

## Octasilsesquioxane Chemistry I. Attachment of Four Surface Bridges to Octasilsesquioxane Quasi-cube Framework

Ling-Kang Liu\* (劉陵崗), Jiann-Bond Chu (朱建邦),  
Zdenek Slanina (史蘭尼) and Tahsin J. Chow (周大新)

*Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan 11529 and  
Department of Chemistry, National Taiwan University, Taipei, Taiwan 10767, R.O.C.*

The Pt/C catalyzed hydrosilylation of  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$  and 8 equiv of  $\text{HSiMe}_2\text{Cl}$  produced  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_8$  that was de-hydrochlorinated with 4 equiv of  $Z\text{-HOCH}_2\text{CH}_2=\text{CHCH}_2\text{OH}$  in the presence of excess TMEDA. This preparation resulted in the attachment of four surface bridges ( $-\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OCH}_2\text{CH}=\text{CHCH}_2\text{OSiMe}_2\text{CH}_2\text{CH}_2\text{-Z-}$ ) on the quasi-cube  $\text{Si}_8\text{O}_{12}$  framework. As a parallel study, the theoretical calculations of  $\text{Si}_8\text{O}_{12}(-\text{CH}_2\text{CH}_2\text{SiH}_2\text{OCH}_2\text{CH}=\text{CHCH}_2\text{OSiH}_2\text{CH}_2\text{CH}_2\text{-Z-})_4$  were carried out at PM3 semi-empirical level to find optimized geometries for use in four subsequent *ab initio* computations using standard basis sets of 3-21G\* and 6-31G\*. The calculations suggest that one should expect about equimolar mixture of the tetra-adducts produced by the bridging over the edges of the quasi-cube, either over four parallel edges or over two orthogonal pairs of parallel edges, but not by bridging across the faces of the quasi-cube.

### INTRODUCTION

Polyhedral oligomeric silsesquioxanes with a general formula  $(\text{RSiO}_{3/2})_n$  have a precisely defined inorganic core, where R maybe hydrogen, organic or inorganic substituents, and n is an even number greater than 4. They are topologically ideal in the preparation of intimate nanocomposite materials.<sup>1</sup> With a quasi-cube shape silica core,<sup>2,3</sup> the best-studied octasilsesquioxanes  $\text{Si}_8\text{O}_{12}\text{R}_8$  are commonly obtained in the hydrolytic polycondensation of  $\text{RSiCl}_3$  or  $\text{RSi}(\text{OEt})_3$ .<sup>4</sup> For instance, the acidic hydrolysis of  $(\text{CH}_2=\text{CH})\text{Si}(\text{OEt})_3$  leads to  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$ ,<sup>5</sup> in which the 8 branch-end vinyl groups are equivalently attached to the rigid core, each Si position being mimic to a corner Si-atom of silica surface.

With an electron-withdrawing silica core, the self-metathesis of  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$  is expected to be thermodynamically favorable. Yet the  $^1\text{H}$  NMR spectra of reaction mixtures containing  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$  and either the Grubbs' catalyst  $\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2\text{Cl}_2$ <sup>6</sup> or the Schrock's catalyst  $\text{Mo}(\text{=CHCMe}_2\text{Ph})(\text{=NC}_6\text{H}_3\{2,6\text{-}i\text{-Pr}_2\})(\text{OCMe}\{\text{CF}_3\}_2)$ <sup>7</sup> never exhibit vinylic  $^1\text{H}$  resonances attributable to the formation of products from self-metathesis.<sup>8</sup> Alternatively  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$  alkylates benzene in a linear fashion to produce  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{Ph})_8$ ,<sup>9</sup> whereas normal  $\alpha$ -olefins alkylate to yield favorably branched products instead. These data are in-

dicative that the  $\text{Si}_8\text{O}_{12}$  core next to the vinylic double bonds is sterically demanding and prevents the formation of *gem*  $\text{Si}_8\text{O}_{12}$  and Ph substituents or the formation of metallacyclobutanes containing two adjacent  $\text{Si}_8\text{O}_{12}$  frameworks.

In addition to the large steric energy,  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$  has the most densely populated terminal olefins on its surface. It is surely of interest to build multiple rings on the  $\text{Si}_8\text{O}_{12}$  framework, making use of the vinylic functions for chemical elaboration. This report deals with the calculations of  $\text{Si}_8\text{O}_{12}(-\text{CH}_2\text{CH}_2\text{SiH}_2\text{OCH}_2\text{CH}=\text{CHCH}_2\text{OSiH}_2\text{CH}_2\text{CH}_2\text{-Z-})_4$  **1**, and the experimental preparation of  $\text{Si}_8\text{O}_{12}(-\text{CH}_2\text{CH}_2\text{SiMe}_2\text{OCH}_2\text{CH}=\text{CHCH}_2\text{OSiMe}_2\text{CH}_2\text{CH}_2\text{-Z-})_4$  **2**, each being with 4 macrocyclic rings based on  $\text{Si}_8\text{O}_{12}$  quasi-cage. As the central  $\text{Si}_8\text{O}_{12}$  quasi-cage is looped with four chains, structural isomers (e.g., **1a**, **1b**, and **1c**, vide infra) arise, that are computed in order to clarify the relative energetics. Cage compounds have frequently been computed<sup>10</sup> as species of focused interest of both experiment and theory.

### CALCULATIONS

All geometry optimizations of **1a**, **1b**, and **1c** were carried out at the PM3 semi-empirical level using the Spartan program package.<sup>11</sup> The optimizations were performed with

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\* Corresponding author. E-mail: liuu@chem.sinica.edu.tw





ing to three isomers that are considered for the energetics:

(i) bridging over four parallel edges of the cage **1a**,

(ii) bridging over four edges, one pair of which is orthogonal to the other pair **1b**, and

(iii) bridging over four face diagonals, leaving two *trans*-faces without a bridge, **1c**.

The PM3 optimized structures of (i)/(ii) and (iii) mono-adducts had been finalized at the lowest energy conformation of the chains (global minimum), or at least a conformation particularly low in energy. After calculations of mono-adducts, the species with the four chains were arranged according to the (i) - (iii) patterns. Then again the conformations particularly low in energy were found. Finding the global minimum for the tetra-adducts would be a considerably more demanding task than for the mono-adducts.

Table 1 shows the relative energetics for the tetra-adducts, at the selected five levels of theory. The main conclusion is that species **1a** and **1b** are almost isoenergetic while species **1c** is placed rather high in the potential energy term. The results of the four applied *ab initio* treatments are mutually well consistent. The calculations suggest that we should expect about equimolar mixture of the tetra-adducts produced by the bridging over the edges, either over four parallel edges or over two orthogonal pairs of parallel edges, but not by bridging across the faces. The PM3 optimized structures for the tetra-adducts **1a** and **1b** are illustrated in Figs. 1 and 2, respectively. That of **1c**, the high-energy isomer, is not shown. There is apparently a symmetry lowering in the optimized structures, when compared to the respective idealized topologies ( $D_{4h}$  for **1a**,  $D_{2d}$  for **1b**, and  $D_4$  for **1c**, see molecular drawings).

The computational study is complemented with the PM3 calculations of the vibrational spectra. As none exhibits any imaginary frequency, we have indeed arrived at the true local minima (though we cannot be sure that they are the global minima owing to the complexity of the problem).

### Synthesis of **2**

Because of short arm length of the vinyl groups of  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$ , it is *cross-metathesis ring-formation inert*. We therefore decided to employ other methods to create the surface bridges. A hydrosilylation reaction was carried out on  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$  first. In the presence of a Pt/C catalyst, the H-Si bond of  $\text{HSiMe}_2\text{Cl}$  (1 equiv per olefin) was added to the vinylic double bond of  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$ , forming smoothly  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_8$ .  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_8$  was further stirred with excess TMEDA and 4 equiv of  $Z\text{-HOCH}_2\text{CH}_2=\text{CHCH}_2\text{OH}$  at 60 °C in toluene for 3 h under an inert atmosphere. The de-hydrochlorination reac-

Table 1. Relative Energetics (Kcal/mol) of the Tetra-adducts **1a**, **1b**, and **1c**

Method <sup>a</sup>	<b>1a</b>	<b>1b</b>	<b>1c</b>
	Parallel edges	Orthogonal edges	Face diagonals
PM3	0.0	0.9	6.9
HF/3-21G*	0.0	1.7	9.3
B3LYP/3-21G*	0.0	4.0	15.7
HF/6-31G*	0.0	-1.9	13.4
B3LYP/6-31G*	0.0	0.2	16.7

<sup>a</sup> All computations carried out in the PM3 optimized geometries.

tion gave **2** successfully, as confirmed with NMR spectroscopic methods, EA and MS with satisfactory data.

Despite the multiple chloride nature of  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_8$  and the diol nature of  $Z\text{-HOCH}_2\text{CH}_2=\text{CHCH}_2\text{OH}$ , the de-hydrochlorination reaction didn't produce polymeric film, gel, or solids under the current experimental condition. It was judged accordingly that the reaction here was only intramolecular. The MS data clearly shows a monomeric molecular peak. The  $^1\text{H}$  NMR signals for the olefinic protons are very characteristic: at  $\delta$  5.57 ( $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{O}-Z-$ ) and 4.22, 4.16 ( $-\text{OCH}_2\text{CH}=\text{CHCH}_2\text{O}-Z-$ ).

Given that the dendritic  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_8$ , with a hard-core, is confined within a cube of approximately  $2 \times 2 \times 2$  nm, the chloro-concentration is about 1.6 M, which is an intrinsic constant and is the maximum possible chloro-concentration in a solution of  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_8$ . The

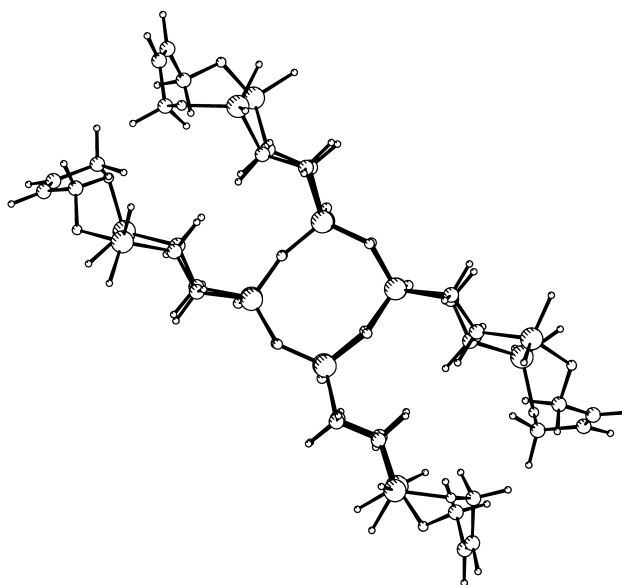
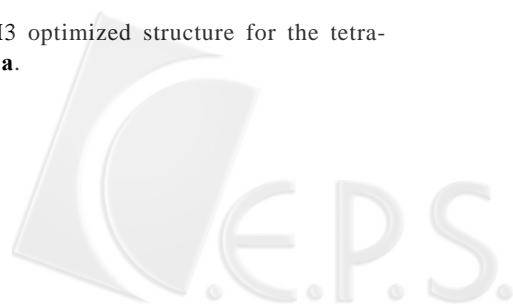


Fig. 1. The PM3 optimized structure for the tetra-adduct **1a**.



apparent molarity of  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_8$  used in the experiment (*ca*  $10^{-3}$  M) was 3 orders of magnitude lower. Because of high chloro-concentration inside the confinements and void elsewhere, a strong proximity effect was present. It is likely that an anionic diol substitutes the chlorides nucleophilically at a much greater rate on the same  $\text{Si}_8\text{O}_{12}$  framework twice than two chlorides on separate  $\text{Si}_8\text{O}_{12}$  frameworks. As a consequence, the products were always intramolecular.

In a nice agreement with the results of computation, the presence of **2a** and **2b** is supported by the split pattern in the  $^1\text{H}$  NMR spectrum, at  $\delta$  4.22 and 4.16 (Fig. 3). Separation of **2a** and **2b** has been attempted but not yet in a success. The

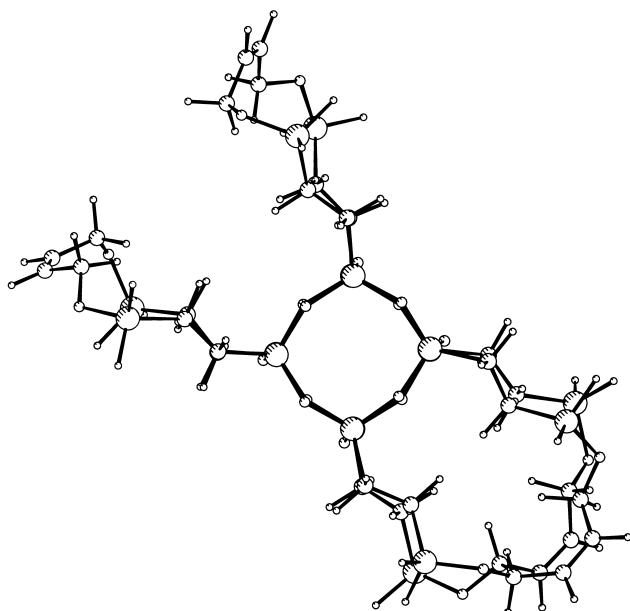


Fig. 2. The PM3 optimized structure for the tetra-adduct **1b**.

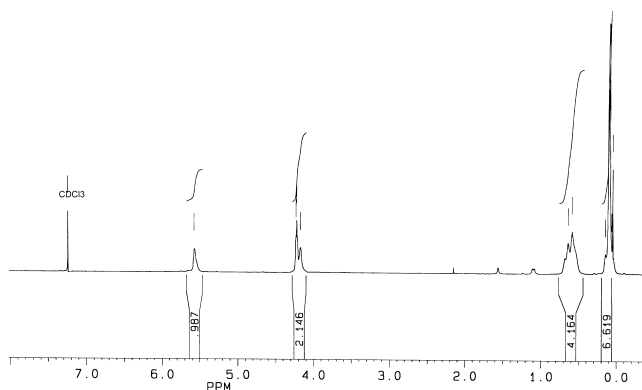


Fig. 3. The  $^1\text{H}$  NMR spectrum of **2**.

line-shape of the peaks is significantly broadened for these nano-sized octasilsesquioxane compounds, reflecting a transition from simple molecules to solid state materials.

As a summary, a Pt/C catalyzed hydrosilylation reaction on the quasi-cube  $\text{Si}_8\text{O}_{12}(\text{CH}=\text{CH}_2)_8$  with 8 equiv of  $\text{HSiMe}_2\text{Cl}$  producing  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_8$ , followed by a de-hydrochlorination reaction on  $\text{Si}_8\text{O}_{12}(\text{CH}_2\text{CH}_2\text{SiMe}_2\text{Cl})_8$ , with 4 equiv of *Z*- $\text{HOCH}_2\text{CH}_2=\text{CHCH}_2\text{OH}$  and excess TMEDA, resulted in four surface bridges on the quasi-cube  $\text{Si}_8\text{O}_{12}$  framework. Computations were performed to reveal relative energetics of the isomers.

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## Key Words

Octasilsesquioxane; Quasi-cube framework; Hydrosilylation; *Ab initio* computation; De-hydrochlorination.

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