

Tip-substituted cage and cyclic silanols

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Abstract

Synthesis of novel cage and cyclic silanols bearing Tip (2,4,6-triisopropylphenyl) groups was performed. Tip-substituted silanetriol, $\text{TipSi}(\text{OH})_3$ (**1**) was prepared from TipSiCl_3 , and can be handled without special care in the air. The versatility of this silanol is amply demonstrated as a starting material of various silanols with novel frameworks. Thus, the condensation of **1** using 2-chloro-1,3-dimethylimidazolium chloride as a dehydrating agent afforded $(\text{TipSi})_5\text{O}_7\text{OH}$ (**2**) in 45% yield. When **1** was treated with $(\text{TipSiCl}_2)_2\text{O}$, *cis,trans*-cyclotrisiloxanetriol (**3**) as well as a novel incompletely condensed silsesquioxane, $(\text{TipSi})_4\text{O}_5(\text{OH})_2$ (**4**) were obtained. In addition, the dehydrochlorinative condensation of $(\text{TipSiCl}_2)_2\text{O}$ and $(\text{TipSi}(\text{OH})_2)_2\text{O}$ afforded **4** as single product. The structures of all these novel silanols were determined by X-ray crystallography, and their unique structures (hydrogen-bonded aggregates or intramolecular hydrogen bonding) were demonstrated.

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Keywords: Silsesquioxane; Silanol; Crystal structure; Hydrogen bonding; Nano-size aggregate

1. Introduction

Cyclic and cage silanols, often quoted as incompletely condensed silsesquioxanes, have been extensively studied, especially on their capability as starting materials of metallosiloxanes [1]. In addition, recent development of the chemistry of cage silsesquioxanes has forced more focus on their synthesis from silanols [2]. Nevertheless, the reactions from silanols are still limited, and only known for readily available silanols [3]. Recently, we have isolated the cyclotetrasiloxanetetraol, $(i\text{-PrSi}(\text{OH})\text{O})_4$, and shown its versatility as precursors of tricyclic laddersiloxane [4], hexasilsesquioxane [4], octasilsesquioxane [5], hydrogen-bonded supramolecular aggregates [6], and pentacyclic laddersiloxanes [7]. These preceding results prompted us to construct cyclic or cage silanols of new types, which may lead to novel silsesquioxane chemistry. In this article, we report the following new results: (1) preparation of Tip-substituted silanetriol (**1**) and disiloxanetetraol (**6**); (2) synthesis and

structure determination of $(\text{TipSi})_5\text{O}_6\text{OH}$ (**2**), *cis,trans*- $(\text{TipSi}(\text{OH})\text{O})_3$ (**3**), and $(\text{TipSi})_4\text{O}_5(\text{OH})_2$ (**4**); (3) structure of the hydrogen-bonded aggregate of **3**.

2. Results and discussion

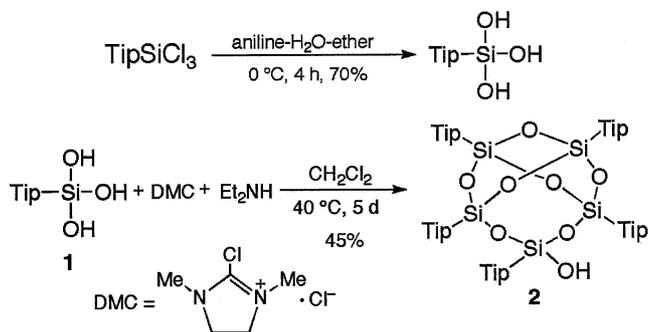
2.1. Synthesis of $(\text{TipSi})_5\text{O}_7\text{OH}$ (**2**)

The starting $\text{TipSi}(\text{OH})_3$ (**1**) was readily prepared by the hydrolysis of the corresponding TipSiCl_3 in 70% yield (Scheme 1). This silanetriol **1** was identified by spectroscopic analyses. Despite the bulkiness of Tip group, NMR spectra showed no hindered rotation; ^1H - and ^{13}C -NMR spectra showed sharp peaks of substituents. The ^{29}Si chemical shift ($\delta -52.30$) was in good accordance with that of 2-naphthylsilanetriol ($\delta -54.3$) [8].

In the present work, the condensation of **1** was carried out using 2-chloro-1,3-dimethylimidazolium chloride (DMC). Previously, we showed that dicyclohexylcarbodiimide (DCC) was effective for the condensation of $\text{RSi}(\text{OH})_3$ ($\text{R} = i\text{-Pr}$ [5], *t*-Bu, and 1,1,2-trimethylpropyl [9]) leading to the hexasilsesquioxane, T_6 . In fact, in the case of **1**, treatment with DCC afforded $(\text{TipSi})_6\text{O}_9$ in

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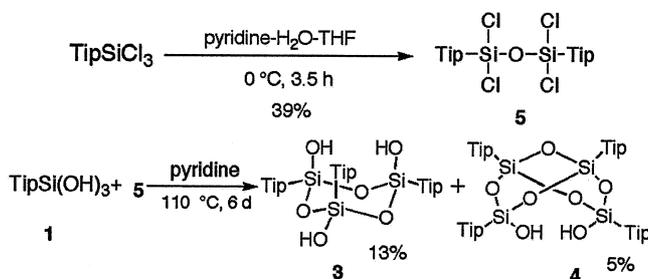


Scheme 1.

20% yield, but no silanols were given [10]. In pursuit of more effective dehydration agent, we came upon DMC; this reagent can be used at lower temperature than DCC, thus more favorable for silanol synthesis. As shown in Scheme 1, reaction of silanetriol **1** with DMC and diethylamine in CH₂Cl₂ led to the formation of cage-type silanol (TipSi)₅O₇(OH) (**2**) in 45% yield. The reaction was monitored by HPLC, and the intermediacy of disiloxanetetraol **6** and following T₄(OH)₂ **4** was confirmed. Obviously, instead of the intramolecular dehydration of **4**, reaction of **4** with **1** predominated to form **2** exclusively.

2.2. Synthesis of cyclotrisiloxanetriol, (TipSi(OH)O)₃ (**3**) and (TipSi)₄O₅(OH)₂ (**4**)

Dehydration of silanols is the most direct synthesis of silsesquioxanes, however, controlling reaction condition is crucial for the synthesis of incompletely condensed silsesquioxanes. Recently, we have demonstrated the dehydrochloric condensation of silanol and chlorosilane proceeded smoothly to give silsesquioxanes [7]. We then applied this reaction to **1** and chlorosilanes (Scheme 2). When TipSiCl₃ was treated with pyridine–water in THF at 0 °C, partial hydrolysis occurred and 1,3-bis(2,4,6-triisopropylphenyl)tetrachlorodisiloxane (**5**) was obtained in 39% yield. The reaction of this tetrachlorodisiloxane **5** with silanetriol **1** in pyridine resulted in the formation of *cis,trans*-cyclotrisiloxanetriol, (TipSi(OH)O)₃ (**3**, 13%) and (TipSi)₄O₅(OH)₂ (**4**, 5%). The result of ²⁹Si-NMR of **3** (2:1 ratio at δ –60.00



Scheme 2.

and –60.84) clearly indicated the generation of *cis,trans*-isomer, and was in good agreement with that of all-*cis*-(PhSi(OH))₃ (δ –64.1) [11]. Compound **3** was probably generated by the dehydration of **1** and **5** to form dichlorohydroxycyclotrisiloxane, followed by hydrolysis at the workup process. Both *cis,cis*- and *cis,trans*-isomers are possibly obtained in this reaction, however, steric hindrance of *cis*-Tip groups overwhelmed the stabilization by more hydrogen bonding expected in *cis,cis*-**3**, resulting in the generation of only *cis,trans*-isomer. Similarly, single isomer of **4** was obtained probably by the steric reason.

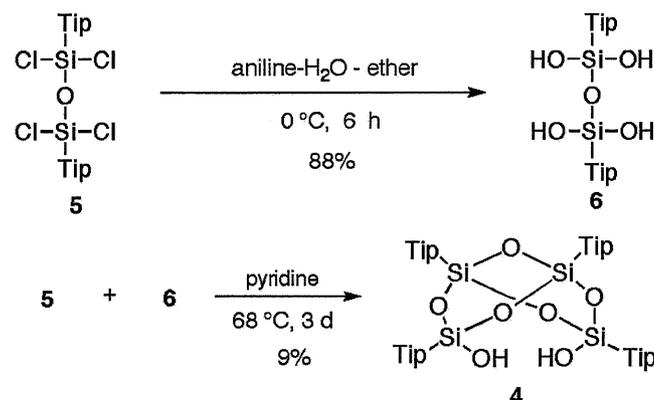
2.3. Synthesis of (TipSi)₄O₅(OH)₂ (**4**) and attempted synthesis of T₄

In order to prepare **4** in a better yield, and also with hoping to synthesize still-unknown tetrasilsesquioxane T₄, we then tried the reaction of tetrachlorosiloxane **5** and disiloxanetetraol **6** (Scheme 3). Preparation of disiloxanetetraol **6** was effected by the hydrolysis of tetrachlorosiloxane **5** with four equivalents of aniline in water and ether. The spectroscopic analysis elucidated its structure (²⁹Si-NMR peak at δ –63.07 vs. –62.4 for di(2-naphthyl)disiloxanetetraol [8]).

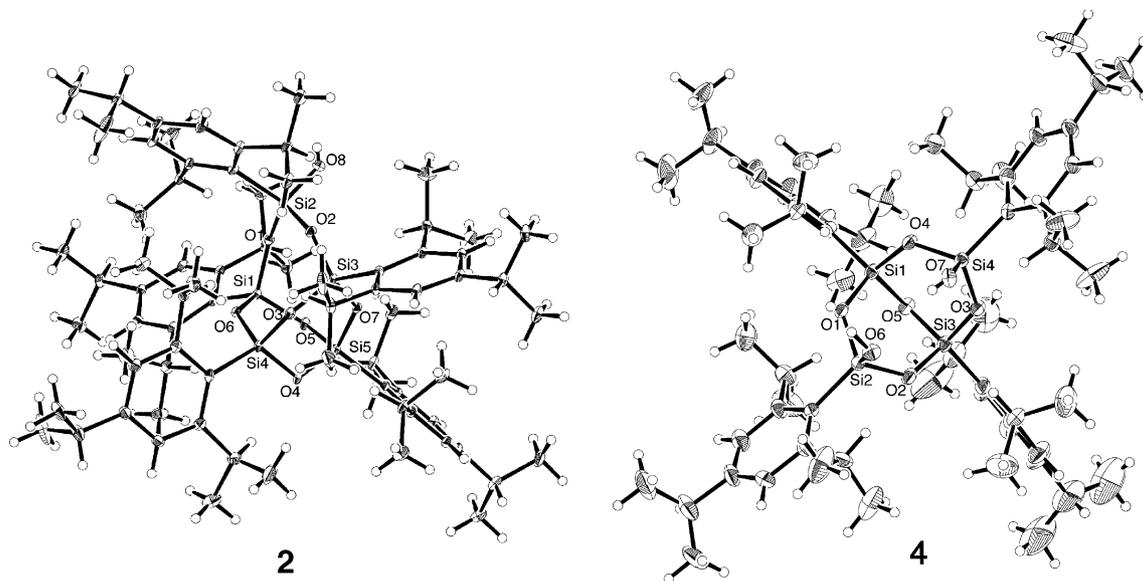
The reaction of tetrachloride **5** and tetraol **6** in pyridine proceeded at 68 °C, and both starting materials disappeared in 3 days. After usual workup, separation with dry column chromatography followed by recrystallization gave **4** in 9% yield. Unfortunately, with multiple trials and investigating reaction conditions, T₄ was not obtained. Compound **4** is stable in the air, and resisted further dehydration with known reagents. Even exposure of **4** to basic or acidic media did not lead to the formation of tetrasilsesquioxane.

2.4. Structure of (TipSi)₅O₇(OH) (**2**) and (TipSi)₄O₅(OH)₂ (**4**)

The structures of **2** and **4** were established by X-ray crystallography [12]. Single crystals of **2** suitable for X-



Scheme 3.

Fig. 1. Molecular drawings of **2** and **4**.

ray analysis were obtained by recrystallization from THF–MeOH. The molecular structure is shown in Fig. 1. Crystallographic data are summarized in Table 1, and selected bond lengths and angles are listed in Table 2. Average Si–O bond length was 1.639 Å, and average Si–O–Si and O–Si–O bond angles were 131.7° and

106.4°, respectively. This T₅OH skeleton has not been reported to date, however, these values are similar to those in hexasilsesquioxanes, i.e., TipT₆ [10] or *i*-PrT₆ [4], consisted of six- and eight-membered siloxane rings. In most cases of silanols, molecules compose intra or intermolecular hydrogen bonding in the crystals. Incidentally, **2** has bulky Tip groups geminal to the hydroxyl groups, thus intramolecular hydrogen bonding was impossible. Instead, one molecule of methanol was inserted between two molecules of **2**, and single crystal was composed. The packing scheme is shown in Fig. 2.

Table 1
Summary of crystal data, data collection, and refinement of **2–4**

	2	3	4
Formula	C ₇₆ H ₁₂₀ Si ₅ O ₉	C ₅₁ H ₈₈ Si ₃ O ₉	C ₆₀ H ₉₄ Si ₄ O ₇
Molecular weight	1318.21	929.51	1039.74
Crystal description	Colorless prism	Colorless prism	Colorless prism
Crystal size (mm)	0.40 × 0.40 × 0.40	0.40 × 0.40 × 0.30	0.40 × 0.40 × 0.20
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	15.250(1)	14.257(3)	15.022(1)
<i>b</i> (Å)	18.800(1)	17.414(4)	18.097(1)
<i>c</i> (Å)	15.028(1)	13.032(3)	12.8776(8)
α (°)	98.721(4)	106.78(1)	108.532(2)
β (°)	112.053(3)	97.71(1)	93.203(6)
γ (°)	81.242(4)	103.90(1)	108.274(6)
<i>V</i> (Å ³)	3925.6(5)	2933(1)	3104.4(4)
<i>Z</i>	2	2	2
Temperature (°C)	−180.0	−12.0	−20.0
μ (cm ^{−1})	1.42	1.27	1.43
Reflections measured	12 915	8047	7732
Reflections observed	11 209	5113	5688
Parameters	810	576	649
<i>R</i> ₁ [<i>I</i> > 2.0σ(<i>I</i>)]	0.071	0.085	0.076
<i>wR</i> ₂ (for all data)	0.161	0.094	0.164
(Δ/σ) _{max}	0.047	0.474	0.008
(Δ/ρ) _{max} (e Å ^{−3})	1.42	0.62	0.54
(Δ/ρ) _{min} (e Å ^{−3})	−1.09	−0.51	−0.46

Table 2
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Si(1)–O(1)	1.625(2)	Si(1)–O(5)	1.639(3)
Si(1)–O(6)	1.640(2)	Si(1)–C(1)	1.861(4)
Si(2)–O(1)	1.635(2)	Si(2)–O(2)	1.631(3)
Si(2)–O(8)	1.620(3)	Si(2)–C(16)	1.881(4)
Si(3)–O(2)	1.619(2)	Si(3)–O(3)	1.637(2)
Si(3)–O(7)	1.647(2)	Si(3)–C(31)	1.866(4)
Si(4)–O(3)	1.643(2)	Si(4)–O(4)	1.650(3)
Si(4)–O(6)	1.642(2)	Si(4)–C(46)	1.852(3)
Si(5)–O(4)	1.659(2)	Si(5)–O(5)	1.641(3)
Si(5)–O(7)	1.640(2)	Si(5)–C(61)	1.862(4)
Bond angles			
O(1)–Si(1)–O(5)	109.3(1)	O(1)–Si(1)–O(6)	104.5(1)
O(5)–Si(1)–O(6)	106.6(1)	O(1)–Si(2)–O(2)	107.3(1)
O(1)–Si(2)–O(8)	105.7(1)	O(2)–Si(2)–O(8)	109.3(1)
O(2)–Si(3)–O(3)	107.4(1)	O(2)–Si(3)–O(7)	108.4(1)
O(3)–Si(3)–O(7)	105.0(1)	O(3)–Si(4)–O(4)	104.0(1)
O(3)–Si(4)–O(6)	107.7(1)	O(4)–Si(4)–O(6)	104.3(1)
O(4)–Si(5)–O(5)	103.8(1)	O(4)–Si(5)–O(7)	105.9(1)
O(5)–Si(5)–O(7)	106.6(1)	Si(1)–O(1)–Si(2)	141.6(2)
Si(2)–O(2)–Si(3)	150.3(2)	Si(3)–O(3)–Si(4)	124.4(1)
Si(4)–O(4)–Si(5)	116.8(1)	Si(1)–O(5)–Si(5)	125.3(1)
Si(1)–O(6)–Si(4)	131.9(2)	Si(3)–O(7)–Si(5)	131.1(1)

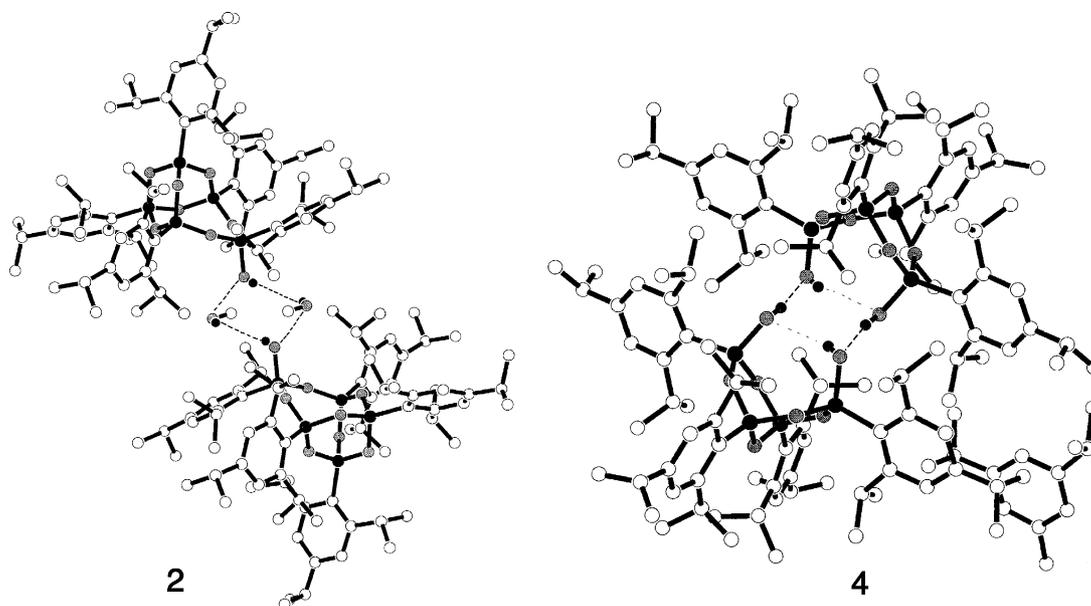


Fig. 2. Hydrogen bonding observed in **2** and **4**.

The length of hydrogen bonding (O...O distance) was 2.91 and 3.06 Å.

Siloxanediol **4** ($T_4(OH)_2$) was recrystallized from THF–MeOH–H₂O, and colorless single crystals were obtained. Crystallographic data are summarized in Table 1, and selected bond lengths and angles are listed in Table 3. Average Si–O bond length was 1.639 Å, and average Si–O–Si and O–Si–O bond angles were 127.4° and 105.9°, respectively. Because this molecule is

comprised only six-membered siloxane rings, Si–O–Si bond angles were smaller than those in **2**, **3**, or T_6 . Other values are within the normal range. As shown in Fig. 2, siloxanediol **4** possesses both intra and intermolecular hydrogen bonding to form dimer in the crystal. The distance of oxygen atoms were 2.98 Å for intramolecular hydrogen bonding, and 3.06 Å for intermolecular one. This is the first example for bicyclo [3.3.1]siloxanes, and the smallest cage silanol ever reported.

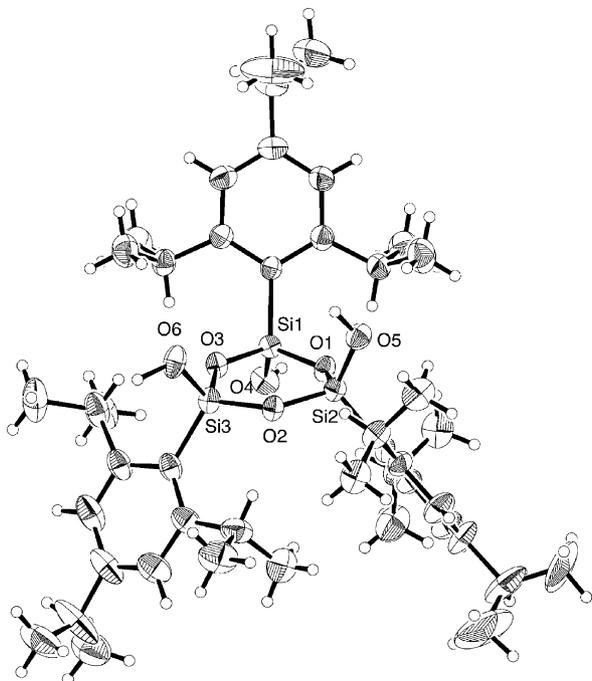
Table 3

Selected bond lengths (Å) and angles (°) for **4**

Bond lengths			
Si(1)–O(1)	1.633(3)	Si(1)–O(4)	1.628(3)
Si(1)–O(5)	1.655(3)	Si(1)–C(1)	1.853(5)
Si(2)–O(1)	1.634(3)	Si(2)–O(2)	1.629(3)
Si(2)–O(6)	1.635(4)	Si(2)–C(16)	1.857(5)
Si(3)–O(2)	1.639(3)	Si(3)–O(3)	1.637(4)
Si(3)–O(5)	1.659(3)	Si(3)–C(31)	1.851(5)
Si(4)–O(3)	1.631(3)	Si(4)–O(4)	1.644(3)
Si(4)–O(7)	1.634(4)	Si(4)–C(46)	1.865(5)
Bond angles			
O(1)–Si(1)–O(4)	109.7(2)	O(1)–Si(1)–O(5)	103.4(2)
O(1)–Si(1)–C(1)	108.4(2)	O(4)–Si(1)–O(5)	104.6(2)
O(4)–Si(1)–C(1)	110.7(2)	O(5)–Si(1)–C(1)	119.6(2)
O(1)–Si(2)–O(2)	106.2(2)	O(1)–Si(2)–O(6)	105.6(2)
O(1)–Si(2)–C(16)	112.2(2)	O(2)–Si(2)–O(6)	106.1(2)
O(2)–Si(2)–C(16)	112.5(2)	O(6)–Si(2)–C(16)	113.6(2)
O(2)–Si(3)–O(3)	109.2(2)	O(2)–Si(3)–O(5)	103.8(2)
O(2)–Si(3)–C(31)	108.1(2)	O(3)–Si(3)–O(5)	103.6(2)
O(3)–Si(3)–C(31)	111.5(2)	O(5)–Si(3)–C(31)	120.1(2)
O(3)–Si(4)–O(4)	106.5(2)	O(3)–Si(4)–O(7)	107.0(2)
O(3)–Si(4)–C(46)	112.3(2)	O(4)–Si(4)–O(7)	105.2(2)
O(4)–Si(4)–C(46)	111.8(2)	O(7)–Si(4)–C(46)	113.5(2)
Si(1)–O(1)–Si(2)	129.9(2)	Si(2)–O(2)–Si(3)	130.7(2)
Si(3)–O(3)–Si(4)	129.2(2)	Si(1)–O(4)–Si(4)	129.3(2)
Si(1)–O(5)–Si(3)	117.7(2)		

2.5. Structure of $(TipSi(OH)HO)_3$ (**3**)

Several structural reports have appeared for cyclo-trisiloxanetriols ($T_3(OH)_3$). In 1980, Russian group reported the synthesis and structure determination of $(PhSi(ONa)O)_3$, which was obtained in two step from $PhSiCl_3$ [13]. Later, Roesky and his group reported the first synthesis of free cyclic triol, *cis,trans*-[(2.6- $Me_2C_6H_3$)(N(SiMe₃)Si(OH)O)₃] starting from the respective chlorosilane [14]. They also described the synthesis of all-*cis*-[(Me_3Si)₂CHSi(OH)O]₃ by the reaction of tetraaminodisilane with H₂O₂/H₂O [15]. Additionally, Fujita's group reported the ship-in-a-bottle formation of all-*cis*-(ArSi(OH)O)₃ (Ar = Ph, 3,5-dimethylphenyl, 2-naphthyl) taking advantage of the self-assembled coordination cage [8,11]. However, only the structures with all-*cis* form were determined by crystallography, and the structure of *cis,trans*-cyclo-trisiloxanetriol is still unknown to the best of our knowledge. The obtained solid of **3** was recrystallized from THF–MeOH by slow evaporation at room temperature to give the crystals suitable for X-ray analysis [12]. The molecular structure is shown in Fig. 3; crystallographic data are summarized in Table 1, and selected bond

Fig. 3. Molecular drawings of **3**.

lengths and angles are listed in Table 4. Interestingly, compound **3** adopted almost planar conformation unlike cyclohexane. Average Si–O bond length in the six-membered ring was 1.645 Å, and average angles were 134.1° for Si–O–Si and 104.8° for O–Si–O. Those values are similar to those in [(Me₃Si)₂CHSi(OH)O]₃ [15]. Most interesting feature of **3** is revealed in its packing diagram. In Fig. 4, possible hydrogen bonding in the packing is shown. Two of the hydroxyl groups in **3** were connected via MeOH by hydrogen bonding, resulted in the formation of infinite nano-size wire. The

Table 4
Selected bond lengths (Å) and angles (°) for **3**

Bond lengths			
Si(1)–O(1)	1.631(4)	Si(1)–O(3)	1.647(4)
Si(1)–O(4)	1.647(5)	Si(1)–C(1)	1.899(5)
Si(2)–O(1)	1.651(5)	Si(2)–O(2)	1.647(4)
Si(2)–O(5)	1.622(4)	Si(2)–C(16)	1.888(6)
Si(3)–O(2)	1.633(4)	Si(3)–O(3)	1.661(5)
Si(3)–O(6)	1.636(5)	Si(3)–C(31)	1.876(5)
Bond angles			
O(1)–Si(1)–O(3)	104.6(2)	O(1)–Si(1)–O(4)	109.2(2)
O(1)–Si(1)–C(1)	111.9(2)	O(3)–Si(1)–O(4)	107.6(2)
O(3)–Si(1)–C(1)	110.5(3)	O(4)–Si(1)–C(1)	112.6(3)
O(1)–Si(2)–O(2)	105.2(2)	O(1)–Si(2)–O(5)	107.5(2)
O(1)–Si(2)–C(16)	114.9(3)	O(2)–Si(2)–O(5)	111.2(3)
O(2)–Si(2)–C(16)	109.5(2)	O(5)–Si(2)–C(16)	108.6(2)
O(2)–Si(3)–O(3)	104.6(2)	O(2)–Si(3)–O(6)	108.7(2)
O(2)–Si(3)–C(31)	114.9(3)	O(3)–Si(3)–O(6)	108.5(2)
O(3)–Si(3)–C(31)	111.0(3)	O(6)–Si(3)–C(31)	108.9(3)
Si(1)–O(1)–Si(2)	133.3(3)	Si(2)–O(2)–Si(3)	134.1(3)
Si(1)–O(3)–Si(3)	134.9(3)		

space-filling model (Fig. 5) clearly shows this structure: hydrophilic groups compose a core surrounded by hydrophobic Tip groups. The shape of this nano-wire is rectangular with 1.4 nm by 1.7 nm. This kind of hydrogen-bonded aggregate have been observed only in siloxanepolyols, and observed for cyclotrisiloxanetriol for the first time.

In summary, we have synthesized novel ring systems, T₅OH (**2**) and T₄(OH)₂ (**4**), and also the first *cis,trans*-T₃(OH)₃ (**3**). The crystallographic analyses of these compounds revealed their unique features, i.e., inter and intramolecular hydrogen bonding, or nano-size aggregates. Currently we are investigating the transformation of these silanols into novel siloxane cage systems.

3. Experimental

Analytical HPLC was performed on a JASCO 875UV/880PU with a Chemco 4.6 × 250 mm 5-ODS-H column. Preparative recycle-type HPLC was carried out using JAI LC-908 with a Chemco 20 × 250 mm 7-ODS-H column. Fourier transform nuclear magnetic resonance spectra were obtained by a JEOL Model α-500 (¹H at 500.00 MHz, ¹³C at 125.65 MHz, and ²⁹Si at 99.25 MHz). Chemical shift were reported as δ units (ppm) relative to SiMe₄, and residual solvents peaks were used for standard. Electron impact mass spectrometry was performed with a JEOL JMS-DX302. Infrared spectra were measured with a SHIMADZU FTIR-8700.

3.1. Preparation of TipSi(OH)₃ (**1**)

Ether (30 ml) solution of TipSiCl₃ (2.06 g, 6.1 mmol) was added to vigorously stirred emulsion of aniline (1.94 g, 21 mmol) and water (10.0 g, 0.56 mmol) in ether (30 ml) at 0 °C for 60 min. The mixture was stirred at 0 °C for 3 h, then filtered through a glass filter. The filtrate was concentrated, and colorless solid was obtained. The solid was recrystallized from hexane to give analytically pure TipSi(OH)₃ (**1**, 1.71 g, 70%). **1**: Colorless solid, m.p. 98–104 °C; ¹H-NMR (DMSO-*d*₆) 1.14 (d, 12H), 1.16 (d, 6H), 2.79 (sep, 1H), 3.90 (sept, 2H), 6.21 (s, 3H), 6.95 (s, 2H); ¹³C-NMR (DMSO-*d*₆) 24.06, 25.40, 31.71, 33.79, 120.40, 130.20, 148.87, 155.71; ²⁹Si-NMR (DMSO-*d*₆) δ –52.30; MS (70 eV) *m/z* (%) 282 ([M]⁺, 70), 249 (100), 240 (45), 231 (40), 225 (60); IR (KBr) 3296, 2960, 2869, 1604, 1554, 1461, 1361, 1193, 1137, 1047, 877, 846, 758, 632 cm^{–1}.

3.2. Preparation of (TipSiCl₂)₂O (**5**)

Water (90 mg, 5.0 mmol) and pyridine (0.79 g, 10 mmol) in THF (0.5 ml) was added dropwise to a

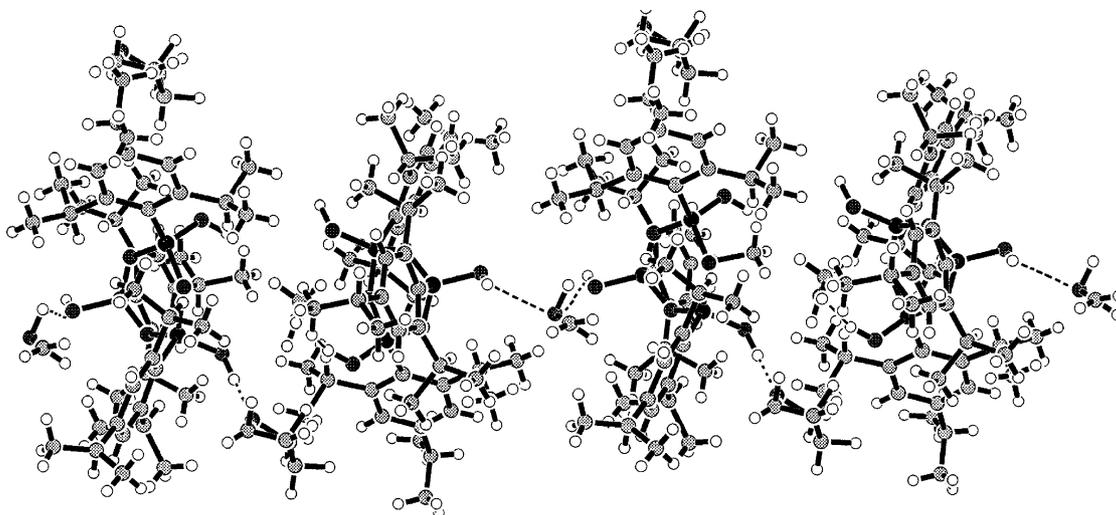


Fig. 4. Hydrogen bonding observed in 3.

solution of TipSiCl_3 (3.37 g, 10 mmol) in 13 ml of THF and 2.5 ml of ether at 0°C for 30 min. The mixture was stirred at 0°C for additional 3 h. After removal of solvent, hexane was added to the semisolid, and the generated salt was filtered under nitrogen atmosphere. Bulb-to-bulb distillation of the concentrated filtrate gave 1,3-bis(2,4,6-triisopropylphenyl)tetrachlorodisiloxane (1.21 g, 39%). **5**: Colorless semisolid, b.p $240^\circ\text{C}/3$ mmHg; $^1\text{H-NMR}$ (CDCl_3) 1.18 (d, 24H), 1.24 (d, 12H), 2.87 (sept, 2H), 3.69 (sept, 4H), 7.06 (s, 4H); $^{13}\text{C-NMR}$ (CDCl_3) 23.60, 24.86, 32.87, 34.30, 122.23, 123.57, 152.98, 156.15; $^{29}\text{Si-NMR}$ (CDCl_3) -30.96 ; MS (70 eV) m/z (%) 620 ($[\text{M}^+]$, 53), 577 (18), 535 (10), 415 (100); IR (NaCl) 3723, 3055, 2964, 2869, 1604, 1554, 1541, 1461, 1421, 1382, 1361, 1047, 846, 812 cm^{-1} .

3.3. Preparation of $(\text{TipSi}(\text{OH})_2)_2\text{O}$ (**6**)

Acetone (15 ml) solution of TipSiCl_3 (4.03 g, 11.9 mmol) was added dropwise to water (150 ml) at 0°C for 10 min. The mixture was stirred at 0°C for 6 h, then warmed to room temperature (r.t.). The solid was filtered, and the filtration was washed with hexane,

dried, and concentrated to give 1,3-bis(2,4,6-triisopropylphenyl)-1,1,3,3-tetrahydroxydisiloxane (2.86 g 88%). **6**: Colorless solid, m.p. $144\text{--}147^\circ\text{C}$; $^1\text{H-NMR}$ ($\text{DMSO-}d_6$) 1.05 (d, 24H), 1.14 (d, 12H), 2.77 (sept, 2H), 3.80 (sept, 4H), 6.21 (s, 4H), 6.91 (s, 4H); $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$) 24.15, 25.52, 31.89, 33.90, 120.53, 130.21, 149.08, 155.89; $^{29}\text{Si-NMR}$ ($\text{DMSO-}d_6$) -63.07 ; MS (70 eV) m/z (%) 341 ($[\text{M}^+]$ —Tip, 20%), 326 (5), 298 (5), 281 (60), 267 (45); IR (KBr) 3723, 3055, 2964, 2869, 1604, 1554, 1541, 1461, 1421, 1382, 1361, 1047, 846, 812 cm^{-1} .

3.4. Synthesis of $(\text{TipSi})_5\text{O}_7\text{OH}$ (**2**)

In a two-necked flask were placed $\text{TipSi}(\text{OH})_3$ (1.41 g, 5.00 mmol), diethylamine (3.53 g, 48.3 mmol), dry CH_2Cl_2 (10 ml), and DMC (2.15 g, 11.3 mmol). The solution was heated 40°C for 5 days. Water (20 mg) was added dropwise to the mixture, and the aqueous phase was extracted three times with ether (30 ml each). The combined organic phase was dried over anhydrous magnesium sulfate and evaporated. The resulting semisolid was separated by recycle-type preparative GPC and further recrystallized from THF-MeOH to give 3-

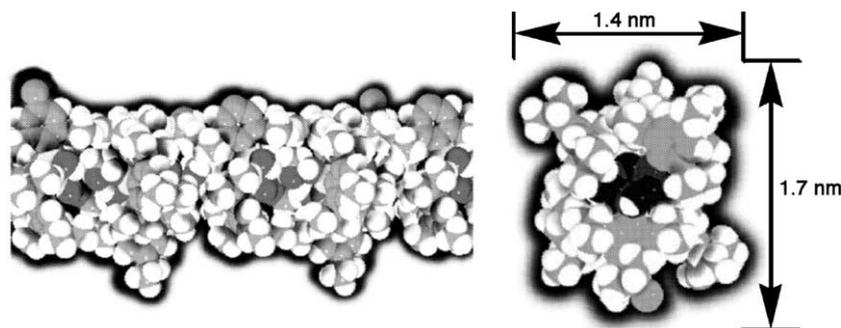


Fig. 5. Space-filling drawing of 3.

hydroxy-1,3,5,7,10-pentakis(2,4,6-triisopropylphenyl)tricyclo[3.3.3.1^{7,10}]pentasiloxane (0.58 g, 45%). **2**: Colorless crystals, m.p. 229–231 °C; ¹H-NMR (CDCl₃) 0.80 (d), 0.89 (d), 0.95 (d) 1.05 (d), 1.21 (m), 2.83 (sept), 3.40–3.64 (m), 3.66–3.74 (m), 6.91 (m), 6.96 (m); ¹³C-NMR (CDCl₃) 23.64, 23.72, 23.81, 24.23, 24.69, 24.92, 25.52, 32.21, 32.59, 32.67, 32.78, 34.35, 120.65, 120.77, 121.30, 121.46, 123.89, 151.10, 151.61, 156.45, 156.67, 156.87, 157.17; ²⁹Si-NMR (CDCl₃) –59.34, –67.55, –68.21, MS (70 eV) *m/z* (%) 1285 ([M]⁺, 80), 1081 ([M]⁺–Tip, 81); IR (KBr) 3420, 2963, 2870, 1605, 1458, 1420, 1383, 1362, 1086, 1057, 1001, 961, 878, 735, 625 cm^{–1}.

3.5. Synthesis of cyclotrisiloxanetriol, Tip₃Si₃(OHO)₃ (**3**) and (TipSi)₄O₅(OH)₂ (**4**)

THF (50 ml) solution of (TipSiCl₂)₂O (**5**, 0.657 g, 1.06 mmol) was added dropwise to a solution of TipSi(OH)₃ (**1**, 0.600 g, 2.13 mmol) and pyridine (1.02 g, 12.9 mmol) at r.t. for 120 min. The solution was stirred for 2 days, and then heated to 110 °C for 6 days. The mixture was washed with water (50 ml), and the aqueous phase was extracted three times with ether (50 ml each). The combined organic phase was dried over anhydrous magnesium sulfate and evaporated. The resulting semisolid was separated by dry column chromatography (hexane/ether = 8/2), and further recrystallized from THF and MeOH to give 1,3,5-trihydroxy-1,3,5-tris(2,4,6-triisopropylphenyl)cyclotrisiloxane (**3**, 0.109 g, 13%) and *cis*-3,7-dihydroxy-1,3,5,7-tetrakis(2,4,6-triisopropylphenyl)bicyclo[3.3.1]tetrasiloxane (**4**, 0.025 g, 5%). **3**: Colorless needles, m.p. 174–177 °C; ¹H-NMR (CDCl₃) 1.11 (d, 12H), 1.15 (d, 12H), 1.23 (d, 12H), 1.26 (d, 6H), 1.29 (d, 12H), 2.81–2.91 (m, 3H), 3.68 (sept, 4H), 3.84 (sept, 2H), 7.03 (m, 4H), 7.09 (m, 2H); ¹³C-NMR (CDCl₃) 23.72, 23.77, 23.80, 25.06, 25.21, 25.28, 32.66, 32.74, 34.32, 121.19, 121.49, 124.23, 124.65, 151.14, 151.19, 156.32, 156.43; ²⁹Si-NMR (CDCl₃) –60.00, –60.84; MS (EI, 70 eV) *m/z* (%) 792 ([M]⁺, 12), 588 ([M]⁺–Tip, 100); IR (KBr) 447, 2961, 2930, 2870, 1605, 1555, 1541, 1464, 1420, 1383, 362, 1084, 1024, 878, 735, 633 cm^{–1}. **4**: Colorless crystals, m.p. 280–281 °C; ¹H-NMR (acetone-*d*₆) 0.96 (d, 24H), 1.15 (d, 36H), 1.23 (d, 12H), 2.90 (sept, 4H), 3.75 (sept, 4H), 3.82 (sept, 4H), 7.00 (s, 4H), 7.12 (s, 4H); ¹³C-NMR (CDCl₃) 17.89, 18.26, 23.71, 23.75, 24.11, 24.82, 24.96, 25.06, 25.15, 32.52, 32.65, 32.80, 34.24, 34.38, 58.50, 59.63, 121.02, 121.19, 121.30, 121.57, 122.04, 148.64, 151.78, 152.03, 156.40, 156.46, 156.59, 156.62, 156.96; MS (EI, 70 eV) *m/z* (%) 1038 ([M]⁺, 65), 835 ([M]⁺–Tip, 100); IR (KBr) 3368, 2963, 2870, 1605, 1460, 1420, 1383, 1362, 1084, 1003, 878, 768, 708, 627, 490, 459 cm^{–1}.

3.6. Reaction of (TipSiCl₂)₂O (**5**) and (TipSi(OH)₂)₂O (**6**)

In a two-necked flask were placed **5** (0.31 g, 0.50 mmol), **6** (0.30 g, 0.55 mmol), and pyridine (3.4 mg). The solution was heated to 68 °C for 3 days. Water (30 ml) was added to the mixture, which was then stirred for 30 min. The mixture was washed with water (30 ml), and the aqueous phase was extracted three times with ether (30 ml each). The combined organic phase was dried with anhydrous magnesium sulfate and evaporated. The resulting semisolid was separated by dry column chromatography (hexane/ether = 8/2) and further recrystallized from THF-MeOH to give (TipSi)₄O₅(OH)₂ (**4**, 0.024 g, 9%).

3.7. X-ray crystallography (general procedure)

Single crystals were coated and mounted on the glass fiber using epoxy adhesive, and were cooled by a Rigaku nitrogen-flow low-temperature apparatus. All measurements were made on a Rigaku RAXIS-IV⁺⁺ imaging plate diffractometer using graphite monochromated Mo-K_α radiation. Indexing was performed from four stills that were exposed for 60 s. The data were collected to a maximum 2θ value of 64.6°. A sweep of data was done using φ oscillations from in 0.5° steps. The exposure rate was 180.0 s per degree. The detector swing angle was –0.15°. The crystal-to-detector distance was 99.89 mm. Readout was performed in the 0.100 mm pixel mode. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. All calculations were performed using the CRYSTALSTRUCTURE crystallographic software package.

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