ = 157, 2B), −10.0 ($^1J_{(B,H)}$ = 151, 4B), −17.3 ($^1J_{(B,H)}$ = 122, 8B), −33.8 (dd,$^1J_{(B,H)}$ = 126, $^1J_{(B,H)}$ = 45, 2B), −36.3 ($^1J_{(B,H)}$ = 138, 2B). ^{13}C{^{1}H} NMR δ 55.2 ($N(CH_3)_4$). 40.2, 40.0 (CH_2), 24.4 (CH_2), 21.5 (C_c-CH_3), 18.9, 18.7 (CH_2), −0.1, −0.7 (Si-CH_3). ^{29}Si{^{1}H} NMR δ 6.7. 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)). Anal. Calcd for $C_{24}H_{74}B_{18}N_2OSi_2$: C, 43.83; H, 11.34; N, 4.26. Found: C, 44.40; H, 11.83; N, 4.27. ESI-MS (*m*/*z*) calcd, 255.2, {[15]-[$N(CH_3)_4]_2$}$^{2-}$; found, 254.5.

Synthesis of $[N(CH_3)_4]_2$[(7-(C_6H_5)-$CH_2CH_2CH_2(CH_3)_2$Si-7,8-*nido*-$C_2B_9H_{10})_2O]$ $[N(CH_3)_4]_2$[16]. 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 **4** (0.12 g, 0.18 mmol). The mixture was stirred and refluxed during 14 h. After this time, the solvent was evaporated and a white solid was isolated by precipitation after addition of saturated aqueous $[N(CH_3)_4]$Cl solution. The solid is filtered off, washed with water (3 × 15 mL) and dried under vacuum to obtain $[N(CH_3)_4]_2$[**16**]. Yield: 0.55 g,

40%. ^{1}H NMR (CD_3OCD_3) δ 7.30−7.03 (m, 10H, C_6H_5), 3.38 (s, 24H, $N(CH_3)_4$), 1.24 (m, 8H, C_c-CH_2CH_2), −0.04 (m, 4H, CH_2), −0.18 (s, 12H, Si-CH_3), −2.19 (br s, 2H, B*H*B). ^{1}H{^{11}B} NMR δ 7.30−7.03 (m, 10H, C_6H_5), 3.38 (s, 24H, $N(CH_3)_4$), 1.50 (br s, B-*H*), 1.24 (m, 8H, C_c-CH_2CH_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, $^1J_{(B,H)}$ = 145, 2B), −8.1 (d, $^1J_{(B,H)}$ = 141, 2B), −10.9 (2B), −14.0 (d, $^1J_{(B,H)}$ = 156, 2B), −15.3 (d, $^1J_{(B,H)}$ =127, 4B), −16.4 (2B), −30.8 (d, $^1J_{(B,H)}$ = 131, 2B), −33.8 (d, $^1J_{(B,H)}$ = 144, 2B). ^{29}Si{^{1}H} NMR δ 6.9. FTIR (KBr), cm^{-1} 2930−2870 (ν (C_{alkyl}-H)), 2515 (ν (B-H)), 1481 (ν (C-N)), 1250 (δ (Si-CH_3)), 1034 (ν (Si-O)).

Synthesis of $[N(CH_3)_4]_8[7\text{-}(CH_3)\text{-}CH_2CH_2CH_2SiO_{1.5}\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]_8$ $[N(CH_3)_4]_8$[17]. 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 **13** (0.10 g, 0.05 mmol) in 1 mL of THF. The mixture was refluxed during 6 h. Then, the volatiles were evaporated in the vacuum and an excess of $[N(CH_3)_4]Cl$ in water was added to obtain a white solid. This was filtered off, washed with water (3 × 10 mL), and dried under vacuum to obtain $[N(CH_3)_4]_8$[**17**] 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 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, $CH_2CH_2CH_2$), 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, $^1J_{(B,H)}$ = 115, $^1J_{(B,H)}$ = 43, 8B), −34.6 (d, $^1J_{(B,H)}$ = 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). ^{29}Si CP MAS NMR δ −66.2. FTIR (KBr, cm^{-1}) 2932−2893 (ν (C_{alkyl}-H)), 2515 (ν (B−H)), 1489 (ν (C−N)), 1111 (ν (Si−O)). Anal. Calcd for $C_{80}H_{248}B_{72}N_8O_{12}Si_8$: C, 38.16; H, 9.93; N, 4.45. Found: C, 37.62; H, 9.31; N, 3.99.

X-ray Structure Determination of 3. Hexane vapor diffusion of compound **3** into $CHCl_3$ solution gave crystalline material with the specimen formed of very thin plate-like sheets connected together. Single-crystal data collection for **3** was performed at −100° with an Enraf Nonius KappaCCD diffractometer using graphite monochromatized Mo Kα radiation. The structure was solved by direct methods and refined on F^2 by the SHELXL97 program.[31] The structure was refined in centrosymmetric space group $P2_1/c$ as also calculations in lower symmetry space groups resulted partial disordering for the central oxygen atom. The oxygen atom is disordered in two positions at the vicinity of inversion center, and also Si, C17, and C18 each occupies two neighboring positions. The disordered carbon atoms were refined with isotropic thermal displacement parameters but rest of the non-hydrogen atoms with anisotropic displacement parameters. The hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

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

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