Synthesis of laddersiloxanes by novel stereocontrolled approach

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Abstract

Three new pentacyclic laddersiloxanes were prepared by a new method utilizing single stereoisomer of disiloxanediol as a growing unit. Thus, one diastereomer of disiloxanediol, (RS)–[i-PrPhSi(OH)]$_2$O was isolated and treated with tetrachlorocyclotetrasiloxane, resulting in the formation of tricyclic laddersiloxanes with cis-Ph groups at terminals. All of the obtained isomers could be transformed into pentacyclic laddersiloxanes by dephenylchlorination followed by the reaction with (RS)–[i-PrPhSi(OH)]$_2$O. The structures of new tricyclic and pentacyclic laddersiloxanes were determined by X-ray crystallography. The thermogravity properties of laddersiloxanes depending on the molecular weight and structures were summarized.
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Keywords: Cyclic silanol; Silsesquioxane; Crystal structure; Laddersiloxane; Diastereomer

1. Introduction

Recently, much effort has been directed toward the syntheses of ladder-type polysilsesquioxanes because of their expected high thermal stability [1]. Although ladder skeleton have been claimed to generate under certain conditions [2], their structures are not universally accepted [3]. Thus, the construction of polysilsesquioxanes having true ladder structures represents an important synthetic goal. As a part of our program toward the synthesis of laddersiloxanes (ladder silsesquioxanes with defined structure) [4], we have recently reported the synthesis of pentacyclic laddersiloxane starting from cyclic tetraol **1** [5] and dichlorosiloxane (**2**) (Scheme 1) [4a]. As shown in this Scheme, it is theoretically possible to build up rings by repeating last two steps. Because of the generation of stereoisomers, the yield of each step must be optimized in order to construct longer laddersiloxanes. In the synthesis of pentacyclic laddersiloxanes, tricyclic laddersiloxanes were obtained in a good yield (85%), however, pentacyclic **3** was not obtained in a satisfactory yield (47%, mixture of five stereoisomers). This can be explained by the generation of disadaptive isomers. As

seen in Scheme 2, when a diastereomeric mixture of dichlorodisiloxane **2** is used, obtained laddersiloxanes possess *cis* or *trans* conformation at the terminals. For the sake of homologation, laddersiloxanes must possess *cis*-phenyl groups at both terminals [6]; however, the ratio of this isomer is statistically only 25% (50% at each terminal). This is the reason why the yields of the laddersiloxanes decreased by going to higher analogues. Our strategy to overcome this problem is as follows. Out of three diastereomers of dichlorosiloxanes, only *RS*-form satisfies *cis*-requisite. When this isomer is separated and utilized in the reaction, only laddersiloxanes capable of affording ring homologation can be obtained.

2. Results and discussion

In the former synthesis, we used dichlorosiloxane **2** as a growing unit (Scheme 3). However, separation of diastereomers of **2** is seemingly difficult because dichloride **2** is liquid and relatively unstable towards moisture. Then we examined the dihydrosiloxane **4**, which can be transformed to **2**. Unfortunately, the attempt for the separation of *RS*- and *RR*/*SS*-isomers of **4** met with failure despite a considerable attempts. We then focused on diol **5**. Fortunately in this case, we could separate diastereomers with recrystallization

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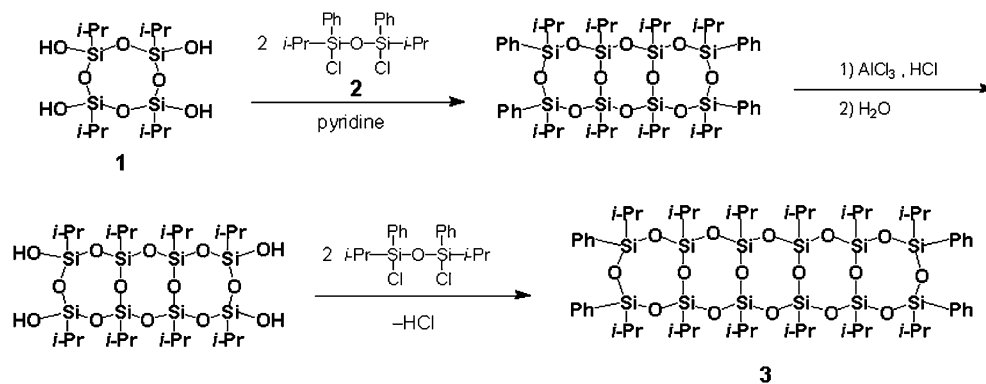
Scheme 1. Synthesis of pentacyclic laddersiloxane.
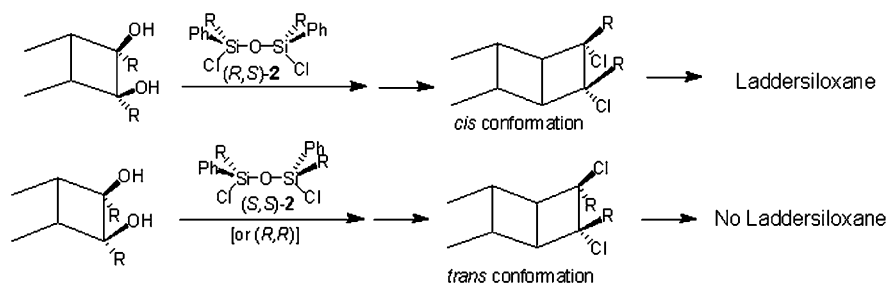
Scheme 2. *Cis*-requisite of laddersiloxane.
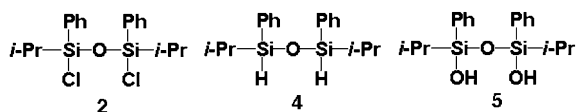
Scheme 3.

or HPLC separation [7]. As illustrated in Scheme 4, repeating recrystallization from hexane afforded *RS*-isomer **5a** in gram quantities. Furthermore, separation with HPLC was also applied for complete separation although the amount

was limited. We combined these two separations, and obtained pure **5a** for the next step. The structure of **5a** was established on the basis of spectroscopic data, and further corroborated by X-ray crystallography. Crystallographic parameters are summarized in Table 1.

With desired pure diastereomer in hand, we first investigated the preparation of tricyclic laddersiloxanes. As shown in Scheme 5, tetrachlorocyclotetrasiloxane, generated from all-*cis*-[*i*-PrPhSiO]₄, was treated with **5a**, and three stereoisomers of tricyclic laddersiloxanes **6a–6c** were
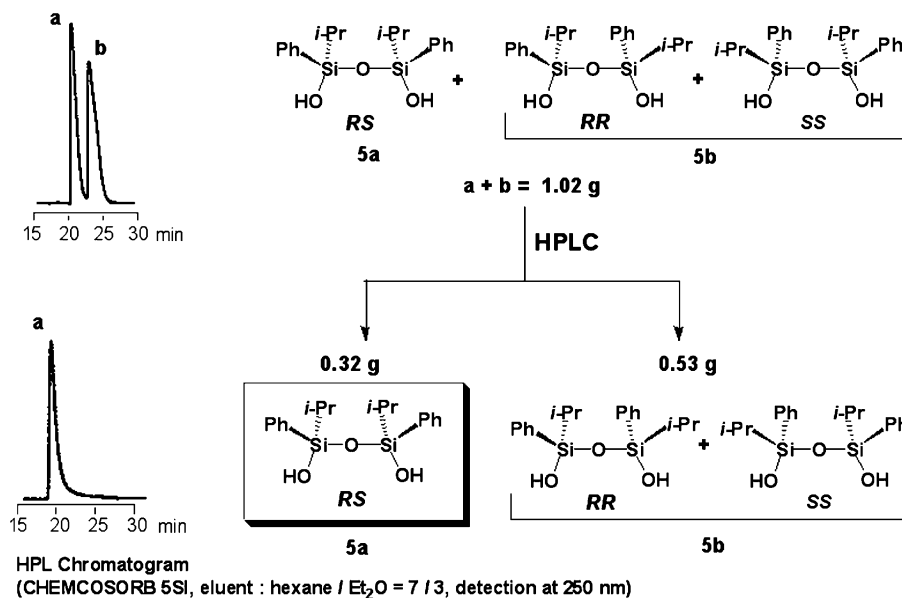
Scheme 4. Separation of diastereomers.

Table 1
Crystallographic data for **5a** and **6a**

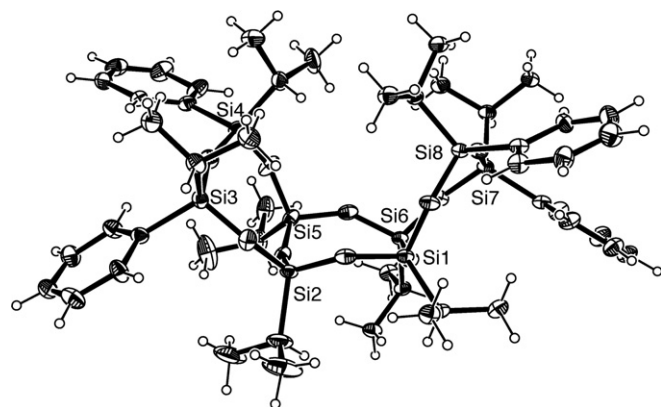|	**5a**	**6a**
Formula	$C_{18}H_{26}Si_2O_3$	$C_{48}H_{76}Si_8O_{10}$
Molecular weight	346.57	1037.81
Crystal description	Colorless platelet	Colorless prism
Crystal size (mm)	$0.30 \times 0.30 \times 0.10$	$0.50 \times 0.50 \times 0.50$
Crystal system	Monoclinic	Orthorhombic
a (Å)	7.787(5)	30.926(1)
b (Å)	21.80(1)	15.6122(7)
c (Å)	12.602(8)	11.9411(5)
β (°)	111.59(1)	
V (Å^3)	1989(2)	5765.4(4)
Space group	$P2_1/a$ (#14)	$Pna2_1$ (#33)
Z	4	4
D_{calc} (g cm^{-1})	1.157	1.196
μ (Mo Kα) (cm^{-1})	1.89	2.36
Number of reflections measured	20 162	27 182
Number of independent reflections (R_{int})	5966(0.156)	11 079(0.061)
Number of observed reflections ($I > 2.00\sigma(I)$)	4999	11 079
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$
Number of parameters	209	596
Reflections/parameters ratio	23.92	18.59
R_1 ($I > 2.00\sigma(I)$)	0.094	0.068
wR_2 (all reflections)	0.115	0.240
S	0.85	2.02
$(\Delta/\sigma)_{max}$	0.00	0.06
$(\Delta\rho)_{max}$ (e Å^{-3})	2.69	0.85
$(\Delta\rho)_{min}$ (e Å^{-3})	−1.41	−0.72

Fig. 1. The molecular structure and numbering of **6a** with 30% probability thermal ellipsoids; selected bond lengths (Å) and angles (°): Si(1)–O(8) 1.619(4), Si(1)–O(9) 1.618(4), Si(1)–O(1) 1.615(4), Si(6)–O(9) 1.633(4), Si(6)–O(6) 1.634(4), Si(6)–O(5) 1.630(4), Si(7)–O(6) 1.616(4), Si(7)–O(7) 1.629(4), Si(2)–O(10) 1.626(4), Si(2)–O(1) 1.628(4), Si(2)–O(2) 1.621(4), Si(8)–O(8) 1.630(4), Si(8)–O(7) 1.623(4), Si(3)–O(3) 1.625(4), Si(3)–O(2) 1.630(4), Si(4)–O(4) 1.627(4), Si(4)–O(3) 1.620(4), Si(5)–O(10) 1.620(5), Si(5)–O(4) 1.610(5), Si(5)–O(5) 1.609(5); O(8)–Si(1) O(9) 109.8(2), O(8)–Si(1)–O(1) 107.8(2), O(9)–Si(1)–O(1) 110.0(2), O(9)–Si(6)–O(6) 108.2(2), O(6)–Si(6)–O(5) 107.9(2), O(6)–Si(7)–O(7) 110.8(2), O(10)–Si(2) –O(1) 110.6(2), O(10)–Si(2)–O(2) 109.3(2), O(1)–Si(2)–O(2) 106.8(2), O(8)–Si(8)–O(7) 110.9(2), O(3)–Si(3)–O(2) 110.6(2), O(4)–Si(4)–O(3) 110.2(2), O(10)–Si(5)–O(4) 110.1(2), O(10)–Si(5)–O(5) 109.0(2), O(4)–Si(5)–O(5) 108.5(3), Si(1)–O(8)–Si(8) 150.6(3), Si(2)–O(10)–Si(5) 151.7(3), Si(1)–O(9)–Si(6) 151.3(3), Si(4)–O(4)–Si(5) 150.9(3), Si(1)–O(1)–Si(2) 145.5(3).

obtained. The yields were 3% (**6a**), 10% (**6b**), and 1% (**6c**). Isomers **6b** and **6c** have previously been separated and structurally determined by X-ray analyses [4a]; we identified them by comparing their spectra. Compound **6a** is an unknown isomer, thus crystallographic analysis was performed, and structure was established. In Fig. 1, the molecular structure is shown, and crystallographic parameters are summarized in Table 1. Although the yields were not optimized yet [8], generated laddersiloxanes possesses *cis*-Ph groups in the terminal, and number of generated isomers was diminished (six isomers when mixture of diastereomers were used) [4a]. It should also be noted that stereostructure (all-*cis* of starting compound) was main-

tained throughout the reactions and only laddersiloxanes with *syn*-configuration in the center rings were obtained. This is a good contrast to the case of oligosilanes, since dearylchlorination of oligosilanes were reported to give mixture of stereoisomers regardless whether *cis* or *trans* isomer was employed [9] (see Table 2)

We then prepared pentacyclic laddersiloxanes. Because of the limited amount of the tricyclic tetrachlorides, we used isomeric mixture of **6a**–**6c**. Dephenylchlorination followed by the reaction with **5a** again proceeded smoothly, affording three pentacyclic laddersiloxanes **7a**–**7c** in 4%, 8%, and 14% yields, respectively [10]. The HPL chromatogram at the end of the reaction clearly indicated the generation of only three isomers. It is noteworthy that all the
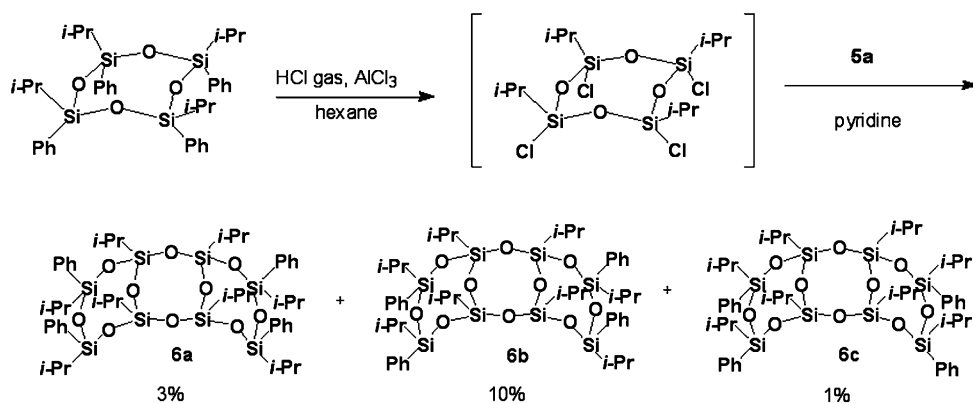
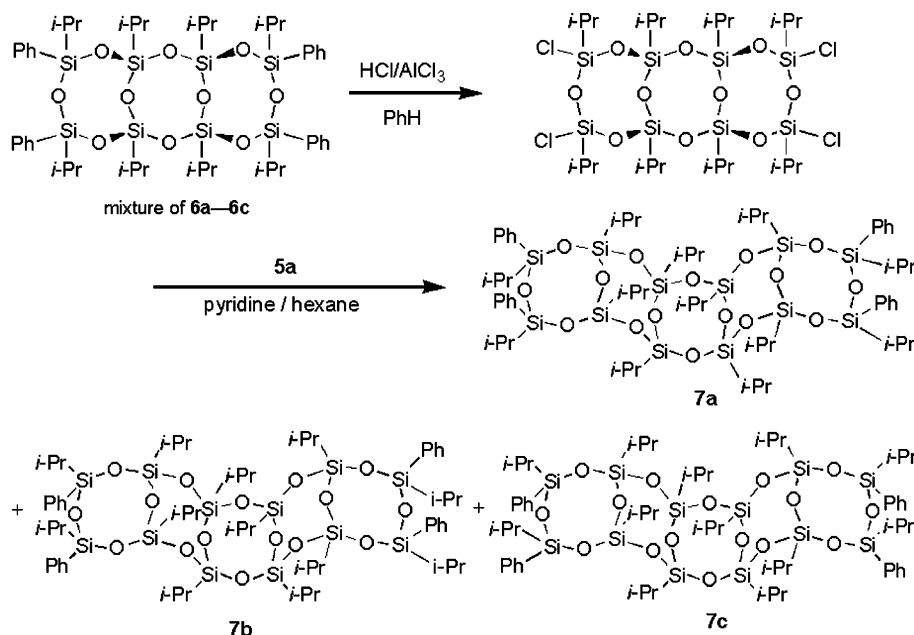Scheme 5. Preparation of tricyclic laddersiloxanes.

Table 2
Thermal properties of laddersiloxanes

Compounds	Td$_5$ (°C)	end of sublimation (°C)
(*i*-Pr$_2$SiO)$_4$	202	345
Tricyclic Laddersiloxane (in Ref. [4a])	253	390
Pentacyclic Laddersiloxane (in Ref. [4a])	287	423
7 (isomeric mixture)	340	428

compounds possess *anti–syn–anti* framework, and those could be generated from only **6a**. Presumably, *syn–syn* framework causes steric congestion, thus no other frameworks were obtained. The stereochemistry of **7a**–**7c** was determined by X-ray crystallography (see Scheme 6).

Higher thermal stability was expected for laddersiloxanes especially with longer framework. Table 1 summarizes the result of thermogravity analysis; the result of thermogravity analysis is shown in Fig. 2. Pentacyclic laddersiloxane **7** started subliming at 340 °C, and lost its total weight at 428 °C. It showed higher Td$_5$ (5% weight decrease) and sublimation temperature than any laddersiloxanes previously reported. In addition, the thermal stability increased by adding rings to laddersiloxanes, showing their advantage over existing chain polysiloxanes. Interestingly, **7** showed more stability than previously reported *anti–syn–syn* pentacyclic laddersiloxane [4a], which is stereoisomer of **7**. It should be noted that the thermal properties depends on not only the molecular weights, but structure of the framework.

In summary, heptacyclic laddersiloxane was prepared for the first time by new synthetic method utilizing stereo-controlled procedure. Further investigation towards the synthesis of laddersiloxanes with various frameworks is now due course.
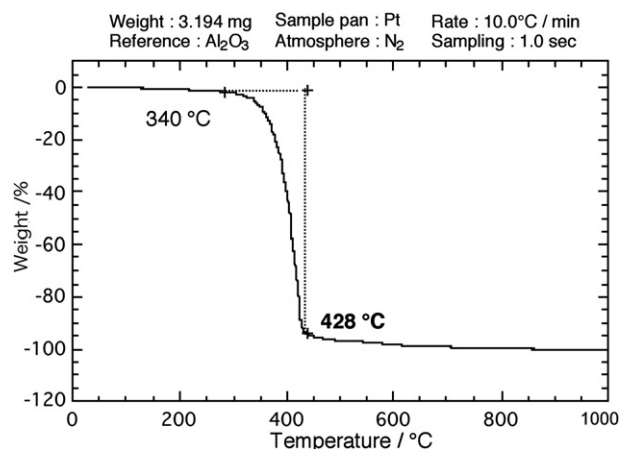

Fig. 2. Thermogravity analysis of **7**.

3. Experimental

3.1. General remarks

GLC analysis were performed on a SHIMADZU GC-8A model using a 3.5 mm × 1000 mm glass column packed with 10% silicon KF-96 on 60–80 mesh Celite 545sk. HPLC analysis was carried out a JASCO 880-PU with a JASCO CHEMICOSORB 4.6 mm × 250 mm 5-ODS-H column detected by JASCO 875-UV. Preparative recycle-type HPLC was carried out using JAI LC-908 with Chemco 20 mm × 250 mm 7-ODS column. FT-NMR spectra were obtained on JEOL Model α-500 and λ-500 (¹H at 500.00 MHz, ¹³C at 125.65 MHz, and ²⁹Si at 99.25 MHz). Chemical shifts were reported as δ unit (ppm) relative to SiMe$_4$, and residual solvents peaks were used for standards. For ²⁹Si NMR, SiMe$_4$ was used as an external stan-

Scheme 6. Preparation of pentacyclic laddersiloxanes.

dard. EI mass spectrometry was performed with a JEOL JMS-DX302 and JMS-700. Infrared spectra were measured with a SHIMADZU FTIR-8700.

3.2. Synthesis of 1,3-dihydroxy-1,3-diisopropyl-1,3-diphenyldisiloxane (5)

Saturated aqueous $NaHCO_3$ solution was added dropwise to vigorously stirred 1,3-dichloro-1,3-diisopropyl-1,3-diphenyldisiloxane (15.1 g, 40.0 mmol) in ether (60 mL) for 20 min at 0 °C. Then, the reaction mixture was stirred for 20 min at 0 °C and was poured into water and the organic layer was extracted with ether. The combined organic phase was washed with water. The organic phase was dried over anhydrous magnesium sulfate. Removing the solvent gave 1,3-dihydroxy-1,3-diisopropyl-1,3-diphenyldisiloxane ([i-PrPhSi(OH)]$_2$O) (5) (12.49 g, 90%). Most proportion of *RS*-isomer contained was filtered off and recrystallized from hexane. *RS*-1,3-dihydroxy-1,3-diisopropyl-1,3-diphenyldisiloxane (5a): colorless solid, mp 101–102 °C; ^{1}H NMR (DMSO-d_6) δ 0.87–0.88 (m, 14H), 6.69 (s, 2H), 7.32–7.62 (m, 10H) ppm; ^{13}C NMR (DMSO-d_6) δ 14.26, 17.06, 127.56, 129.52, 134.22, 136.48 ppm; ^{29}Si NMR (DMSO-d_6) δ-28.92 ppm; MS (70 eV) m/z (%) 303 (M$^+$−i-Pr, 100), 275 (4), 225 (10), 183 (13); IR (NaCl) v 3304, 3069, 3053, 3024, 3013, 2924, 2891, 2864, 1960, 1888, 1827, 1589, 1460, 1429, 1383, 1366, 1327, 1306, 1246, 1123, 1059, 1028, 988, 920, 889, 851, 739, 702, 642 cm^{-1}.

3.2.1. Preparation of 1,3,5,7-tetrachloro-1,3,5,7-tetraisopropyltetracyclosiloxane

To a solution of all-*cis*-1,3,5,7-tetraisopropyl-1,3,5,7-tetraphenylcyclotetrasiloxane (0.37 g, 0.56 mmol) and anhydrous aluminum chloride (0.15 g, 1.13 mmol) in 15 mL of benzene was passed hydrogen chloride for 30 min at room temperature. Analysis by gas chromatography showed the formation of 1,3,5,7-tetrachloro-1,3,5,7-tetraisopropylcyclotetrasiloxane, then argon gas was bubbled. After filtration of aluminum chloride, and removal of benzene, the product was purified by Kugelrohr distillation to give analytically pure 3 (0.226 g, 83%). Identification was made by mass spectrum; MS (70 eV) m/z (%) 447 (M$^+$+2−i-Pr, 100), 445 (M$^+$−i-Pr, 68), 363 (18).

3.2.2. Synthesis of syn-1,3,5,7,9,11,13,15-octaisopropyl-5,7,13,15-tetraphenyltricyclo[9.5.1.1^{3,9}]octasiloxanes (6)

A solution of [i-PrPhSi(OH)]$_2$O (5b) [*RS* (70% HPLC purity) 0.28 g, 0.80 mmol] in pyridine (0.6 mL) was added dropwise to a solution of tetrachlorocyclotetrasiloxane (0.19 g, 0.39 mmol) in hexane (0.5 mL) for 3 min at 0 °C. The mixture was stirred for 14 h. The reaction mixture was added to saturated aqueous NH_4Cl and hexane, and separated. The separated aqueous phase was extracted with hexane. The organic phase was washed with saturated aqueous NH_4Cl, then dried over anhydrous magnesium sulfate, and concentrated. The crude product was sepa-

rated by preparative TLC (eluent: hexane/Et_2O = 9/1) followed by the separation with recycle-type HPLC (eluent: MeOH/THF = 8/2) to give mainly three isomers of tricyclic laddersiloxanes (6a–6c). The yields were 3%, 10%, 1%, respectively. Compound 6a was structurally determined the by X-ray crystallography. The other compounds (6b and 6c) were identified by the comparison with authentic sample. *exo*-all-*cis*–*syn* (6a): colorless solid, mp 181–182 °C; ^{1}H NMR (CDCl$_3$) δ 0.620–1.273 (m, 56), 7.198–7.533 (m, 20) ppm; ^{13}C NMR (CDCl$_3$) δ 12.30, 14.68, 16.66, 16.76, 16.96, 127.37, 129.62, 134.23, 134.36 ppm; ^{29}Si NMR (CDCl$_3$) δ-65.94, −33.17 ppm; MS (EI, 70 eV) m/z (%) 993 (M$^+$−i-Pr, 28), 915 (3), 829 (6), 725 (8), 691 (7), 225 (100), 183 (23); IR (NaCl) v 3071, 3051, 2947, 2895, 2868, 1464, 1429, 1385, 1258, 1119, 1094, 1047, 993, 320, 887, 721, 700 cm^{-1}.

3.2.3. Chlorination of tricyclic laddersiloxanes (6)

Chlorination of tricyclic laddersiloxanes was performed according to our reported method [4a].

3.2.4. Synthesis of 1,3,5,7,9,11,13,15,17,19,21,23-dodecaisopropyl-9,11,21,23-tetraphenylpentacyclo-[17.5.1.1^{3,17}.1^{5,15}.1^{7,13}]dodecasiloxanes (7)

A solution of [i-PrPhSi(OH)]$_2$O (5b) [*RS* (>99% HPLC purity) 0.20 g, 0.59 mmol] in pyridine (2.5 mL) was added dropwise to a solution of tetrachlorotricyclic laddersiloxane (0.26 g, 0.29 mmol) in hexane (1 mL) for 25 min at room temperature. The mixture was stirred for 16 h. The reaction mixture was added to saturated aqueous NH_4Cl and hexane, and separated. The separated aqueous phase was extracted with hexane. The organic phase was washed with saturated aqueous NH_4Cl, then dried over anhydrous magnesium sulfate, and concentrated. The crude product was separated by dry column chromatography (eluent: hexane) followed by the separation with recycle-type HPLC (eluent: MeOH/THF = 7/3) to give mainly three isomers of pentacyclic laddersiloxanes (7a–7c), and the yields were 4%, 8%, and, 14% respectively. 7a: colorless solid, mp 195–197 °C; ^{1}H NMR (CDCl$_3$) δ 0.71–1.10 (m, 84H), 7.18–7.50 (m, 20H) ppm; ^{13}C NMR (CDCl$_3$) δ 11.85, 12.37, 14.48, 16.31, 16.62, 16.68, 16.84, 127.38, 129.62, 134.09, 134.58 ppm; ^{29}Si NMR (CDCl$_3$) δ −66.01, −33.67 ppm; MS (EI, 70 eV) m/z (%) 1375 (M$^+$−i-Pr, 100); IR (NaCl) v 3071, 3051, 2947, 2895, 2868, 1466, 1429, 1385, 1364, 1364, 1259, 1165, 1121, 1069, 1042, 995, 920, 887, 770, 700 cm^{-1}. 7b: colorless solid, mp 179–180 °C; ^{1}H NMR (CDCl$_3$) δ 0.30–1.14 (m, 84H), 7.17–7.50 (m, 20H) ppm; ^{13}C NMR (CDCl$_3$) δ 11.69, 11.91, 12.12, 12.31, 14.49, 14.70, 16.27, 16.39, 16.43, 16.52, 16.68, 16.81, 16.84, 16.87, 127.28, 127.39, 129.50, 129.61, 134.11, 134.17 ppm; ^{29}Si NMR (CDCl$_3$) δ −66.23, −66.18, −65.86, −64.87, −34.44, −33.60 ppm; MS (EI, 70 eV) m/z (%) 1375 (M$^+$−i-Pr, 100); IR (NaCl) v 3071, 3051, 2947, 2895, 2868, 1466, 1429, 1385, 1366, 1259, 1121, 1042, 995, 920, 887, 770, 700 cm^{-1}. 7c: colorless solid, mp 222–223 °C; ^{1}H NMR (CDCl$_3$) δ 0.24–1.25 (m, 84H), 7.17 (t, 8H,

$J = 7.3$ Hz), 7.27 (tt, 4H, $J = 7.3$ Hz,1.5 Hz), 7.47 (dd, 8H, $J = 7.3$ Hz, 1.5 Hz) ppm.; ^{13}C NMR (CDCl$_3$) δ 11.62, 12.15, 14.71, 16.39, 16.47, 16.79, 16.93, 127.26, 129.41, 129.47, 134.14 ppm; ^{29}Si NMR (CDCl$_3$) δ -66.46, -65.88, -34.44 ppm; MS (EI, 70 eV) m/z (%) 1375 (M^+-i-Pr, 100); IR (NaCl) v 3071, 3049, 2945, 2930, 2866, 1464, 1429, 1385, 1364, 1259, 1121, 1096, 1068, 1047, 997, 920, 887, 770, 698 cm^{-1}.

3.2.5. X-ray crystallography (General procedure)

A colorless prism crystal was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS–IV++ imaging plate area detector with graphite monochromated Mo Kα radiation. Indexing was performed from 4 oscillations that were exposed for 60 seconds. The data were collected at a temperature of -160 °C to a maximum 2θ value of 64.7°. A sweep of data was done using ϕ oscillations from 7.0 to 154.0° in 0.5° steps. The exposure rate was 360.0 [s/°]. The detector swing angle was 1.10°. The crystal-to-detector distance was 100.40 mm. Readout was performed in the 0.100 mm pixel mode. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated and refined using the riding model. The final cycle of full-matrix least squares refinement on F^2 was converged. All calculations were performed using the CrystalStructure software of Rigaku/MSC.

Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures of compounds **5a** and **6a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC–605456 for **5a**, and 605457 for **6a**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.068.

References

[1] R.H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, Chem. Rev. 95 (1995) 1409–1430.
[2] (a) E.–C. Lee, Y. Kimura, Polym. J. 29 (1997) 678–684;
    (b) E.–C. Lee, Y. Kimura, Polym. J. 30 (1998) 234–242;
    (c) W.–Y. Chen, Y. Lin, K.P. Pramoda, K.X. Ma, T.S. Shung, J. Polym. Sci. B: Polym. Phys. 38 (2000) 138–147;
    (d) S. Hayashida, S. Imamura, J. Polym. Sci. A: Polym. Chem. 33 (1995) 55–62.
[3] (a) C.L. Frye, J.M. Klosowski, J. Am. Chem. Soc. 93 (1971) 4599–4601;
    (b) M.A. Brook, in: Silicon in Organic, Organometallic, and Polymer Chemistry, John Willey & Sons, New York, 2000, p. 322.
[4] (a) M. Unno, A. Suto, H. Matsumoto, J. Am. Chem. Soc. 124 (2002) 1475–1574;
    (b) M. Unno, R. Tanaka, S. Tanaka, T. Takeuchi, S. Kyushin, H. Matsumoto, Organometallics 24 (2005) 765–768;
    (c) M. Unno, S. Chang, H. Matsumoto, Bull. Chem. Soc. Jpn. 78 (2005) 1105–1109;
    (d) M. Unno, A. Suto, K. Takada, H. Matsumoto, Bull. Chem. Soc. Jpn. 73 (2000) 215–220;
    (e) M. Unno, B.A. Shamsul, M. Arai, K. Takada, R. Tanaka, H. Matsumoto, Appl. Organomet. Chem. 13 (1999) 1–8.
[5] (a) M. Unno, Y. Kawaguchi, Y. Kishimoto, H. Matsumoto, J. Am. Chem. Soc. 127 (2005) 2256–2263;
    (b) M. Unno, K. Takada, H. Matsumoto, Chem. Lett. (2000) 242–243;
    (c) M. Unno, K. Takada, H. Matsumoto, Chem. Lett. (1998) 489–490.
[6] The result of MM2 calculation showed that *trans*-fused bicyclic laddersiloxane was substantially less stable than *cis*-fused ones (due to increasing bond stretch and bent energy). Additionally, no *trans*-fused laddersiloxanes have been obtained in our previous experiments.
[7] (a) Separation of the stereoisomers of disiloxanediol ((PhMe(OH)-Si)$_2$O) appeared in the literature: A.W.P. Jarvie, A. Holt, J. Hickton, J. Chem. Soc. (B) (1969) 978–979;
    (b) M. Oishi, Y. Kawakami, Org. Lett. 1 (1999) 549–551.
[8] The HPLC analysis at the end of the reaction indicated the generation of incompletely condensed siloxanes. Presumably, the steric shielding of cyclic tetrachloride causes a lower yield. Although the *R*-value of the crystallographic analysis is not satisfactory low, the stereostructure was unequivocally established.
[9] K. Tamao, M. Kumada, M. Ishikawa, J. Organomet. Chem. 31 (1971) 17–34.
[10] Because of the poor crystallinity, the X-ray analysis of **7a**–**7c** have not been fully accomplished. However, the structure of frameworks and positions of substituents were unequivocally determined.