

# Synthesis and Characterization of Cage and Bicyclic Silsesquioxanes via Dehydration of Silanols

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Synthesis of cage and ladder silsesquioxanes by the dehydration of silanols using dicyclohexylcarbodiimide (DCC) is described. The reaction of 1,3-dicyclohexyldisiloxane-1,1,3,3-tetraol with DCC gave octa(cyclohexylsilsesquioxane) in 13% yield. The bicyclic ladder siloxane **3** ( $\text{Ph}_8\text{Thex}_2\text{Si}_6\text{O}_7$ ) was prepared from 1,1,3,3-tetraphenyldisiloxane-1,3-diol and 1,3-dithexyldisiloxane-1,1,3,3-tetraol (Thex or thexyl denotes 1,1,2-trimethylpropyl) at 80 °C. In this reaction, the propellane-type cage siloxane **2** ( $\text{Ph}_6\text{Thex}_2\text{Si}_5\text{O}_6$ ) was generated also. Upon reaction completion at 120 °C, only **2** was obtained. The reaction from the same starting compounds with diisopropylcarbodiimide at 80 °C resulted in another caged siloxane,  $\text{Ph}_4\text{Thex}_4\text{Si}_6\text{O}_8$  (**5**). The structures of **2**, **3** and **5** were determined by X-ray crystallography. Copyright © 1999 John Wiley & Sons, Ltd.

**Keywords:** silsesquioxane; ladder polysiloxane; cage polysiloxane; X-ray structure; silanol

## INTRODUCTION

As a part of our investigation of the chemistry of polycyclic silicon compounds,<sup>1–3</sup> we have been

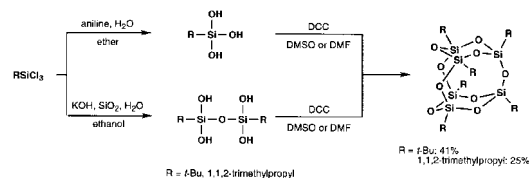
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Contract/grant sponsor: Ministry of Education, Science and Culture, Japan.

Contract/grant sponsor: REIMEI Research of Japan Atomic Energy Research Institute.

interested in the synthesis and characterization of polycyclic oligosiloxanes with well-defined structures. In a previous paper, we reported a new synthetic procedure for the preparation of cage siloxanes, hexa(thexylsilsesquioxane) (thexyl or Thex denotes 1,1,2-trimethylpropyl hereafter) and hexakis(*t*-butylsilsesquioxane) from the corresponding silanetriol or disiloxanetetraol, utilizing dicyclohexylcarbodiimide (DCC) as a dehydrating reagent (Scheme 1).<sup>4</sup> This procedure requires slightly forced conditions, but the reaction was completed in a shorter time and resulted in higher



Scheme 1

yield than the hydrolysis of the corresponding organotrichlorosilanes.

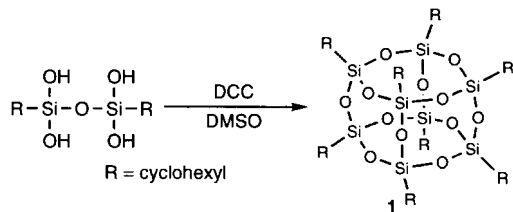
Here we report the syntheses and structures of cage and bicyclic oligosiloxanes containing thexyl, phenyl and cyclohexyl groups using DCC.

## RESULTS AND DISCUSSION

### Synthesis of octa (cyclohexylsilsesquioxane)

Octa(cyclohexylsilsesquioxane) was known in the literature, but in each case preparations were made by multistep syntheses, i.e. alkali-catalyzed siloxane cracking at 340–440 °C of the hydrolysis product of cyclohexyltrichlorosilane,<sup>5</sup> hydrogen-

tion of octa(phenylsilsesquioxane)<sup>6</sup> or the reaction of 7,13-dihydroxytetracyclo[9.5.1.1<sup>3,9</sup>.1<sup>5,15</sup>]octasiloxane [ $R_7Si_7O_9(OH)_3$ ], which was obtained by condensation of cyclohexyltrichlorosilane in aqueous acetone for four months using  $RSiCl_3$  ( $R = \text{cyclohexyl}$ ).<sup>7</sup> When cyclohexyltrichlorosilane or cyclohexylsilanetriol was condensed in aqueous solution, the cage compound obtained was hexasilsesquioxane ( $T_6$ ), and octasilsesquioxane ( $T_8$ ) was not produced.<sup>8</sup> Here we applied our method to a one-pot synthesis of octa(cyclohexylsilsesquioxane). The procedure is shown in Scheme 2. The starting 1,3-dicyclohexyldisiloxane-1,1,3,3-tetraol was prepared by the reported method,<sup>7</sup> and after the reaction with DCC for three days at 120 °C octasilsesquioxane **1** was obtained in 13% yield after separation by column chromatography (silica/hexane). The other fractions were collected carefully; NMR and mass spectral results indicate these were all polymeric siloxanes. Compound **1** was identified by NMR and MS, and these spectra were identical to those in the literature.<sup>4</sup>



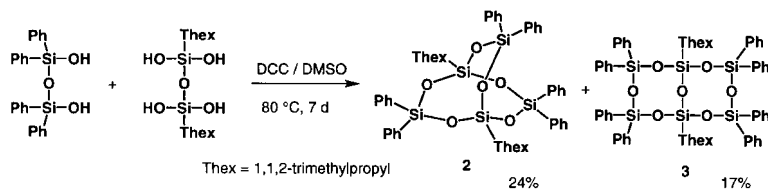
Scheme 2

## Synthesis of ladder silsesquioxane

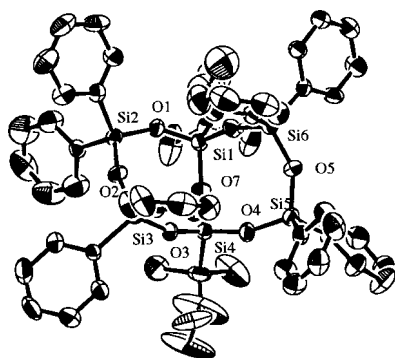
Ladder polysilsesquioxanes were first reported by Brown *et al.* in 1960;<sup>9</sup> however, their results were without structural evidence, and the real structure is still controversial.<sup>10</sup> Until now, polysiloxanes containing ladder structures have been widely used as materials with improved properties, e.g. high thermal stability.<sup>10</sup> In order to examine the synthesis and structure of ladder siloxanes, we prepared

bicyclic oligosiloxane as a model system. Bicyclic oligosilsesquioxane [ $(C_7H_{13})_6Si_6O_7(OH)_4$ ] has also been obtained in the condensation reaction from cycloheptytrichlorosilane<sup>11</sup>.

For the preparation of ladder polysilsesquioxanes, we have examined the condensation of 1,3-dithexyldisiloxane-1,1,3,3-tetraol and 1,1,3,3-tetraphenyldisiloxane-1,3-diol with DCC. The reaction pathway is shown in Scheme 3. Preparation of 1,1,3,3-tetraphenyldisiloxane-1,3-diol<sup>12</sup> and 1,3-dithexyldisiloxane-1,1,3,3-tetraol<sup>4</sup> was effected by following the reported methods. A 1:1 mixture of the tetraol and diol was heated with DCC at 80 °C in dimethyl sulfoxide (DMSO). Analysis with HPLC indicated that **2** and **3** existed as isolable products which could be separated easily by reverse-phase recycle-type HPLC; yields were 24% for **2** and 17% for **3**. For product **2**, unfortunately a suitable crystal for X-ray analysis could not be obtained and the structure was confirmed by IR, mass and NMR ( $^1H$ ,  $^{13}C$ ,  $^{29}Si$ ) spectroscopy. Mass spectra indicated a molecular weight of 868, which was the evidence for a composition  $Ph_6Thex_2Si_5O_7$ . In  $^1H$  NMR, the resonances for single thexyl and phenyl groups were observed, indicating the high symmetry of the structure. The integration ratio was  $Thex/Ph = 1:3$ . The result of  $^{13}C$  NMR also supported this high symmetry (four peaks for the thexyl group, and four peaks for the phenyl group). In  $^{29}Si$  NMR, two resonances were observed at  $-21.4$  and  $-58.8$  ppm, which means that the compound possesses one kind of T-type  $RSiO_3$  and one kind of D-type  $R_2SiO_2$ . From the IR and  $^1H$  NMR spectra, no  $Si-H$  or  $Si-OH$  groups existed. With these results, compound **2** was identified as 1,5-bis(1,1,2-trimethylpropyl)-3,3,7,7,10,10-hexaphenylbicyclo[3.3.3]pentasiloxane. Compound **3** was determined to be bicyclic ladder-type siloxane from spectral data as well as X-ray crystallography. It also showed two resonances in  $^{29}Si$  NMR at  $-24.4$  and  $-65.8$  ppm, and all the other spectra satisfied the same structure.



Scheme 3



**Figure 1** ORTEP drawing of **3**. Thermal ellipsoids are drawn at the 30% probability level.

### Structure of bicyclic ladder siloxanes

The crystal structure of **3** is shown in Fig. 1. The summary of crystal data, data collection and refinement is shown in Table 1; selected bond lengths and angles are shown in Table 2. In 1980, Shklover *et al.* reported the synthesis and structure of 3,3,5,5,9,9,11,11-octamethyl-1,7-diphenylbicyclo[5,5,1]hexasiloxane ( $\text{Me}_6\text{Ph}_2\text{Si}_5\text{O}_6$ ),<sup>13</sup> and our result is the second example of a bicyclic ladder polysiloxane.

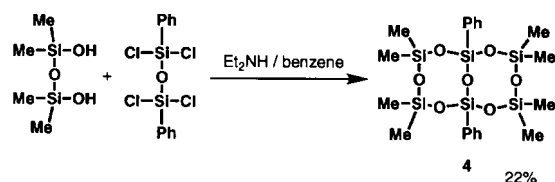
In order to compare the structures of these two compounds more intensively, we prepared  $\text{Me}_6\text{Ph}_2\text{Si}_5\text{O}_6$  (**4**) using the method of Shklover *et al.*<sup>13</sup> Thus the reaction of tetramethyldisiloxanediol and diphenyltetrachlorodisiloxane with diethylamine in benzene gave **4** in 22% yield (Scheme 4). In <sup>29</sup>Si NMR, two resonances were observed at  $-17.3$  and

**Table 1.** X-ray diffraction analysis data for **3** and **4**

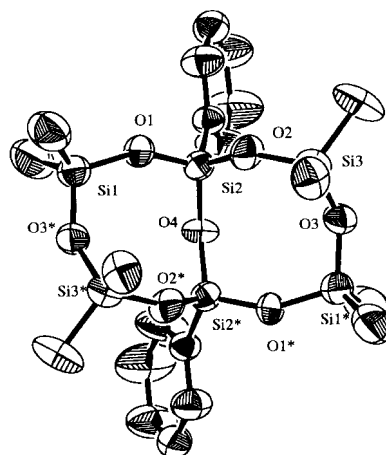
	$\text{Thex}_2\text{Ph}_8\text{Si}_6\text{O}_7$ , <b>3</b>	$\text{Ph}_2\text{Me}_8\text{Si}_6\text{O}_7$ , <b>4</b>
<i>Crystal data</i>		
Formula	$\text{C}_{60}\text{H}_{66}\text{Si}_6\text{O}_7$	$\text{C}_{20}\text{H}_{34}\text{Si}_6\text{O}_7$
Mol wt	1067.69	555.00
Crystal dimensions ( $\text{mm}^3$ )	$0.20 \times 0.20 \times 0.10$	$0.40 \times 0.10 \times 0.10$
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
$a$ (Å)	14.182(1)	12.749(5)
$b$ (Å)	20.149(3)	14.967(7)
$c$ (Å)	11.047(1)	16.470(4)
$\alpha$ (deg)	97.49(1)	
$\beta$ (deg)	109.300(9)	105.59(2)
$\gamma$ (deg)	81.690(10)	
$V$ (Å <sup>3</sup> )	2936.5(6)	3026(1)
$Z$	2	4
$d_{\text{calc}}$ ( $\text{gcm}^{-3}$ )	1.21	1.22
<i>Data collection</i>		
Diffractometer	Rigaku AFC7S	Rigaku AFC7S
Radiation	$\text{Cu K}_\alpha$ (1.54178 Å)	$\text{Cu K}_\alpha$ (1.54178 Å)
$\mu$ ( $\text{cm}^{-1}$ )	17.30	28.78
$2\theta$ range (deg)	4–120.1	4–120.1
Scan type	$\omega$ - $2\theta$	$\omega$ - $2\theta$
No. of reflections measured	9156	2463
No. of independent reflections	8745	2341
No. of reflections observed ( $ F_0  \geq 3\sigma(F_0)$ )	3917	769
$R$	0.072	0.073
$R_w$	0.065	0.055
Weighting scheme	$w = 4(F_0)^2/\sigma^2(F_0)^2$	$w = 4(F_0)^2/\sigma^2(F_0)^2$
$S$	2.57	2.50
$(\Delta/\sigma)_{\text{max}}$	0.08	0.01
$(\Delta\rho)_{\text{max}}$ ( $\text{e}\text{Å}^{-3}$ )	0.92	0.26
$(\Delta\rho)_{\text{min}}$ ( $\text{e}\text{Å}^{-3}$ )	-0.68	-0.25
No. of parameters	639	150

**Table 2. Selected bond lengths (Å) and angles (deg) of 3**

<i>Bond Lengths</i>			
Si(1)–O(1)	1.608(5)	Si(1)–O(6)	1.615(7)
Si(1)–O(7)	1.614(7)	Si(2)–O(1)	1.618(7)
Si(2)–O(2)	1.615(8)	Si(3)–O(2)	1.618(7)
Si(3)–O(3)	1.613(6)	Si(4)–O(3)	1.602(6)
Si(4)–O(4)	1.615(6)	Si(4)–O(7)	1.618(7)
Si(5)–O(4)	1.626(7)	Si(5)–O(5)	1.625(8)
Si(6)–O(5)	1.620(6)	Si(6)–O(6)	1.606(6)
<i>Bond Angles</i>			
O(1)–Si(1)–O(6)	107.2(3)	O(1)–Si(1)–O(7)	110.1(3)
O(6)–Si(1)–O(7)	107.5(3)	O(1)–Si(2)–O(2)	110.6(3)
O(2)–Si(3)–O(3)	109.4(4)	O(3)–Si(4)–O(4)	109.0(3)
O(3)–Si(4)–O(7)	108.0(3)	O(4)–Si(4)–O(7)	108.8(4)
O(4)–Si(5)–O(5)	110.4(3)	O(5)–Si(6)–O(6)	108.7(4)
Si(1)–O(1)–Si(2)	151.4(5)	Si(2)–O(2)–Si(3)	156.7(4)
Si(3)–O(3)–Si(4)	160.0(5)	Si(4)–O(4)–Si(5)	158.8(5)
Si(5)–O(5)–Si(6)	148.2(5)	Si(1)–O(6)–Si(6)	163.3(5)
Si(1)–O(7)–Si(4)	145.8(4)		

**Scheme 4**

–76.4 ppm, and these values are in good agreement with those of **3**, considering the difference between the substituents. The crystal structure of **4** is shown in Fig. 2; the summary of crystal data, data collection and refinement is shown in Table 1; selected bond lengths and angles are shown in Table 3. Shklover reported that **4** crystallized in the  $P2_1/c$  space group, and the molecule did not have a symmetry axis; however, in our case, the space

**Figure 2** ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 30% probability level.**Table 3. Selected bond lengths (Å) and angles (deg) of 4**

<i>Bond Lengths</i>			
Si(1)–O(1)	1.61(1)	Si(1)–O(3*)	1.630(8)
Si(2)–O(1)	1.59(1)	Si(2)–O(2)	1.57(1)
Si(2)–O(4)	1.627(7)	Si(3)–O(2)	1.63(1)
Si(3)–O(3)	1.609(10)		
<i>Bond Angles</i>			
O(1)–Si(1)–O(3*)	109.7(5)	O(1)–Si(2)–O(2)	106.3(6)
O(1)–Si(2)–O(4)	110.5(4)	O(2)–Si(2)–O(4)	112.2(5)
O(2)–Si(3)–O(3)	110.9(6)	Si(1)–O(1)–Si(2)	147.8(6)
Si(2)–O(2)–Si(3)	146.1(7)	Si(3)–O(3)–Si(1*)	145.5(7)
Si(2)–O(4)–Si(2*)	140.8(9)		

group was identified as  $C2/c$ , and there is a symmetry axis through O(4). The structural parameters, including bond lengths and angles, were similar to each other.

As compound **3** has larger substituents, thexyl groups, the Si–O–Si angles were greater than those of **4**. Thus, the average Si–O–Si angles were  $154.9^\circ$  for **3** and  $145.1^\circ$  for **4**. On the other hand, the Si–O bond lengths and O–Si–O angles were similar to each other; the average Si–O bond lengths were 1.615 Å for **3** and 1.61 Å for **4**, and the average O–Si–O angles were  $109.0^\circ$  for **3** and  $109.9^\circ$  for **4**. Interestingly, the Si–O–Si angles were very scattered for **3**,  $145.8(4)$ – $163.3(5)^\circ$ . In the case of **4**, scattering was not so great [ $140.8(9)$ – $147.8(6)$ ]; it seems that the relatively flexible Si–O–Si bond angle changed in order to release the steric repulsion of the substituents. In both compounds, two rings were in *cis*-fused orientation.

### Products under different reaction conditions

To investigate the effect of temperature and dehydrating reagent, we then tried the condensation reaction of disiloxanediol and disiloxanetetraol at  $120^\circ\text{C}$ , and with diisopropylcarbodiimide (DIC). The reactions are depicted in Scheme 5. When the same starting materials as in the case of **3** were stirred with DCC at  $120^\circ\text{C}$  for seven days the product was only **2**, and no other products were isolated. The reaction from the same starting materials with DIC gave neither **2** nor **3**, and the product was **5**. The structure of **5** could be determined by the following spectral data: one kind each of thexyl and phenyl groups was observed in  $^1\text{H}$  NMR, indicating a high symmetry of the molecule, as in the case of **2**. The Ph/Thex ratio by integration was 1:1. In  $^{13}\text{C}$  NMR, similar

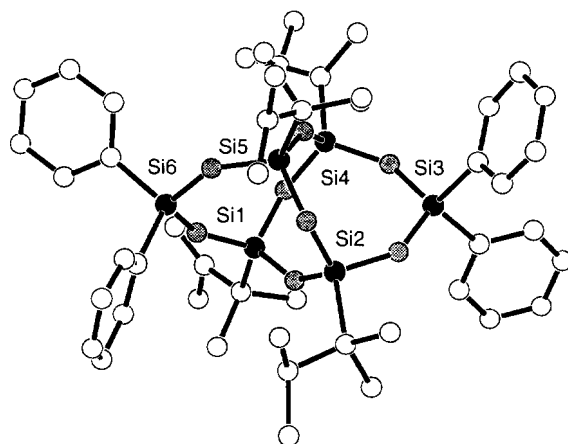
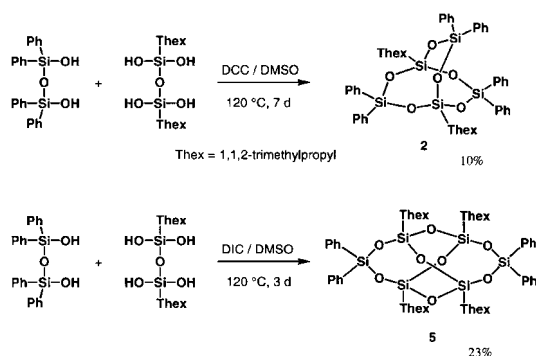


Figure 3 Molecular drawing of **5**.

results were given; thus, four peaks for the thexyl ( $\delta = 18.53, 20.59, 24.18, 34.12$  ppm), and four peaks for the phenyl group (127.45, 129.80, 133.92, 135.20 ppm). Two resonances ( $-43.65, -60.40$  ppm) were obtained in  $^{29}\text{Si}$  NMR, and mass and IR spectra satisfied the structure 1,3,7,9-tetrakis(1,1,2-trimethylpropyl)-5,5,11,11-tetraphenyltricyclo[5.5.1.1<sup>3,9</sup>]hexasiloxane ( $\text{Ph}_4\text{Thex}_4\text{Si}_6\text{O}_8$ ). Preliminary results of X-ray crystallography established the structure of the framework [Fig. 3]: due to the severe disorder we could not determine the positions of substituents. Crystal data: monoclinic,  $P2_1/c$ ,  $a = 17.903(1)$  Å,  $b = 14.552(1)$  Å,  $c = 20.944(1)$  Å,  $V = 5428.8(7)$  Å<sup>3</sup>,  $\beta = 95.752(6)^\circ$ ,  $Z = 4$ ,  $R = 0.110$ ,  $R_w = 0.102$  for 505 variables. These results show that the reaction conditions are important for the construction of the ladder structure, in addition to the selection of the substituents. So far as our investigations went, thexyl groups were rather large and preferred a twisted structure.

In summary, we extended the reaction using DCC to prepare octa(cyclohexylsilsesquioxane) and ladder-type siloxane, and the structures of some bicyclic ladder siloxanes were determined. In addition, the modification of the reaction gave different products, e.g. twisted siloxanes. Now we are investigating the application of different substituents to construct longer ladder siloxanes.



Scheme 5

### EXPERIMENTAL

NMR spectra were recorded on a JEOL Model  $\alpha$ -500 ( $^1\text{H}$ , 500.0 MHz;  $^{13}\text{C}$ , 125.7 MHz;  $^{29}\text{Si}$ ,

99.3 MHz). Mass spectrometry was performed by JEOL JMS-D300. Infrared spectra were measured with a JASCO A-102 spectrometer. Analytical HPLC was performed with JASCO 875UV/880PU and UV-970/880PU equipment with Chemco 4.6 mm  $\times$  250 mm 5-ODS-H columns. Preparative recycle-type HPLC was performed on JAI LC-908 apparatus with Chemco 20  $\times$  250 (w) 7-ODS-H columns.

### Synthesis of 1,3,5,7,9,11,13,15-octacyclohexylpentacyclo-[9.5.1.1<sup>3,9</sup>.1<sup>5,15</sup>.1<sup>7,13</sup>]octasiloxane (1)

Dicyclohexyldisiloxanetraol (1.00 g, 3.26 mmol), DCC (1.48 g, 7.18 mmol) and DMSO (11 ml) were placed in a flask and the solution was heated at 120 °C. After three days the mixture was cooled to room temperature, and benzene (16 ml) was added. The solid generated was filtered and the filtrate was washed with water (40 ml), then the water phase was extracted with hexane three times (40 ml each). The combined organic phase was dried and evaporated. The crude mixture obtained was purified by column chromatography (silica hexane) to give pure octa(cyclohexylsilsequioxane) **1** (114 mg, 13% yield).

**1**: colorless solid. <sup>1</sup>H NMR(CDCl<sub>3</sub>):  $\delta$  = 0.65–0.85 (m, 8H), 1.14–1.36 (m, 40H), 1.60–1.88 (m, 40H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 23.20, 26.66, 26.91, 27.51 ppm. <sup>29</sup>Si NMR (CDCl<sub>3</sub>):  $\delta$  = –71.19 ppm. IR (KBr):  $\nu$  = 2930, 2860, 1445, 1270, 1195, 1110, 1050, 1025, 895, 845, 825, 735 cm<sup>-1</sup>. MS (30 eV):  $m/z$  = 1082 (M<sup>+</sup>, 3%), 997 (base), 915 (30%), 833 (10%).

### Reaction of dithexyldisiloxanetraol and tetraphenyldisiloxanediol with dicyclohexylcarbodiimide

The starting compounds were prepared by the reported methods. Dithexyldisiloxanetraol<sup>4</sup> (0.44 g, 1.1 mmol), tetraphenyldisiloxanediol<sup>12</sup> (0.31 g, 1.0 mmol) and dicyclohexylcarbodiimide (0.82 g, 4.0 mmol) were dissolved in 10 ml DMSO and the solution was heated to 80 °C for seven days. Water was added to the reaction mixture, which was extracted with ether. After drying and removal of the solvent, methanol was added to the residue, and 0.38 g of colorless solid was obtained. Separation with recycle-type HPLC (eluent: MeOH/THF,

9:1) gave 1,5-bis(1,1,2-trimethylpropyl)-3,3,7,7,10,10-hexaphenylbicyclo[3.3.3]pentasiloxane **2** (0.14 g, 24%) and 1,7-bis(1,1,2-trimethylpropyl)-3,3,5,5,9,9,11,11-octaphenyl[5.5.1]hexasiloxane **3** (0.090 g, 17%).

Ph<sub>6</sub>Thex<sub>2</sub>Si<sub>6</sub>O<sub>7</sub> **2**: colorless solid, mp 116–119 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.04 (d,  $J$  = 7.0 Hz, 12H), 1.27 (s, 12H), 1.89 (sept,  $J$  = 6.7 Hz, 2H), 7.02 (t,  $J$  = 7.6 Hz, 6H), 7.12 (t,  $J$  = 7.6 Hz, 12H), 7.63 (d,  $J$  = 7.6 Hz, 12H) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 19.04, 21.68, 25.02, 35.02, 128.29, 130.15, 134.46, 134.95 ppm. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = –21.39, –58.79 ppm. IR (NaCl plate):  $\nu$  = 2955, 1450, 1150, 1080 cm<sup>-1</sup>. MS (30 eV):  $m/z$  = 783 (M<sup>+</sup>–Thex, 100%), 713 (75%).

Ph<sub>8</sub>Thex<sub>2</sub>Si<sub>6</sub>O<sub>7</sub> **3**: colorless solid, mp 243–246 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 0.69 (d,  $J$  = 6.7 Hz, 12H), 0.72 (s, 12H), 1.49 (sept,  $J$  = 6.7 Hz, 2H), 6.82 (t,  $J$  = 7.3 Hz, 6H), 7.10 (t,  $J$  = 7.6 Hz, 3H), 7.17 (t,  $J$  = 7.6 Hz, 6H), 7.29 (dd,  $J$  = 7.3, 6.7 Hz, 9H), 7.47 (d,  $J$  = 6.7 Hz, 6H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 18.42, 20.00, 24.32, 33.12, 127.42, 127.47, 129.68, 129.94, 133.81, 134.26, 134.41, 135.15 ppm. <sup>29</sup>Si NMR (CDCl<sub>3</sub>):  $\delta$  = –24.4, –65.8 ppm. IR (NaCl plate):  $\nu$  = 3100, 2955, 1450, 1150, 1095, 1055 cm<sup>-1</sup>. MS (30 eV):  $m/z$  = 981 (M<sup>+</sup>–Thex, 25%), 259 (base).

### X-ray crystallographic analysis of 3

A crystal specimen of dimensions 0.20 mm  $\times$  0.20 mm  $\times$  0.10 mm was mounted on a glass fiber, and used for data collection on a Rigaku AFC7S diffractometer using graphite-monochromated Cu K $\alpha$  radiation. Cell parameters were refined by the least-squares method using 25 reflections in the range 53.22° < 2 $\theta$  < 56.13°. Intensity data were collected at 2 $\theta$  < 120.2° by the  $\omega$ –2 $\theta$  scan technique at 20  $\pm$  1 °C. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be  $P\bar{1}$ . Of the 9156 reflections collected, 8745 were unique, and 3917 observed reflections ( $|F_o| \geq 3\sigma(F_o)$ ) were obtained and corrected for Lorentz polarization and empirical absorption based on a  $\psi$  scan. The structure was solved by SIR88.<sup>14</sup> Non-hydrogen atoms were found from subsequent Fourier syntheses and refined anisotropically by the full-matrix least-squares method. Hydrogen atoms were included but not refined. Final  $R$  and  $R_w$  values are 0.072 and 0.065, respectively. All calculations were

carried out by teXsan<sup>15</sup> with a SiliconGraphics INDY computer.

### Synthesis of 1,7-diphenyl-3,3,5,5,9,9,11,11-octamethyl-2,4,6,8,10,13-hexaoxabicyclo[5.5.1]tridecasilane (4)

Under a nitrogen atmosphere, tetramethyldisiloxanediol<sup>16</sup> (0.16 g, 1.0 mmol) and diethylamine (0.29 g, 4.0 mmol) were dissolved in 5 ml of benzene. Diphenyltetrachlorodisiloxane<sup>17</sup> (0.18 g, 0.50 mmol) in 5 ml of benzene was added dropwise at room temperature. The mixture was stirred for an additional 5 h, and 5 ml of hexane was added. The salt generated was removed by filtration and the solvent was removed. Hexane (2 ml) and benzene (3 ml) were added to the residue and the mixture was passed through a silica-gel column. After concentration, the resultant mixture was purified with recycle-type HPLC (eluent: MeOH/THF, 9:1) to give the product (62 mg, 22%).

Me<sub>8</sub>Ph<sub>2</sub>Si<sub>6</sub>O<sub>7</sub> **4**: colorless solid, mp 78–79 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 0.14 (s, 12H), 0.32 (s, 12H), 7.15 (br s, 4H), 7.18 (dd, *J* = 7.3, 6.7 Hz, 2H), 7.90 (dd, *J* = 7.3, 6.7 Hz, 4H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 0.72, 0.86, 128.29, 130.56, 133.34, 134.28 ppm. <sup>29</sup>Si NMR (CDCl<sub>3</sub>): δ = -17.31, -76.43 ppm. IR (NaCl plate): ν = 3150, 3010, 1440, 1280, 1145, 1090, 805 cm<sup>-1</sup>. MS (30 eV): *m/z* = 539 (M<sup>+</sup> - Me, 100%), 135 (88%).

### X-ray crystallographic analysis of 4

A crystal specimen of dimensions 0.40 mm × 0.10 mm × 0.10 mm was mounted on a glass fiber, and used for data collection on a Rigaku AFC7S diffractometer with graphite-monochromated Cu K<sub>α</sub> radiation. Cell parameters were refined by the least-squares method using 25 reflections in the range 20.85° < 2θ < 56.13°. Intensity data were collected at 2θ < 120.1° by the ω-2θ scan technique at 20 ± 1°C. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be C2/c. Of the 2463 reflections collected, 2341 were unique, and 769 observed reflections ( $|F_0| \geq 3\sigma(F_0)$ ) were obtained and corrected for Lorentz polarization and empirical absorption based on a ψ-scan. The structure was solved by SHELXS86.<sup>18</sup> Non-hydrogen atoms were found from subsequent Fourier syntheses and refined anisotropically by the full-matrix least-

squares method. Hydrogen atoms were included but not refined. Final *R* and *R<sub>w</sub>* values are 0.073 and 0.055, respectively. All calculations were carried out by teXsan<sup>15</sup> with a SiliconGraphics INDY computer.

### Reaction of dithexyldisiloxanetetraol and tetraphenyldisiloxanediol with dicyclohexylcarbodiimide at 120 °C

The procedure was similar to the experiment at 80 °C. From dithexyldisiloxanetetraol (0.87 g, 2.1 mmol), tetraphenyldisiloxanediol (0.63 g, 2.0 mmol) and dicyclohexylcarbodiimide (1.72 g, 8.3 mmol) in 20 ml of DMSO, 0.060 g (10%) of **2** was obtained.

### Reaction of dithexyldisiloxanetetraol and tetraphenyldisiloxanediol with diisopropylcarbodi-imide

Dithexyldisiloxanetetraol (0.31 g, 0.75 mmol), tetraphenyldisiloxanediol (0.22 g, 0.70 mmol) and diisopropylcarbodi-imide (0.39 g 3.1 mmol) were dissolved in 5 ml DMSO and the solution was heated to 120 °C for three days. Methanol was added to the reaction mixture and 0.37 g of colorless solid was obtained. Separation with recycle-type HPLC (eluent: MeOH/THF, 9:1) to give 1,3,7,9-tetrakis(1,1,2-trimethylpropyl)-5,5,11,11-tetraphenyltricyclo[5.5.1.1<sup>3,9</sup>]hexasiloxane **5** (0.070 g, 23%).

Ph<sub>4</sub>Thex<sub>4</sub>Si<sub>6</sub>O<sub>8</sub> **5**: colorless solid, m.p. 320–324 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ = 0.75 (d, *J* = 6.7 Hz, 24H), 0.78 (s, 24H), 1.54 (sept, *J* = 6.7 Hz, 4H), 7.23 (t, *J* = 7.6 Hz, 8H), 7.28 (t, *J* = 7.6 Hz, 4H), 7.58 (d, *J* = 7.6 Hz, 8H) ppm. <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ = 18.53, 20.59, 24.18, 34.12, 127.45, 129.80, 133.92, 135.20 ppm. <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>): δ = -43.65 -60.40 ppm. IR (NaCl plate): ν = 2955, 1450, 1100, 780 cm<sup>-1</sup>. MS (30 eV): *m/z* = 858 (M<sup>+</sup> - Thex, 100%), 788 (39%).

*Acknowledgements* The present study is partially supported by the REIMEI Research Resources of Japan Atomic Energy Research Institute, and by a Grant-in-aid from the Ministry of Education, Science and Culture of Japan. We thank Shin-Etsu Chemical Co. Ltd and Toshiba Silicon Co. Ltd for financial support.

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