

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

Arántazu González-Campo,[†] Emilio José Juárez-Pérez,^{†,‡} Clara Viñas,[†] Bruno Boury,[§] Reijo Sillanpää,^{||} Raikko Kivekäs,[⊥] and Rosario Núñez^{*,†}

Department of Chemistry, Institut de Ciència de Materials de Barcelona (CSIC), Campus de la U.A.B., 08193 Bellaterra, Spain, Institut Charles Gerhardt Montpellier - UMR 5253 - CNRS-UM2-ENSCM-UM1, CMOS - Place E. Bataillon, 34095 Montpellier, France, Department of Chemistry, University of Jyväskylä, FIN-40351, Jyväskylä, Finland, and Department of Chemistry, University of Helsinki, Post Office Box 55, FIN-00014, Finland

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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 chlorosilane 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 mesostructure 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 source¹⁸ or the condensation between Si–H and Si–OMe.¹⁹ This former method has recently been used to prepare hexasilsesquioxanes (T₆),^{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.

* To whom correspondence should be addressed. Tel.: +34 93 580 1853. Fax: +34 93 580 5729. E-mail: rosario@icmab.es.

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

[‡] Enrolled in the UAB Ph.D. program.

[§] Institut Charles Gerhardt Montpellier.

^{||} University of Jyväskylä.

[⊥] University of Helsinki.