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cis-*trans*-*cis*-Tetrabromotetramethylcyclotetrasiloxane: a Versatile Precursor of Ladder Silsesquioxanes

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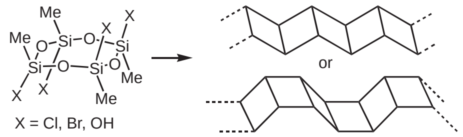
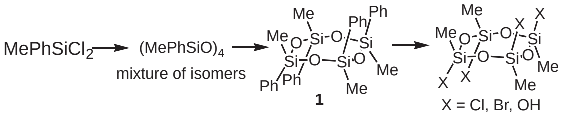
The title compound was isolated for the first time by a novel procedure including dephenylbromination of cyclotetrasiloxane. The stereostructure of the tetrabromide was confirmed by condensation with diphenylsilanediol, affording *anti*-tricyclo[7.3.1.1^{3,7}]hexasiloxane. This tetrabromide spontaneously decomposed in air to afford a white powder insoluble in organic solvents. Measurements of the TG, IR, and solid-state NMR spectra of the product revealed that a ladder polysilsesquioxane with high thermal stability and stereoregularity was obtained.

Sila-functional cyclotetrasiloxanes have received growing interest in recent years because of their potential applications as precursors of various silsesquioxanes.[1] Among them, functionalized *cis-trans-cis*-cyclotetrasiloxane is a good precursor of ladder silsesquioxanes, as depicted in Scheme 1. The condensation of this isomer affords all-*anti*, *anti-syn-anti*, or mixed-type polymers, and in all cases infinite-length ladder polysilsesquioxanes are possibly generated. Much effort has been directed towards the syntheses of ladder polysilsesquioxanes,[2] since Brown and co-worker proposed a ladder structure for phenylsilsesquioxanes $(PhSiO_{1.5})_n$.[3] It has been suggested that ladder structures resulted under certain conditions; however, the evidence, such as IR and NMR spectra, or X-ray powder diffraction[2] is not universally accepted.[4] Recently, we isolated the first pentacyclic laddersiloxane[5] and determined the structure.[6] This laddersiloxane could be obtained from all-*cis*-[*i*-PrSi(OH)O]$_4$,[1a] and also the surprising versatility of this cyclotetrasiloxane as a precursor of tricyclic laddersiloxane,[1b] hexasilsesquioxane,[1b] octasilsesquioxane,[1a] and hydrogen-bonded supermolecule[1c] was shown. Therefore, functionalized *cis-trans-cis*-cyclotetrasiloxane will no doubt be an intriguing building block of sterically-regulated siloxanes, especially that of ladder polysilsesquioxanes, which have been desired for industrial use.

Until now, three types of functionalized tetramethylcyclotetrasiloxanes have been reported in the scientific literature. In 1956, the synthesis of [MeSi(Cl)O]$_4$ was accomplished by the chlorination of [MeSi(H)O]$_4$.[7] Later in 1984, Harrod and Pelletier reported on the preparation of [MeSi(Br)O]$_4$ from [MePhSiO]$_4$,[8] and an NMR observation as a mixture of four isomers was shown.[9] In both cases, however, inseparable isomeric mixtures were obtained, and no further reaction or structure determination was given. As a relevant compound, the synthesis and isolation of *cis*,*trans*,*cis*-[MeSi(NCO)O]$_4$ was quite recently reported, and the structure was determined by X-ray crystallographic analysis.[10] We report herein on the preparation and characterization of *cis*,*trans*,*cis*-2,4,6,8-tetrabromo-2,4,6,8-tetramethylcyclotetrasiloxane, and its application to the synthesis of ladder polysilsesquioxanes.



Scheme 1. Ladder polysilsesquioxane.



Scheme 2. Preparation of the single isomer.

Results and Discussion

Considering the instability of the target compound towards moisture, we devised the strategy shown in Scheme 2. Cyclotetrasilane (MePhSiO)$_4$ is prepared from dichloro(methyl)-phenylsilane as a mixture of isomers, and then *cis-trans-cis* isomer **1** is separated. Subsequent dephenylhalogenation of **1** with retained stereostructure affords the target compound.

Preparation of Cyclotetrasiloxane 1. The first synthesis of (MePhSiO)$_4$ was reported in 1948 by Lewis,[11] followed by a report in which partial separation and an IR measurement were performed.[12] Eighteen years later, isolation of the *cis-trans-cis* isomer was effected by distillation and fractional crystallization over a period of two months.[13] Since then, the structure elucidation of four isomers by ^{1}H NMR,[14] and X-ray crystallographic analysis of *cis-trans-cis* isomer have been accomplished.[15] We employed the reaction of MePhSiCl$_2$ with aqueous KOH in THF at 80 °C, and obtained (MePhSiO)$_4$ (D$_4$) in 40% yield as a mixture of isomers. Condensation with ZnO was also examined; in this case, cyclotrisiloxane was obtained in a better yield, while the yield of cyclotetrasiloxane decreased, as previously shown in the lietarature.[16] We separated D$_3$, D$_4$, D$_5$, and higher oligomers by distillation. The ratio of the isomers of D$_4$ was determined by the ^{1}H NMR spectra,[14] and *cis-cis-cis*- (3%), *cis-cis-trans*- (21%), *cis-trans-cis*- (10%),

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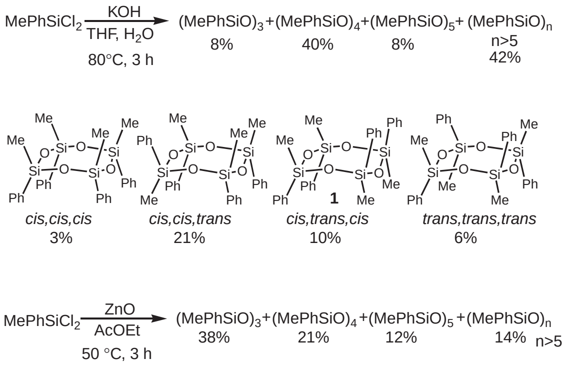
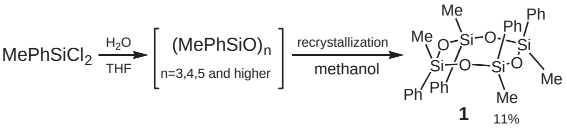


Scheme 3. Preparation of cyclotetrasiloxanes.

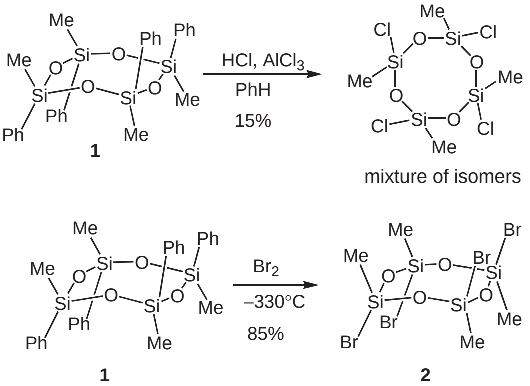


Scheme 4. One-step separation of *cis*,*trans*,*cis*-$(PhMeSiO)_4$, **1**.

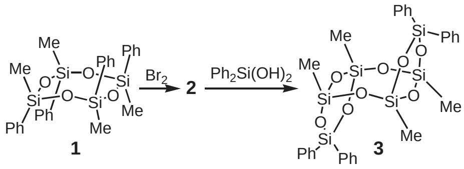
and *trans-trans-trans*-cyclotetrasiloxanes (6%) were obtained (Scheme 3). The ratio of four isomers is close to the statistical one (1:4:2:1, respectively); this value was similar in various reaction conditions.

According to the literature, the *cis-trans-cis* isomer of $(MePhSiO)_4$ possesses better crystallinity than other isomers, and the fractional crystallization of an isomeric mixture of D_4 successfully afforded the *cis*,*trans*,*cis* isomer.[13] We further examined separation methods, and could obtain *cis-trans-cis*-$(MePhSiO)_4$ **1** by crystallization at −40 °C from methanol without separating D_3, D_4, or D_5. When we separated **1** from a mixture obtained by a reaction with aqueous KOH in THF, the yield was 5% after recrystallization. This yield was improved if we performed hydrolytic condensation in water and THF. The yield of **1** by this method was 11%. As a result, we could obtain **1** in a bulk amount (Scheme 4). In view of the industrial application, HPLC separation is not practical. Thus, it is promising that the desired isomer is obtained by facile single-step crystallization.

Dearylhalogenation Reaction. In our previous report on laddersiloxanes, we described that dephenylchlorination proceeded in high yields by the action of $AlCl_3/HCl$.[6] We thus applied this reaction to **1**. As shown in Scheme 5, the reaction of **1** with HCl and a catalytic amount of $AlCl_3$ successfully afforded tetrachloride in 15% yield. Unfortunately, an NMR analysis of the products revealed that all four isomers were generated, showing that the reaction was not stereospecific. We supposed that this stereoselectivity was a result of the reaction temperature (20 °C) and the use of $AlCl_3$. The cleavage of cyclotetrasiloxane by $AlCl_3$ was reported;[17] thus, ring cleavage and closing also occurred in our case, resulting in isomerization of the products. We then examined the reaction with Br_2 at −30 °C by following the reported method.[8] After purification by sublimation, pure tetrabromide **2** was obtained in 85% yield as a moisture-sensitive white solid. A spectroscopic analysis supported the structure of **2** as well as the generation of a single isomer. However, the stereostructure was not determined equivocally, because three isomers (all-*cis*, all-*trans*, *cis-trans-cis*) could not be identified by spectroscopic methods. Unfortunately, all attempts to make single crystals of tetrabromide met with failure.



Scheme 5. Dephenylhalogenation of **1**.



Scheme 6. Preparation of tricyclic laddersiloxane **3**.

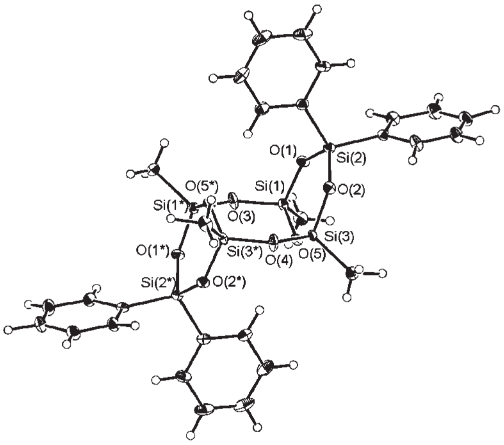


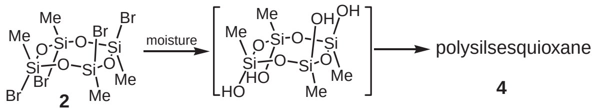
Fig. 1. Molecular drawing of **3**. Thermal ellipsoids are drawn in 30% probability level.

Preparation of Laddersiloxanes. In order to determine the stereostructure of **2**, we then transferred **2** to the tricyclic laddersiloxane **3**. As outlined in Scheme 6, tetrabromide **2** obtained from **1** was not isolated, and directly treated with diphenylsilanediol after sublimation because of the lability of **2** in air. As a result, the expected **3** was obtained in 65% yield from **1**. The obtained tricyclic laddersiloxane was identified by spectroscopic methods, and the structure was determined by X-ray crystallographic analysis. In Fig. 1, the molecular structure of **3** is shown; crystallographic data are summarized in Table 1, and selected bond lengths and angles are listed in Table 2. There exists a symmetry axis passing through atoms O(3) and O(4), and all three planes are virtually planar. Previously, one tricyclic siloxane with the same framework was prepared and the structure was determined.[18] That compound possesses phenyl groups in the center ring and methyl groups at the terminal silicon atoms. The average bond lengths and angles in each ring are similar, indicating the strain-free structure of **3**.

We can identify the structure of tetrabromide **2** as a *cis-trans-cis* isomer based on the following two reasons: (1) We previously observed that the stereostructure was maintained in the reaction of dehydrochlorinative condensation.[6] (2) If **2** was all-*cis* isomer, *syn*-tricyclic laddersiloxane must be obtained. In this case, no laddersiloxane other than **3** was generated.

Condensation from Tetrabromide. In the case of isopropyl-substituted cyclotetrasiloxanes, tetrols are stable in air, and crystallographic analyses have been performed without problems. However, methyl groups are not large enough for stabilization, and the isolation of tetrol by the hydrolysis of tetrabromide **2** met with failure. Actually, **2** spontaneously decomposed in air to give a white solid **4** (Scheme 7). Judging from the structure of **2**, the intermediate is evidently *cis-trans-cis*-[Me(OH)Si]$_4$, which was spontaneously dehydrated to afford polysilsesquioxane **4**.

As depicted in Fig. 2, the result of a TG analysis showed its remarkable stability (5% weight loss was at 645 °C; only 13% weight loss at 1000 °C in N_2). It is also noteworthy that the reported ladder-like polymers showed a much lower 5% weight-loss temperature. For example, poly(methylsilsesquioxanes), obtained by the hydrolysis of $MeSiCl_3$ or $MeSi(OMe)_3$, showed a 5% weight loss in a range of 400–500 °C.[19] Presumably, this stability of **4** is the result of a flawless ladder structure. For less regulated ladder-like polymers, decomposition is initiated at the weakest point, and then further bond fission may occur. Additionally, IR and solid-state NMR spectra show its unique structure. As can be seen in Fig. 3, two sharp Si–O–Si stretching bands are observed at 1128 and 1032 cm^{-1} for **4**. These bands were observed for other ladder-like poly(methylsilsesquioxanes); however, the shape of the peaks is broad,[20]



Scheme 7. Condensation to poly(methylsilsesquioxanes).

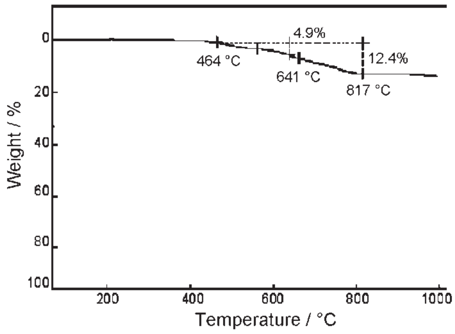


Fig. 2. TG analysis of **4**.

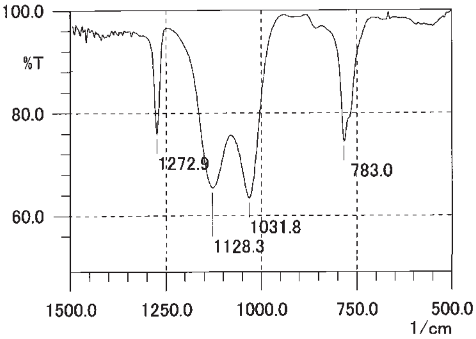


Fig. 3. IR spectrum of **4**.

Table 1. Crystallographic Data for **3**

Formula	$C_{28}H_{32}O_8Si_6$
fw	665.07
Crystal size/mm^3	0.30 × 0.20 × 0.15
Temp/K	113
Crystal system	orthorhombic
Space group	*Pnn*2 (#34)
a/Å	9.11(1)
b/Å	18.68(3)
c/Å	9.74(2)
V/Å^3	1658(4)
Z	2
D_{calc}/g cm^{-3}	1.332
μ(Mo Kα)/cm^{-1}	2.97
θ max/deg	64.7
No. of data collected	19210
No. of unique data	9246
No. of data obsd	3166
No. of variables	193
$R1$ ($I > 3\sigma(I)$)	0.048
R (all data)	0.050
$wR2$ (all data)	0.168
Largest diff peak/hole/eÅ^{-3}	0.47/−0.53
GOF	0.975

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **3**

Si(1)–O(1)	1.635(3)	Si(1)–O(3)	1.628(2)	Si(1)–O(5)	1.654(4)
Si(2)–O(1)	1.648(3)	Si(2)–O(2)	1.637(3)	Si(3)–O(2)	1.607(3)
Si(3)–O(4)	1.615(2)	Si(3)–O(5)	1.626(4)		
O(1)–Si(1)–O(3)	108.6(1)	O(1)–Si(1)–O(5)	107.1(1)	O(3)–Si(1)–O(5)	109.2(2)
O(1)–Si(2)–O(2)	106.7(1)	O(2)–Si(3)–O(4)	109.3(1)	O(2)–Si(3)–O(5)	106.4(1)
O(4)–Si(3)–O(5)	108.4(2)	Si(1)–O(1)–Si(2)	131.3(2)	Si(2)–O(2)–Si(3)	134.1(2)
Si(1*)–O(3)–Si(1)	139.3(3)	Si(3*)–O(4)–Si(3)	140.9(3)	Si(1)–O(5)–Si(3)	131.19(9)

indicating the various structures of their Si–O skeleton. Furthermore, a single peak was observed at −64.5 ppm in solid-state ^{29}Si NMR. This chemical shift is in good accordance with those of laddersiloxanes (e.g., −65 to −67 ppm for tricyclic laddersiloxanes, and −64 to −66 ppm for pentacyclic laddersiloxanes both with isopropyl groups[6]). These results indicate that the structure of **4** is highly regulated, and thus the hydrolysis–dehydration of tetrabromide proceeded in a stereospecific manner.

Summary

We performed the synthesis of functionalized tetramethylcyclotetrasiloxane. The first isomeric pure 2,4,6,8-tetrabromo-2,4,6,8-tetramethylcyclotetrasiloxane was obtained in a facile two-step reaction from chlorosilane. The reaction starting from this potential precursor will be presented in due course.

Experimental

All of the reactions were carried out under an argon or dry nitrogen atmosphere, except when otherwise noted. The solvents used in the reactions were purified and dried according to literature procedures. NMR spectra were obtained on a JEOL α-500 (^{1}H, 500.00 MHz, ^{13}C, 125.65 MHz, ^{29}Si, 99.25 MHz) spectrometer. Solid state MAS NMR was measured by a Bruker DMX-300 wide-bore spectrometer operating at 59.6 MHz. The spinning rate was 3 kHz. EI mass spectrometry was performed with a JEOL JMS-DX302. Infrared spectra were recorded on a SHIMADZU FTIR-8700. Analytical HPLC was performed on a Jasco UV-970 and 880-PU instrument with a Chemcosorb 4.6 mm × 500 mm 5-ODS-UH column.

Preparation of Methylphenylcyclooligosiloxanes (General Procedure). An aqueous KOH solution (2.0 equiv) was added dropwise to $\mathrm{MePhSiCl_2}$ in THF for 30 min. After the mixture was heated to 80 °C for 15 h, THF was removed. The resulting mixture was extracted with ether three times. The combined organic phases were washed with water twice. The organic phase was dried with anhydrous $\mathrm{MgSO_4}$ and concentrated. The residue was separated by bulb-to-bulb distillation, and $\mathrm{(MePhSiO)_3}$, $\mathrm{(MePhSiO)_4}$, and $\mathrm{(MePhSiO)_5}$ were obtained. The ratio of isomers were determined by NMR spectra previously shown in the literature.[13,16] Trimethyltriphenylcyclotrisiloxane (isomeric mixture): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.36 (s), 0.42 (s), 0.50 (s), 7.15–7.60 (m); ^{13}C NMR ($\mathrm{CDCl_3}$) δ −0.43, −0.27, −0.07, 127.7, 127.8, 127.9, 130.0, 130.1, 130.2, 133.1, 133.2, 133.3, 135.8, 136.2, 136.6. MS (70 eV) m/z (%) 408 ($\mathrm{M^+}$, 20), 393 ($\mathrm{M^+}$ − Me, 70). Tetramethyltetraphenylcyclotetrasiloxane (isomeric mixture): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.14 (s), 0.26 (s), 0.29 (s), 0.39 (s), 0.41 (s), 0.49 (s), 7.1–7.7 (m) ppm; ^{13}C NMR ($\mathrm{CDCl_3}$) δ −0.39, −0.34, −0.20, −0.17, −0.08, −0.06, 127.52, 127.63, 127.68, 127.77, 127.80, 127.86, 127.88, 129.66, 129.78, 129.79, 129.88, 129.94, 133.12, 133.28, 133.35, 133.40, 133.44, 136.29, 136.46, 136.68, 136.84, 137.08, 137.23; ^{29}Si NMR ($\mathrm{CDCl_3}$) δ −21.04, −20.99, −20.96. MS (70 eV) m/z (%) 544 ($\mathrm{M^+}$, 15), 529 ($\mathrm{M^+}$ − Me, 100). Pentamethylpentaphenylcyclopentasiloxane (isomeric mixture): ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.03 (s), 0.25 (s), 0.37 (s), 0.40 (s), 0.48 (s), 0.52 (s), 0.57 (s), 7.13–7.7 (m); ^{13}C NMR ($\mathrm{CDCl_3}$) δ −0.57, −0.38, −0.34, −0.28, −0.16, −0.13, −0.07, 0.02, 0.04, 127.57, 127.61, 127.63, 127.69, 127.71, 127.74, 127.77, 129.47, 129.61, 129.64, 129.68, 129.72, 129.73, 129.76, 129.78, 133.22, 133.27, 133.33, 133.36, 133.41, 136.87, 137.05, 137.20, 137.35. MS (70 eV) m/z (%) 680 ($\mathrm{M^+}$, 20), 665 ($\mathrm{M^+}$ − Me, 60).

Synthesis of *cis-trans-cis*-2,4,6,8-Tetraphenyl-2,4,6,8-tetramethylcyclotetrasiloxanes (1). Dichloro(methyl)phenylsilane (200.3 g, 1.05 mol) was treated with water in THF. After refluxing for 10 h, water and ether were added to the mixture, and the organic layer was separated. The aqueous phase was extracted three times with ether. The combined organic phases were dried over anhydrous $\mathrm{MgSO_4}$ and concentrated. *cis-trans-cis* Isomer **1** (16.4 g, 12%) was separated from the mixture by fractional crystallization from methanol at −40 °C for 7 d. Further recrystallization was carried out in ether and methanol to give single crystals of **1** (16.1 g, 11%). **1**: colorless crystals, mp 95–98 °C. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.29 (s, 3H), 7.35 (t, 1H, $J = 6.8$ Hz), 7.40 (q, 2H, $J = 6.8$ Hz), 7.62 (d, 2H, $J = 6.8$ Hz); ^{13}C NMR ($\mathrm{CDCl_3}$) δ −0.21, 127.73, 129.83, 133.34, 136.84; ^{29}Si NMR ($\mathrm{CDCl_3}$) δ −30.80 ppm. MS (70 eV) m/z (%) 544 ($\mathrm{M^+}$, 10), 529 ($\mathrm{M^+}$ − Me, 100).

Dephenylchlorination of *cis-trans-cis*-Tetraphenyl-2,4,6,8-tetramethylcyclotetrasiloxane (1). To a suspension of **1** (2.1 g, 4.0 mmol) and anhydrous aluminum chloride (1.4 g, 11 mmol) in benzene (100 mL) was passed hydrogen chloride for 30 min at room temperature. Then, argon gas was bubbled for 1 h. After filtration of aluminum chloride and the removal of benzene, the product was distilled at 70 °C/0.5 mmHg with a bulb-to-bulb distillation apparatus to give pure tetrachlorotetramethylcyclotetrasiloxane (0.22 g, 15%). The result of the MS and NMR spectra indicated that a mixture of isomer was obtained. Decomposition was observed during further purification, and no other identification was performed. 2,4,6,8-Tetrachloro-2,4,6,8-tetramethylcyclotetrasiloxanes: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 0.42 (s), 0.43 (s), 0.46 (s), 0.47 (s), 0.50 (s), 0.51 (s). MS (70 eV) m/z (%) 363 ($\mathrm{M^+}$ − Me, 100), 343 ($\mathrm{M^+}$ − Cl, 20).

Synthesis of *cis-trans-cis*-2,4,6,8-Tetrabromo-2,4,6,8-tetramethylcyclotetrasiloxanes (2). In the sublimation apparatus, **1** (504 mg, 0.925 mmol) was placed and cooled to −30 °C under Ar. Bromine (778 mg, 4.86 mmol) was then added with vigorous stirring. After 30 min, all volatiles were slowly pumped off (0.4 mmHg), resulting a light-yellow solid. Further purification by sublimation was carried out at 0.2 mmHg with a 75 °C oil bath. The product was collected in a glove box, and pure *cis-trans-cis*-tetrabromotetramethylcyclotetrasiloxane (**2**) (437 mg, 85%) was obtained. *cis-trans-cis*-2,4,6,8-Tetrabromo-2,4,6,8-tetramethylcyclotetrasiloxane (**2**): colorless solid, ^{1}H NMR ($\mathrm{C_6D_6}$) δ 0.39 ppm; ^{13}C NMR ($\mathrm{C_6D_6}$) δ 3.61 ppm; ^{29}Si NMR ($\mathrm{C_6D_6}$) δ −44.01 ppm. MS (70 eV) m/z (%) 556 ($\mathrm{M^+}$, 5), 541 ($\mathrm{M^+}$ − Me, 100).

Synthesis of *anti*-1,3,7,9-Tetramethyl-5,5,11,11-tetraphenyltricyclo[7.3.1.1^{3,7}]hexasiloxane (3). Tetrabromide **2** was generated from **1** (1.2 g, 2.2 mmol) with bromine (0.5 mL, 9.8 mmol) in a similar manner. Then, **2** was dissolved in pyridine (20 mL), and diphenylsilanediol (0.90 g, 4.2 mmol) in $\mathrm{Et_2O}$ (30 mL) was added. After 12 h, the solution was subjected to a work-up. The crystals of *anti*-tricyclic laddersiloxane (**3**, 0.94 g, 65%) were obtained when hexane and $\mathrm{Et_2O}$ were added to the mixture. *anti*-1,3,7,9-Tetramethyl-5,5,11,11-tetraphenyltricyclo[7.3.1.1^{3,7}]hexasiloxane (**3**): colorless crystals; mp 193–194 °C. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.18 (s, 12H), 7.31–7.69 (m, 20H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ −4.24, 127.62, 127.91, 130.38, 130.46, 133.98, 134.27; ^{29}Si NMR ($\mathrm{CDCl_3}$) δ −51.91, −34.71. MS (70 eV) m/z (%) 664 ($\mathrm{M^+}$, 5), 649 ($\mathrm{M^+}$ − Me, 10), 597 ($\mathrm{M^+}$ − Ph, 100). IR (KBr): 507, 596, 619, 721, 742, 775, 841, 926, 995, 1120, 1159, 1168, 1193, 1271, 1429, 1593, 1780, 1832, 1900, 1967, 2854, 3074 cm^{-1}; Found: C, 50.47; H, 5.00%. Calcd for $\mathrm{C_{28}H_{32}O_8Si_6}$: C, 50.57; H, 4.85%.

X-ray Crystallography. Intensity data were collected on a

Rigaku RAXIS-IV++ diffractometer with Mo Kα radiation ($\lambda = 0.71070$ Å). An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. All calculations were performed using the CrystalStructure software of Molecular Structure Corporation. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-262988 for compound **3**. Copies of the data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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