

Approaches to the Preparation of Carborane-Containing Carbosilane Compounds

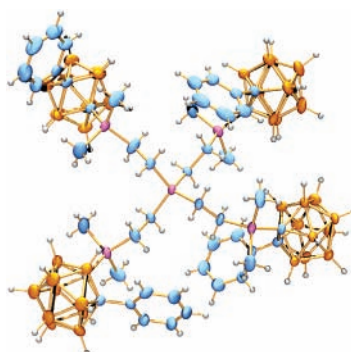
Rosario Núñez,[†] Arántzazu González,^{†,‡} Clara Viñas,[†] Francesc Teixidor,^{*,†}
Reijo Sillanpää,[§] and Raikko Kivekäs^{||}

*Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB,
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*

teixidor@icmab.es

Received October 20, 2004

ABSTRACT



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

The *o*-carborane and its derivatives present properties such as high stability, hydrophobicity, so-called three-dimensional “aromaticity”, and synthetic versatility.¹ This makes them suitable for a wide range of applications in organometallic chemistry and materials science such as extraction of radionuclides,² BNCT,³ and catalysis,⁴ among others. Al-

though some carborane-containing dendrimers have been reported, none of them have been integrated into carbosilane structures.⁵ Dendrimers⁶ constitute a class of spherical and monodisperse macromolecules that can be constructed from a multifunctional central core and expand to a periphery. Today, the technology of dendrimers is focused on the modification of their properties and potential applications by introduction of reactive functional groups⁷ or metals in their interior or on their periphery.^{8,9} Of the multitude of

[†] Institut de Ciència de Materials de Barcelona (CSIC).

[‡] A.G. is enrolled in the UAB Ph.D. Program.

[§] University of Jyväskylä.

^{||} University of Helsinki.

(1) (a) Plešek, J. *Chem. Rev.* **1992**, 92, 269. (b) King, R. B. *Chem. Rev.* **2001**, 101, 1119.

(2) (a) Viñas, C.; Gómez, S.; Bertrán, J.; Teixidor, F.; Dozol, J.-F.; Rouquette, H. *Chem. Commun.* **1998**, 191. (b) Viñas, C.; Gómez, S.; Bertrán, J.; Teixidor, F.; Dozol, J.-F.; Rouquette, H. *Inorg. Chem.* **1998**, 37, 3640. (c) Grüner, B.; Plešek, J.; Baca, J.; Cisarova, I.; Dozol, J.-F.; Rouquette, H.; Viñas, C.; Seluckx, P.; Rais, J. *New J. Chem.* **2002**, 26, 1519.

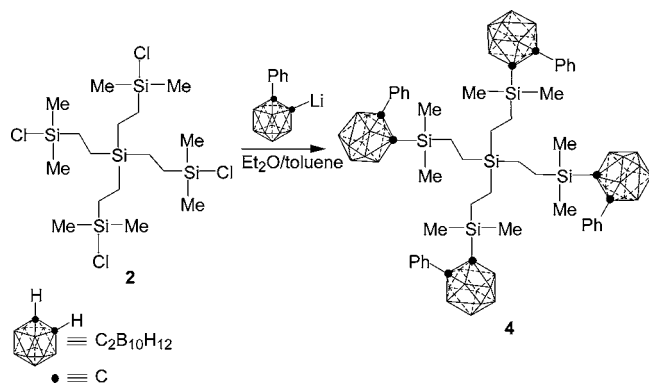
(3) Hawthorne, M. F.; Maderna, A. *Chem. Rev.* **1999**, 99, 3421.

(4) (a) Teixidor, F.; Flores, M. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Angew. Chem., Int. Ed. Engl.* **1996**, 108, 2388. (b) Teixidor, F.; Flores, M. A.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *J. Am. Chem. Soc.* **2000**, 122, 1963. (c) Tutusaus, O.; Viñas, C.; Núñez, R.; Teixidor, F.; Demonceau, A.; Delfosse, S.; Nöels, A. F.; Mata, I.; Molins, E. *J. Am. Chem. Soc.* **2003**, 125, 11830.

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

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

Scheme 1. Preparation of **4** from **2** and Li[1-Ph-1,2-C₂B₁₀H₁₀]

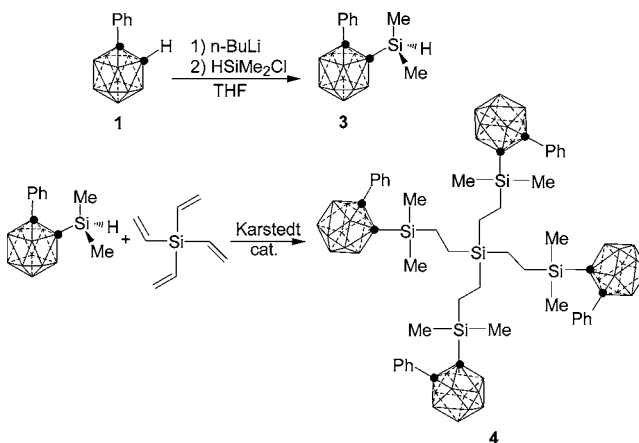


solution of **1** in diethyl ether was treated with *n*-buthyllithium at 0 °C to afford the monolithiated species, and subsequently a solution of **2** in toluene was added. The mixture was stirred for 5 min at 0 °C and then filtered. After evaporation of solvents, the residue was treated with cold diethyl ether (0

°C), affording compound **4** as an air-stable white solid in 62% yield.

Analysis (vide infra) shows that a carbosilane core with four phenyl-*o*-carborane clusters on the periphery was obtained. In principle, compound **4** could be prepared by a hydrosilylation reaction following Cuadrado and collaborators' procedure.¹² Thus, considering the properties of carboranes, the hydrosilylation of tetravinylsilane with the corresponding carboranylsilane was investigated. For this purpose, 1-dimethylsilyl-2-phenyl-1,2-dicarba-*closo*-dodecaborane (**3**) was prepared. The synthesis of **3** was achieved by reaction of the lithium salt of **1** with HSiMe₂Cl in THF (Scheme 2). Compound **3** was isolated as a white solid in

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



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

No reaction was observed, however, when **3** was mixed with tetravinylsilane in the reported reaction conditions using Pt catalysts.^{11,12} The permanence of the Si–H signal in the IR and ¹H NMR spectra indicated its lack of reactivity under those conditions. Formation of **4** in 85% yield was successfully achieved by the addition of **3** to tetravinylsilane in the absence of solvent, at 50 °C overnight, using the Karstedt catalyst¹³ (Scheme 2). In view of these results, the hydrosi-

(5) (a) Newkome, G. R.; Moorefield, C. N.; Keith, J. M.; Baker, G. R.; Escamilla, G. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 666. (b) Armspach, D.; Cattalini, M.; Constable, E. C.; Housecroft, C. E.; Phillips, D. *Chem. Commun.* **1996**, 1823. (c) Qualman, B.; Kessels, M. M.; Musiol, H.-J.; Sierralta, W. D.; Jungblut, P. W.; Moroder, L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 909. (d) Parrott, M. C.; Marchington, E. B.; Valliant, J. F.; Adronov, A. *Macromol. Symp.* **2003**, *196*, 201. (e) Yao, H.; Grimes, R. N.; Corsini, M.; Zanello, P. *Organometallics* **2003**, *22*, 4381.

(6) (a) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Synthesis, Applications*; Wiley: New York, 2002. (b) Beletskaya, I. P.; Chuchurjukin, A. V. *Russ. Chem. Rev.* **2000**, *69*, 639. (c) Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991.

(7) (a) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74. (b) Stiriba, A.-E.; Frey, H.; Haag, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 1329. (c) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681. (d) Boury, B.; Corriu, R. J. P.; Núñez, R. *Chem. Mater.* **1998**, *10*, 1795.

(8) (a) Oosterom, G. E.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1828. (b) Seebach, D.; Rheiner, P. B.; Greiveldinger, G.; Butz, T.; Sellner, H. *Top. Curr. Chem.* **1998**, *197*, 125. (c) Gossage, A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423.

(9) Kleij, A. W.; Gossage, R. A.; Jastrzebski, J. T. B. H.; Boersma, J.; van Koten, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 176.

(10) (a) Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1951. (b) Frey, H.; Schlenk, C. *Top. Curr. Chem.* **2000**, *210*, 69. (c) Kreiter, R.; Kleij, A. W.; Klein Gebbink, R. J. M.; van Koten, G. *Top. Curr. Chem.* **2001**, *217*, 163.

(11) Seyferth, D.; Kugita, T.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1995**, *14*, 5362.

(12) Lobete, F.; Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada J. J. *Organomet. Chem.* **1996**, *509*, 109.

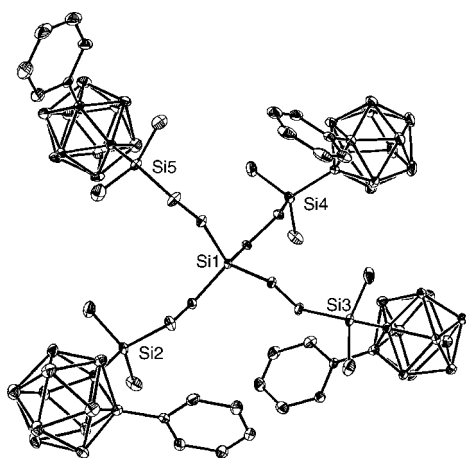


Figure 1. Structure of **4**. Thermal ellipsoids are drawn at the 20% probability level.

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

The structure of **4** was straightforwardly established on the basis of IR, ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B , and ^{29}Si NMR, elemental analysis, and electrospray-ionization mass spectrometry (ESI-MS) and unequivocally confirmed by X-ray diffraction analysis. The IR spectrum shows two bands at 2568 and 1253 cm^{-1} corresponding to $\nu(\text{B}-\text{H})$ and $\delta(\text{Si}-\text{Me})$, respectively. The ^1H NMR spectrum exhibits a singlet at -0.13 ppm assigned to the $\text{Si}-\text{Me}$ protons and a multiplet at 0.14 ppm due to the $\text{Si}-(\text{CH}_2)_2-\text{Si}$ protons. Such protons appear at higher field with respect to precursor **2** (from 0.44 to -0.13 ppm for $\text{Si}-\text{Me}$ and from 0.65 to 0.14 ppm for $\text{Si}-\text{CH}_2$). This effect has been attributed to the influence of the ring electronic currents with these protons (vide infra).¹⁴ The $^{13}\text{C}\{^1\text{H}\}$ NMR resonances of the CH_2 and CH_3 groups have also been shifted to higher field with respect to **2**. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **4** shows four resonances in a range $\delta -10.14$ to $+1.41$ ppm that were assigned by comparison with **3**. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum displays two close signals at 10.56 ppm (Si core) and 10.36 ppm (Si periphery). The latter corresponds to the Si atom bonded to

the $\text{C}_{\text{cluster}}$. The corresponding Si resonance is shifted to higher field with respect to the peripheral $\text{Si}-\text{Cl}$ (32.71 ppm) for **2**, due to the presence of the cluster. The ESI mass spectrum of **4** shows various peaks, among them one at $m/z = 1312.1$ corresponding to $[\text{M} + 2(\text{CH}_3\text{OH})]^-$. Crystals suitable for X-ray structural determination were isolated, and the structure is shown in Figure 1. The molecule assumes C_1 symmetry with mutually different orientations of the clusters. The $\text{C}_{\text{cluster}}-\text{C}_{\text{cluster}}$ distances of 1.649(4)–1.720(4) Å are comparable to values found for 1,1',2,2'-(SiMe_2)₂- and 1,2- Ph_2 -disubstituted *o*-carborane derivatives [1.688(5) and 1.720(4), and 1.733(4) Å, respectively].¹⁵ The $\text{Si}-\text{C}_{\text{cluster}}$ distances are around 1.93 Å, longer than the dendrimeric $\text{Si}-\text{C}$ distance (1.85 Å). The $\text{C}_{\text{cluster}}-\text{C}_{\text{cluster}}-\text{Si}$ angle is 122.8°.

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

Acknowledgment. This work was supported by CICYT, MAT01-1575, and the Generalitat de Catalunya, 2001/SGR/00337.

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

OL0478335

(13) Karstedt's catalyst: platinum divinyltetramethyldisiloxane complex, 3–3.5% platinum in vinyl-terminated poly(dimethylsiloxane).

(14) (a) Llop, J.; Viñas, C.; Teixidor, F.; Victori, L.; Kivekäs, R.; Sillanpää, R. *Organometallics* **2002**, *21*, 355. (b) Mitchell, R. H. *Chem. Rev.* **2001**, *101*, 1301.

(15) (a) Kivekäs, R.; Romerosa, A.; Viñas, C. *Acta Crystallogr.* **1994**, *C50*, 638. (b) Lewis, Z. G.; Welch, A. *Acta Crystallogr.* **1993**, *C49*, 705.