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Preliminary communication

Oxaoctasilahomocubane and dioxaoctasilabishomocubane: novel silicon ring systems [1]

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Abstract

The novel silicon ring systems, 9-oxaoctasilahomocubane ($(SiThex)_8O$, 2) and 5,10-dioxaoctasilabishomocubane ($(SiThex)_8O_2$, 3) (Thex = 1,1,2-trimethylpropyl) were obtained by the photo-induced reaction of octasilacubane, $(SiThex)_8$ (1) with dimethylsulfoxide. A significant distortion of the framework is revealed by X-ray crystallography; the Si–Si bond distances vary from 2.423(4) and 2.559(4) Å.

Keywords: Silicon; Octasilacubane; Photo-oxidation; X-ray analysis; Oxaoctasilahomocubane; Dioxaoctasilabishomocubane

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1. Introduction

Octasilacubanes are of special interest because they are expected to exhibit interesting chemical and physical properties arising from high energy of the Si–Si σ-bonding electrons [1–5]. Following the construction of the octasilacubanes ($(SiR)_8$, R = t-$BuMe_2Si$ [1], and Thex [2] (Thex = 1,1,2-trimethylpropyl)), we have recently reported the ring-opening halogenation of the peralkyloctasilacubane $(SiThex)_8$ (**1**), which led to an unusual skeletal rearrangement [6,7]. As an extension of our work, we report here the partial oxidation of **1**, which gives the novel polyhedral compounds, octakis(1,1,2-trimethylpropyl)pentacyclo[$4.3.0.0^{2,5}.0^{3,8}.0^{4,7}$]-9-oxanonasialne, $(SiThex)_8O$ (**2**) and octakis(1,1,2-trimethylpropyl)pentacyclo[$5.3.0.0^{2,6}.0^{3,9}.0^{4,8}$]-5,10-dioxadecasilane, $(SiThex)_8O_2$ (**3**). To our knowledge, no examples of the partial oxidation have been reported for the polyhedranes of the Group 14 elements; two examples have appeared on the conversion of $(MR)_8$ to $(MR)_8O_{12}$: for M = Si, R = t-$BuMe_2Si$ see Ref. [8], and for M = Sn, R = 2,6-diethylphenyl see Ref. [9].

2. Experimental

Taking advantage of our observation that the octasilacubane **1** is photoactive under UV irradiation [2,10], the oxidation was carried out by the photoreaction of **1** (Scheme 1) in the presence of a large excess dimethylsulfoxide (DMSO) [11]. Thus, irradiation of **1** and DMSO in benzene with a high pressure mercury lamp for 5 h resulted in formation of **2** (46% yield) and **3** (39% yield) with recovery of some **1** (10%).

Procedure: a mixture of **1** (34 mg, 38 μmol) and DMSO (2 ml, 28 mmol) in benzene (15 ml) was placed in a sealed Pyrex glass tube and degassed. After irradiating with a high pressure mercury lamp (400 W, > 300 nm) for 5 h, benzene and DMSO were removed and the resulting orange solid (38 mg) was separated with recycle-type preparative HPLC. With the recovery of starting material (3.0 mg, 10%), $(SiThex)_8O$ (**2**) and $(SiThex)_8O_2$ (**3**) were obtained. Yields were 14 mg (47%) for **2** and 12 mg (37%) for **3**.

Without irradiation, **1** did not give **2** or **3** even at elevated temperature. Thus, when a toluene solution of **1** and DMSO was heated at 115 °C in a sealed tube for 100 h, only starting **1** was recovered (90%).

3. Results and discussion

Oxaoctasilahomocubane **2** and dioxaoctasilabishomocubane **3** were fully characterized by X-ray crystallography and spectroscopic methods.

Crystal data for 2: $C_{48}H_{104}OSi_8$, monoclinic, $C2/c$; $a = 13.894(3)$ Å, $b = 19.223(4)$ Å, $c = 21.27(1)$ Å, $\beta = 98.67(3)°$, $V = 5616(3)$ Å^3, $Z = 4$, $R = 0.083$, $R_w = 0.060$ for 3067 reflections. *Crystal data for 3*: $C_{48}H_{104}O_2Si_8$, monoclinic, $C2/c$; $a = 13.918(2)$ Å, b

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[1] Dedicated to Professor Robert Corriu.

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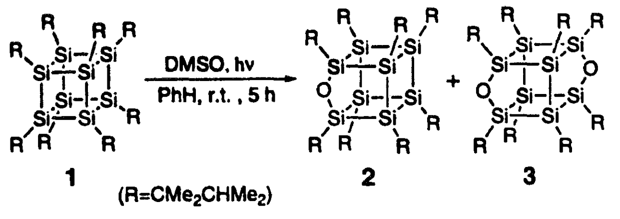

Scheme 1.

= 19.235(6) Å, $c = 21.411(5)$ Å, $\beta = 98.57(1)°$, $V = 5668(2)$ Å^3, $Z = 4$, $R = 0.089$, $R_w = 0.062$ for 2566 reflections. Tables of anisotropic thermal parameters, atomic coordinates and isotropic thermal parameters involving H atoms, bond lengths and angles for **2** and **3** have been deposited at the Cambridge Crystallographic Data Centre.

Spectroscopic data. **2**: wine red prisms, m.p. 218–220°C. ^{1}H NMR (C_6D_6): δ 2.53 (sept, $J = 6.7$ Hz, 1H), 2.43 (sept, $J = 6.7$ Hz, 1H), 2.22 (sept, $J = 6.7$ Hz, 2H), 1.56 (s, 6H), 1.49 (s, 6H), 1.44(s, 6H), 1.39 (s, 6H), 1.21 (d, $J = 6.7$ Hz, 6H), 1.14 (d, $J = 6.7$ Hz, 6H), 1.09 (d, $J = 5.8$ Hz, 6H), 1.03 (d, $J = 6.7$ Hz, 6H) ppm. ^{13}C NMR (C_6D_6): δ 37.87, 37.70, 36.30, 36.13, 35.70, 32.70, 27.05, 26.99, 26.39, 22.67, 20.63, 19.73 ppm. ^{29}Si NMR (C_6D_6): δ 63.32, 39.84, 22.96, −22.57 ppm. UV–vis (hexane) λ (ε): 484 (80), 415 (180), 328 (1100), 292 (1600), 262 (13200), 254 (16300), 238 (19600) nm. MS (EI) *m/z*: 920 (7, M^+), 835 (27), 751 (12), 665 (17), 415 (6), 69 (100). HRMS calcd. for $C_{42}H_{91}OSi_8$ (M^+ − thexyl) 835.5224; found, 835.5195. **3**: yellow prisms, m.p. 212–213.5°C (dec.). ^{1}H NMR (C_6D_6): δ 2.54 (sept, $J = 6.9$ Hz, 2H), 2.43 (sept, $J = 6.9$ Hz, 2H), 2.27 (sept, $J = 6.9$ Hz, 2H), 2.22 (sept, $J = 6.9$ Hz, 2H), 1.49 (s, 3H), 1.48 (s, 3H), 1.47 (s, overlap, 9H), 1.454 (s, 3H), 1.446 (s, 3H), 1.433 (s, 3H), 1.429 (s, 3H), 1.41 (s, overlap, 9H), 1.38 (s, overlap, 6H), 1.34 (s, overlap, 6H), 1.22 (d, $J = 6.7$ Hz, 6H), 1.14 (d, $J = 6.7$ Hz, 6H), 1.13 (d, $J = 6.7$ Hz, 6H), 1.12 (d, $J = 6.7$ Hz, 6H), 1.07 (d, overlap, $J = 6.7$ Hz, 12H), 1.04 (d, $J = 6.7$ Hz, 6H), 1.01 (d, $J = 6.7$ Hz, 6H) ppm. ^{13}C NMR (C_6D_6): δ 38.18, 37.72, 37.55, 36.51, 35.83, 35.64, 35.05, 35.01, 34.24, 33.36, 31.85, 31.55, 28.03, 27.55, 27.27, 23.18, 22.93, 22.75, 21.60, 21.36, 20.07, 19.48 (overlap), 19.03 ppm. ^{29}Si NMR (C_6D_6): δ 28.37, 18.84, 33.00 ppm. UV–vis (hexane) λ (ε): 450 (40), 400 (100), 336 (730), 300 (4500), 280 (9600), 262 (12400), 244 (12400) nm. MS (EI) *m/z*: 936 (5, M^+), 851 (45), 767 (17), 681 (22), 599 (5), 515 (4), 431 (6), 69 (100). HRMS calcd. for $C_{42}H_{91}OSi_8$ (M^+ − thexyl) 851.5174; found, 851.5198.

In Fig. 1, the ORTEP drawing of **2**, is shown with selected bond lengths and angles. Compound **2** crystallizes in the *C*2/*c* space group, and the symmetry axis passes through the oxygen atom and the midpoint of Si(3) and Si(3*). The most important feature is that Si–Si bond lengths vary between 2.423(3) and 2.556(3) Å; the longest distance is Si(3)–Si(3*) and this value is among the longest Si–Si bonds in cyclic polysilanes. In comparison, the Si–Si bond lengths of **1** vary only between 2.398(2) and 2.447(4) Å. It is thus clear that insertion of an oxygen atom into the octasilacubane framework causes significant distortions of the Si–Si bonds. Interestingly, in the case of **3** the second oxygen inserted into the longest Si–Si bond in **2**. Another experiment proved that **3** was generated from **2**; (monoxide **2** (1.4 mg, 0.0015 mmol) was dissolved in benzene in the Pyrex tube and DMSO (0.1 ml) was added. The solution was degassed by freeze–thaw cycles and sealed in vacuum. The mixture was irradiated with a high pressure mercury lamp at room temperature for 5 h. After removal of the solvent, the mixture was separated with recycle-type preparative HPLC (eluent, MeOH/THF = 6/4) and 0.8 mg of **3** (57%) was obtained.) We can safely conclude that the elongated bond distance of **2** is responsible for the formation of **3** as the only product out of the four possible isomers.

We consider that the distortions observed for **2** are a consequence of the increase in the steric congestion generated by the bulky thexyl substituents; insertion of the oxygen atom in the Si(1)–Si(1*) bond pushes the two thexyl groups of the neighboring Si atoms backwards, so elongating the opposite Si(3)–Si(3*) bond.

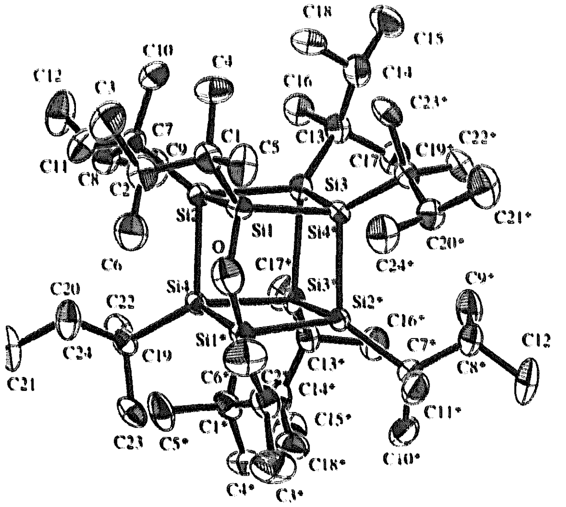

Fig. 1. The molecular structure of $(SiThex)_8O$ **2**. Thermal ellipsoids are shown at 30% probability level. Selected bond lengths: Si(1)–Si(2), 2.423(3); Si(1)–Si(4*), 2.445(3); Si(2)–Si(3), 2.464(3); Si(2)–Si(4), 2.437(3); Si(3)–Si(4*), 2.428(3); Si(3)–Si(3*), 2.556(3); Si(4)–O, 1.612(5). Selected angles (deg): Si(2)–Si(1)–O, 107.9(2); Si(2)–Si(1)–Si(4*), 90.7(1); O–Si(1)–Si(4*), 102.7(2); Si(1)–Si(2)–Si(3), 89.1(1); Si(1)–Si(2)–Si(4), 92.5(1); Si(3)–Si(2)–Si(4), 92.2(1); Si(2)–Si(3)–Si(4*), 90.1(1); Si(2)–Si(3)–Si(3*), 86.9(1); Si(3*)–Si(3)–Si(4*), 90.1(1); Si(2)–Si(4)–Si(3*), 90.5(1); Si(2)–Si(4)–Si(1*), 96.7(1); Si(1*)–Si(4)–Si(3*), 89.4(1); Si(4)–Si(1*)–O, 102.7(2); Si(1)–O–Si(1*), 122.5(6).

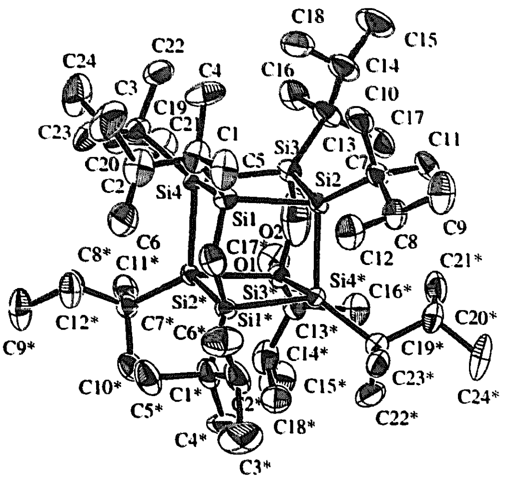

Fig. 2. The molecular structure of $(\mathrm{SiThex})_8\mathrm{O}_2$ **3**. Thermal ellipsoids are shown at 30% probability level. Selected bond lengths (Å): Si(1)–Si(2), 2.468(4); Si(1)–Si(4), 2.422(4); Si(2)–Si(3), 2.415(4); Si(2)–Si(4*), 2.419(3); Si(3)–Si(4), 2.506(4); Si(1)–O(1), 1.598(5); Si(3)–O(2), 1.540(7). Selected angles (deg): Si(2)–Si(1)–O(1), 102.0(2); Si(2)–Si(1)–Si(4), 90.9(1); Si(4)–Si(1)–O(1), 107.3(2); Si(1)–Si(2)–Si(3), 89.4(1); Si(1)–Si(2)–Si(4*), 96.3(1); Si(3)–Si(2)–Si(4*), 93.2(1); Si(2)–Si(3)–Si(4), 90.1(1); Si(2)–Si(3)–O(2), 107.7(4); Si(4)–Si(3)–O(2), 102.0(4); Si(1)–Si(4)–Si(3), 88.4(1); Si(1)–Si(4)–Si(2*), 93.1(1); Si(3)–Si(4)–Si(2*), 94.3(1); Si(1)–O(1)–Si(1*), 124.2(6); Si(3)–O(2)–Si(3*), 126(1).

For **3**, the space group is also $C2/c$ and the symmetry axis passes through two oxygen atoms. Interestingly, the lattice constants of **3** are essentially similar to those of **2**, indicating that the slight modification of the frameworked does not affect the crystal system. The ORTEP drawing of **3** is shown in Fig. 2. The average Si–Si bond lengths indicate that **3** is less strained than **2** (2.446 Å vs. 2.458 Å). However, one of the bonds (Si(3)–Si(4)) was 2.506(4) Å, showing that there still exists steric congestion.

In summary, we obtained the oxaoctasilahomocubane and dioxaoctasilabishomocubane as novel ring systems of silicon polyhedral compounds and showed their unique structures.

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