Modular Construction of Neutral and Anionic Carboranyl-Containing Carbosilane-Based Dendrimers

Arántzazu González-Campo,[†] Clara Viñas,[†] Francesc Teixidor,[†] Rosario Núñez,*[,†] Reijo Sillanpää,[‡] and Raikko Kivekäs[§]

Institut de Ciència de Materials, CSIC, Campus U.A.B., 08193 Bellaterra, Spain, Department of Chemistry, University of Jyväskylä, FIN-40351, Jyväskylä, Finland, and Department of Chemistry, P.O. Box 55, University of Helsinki, FIN-00014, Finland

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ABSTRACT: A modular construction of new carbosilane dendrimers, which contain four and eight peripheral carborane derivatives and propyl linkages between the $C_{cluster}$ and the Si atoms, has been developed using different methodologies. Regiospecific hydrosilylation of 1-C_6H_5-2-($CH_2CH{=}CH_2$)-l,2-*closo*-$C_2B_{10}H_{10}$ (**1**) and 1-CH_3-2-($CH_2CH{=}CH_2$)-1,2-*closo*-$C_2B_{10}H_{10}$ (**2**) offers an efficient route to molecular precursors and building blocks that can provide both divergent and convergent strategies for dendritic growth. First generations of neutral carboranyl-containing dendrimers were constructed by two approaches: (a) a divergent approach via hydrosilylation of **1** and **2** with the first generation of a carbosilane dendrimer containing peripheral Si−H functions, Si[$(CH_2)_2$-$(CH_3)_2$SiH]$_4$, **1G-H$_4$**, to give dendrimers **7** and **8**, respectively; (b) a convergent strategy, the growth of which was initiated with the groups that will become the periphery of the dendrimer. In the latter, the hydrosilylation of the allyl group in **1** and **2** with Me_2HSiCl was carried out leading to the formation of 1-$(CH_2)_3$SiCl-2-R-1,2-*closo*-$C_2B_{10}H_{10}$ [R = C_6H_5 (**3**), CH_3 (**4**)], and subsequent reduction with $LiAlH_4$ gave compounds 1-$(CH_2)_3$SiH-2-R-1,2-*closo*-$C_2B_{10}H_{10}$ [R = C_6H_5 (**5**), CH_3 (**6**)], which were treated with tetravinylsilane or the core molecule to yield the first generation dendrimers, **7** and **8**, with four carborane clusters. Next generation dendrimers were built up in a similar manner: (a) by the hydrosilylation using **1G-H$_4$** of the vinyl group in dendrons **9** and **10**, which themselves have been prepared from the alkenylation of **3** and **4** with vinylmagnesium chloride; (b) by growing the carboranylsilane wedges **9** and **10** to a second generation and later assembling all to the core tetravinylsilane to obtain dendrimers **15** and **16**. In addition, another set of a 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[$(CHCH_2)_2$]}$_4$, **1G-Vi$_8$,** with carboranylsilane dendrons **5** and **6**, that contain 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 polyanionic 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 divergent, convergent or combined divergent/convergent methods.[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] The field of dendrimer chemistry is still young; the first synthesis of dendritic macromolecules was only 30 years ago.[3] Nowadays, dendrimers are widely investigated as supports for functional groups and metal fragments, which can be localized at the core or at the periphery. The incorporation of metals in dendritic structures has attracted growing interest as it generates new metallodendrimers with interesting catalytic, redox, magnetic, and photo-optical properties.[4−6] These have inspired many chemists to develop new materials and several applications have been explored.[2b,7,8] More recently, several research groups have studied the incorporation of carborane derivatives in the interior or on the periphery of macromolecules and dendrimeric systems.[8,9]

In view of the availability of carbosilane dendrimers[10] as inert scaffolds for attaching functional groups on the periphery and the versatility of carborane clusters for application,[11−13] we have started a program to functionalize the surface of star-shaped carbosilanes with carborane moieties by Si−$C_{cluster}$ (Si-C_c) direct bonds.[14] In our opinion, these systems provide an interesting example, from the scientific point of view, for testing the behavior of the carborane derivatives vs different organosilanes and for testing their reactivity as hydrosilylating agents. However, due to the sensitivity of the C_c−Si bond to nucleophilic attack,[11g,15,16] they also present a restraint for further reactions on the peripheral clusters.

Thus, pursuing our work dealing with the preparation, functionalization and study of reactivity of carboranyl-containing carbosilane dendrimers, we report herein the preparation of a family of dendrimers, in which *o*-carborane derivatives are bonded to the Si atom through a propyl spacer. For this purpose, we have used the *divergent* route or alternatively a *convergent* strategy. Because of the versatility of carboranes to be chemically modified,[11,17] they have been an ideal group for the preparation of stable, agile and suitable building blocks that are subsequently attached to a core molecule in the convergent dendrimer synthesis. In addition, the new approach to graft carboranyl building blocks described below could be adapted to assemble other dendrimeric systems and used as a coupling point. In addition, our goal is also to achieve the modification of the peripheral clusters, and the new carborane-containing dendrimeric compounds allow the partial degradation of the *closo* clusters, leading to new polyanionic species, which we expect will endure a further metalation.[11]

* Corresponding author. Telephone: +34 93 580 1853. Fax: +34 93 580 5729. E-mail: rosario@icmab.es.
[†] Institut de Ciència de Materials, CSIC, Campus U.A.B.
[‡] Department of Chemistry, University of Jyväskylä.
[§] Department of Chemistry, P.O. Box 55, University of Helsinki.

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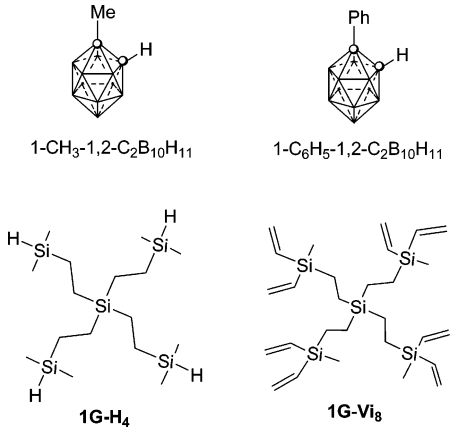
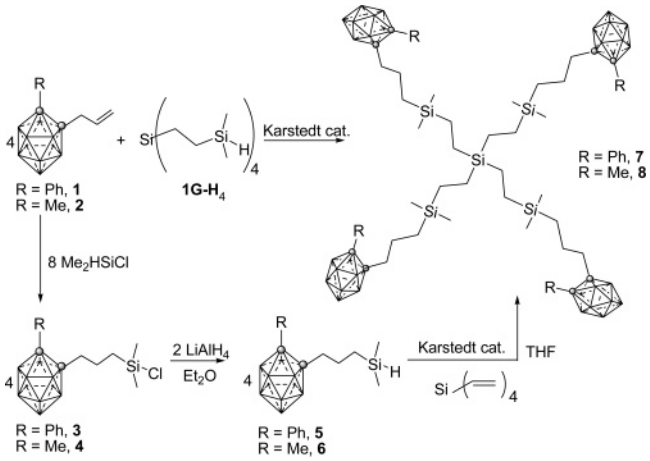
Chart 1



Scheme 1. Preparation of the Carboranyl−Carbosilane First Generation Dendrimers (1G) 7 and 8 Using Two Different Approaches



Results and Discussion

Preparation of First Generation of Carboranyl-Containing Carbosilane Dendrimers. Dendritic carbosilanes are generally prepared using the divergent approach by successive alkenylation and hydrosilylation steps (using silanes as hydrosilylating agents),[10] although a convergent strategy has also been used to attach dendritic carbosilane fragments to core systems.[18] With this idea, silane terminated carboranyl molecules were developed as building blocks for the construction of first and second generation carboranyl-containing dendrimers. *closo*-Carboranes and carbosilane dendrimers used in this study are shown in Chart 1. Dendrimers **1G-H$_4$** and **1G-Vi$_8$** were synthesized according to literature procedures.[10a,e]

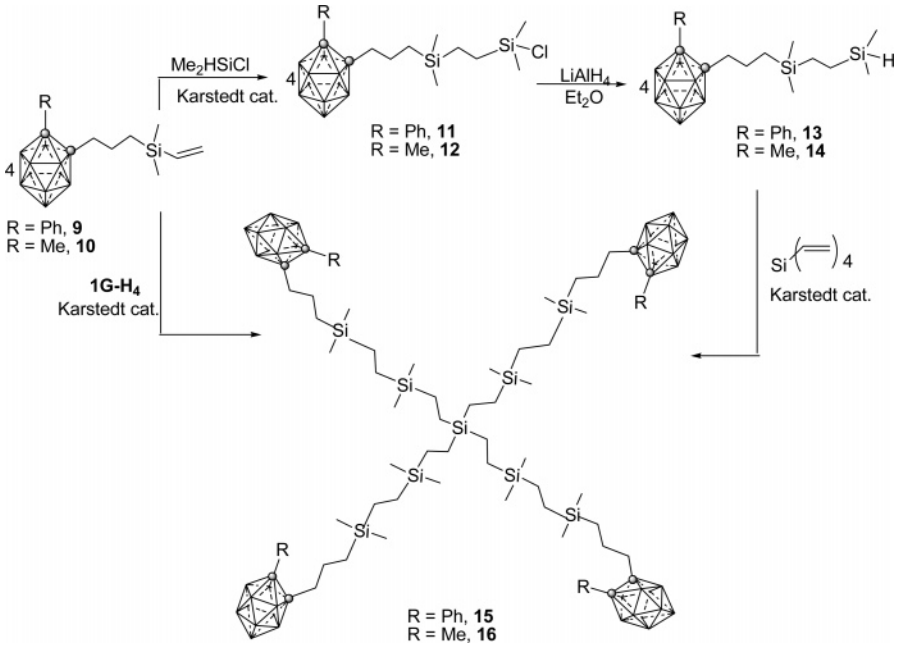
The key starting materials for this work, **1** and **2**, were prepared by the reaction of the respective monolithium salts of 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ and 1-CH_3-1,2-$C_2B_{10}H_{11}$, with stoichiometric amounts of ($CH_2CH{=}CH_2$)Br in a Et_2O/toluene solution at room temperature, to give crystalline air-stable solids in 82 and 88% yield. The presence of the allyl function allowed the platinum-catalyzed hydrosilylation with $(CH_3)_2HSiCl$ to give chloroterminated carboranylsilanes **3** and **4**, respectively (Scheme 1). The ^{1}H NMR olefinic resonances were used to follow the complete hydrosilylation reaction by the disappearance of the double bond protons. Subsequent reduction of the Si−Cl functions in carboranyl-chlorosilanes **3** and **4** was carried out with lithium tetrahydroaluminate, Li[AlH_4], obtaining **5** and **6** as analytical and spectroscopically pure oils in 93 and 72% yield, respectively (Scheme 1).

To obtain the first generation of carboranyl-containing carbosilane dendrimers, two different approaches were followed: (a) In the divergent approach the hydrosilylation reaction of precursors **1** and **2** with dendrimer **1G-H$_4$** was carried out; (b) the hydrosilylation of tetravinylsilane using **5** and **6** as hydrosilylation agents were performed in the convergent method. In the first method, the reaction of **1G-H$_4$** with compounds **1** and **2** in the presence of Karstedt catalyst, at room temperature for 48 h, gave the related dendrimers **7** and **8** respectively in around 36% yields (Scheme 1). It is noticeable that all the hydrosilylation reactions were easily monitored using IR and ^{1}H NMR spectroscopy following the disappearance of the Si−H signals in the spectra. Using the second synthetic approach, **7** and **8** were obtained by the platinum-catalyzed hydrosilylation of tetravinylsilane with the small building blocks **5** and **6** in toluene, at room temperature overnight, in ≈99% yields (Scheme 1). Thus, both methods achieved the expected carbosilane dendrimers containing four *closo*-carboranyl units peripherally attached; however, the *convergent* approach was faster and cleaner affording the formation of **7** and **8** in higher yields.

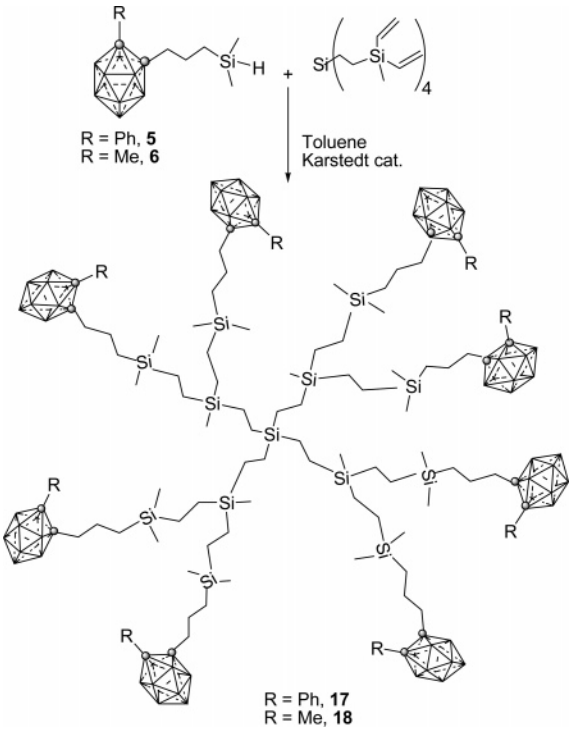
Preparation of Second Generations of Carboranyl-Containing Carbosilane Dendrimers. Two different approaches were also used to prepare second generation dendrimers (**2G**) containing four peripheral *closo*-carborane clusters. First, a convergent method was used that consists of growing the compounds **3** and **4** using a sequence of alkenylation, hydrosilylation and reduction reactions (Scheme 2). The reaction of **3** and **4** with vinylmagnesium chloride in THF at room temperature overnight gave the corresponding vinylsilane-containing carborane derivatives **9** and **10** as yellow oils (Scheme 2). The subsequent hydrosilylation reaction of **9** and **10** with Me_2HSiCl in the presence of Karstedt catalyst at room temperature for 12 and 2 h respectively, led to the formation of **11** and **12** in exceptionally high yield (>99%). The reduction of the Si−Cl function in **11** and **12** with Li[AlH_4] in Et_2O gave, after workup procedures, compounds **13** and **14** that can act as carboranyl building blocks (Scheme 2). Finally, a solvent free platinum-catalyzed hydrosilylation reaction of tetravinylsilane with **13** and **14**, at room temperature overnight, led to the formation of the second generation of carboranyl-carbosilane dendrimers **15** and **16** respectively, as yellow oils in 58 and 61% yield, respectively (Scheme 2). A second approach used to obtain dendrimers **15** and **16** involved the reaction of vinyl-carborane derivatives **9** and **10** with a freshly prepared **1G-H$_4$** in the presence of Karstedt catalyst. As conclusion, the second generation dendrimers **15** and **16,** incorporating four *closo*-carborane clusters on the periphery, were obtained in higher yields following the first approach.

Two second generation dendrimers (**2G′**) containing eight peripheral carborane clusters were prepared from the reaction of compounds **5** and **6** with dendrimer **1G-Vi$_8$** (which contains two vinyl function in each branch). The reaction of **5** and **6** with the dendrimer vinyl functions in the presence of catalytic amounts of Kartestd catalyst, in toluene solution at room temperature overnight, afforded the desired hydrosilylated second generations dendrimers **17** and **18** respectively, in 60−58% yield (Scheme 3). Carbosilane dendrimers **17** and **18** containing eight *closo*-carborane clusters attached on the dendrimeric peripheral Si atoms through a propyl spacer were obtained. It is important to notice that due to the high versatility of the carborane cluster to be functionalized in the C atoms, a high variety of different fragments to be attached to a great

Scheme 2. Preparation of Carboranyl-carbosilane Second Generation Dendrimers (2G) with Four Peripheral Clusters, 15 and 16



Scheme 3. Preparation of Carboranyl-Carbosilane Second Generation Dendrimes (2*G′*) with Eight Peripheral Clusters, 17 and 18

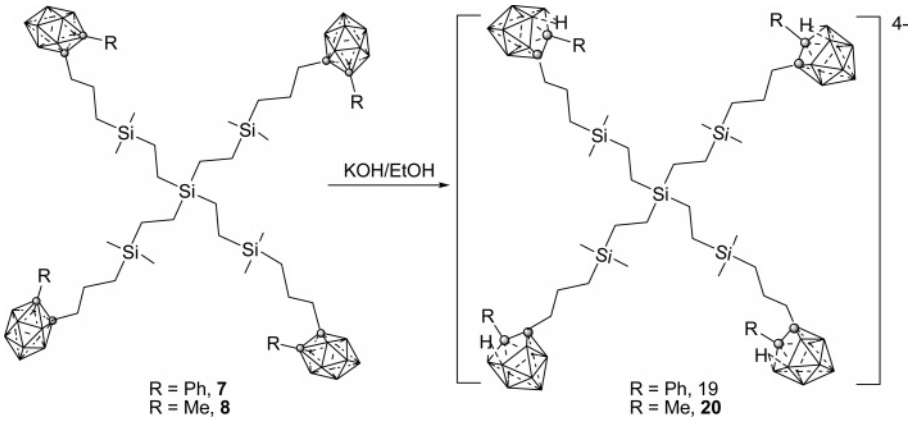


number of generation dendrimers is available depending on the final application.

Preparation of Carboranyl-Containing Polyanionic Dendrimers. We have prepared first and second generations of carboranyl-containing carbosilane dendrimers, in which an alkyl spacer is interposed between the C_c and Si atoms to prevent a direct bond C_c-Si that is sensitive to nucleophiles.[11f,15,16] In addition, our goal in the present work was also the modification of the perypheral *closo*-clusters by using nucleophiles. Thus, herein we present the initial results on the preparation of polianionic dendrimeric structures from carboranyl-containing carbosilane dendrimers. For this purpose, the partial degradation reaction of peripheral *closo*-carboranes incorporated in dendrimers **7** and **8** was achieved, using KOH/EtOH at reflux (Scheme 4). The nucleophilic attack of the EtO^- ion on the clusters caused their degradation producing the corresponding anionic *nido* species, without alteration of the dendrimeric structure. Thus, polyanionic compounds **19** and **20** were isolated as tetramethylammonium salts in 89 and 70% yield, respectively. The presence of the alkyl spacer between the $C_{cluster}$ and the Si atoms has allowed the partical degradadation of the cluster with nucleophiles and opens the way to the modification and metalation of the cluster in order to obtain metallodendrimers.

Characterization of Compounds. The structures of compounds **1**−**20** were established on the basis of elemental analysis, IR, ^1H, ^{13}C, ^{11}B, ^{29}Si NMR and mass spectrometry and for **1** and **2** 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 $\delta(Si-CH_3)$. 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** and **20** the υ(B−H) appears around 2517 cm^{-1}, due to the presence of *nido* clusters. The ^1H NMR spectra for **1** and **2** exhibit resonances for allyl protons in the region 5.80−4.75 ppm, while **9** and **10** show the vinyl protons in the region 6.15−5.58 ppm. The ^1H NMR spectra of **3**−**18** exhibit resonances at high field, for Si−CH_3 protons in the region from −0.15 to 0.45 ppm and for methylene protons between 0.25 and 0.56 ppm, which has been unambiguously assigned in the majority of cases. For anionic **19** and **20**, the C_c-CH_2 protons are shifted to higher field with respect to the *closo* precursors **7** and **8**, due to the electrodonor character of the *nido* clusters. Additionally, for compounds **5**, **6**, **13**, and **14**, the presence of Si−*H* bonds in the molecule is confirmed by a multiplet displayed between 3.89 and 3.70 ppm. Figure 1 shows the ^1H NMR spectra of compounds **6**, **8**, and **18** as examples. The $^{13}C\{^1H\}$ NMR spectra for 1-C_6H_5-1,2-*closo*-$C_2B_{10}H_{11}$ derivatives show resonances from 83.5 to 80.6 ppm attributed to the $C_{cluster}$ atoms, whereas for 1-CH_3-1,2-*closo*-$C_2B_{10}H_{11}$ derivatives these resonances appear between 78.2 and 74.4 ppm and the Si−CH_3 carbon resonances appear in the range between −4.9 and +1.5 ppm in the ^{13}C NMR spectra. Finally,

Scheme 4. Preparation of Carboranyl-Carbosilane First Generation Polyanionic Dendrimers 19 and 20



the CH_2 carbons are exhibited from 39.0 (C_c-CH_2) to 2.6 ppm ($Si-CH_2$).

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

The $^{29}Si\{^1H\}$ NMR spectra of compounds **3**−**6** and **9** and **10** exhibit a single signal whose chemical shift is dependent upon the Si atom substituents: resonances for Si−Cl appear around 30.4 ppm, Si−H resonances are observed at higher field, about −14.0 ppm, and the Si−C═C are exhibited at −6.3 ppm. For neutral first generation dendrimers **7** and **8** the $^{29}Si\{^1H\}$ NMR spectra exhibit two signals, whereas for second generation dendrimers, **15**−**18**, three resonances are observed (Table 1). 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 region, 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 branched Si−C (Table 1). Finally, for anionic dendrimers **19** and **20**, the $^{29}Si\{^1H\}$ NMR spectra show two signals at 8.54 and 9.47 ppm, respectively assigned to the Si_{core}, and at 2.97 and 4.06 ppm due to the $Si_{periphery}$.

Table 1. $^{29}Si\{^1H\}$ NMR Data for Dendrimers in ppm

dendrimers	Si_{core}	Si_{middle}	$Si_{periphery}$
7	9.05		3.32
8	8.45		3.56
15	8.92	5.05	3.36
16	7.26	5.21	3.52
17	8.80	6.98	3.38
18	8.99	7.26	3.42
19	8.54		2.97
20	9.47		4.06

X-ray Structures of 1 and 2. Precursors **1** and **2** were isolated as monocrystals from a solution of Et_2O, and were suitable for X-ray structural determination. The molecular structures are presented in Figure 3. X-ray analyses confirmed that **1** and **2** are molecular compounds without any significant intermolecular interactions. The $-CH_2CH=CH_2$ substituent at C1 is disordered in two orientations in **1,** whereas in **2** it is ordered. The bond parameters in both compounds are normal. The C14−C15 bond distances are 1.298(9)−1.312(4) Å which are typical for a $C_{sp2}=C_{sp2}$ bond. The minor difference in the

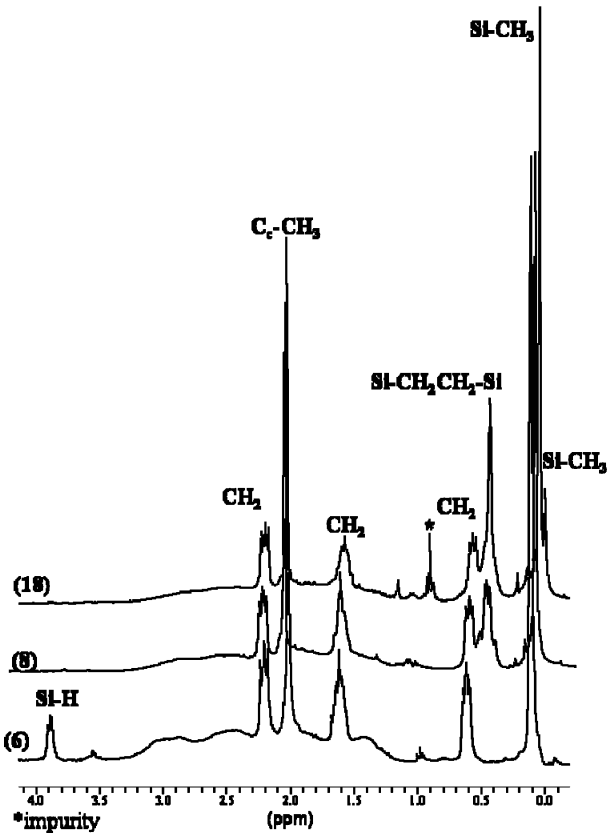


Figure 1. ^1H NMR spectra of compounds **6**, **8**, and **18**.

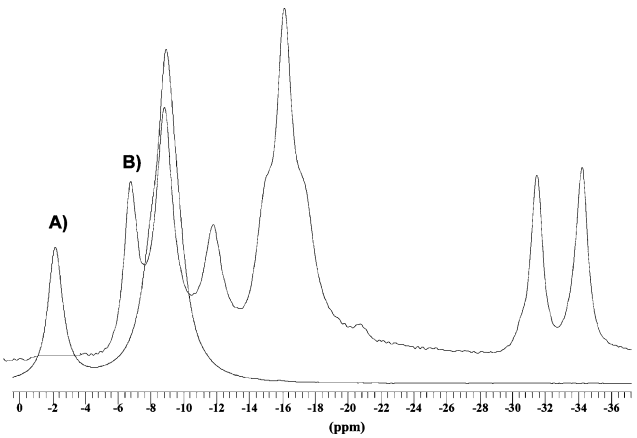
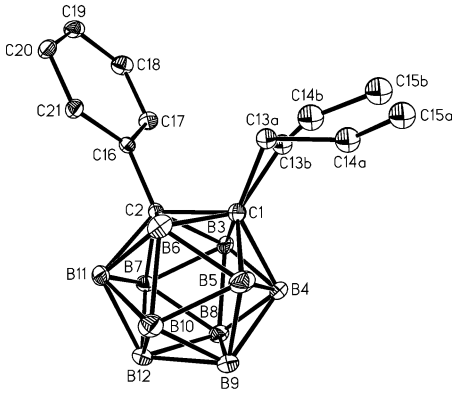


Figure 2. $^{11}B\{^1H\}$ NMR spectra: (A) neutral dendrimer **7**; (B) anionic dendrimer **19**.



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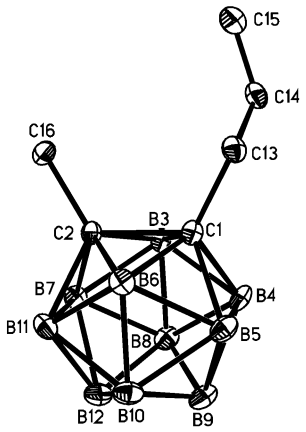

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Figure 3. Molecular structures of precursors **1** and **2**. In **1**, the $-CH_2-CH=CH_2$ substituent is disordered in two orientations.

C1−C2 bond lengths between **1** [1.701(4) Å] and **2** [1.670(3) Å] is a further confirmation that the phenyl substituent at the cluster carbon has a greater contribution to the lengthening of the C_c-C_c bond than that of aliphatic substituent.[20]

Conclusions

First and second generations of neutral carbosilane dendrimers, periphery functionalized with four *closo*-carborane clusters (**7**, **8**, **15** and **16**) have been synthesized. In all cases, the carborane cluster is attached to the dendrimer through a propyl chain between the $C_{cluster}$ and the Si atom, to avoid the direct and sensitive $C_{cluster}-Si$ bond. Two different strategies (divergent and convergent) for the preparation of carborane functional dendrimers **7**, **8**, **15** and **16** have been explored. The divergent approach involves the hydrosilylation of allyl or vinyl-substituted carborane derivatives with the first generation of a carbosilane dendrimer containing peripheral Si−H functions, **1G-H$_4$**. The convergent strategy requires the synthesis of agile and suitable Si−H functionalized carboranyl building blocks, to be attached, at the last step, to the tetravinylsilane core. Additionally, 2 second generation carbosilane dendrimers, **17** and **18**, containing eight peripheral *closo*-clusters have been prepared by hydrosilylation of the vinyl groups in the dendrimer **1G-Vi$_8$** with carboranylsilane dendrons containing Si−H functions. The synthetic methodology described here is suitable to prepare carbosilane dendrimers of higher generations and to functionalize with other peripheral carborane derivatives. When no direct $C_{cluster}-Si$ bond was present in the dendrimeric structure, it was possible to carry out the modification of the peripheral *closo*-carboranes, such as in dendrimers **7** and **8**, to yield the corresponding anionic species. This reaction afforded a new type of polyanionic carbosilane dendrimer that contains *nido*-carborane clusters. These compounds offer the possibility for further complexation of the peripheral carborane clusters to obtain metallodendrimers, which is actually the focus of our studies.

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{^{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 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 ^{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-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. $(CH_3)_2HSiCl$ and Karstedt's catalyst (platinum divinyltetramethyldisiloxane complex, 2.1−2.4% platinum in vinyl terminated polydimethylsiloxane) 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 $CH_2=CHMgCl$ from Aldrich. Dendrimers **1G-H$_4$** and **1G-Vi$_8$** were prepared according to the literature.[10a,e]

Synthesis of 1-C_6H_5-2-$CH_2CH=CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (1). To a solution of 1-C_6H_5-1,2-*closo*-$C_2B_{10}H_{11}$ (0.50 g, 2.3 mmol) in a mixture of toluene (7 mL) and diethyl ether (3.5 mL) at 0 °C, 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 °C, 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 cooled at room temperature, 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 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, ^3J(H,H) = 16.7, ^3J(H,H) = 10.0, ^3J(H,H) = 7.3, 1H, $CH_2CH=CH_2$), 5.05 (d, ^3J(H,H) = 10.0, 1H, $CH_2CH=CH_2$), 4.75 (d, ^3J(H,H) = 16.7, 1H, $CH_2CH=CH_2$), 2.57 (d, ^3J(H,H) = 7.3, 2H, $CH_2CH=CH_2$). ^{1}H{^{11}B} NMR: δ 7.68−7.36 (m, 5H, C_6H_5), 5.65 (ddt, ^3J(H,H) = 16.7, ^3J(H,H) = 10.0, ^3J(H,H) = 7.3, 1H, $CH_2CH=CH_2$), 5.05 (d, ^3J(H,H) = 10.0, 1H, $CH_2CH=CH_2$), 4.75 (d, ^3J(H,H) = 16.7, 1H, $CH_2CH=CH_2$), 2.76 (br s, B−*H*), 2.57 (d, ^3J(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, ^1J(B,H) = 147, 2B), −10.5 (8B). ^{13}C{^{1}H} NMR: δ 132.4 ($CH_2CH=CH_2$), 131.3 ($C_6H_5-C_{meta}$), 130.7 ($C_6H_5-C_{ortho}$), 130.5 ($C_6H_5-C_{ipso}$), 128.8 ($C_6H_5-C_{para}$), 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(CH=CH)), 2967, 2927 ($\nu(C_{alkyl}-H)$), 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-*closo*-$C_2B_{10}H_{10}$ (2). The procedure was the same as for **1** using 1.00 g (6.32 mmol) of 1-CH_3-1,2-*closo*-$C_2B_{10}H_{11}$ 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 h 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, ^3J(H,H) = 16.8, ^3J(H,H) = 10.0, ^3J(H,H) = 7.2, 1H, CH_2CH═CH_2), 5.21 (d, ^3J(H,H) = 10.0, 1H, CH_2CH═CH_2), 5.13 (d, ^3J(H,H) = 16.8, 1H, CH_2CH═CH_2), 2.97 (d, ^3J(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, ^3J(H,H) = 16.8, ^3J(H,H) = 10.0, ^3J(H,H) = 7.2, 1H, CH_2CH═CH_2), 5.21 (d, ^3J(H,H) = 10.0, 1H, CH_2CH═CH_2), 5.13 (d, ^3J(H,H) = 16.8, 1H, CH_2CH═CH_2), 2.97 (d, ^3J(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, ^1J(B,H) = 124, 1B), −4.1 (d, ^1J(B,H) = 135, 1B), −8.2 (3B), −9.1 (d, ^1J(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-(CH═CH)), 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-*closo*-$C_2B_{10}H_{10}$ (3). In a Schlenk flask, **1** (0.32 g, 1.23 mmol), $(CH_3)_2$-HSiCl (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 $(CH_3)_2$HSiCl 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, ^3J(H,H) = 7.5, 2H, C_c−CH_2), 1.52 (tt, 2H, $CH_2CH_2CH_2$), 0.60 (t, ^3J(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, ^3J(H,H) = 7.5, 2H, C_c−CH_2), 1.52 (m, 2H, $CH_2CH_2CH_2$), 0.60 (t, ^3J(H,H) = 8.1, 2H, Si−CH_2), 0.31 (s, 6H, Si−CH_3). ^{11}B NMR: δ −3.6 (d, ^1J(B,H) = 145, 2B), −10.5 (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-*closo*-$C_2B_{10}H_{10}$ (4). The procedure was the same as for compounds **3** using **2** (0.64 g, 3.21 mmol), $(CH_3)_2$HSiCl (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, ^3J(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, ^3J(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., ^3J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.85 (t, ^3J(H,H) = 8.13, 2H, Si−CH_2), 0.45 (s, 6H, Si−CH_3). ^{11}B NMR: δ −2.9 (d, ^1J(B,H) = 132, 1B), −4.2 (d, ^1J(B,H) = 144, 1B), −9.1 (d, ^1J(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-*closo*-$C_2B_{10}H_{10}$ (5). To a solution of $LiAlH_4$ (38.0 mg, 1.00 mmol) in Et_2O (16 mL) at 0 °C 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, ^3J(H,H) = 8.5, 2H, C_c−CH_2), 1.45 (tt, ^3J(H,H) = 8.5, ^3J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.37 (td, ^3J(H,H) = 8.1, ^3J(H,H) = 3.2, 2H, Si−CH_2), −0.02 (d, ^3J(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, ^3J(H,H) = 8.1, 2H, C_c−CH_2), 1.45 (tt, ^3J(H,H) = 8.5, ^3J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.37 (td, ^3J(H,H) = 8.1, ^3J(H,H) = 3.2, 2H, Si−CH_2), −0.02 (d, ^3J(H,H) = 3.7, 6H, Si−CH_3). ^{11}B NMR: δ −2.3 (d, ^1J(B,H) = 146, 2B), −9.1 (d, ^1J(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-*closo*-$C_2B_{10}H_{10}$ (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, ^3J(H,H) = 8.5, 2H, C_c−CH_2), 2.02 (s, 3H, C_c−CH_3), 1.62 (tt, ^3J(H,H) = 8.5, ^3J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.61 (td, ^3J(H,H) = 8.1 ^3J(H,H) = 3.2, 2H, Si−CH_2), 0.11 (d, ^3J(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, ^3J(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, ^3J(H,H) = 8.5, ^3J(H,H) = 8.1, 2H, $CH_2CH_2CH_2$), 0.61 (td, ^3J(H,H) = 8.1 ^3J(H,H) = 3.7, 6H, Si−CH_3). ^{11}B NMR: δ −2.9 (d, ^1J(B,H) = 130, 1B), −4.2 (d, ^1J(B,H) = 140, 1B), −8.3 (3B), −9.1 (d, ^1J(B,H) = 145, 5B). ^{13}C{^{1}H} 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{^{1}H} NMR: δ −14.07. FTIR (NaCl), cm^{-1}: 2957−2901 (ν(C_{alkyl}−H)), 2588 (ν(B−H)), 2114 (ν(Si−H)), 1252 (ν(Si−CH_3)).

Synthesis of 1G-[1-C_6H_5-2-$CH_2CH_2CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$]$_4$ (7). Method A: In a Schlenk flask, **1** (0.55 g, 2.12 mmol), **1G-H_4** (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. 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%. ^{1}H 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). ^{1}H{^{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{^{1}H} 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_2-CH_2−Si), 2.6 (Si−CH_2CH_2−Si), −4.0 (Si−CH_3). ^{29}Si{^{1}H} NMR: δ 9.05 (Si_{core}), 3.32 ($Si_{periphery}$). FTIR (NaCl), cm^{-1}: 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-[1-CH_3-2-$CH_2CH_2CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$]$_4$ (8). Method A: In a Schlenk flask, **2** (0.13 g, 0.64 mmol), **1G-H_4** (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 petroleum ether. 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%. ^{1}H 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). ^{1}H{^{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-{^{1}H} NMR: δ 78.1 (C_c), 74.6 (C_c), 38.9 (C_c−CH_2), 24.4 (CH_2CH_2-CH_2), 23.1 (C_c−CH_3), 14.7 (Si−CH_2), 7.2 (Si−CH_2CH_2−Si), 2.7

(Si−*C*H$_2$CH$_2$−Si), −3.9 (Si−C*H*$_3$). ^{29}Si{^{1}H} NMR: δ 8.45 (*Si*$_{core}$), 3.56 (*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, 1167.9 [M − 1]$^-$, 910.75 [M − Si(CH$_3$)$_2$CH$_2$CH$_2$CH$_2$(C$_3$B$_{10}$H$_{13}$)]$^-$, 527.5 [M − CH$_2$CH$_2$Si(CH$_3$)$_2$-CH$_2$CH$_2$CH$_2$(C$_3$B$_{10}$H$_{13}$)]$^-$, 194.0 [CH$_2$CH$_2$CH$_2$(C$_3$B$_{10}$H$_{13}$)]$^-$, 169.0 [CH$_2$(C$_3$B$_{10}$H$_{13}$)]$^-$, 156 [C$_3$B$_{10}$H$_{13}$]$^-$.

Synthesis of 1-C$_6$H$_5$-2-[CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCH = CH$_2$]-1,2-*closo*-C$_2$B$_{10}$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%. ^{1}H NMR: δ 7.66−7.38 (m, 5H, C$_6$*H*$_5$), 6.05−5.87 (m, 2H), 5.58 (m, 1H), 1.79 (t, ^{3}*J*(H,H) = 8.1, 2H, C$_c$−C*H*$_2$), 1.41 (tt, ^{3}*J*(H,H) = 8.1, 2H, CH$_2$C*H*$_2$CH$_2$), 0.34 (t, ^{3}*J*(H,H) = 8.1, 2H, Si−C*H*$_2$), −0.03 (s, 6H, Si−C*H*$_3$). ^{1}H{^{11}B} NMR: δ 7.66−7.38 (m, 5H, C$_6$*H*$_5$), 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, ^{3}*J*(H,H) = 8.1, 2H, C$_c$−C*H*$_2$), 1.41 (tt, ^{3}*J*(H,H) = 8.1, 2H, CH$_2$C*H*$_2$CH$_2$), 0.34 (t, ^{3}*J*(H,H) = 8.1, 2H, Si−C*H*$_2$), −0.03 (s, 6H, Si−C*H*$_3$). ^{11}B NMR: δ −2.2 (d, ^{1}*J*(B,H) = 146, 2B), −9.0 (d, ^{1}*J*(B,H) = 127, 8B). ^{13}C{^{1}H} NMR: δ 131.0−128.9 (C$_6$H$_5$), 137.8 (*C*H═CH$_2$), 131.8 (CH═*C*H$_2$), 83.3 (*C*$_c$), 81.9 (*C*$_c$), 38.6 (C$_c$−*C*H$_2$), 24.3 (*C*H$_2$), 15.1 (Si−*C*H$_2$), −3.4 (Si−*C*H$_3$). ^{29}Si{^{1}H} NMR: δ −6.25.

Synthesis of 1-CH$_3$-2-[CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCH═CH$_2$]-1,2-*closo*-C$_2$B$_{10}$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%. ^{1}H NMR: δ 6.15−5.98 (m, 2H), 5.70 (m, 1H), 2.19 (t, ^{3}*J*(H,H) = 8.1, 2H, C$_c$−C*H*$_2$), 2.01 (s, 3H, C$_c$−C*H*$_3$), 1.62 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.61 (t, ^{3}*J*(H,H) = 8.5, 2H, Si−C*H*$_2$), 0.10 (s, 6H, Si−C*H*$_3$). ^{1}H{^{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$_c$−C*H*$_3$), 1.62 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.61 (t, ^{3}*J*(H,H) = 8.5, 2H, Si−C*H*$_2$), 0.10 (s, 6H, Si−C*H*$_3$). ^{11}B NMR: δ −2.9 (d, ^{1}*J*(B,H) = 122, 1B), −4.1 (d, ^{1}*J*(B,H) = 141, 1B), −9.1 (d, ^{1}*J*(B,H) = 141, 8B). ^{13}C{^{1}H} NMR: δ 138.2 (*C*H═CH$_2$), 132.2 (CH═*C*H$_2$), 78.2 (*C*$_c$), 74.7 (*C*$_c$), 38.7 (C$_c$−*C*H$_2$), 24.3 (*C*H$_2$), 23.1 (C$_c$−*C*H$_3$), 15.3 (Si−*C*H$_2$), −3.4 (Si−*C*H$_3$). ^{29}Si{^{1}H} NMR: δ −6.27.

Synthesis of 1-C$_6$H$_5$-2-[CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCH$_2$CH$_2$(CH$_3$)$_2$-SiCl]-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (11). In a Schlenk flask, **9** (0.22 g, 0.64 mmol), (CH$_3$)$_2$HSiCl (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$_3$)$_2$-HSiCl gave **11** as a yellow oil. Yield: 0.28 g, > 99%. ^{1}H NMR: δ 7.67−7.41 (m, 5H, C$_6$*H*$_5$), 1.80 (t, ^{3}*J*(H,H) = 8.1, 2H, C$_c$−C*H*$_2$), 1.39 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.61 (m, 2H, C*H*$_2$), 0.39 (m, 8H, Si$_{core}$−C*H*$_2$, Si$_{periphery}$−CH$_3$), 0.30 (m, 2H, C*H*$_2$), −0.11 (s, 6H, Si$_{core}$−C*H*$_3$). ^{1}H{^{11}B} NMR: δ 7.67−7.41 (m, 5H, C$_6$*H*$_5$), 2.73 (br s, 2B, B−*H*), 2.36 (br s, 8B, B−*H*), 1.80 (t, ^{3}*J*(H,H) = 8.1, 2H, C$_c$−C*H*$_2$), 1.39 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.61 (m, 2H, C*H*$_2$), 0.39 (m, 8H, Si$_{core}$−C*H*$_2$, Si$_{periphery}$−CH$_3$), 0.30 (m, 2H, C*H*$_2$), −0.11 (s, 6H, Si$_{core}$−C*H*$_3$). ^{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*$_6$H$_5$), 83.3 (*C*$_c$), 82.3 (*C*$_c$), 38.6 (C$_c$−*C*H$_2$), 24.0 (*C*H$_2$), 14.4 (*C*H$_2$), 11.3 (*C*H$_2$), 6.3 (*C*H$_2$), 0.9 (*C*H$_3$−Si$_{periphery}$), −4.1 (*C*H$_3$−Si$_{core}$).

Synthesis of 1-CH$_3$-2-[CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCH$_2$CH$_2$(CH$_3$)$_2$-SiCl]-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (12). The procedure was the same as for compound **11** using, **10** (0.12 g, 0.43 mmol), (CH$_3$)$_2$HSiCl (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$_3$)$_2$HSiCl 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$_c$−C*H*$_2$), 2.01 (s, 3H, C$_c$−C*H*$_3$), 1.57 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.54 (m, 12H), 0.03 (s, 6H, Si−C*H*$_3$). ^{1}H{^{11}B} NMR: 2.20 (m, C$_c$−C*H*$_2$, B−*H*), 2.01 (s, 3H, C$_c$−C*H*$_3$), 1.57 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.54 (m, 12H), 0.03 (s, 6H, Si−C*H*$_3$). ^{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$_c$−*C*H$_2$), 24.2 (*C*H$_2$), 23.1 (C$_c$−*C*H$_3$), 14.7 (*C*H$_2$), 11.4 (*C*H$_2$), 6.4 (*C*H$_2$), 0.9 (Si$_{periphery}$−*C*H$_3$), −4.0 (Si$_{core}$−*C*H$_3$).

Synthesis of 1-C$_6$H$_5$-2-[CH$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCH$_2$CH$_2$(CH$_3$)$_2$-SiH]-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (13). To a solution of LiAlH$_4$ (12.9 mg, 0. 32 mmol) in Et$_2$O (10 mL) at 0 °C was added dropwise a solution of **11** (0.28 g, 0.64 mmol) in Et$_2$O (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$_6$*H*$_5$), 3.81 (m, 1H, Si−*H*), 1.78 (t, ^{3}*J*(H,H) = 8.1, 2H, C$_c$−C*H*$_2$), 1.39 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.36 (m, 4H, C*H*$_2$), 0.27 (m, 2H, C*H*$_2$), 0.04 (d, J^3(H,H) = 3.7, 6H, Si$_{periphery}$−C*H*$_3$), −0.14 (s, 6H, Si$_{core}$-C*H*$_3$). ^{1}H-{^{11}B} NMR: δ 7.66−7.40 (m, 5H, C$_6$*H*$_5$), 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$_c$−C*H*$_2$), 1.39 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.36 (m, 4H, C*H*$_2$), 0.27 (m, 2H, C*H*$_2$), 0.04 (d, J^3(H,H) = 3.7, 6H, Si$_{periphery}$−C*H*$_3$), −0.14 (s, 6H, Si$_{core}$−C*H*$_3$). ^{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*$_6$H$_5$), 83.3 (*C*$_c$), 82.4 (*C*$_c$), 38.7 (C$_c$−*C*H$_2$), 24.1 (CH$_2$), 14.5 (CH$_2$), 7.7 (CH$_2$), 6.3 (CH$_2$), −4.0 (*C*H$_3$−Si), −4.9 (*C*H$_3$−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$_2$CH$_2$CH$_2$(CH$_3$)$_2$SiCH$_2$CH$_2$(CH$_3$)$_2$-SiH]-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (14). The process was the same as for compound **13** using LiAlH$_4$ (8.5 mg, 0.21 mmol) in Et$_2$O (8 mL) and **12** (0.16 g, 0.43 mmol) in Et$_2$O (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$_c$−C*H*$_2$), 2.02 (s, 3H, C$_c$−C*H*$_3$), 1.55 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.47 (m, 6H), 0.08 (d, ^{3}*J*(H,H) = 3.7, 6H, Si$_{periphery}$−C*H*$_3$), 0.005 (s, 6H, Si$_{core}$−C*H*$_3$). ^{1}H{^{11}B} NMR: δ 3.85 (m, 1H, Si−*H*), 2.15 (m, C$_c$−C*H*$_2$, B−*H*), 2.02 (s, 3H, C$_c$−C*H*$_3$), 1.55 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 0.47 (m, 6H), 0.08 (d, ^{3}*J*(H,H) = 3.7, 6H, Si$_{periphery}$−C*H*$_3$), 0.005 (s, 6H, Si$_{core}$−C*H*$_3$). ^{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$_c$−*C*H$_2$), 24.3 (*C*H$_2$), 23.1 (C$_c$−*C*H$_3$), 14.8 (*C*H$_2$), 7.8 (*C*H$_2$), 6.3 (*C*H$_2$), −3.9 (*C*H$_3$−Si), −4.9 (*C*H$_3$−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-[1-C$_6$H$_5$-2-CH$_2$CH$_2$CH$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$]$_4$ (15). Method A: In a Schlenk flask, **9** (83.9 mg, 0.24 mmol), **1G-H$_4$** (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$_6$*H*$_5$), 1.78 (t, ^{3}*J*(H,H) = 8.5, 8H, C$_c$−C*H*$_2$), 1.39 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 0.33 (m, 40H, Si(1)C*H*$_2$C*H*$_2$Si(2)C*H*$_2$C*H*$_2$Si(3)-C*H*$_2$), −0.05 (s, 24H, Si−C*H*$_3$), −0.15 (s, 24H, Si−C*H*$_3$). ^{1}H{^{11}B} NMR: δ 7.66−7.40 (m, 20H, C$_6$*H*$_5$), 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$_c$−C*H*$_2$), 1.39 (m, 8H, CH$_2$C*H*$_2$CH$_2$), 0.33 (m, 40H, Si(1)-C*H*$_2$C*H*$_2$Si(2)C*H*$_2$C*H*$_2$Si(3)C*H*$_2$), −0.05 (s, 24H, Si−C*H*$_3$), −0.15 (s, 24H, Si−C*H*$_3$). ^{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$_6$H$_5$), 83.4 (*C*$_c$), 82.4 (*C*$_c$), 38.7 (C$_c$−*C*H$_2$), 24.1 (CH$_2$C*H*$_2$CH$_2$), 14.4 (Si*C*H$_2$CH$_2$CH$_2$), 7.1−6.5 (Si*C*H$_2$*C*H$_2$Si*C*H$_2$*C*H$_2$Si), −4.0 (Si−*C*H$_3$), −4.4 (Si−*C*H$_3$). ^{29}Si{^{1}H} NMR: δ 8.92 (Si$_{core}$), 5.05 (Si$_{middle}$), 3.36 (Si$_{periphery}$). 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-[1-CH_3-2-$CH_2CH_2CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$]$_4$ (16). Method A: The procedure was the same as for compound **15** using **10** (0.17 g, 0.59 mmol), **1G-H$_4$** (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, ^3J(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_2-SiCH_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_2-CH_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, ^1J(B,H) = 117, 4B), −4.3 (d, ^1J(B,H) = 143, 4B), −9.2 (d, ^1J(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_2-CH_2), 7.2−6.7 (SiCH_2CH_2SiCH_2CH_2Si), −3.9 ($Si_{periphery}$−CH_3), −4.5 (Si_{middle}−CH_3). ^{29}Si{^{1}H} NMR: δ 7.26 (Si_{core}), 5.21 (Si_{middle}), 3.52 ($Si_{periphery}$). 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′-[1-C_6H_5-2-$CH_2CH_2CH_2$-1,2-closo-$C_2B_{10}H_{10}$]$_8$ (17). In a Schlenk flask, **5** (0.13 g, 0.41 mmol), **1G-Vi$_8$** (27.0 mg, 51 μmol), 0.4 mL of toluene, and Karstedt catalyst were mixed and stirred during 48 h. 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, ^3J(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, ^3J(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, ^1J(B,H) = 122, 16B), −8.8 (br s, 64B). ^{29}Si{^{1}H} NMR: δ 8.80 (Si_{core}), 6.98 (Si_{middle}), 3.38 ($Si_{periphery}$). ^{13}C{^{1}H} NMR: δ 131.1−128.9 (C_6H_5), 83.4 (C_c), 82.1 (C_c), 38.8 (C_c−CH_2), 24.4 ($CH_2CH_2CH_2$), 14.4 (Si$CH_2CH_2CH_2$), 7.1−4.9 (SiCH_2CH_2SiCH_2CH_2Si), −4.0 ($Si_{periphery}$−CH_3), −6.4 (Si_{middle}−CH_3). ^{29}Si{^{1}H} NMR: δ 7.26 (Si_{core}), 5.21 (Si_{middle}), 3.52 ($Si_{periphery}$).

Synthesis of 2G′-[1-CH_3-2-$CH_2CH_2CH_2$-1,2-*closo*-$C_2B_{10}H_{10}$]$_8$ (18). In a Schlenk flask, **6** (0.17 g, 0.67 mmol), **1G-Vi$_8$** (44.1 mg, 84 μmol), 0.4 mL of toluene, and Karstedt catalyst were mixed and stirred during 24 h. 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, ^3J(H,H) = 8.1, 16H, C_c−CH_2), 2.01 (s, 24H, C_c−CH_3), 1.55 (m, 16H, CH_2CH_2-CH_2), 0.53 (t, ^3J(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, ^3J(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, ^3J(H,H) = 8.5, 16H, CH_2CH_2-CH_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, ^1J(B,H) = 144, 8B), −9.1 (d, ^1J(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 (Si$CH_2CH_2CH_2$), 7.3−4.5 (SiCH_2CH_2-SiCH_2CH_2Si), −3.8 (Si−CH_3), −6.5 (Si−CH_3). ^{29}Si{^{1}H} NMR: δ 8.99 (Si_{core}), 7.26 (Si_{middle}), 3.42 ($Si_{periphery}$). 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 [N(CH_3)$_4$]$_4${1G-[7-C_6H_5-8-$CH_2CH_2CH_2$-7,8-*nido*-$C_2B_9H_{10}$]$_4$} (19). To a two necked round-bottom flask containing a solution of KOH (0.12 g, 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 h. Then, the volatiles were evaporated in the vacuum and an excess of tetramethylamonium chloride in water was added to obtain a white solid. This was filtered off, washed with water (3 × 15 mL), diethyl ether (3 × 10 mL), and toluene (3 × 10 mL), and dried under vacuum to obtain **19** as a white solid. Yield: 0.12 g, 89%. ^{1}H NMR (CD_3-OCD_3): δ 7.36−7.12 (m, 20H, C_6H_5), 3.42 (s, 48H, [N(CH_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). ^{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, ^1J(B,H) = 140, 4B), −11.2 (d, ^1J(B,H) = 161, 4B), −15.6 (d, ^1J(B,H) = 128, 16B), −31.3 (dd, ^1J(B,H) = 119, ^1J(B,H) = 31, 4B), −34.1 (d, ^1J(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): 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_3-OH (1:2) *m/z*: calcd for $C_{76}H_{172}B_{36}N_4Si_5$, 1671.8; found, 1597.5 [(M − N(CH_3)$_4$]$^-$.

Synthesis of [N(CH_3)$_4$]$_4${1G-[7-CH_3-8-$CH_2CH_2CH_2$-7,8-*nido*-$C_2B_9H_{10}$]$_4$} (20). To a two necked round-bottom flask containing a solution of KOH (0.10 g, 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 h. Then, the volatiles were evaporated in the vacuum and an excess of tetramethylamonium chloride in water was added to obtain a white solid. This was filtered off, washed with water (3 × 15 mL) 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, Si_{core}−CH_2CH_2−$Si_{periphery}CH_2$), −0.01 (s, 24H, Si−CH_3). ^{1}H{^{11}B} NMR: δ 3.44 (s, 48H, [N(CH_3)$_4$]$^+$), 1.62 (m, 16H, C_c−CH_2CH_2), 1.42 (s, 12H, C_c−CH_3), 0.46 (m, 24H, Si_{core}−CH_2CH_2−$Si_{periphery}CH_2$), −0.01 (s, 24H, Si−CH_3), −2.58 (br s, 4H, B*H*B). ^{11}B NMR: δ −6.0 (d, ^1J(B,H) = 158, 4B), −7.8 (d, ^1J(B,H) = 153, 8B) −15.1 (d, ^1J(B,H) = 112, 16B), −31.6 (dd, ^1J(B,H) = 119, ^1J(B,H) = 45, 4B), −34.1 (d, ^1J(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): 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. Single-crystal data collections for **1** and **2** were performed at −100 °C on a Nonius Kappa diffractometer equipped with CCD area detector and using graphite monochromatized Mo Kα radiation. Totals of 4869 and 4210 reflections were collected for **1** and **2** giving 2860 (R_{int} ≡ 0.0296) and 2259 (R_{int} ≡ 0.0809) unique reflections for **1** and **2**, respectively.

The structures were solved by direct methods and refined on F^2 by the SHELXL97 program.[21] For **1**, the −CH_2CH═CH_2 substituent is disordered assuming two orientations. Refinement of the disordered substituent resulted site occupation parameter of 0.470-(5) for C13a, C14a, C15a, and relevant hydrogen atoms, while the parameter of 0.530(5) was obtained for C13b, C14b, C15b, and relevant hydrogen atoms. The disordered carbons atoms were refined with isotropic thermal displacement parameters, but the rest of the non-hydrogen atoms were refined with anisotropic thermal displacement parameters. The hydrogen atoms were treated as riding atoms using the SHELX97 default parameters.

For **2**, all non-hydrogen atoms were refined with anisotropic thermal displacement parameters and hydrogen atoms were treated

as riding atoms using the SHELX97 default parameters.

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