Organometallics **1999,** *18,* 2326−2330

1,1,3,3,5,5,7,7-Octaphenyl-1,3,5,7-tetrasiloxane-1,7-diol and Its Organotin Derivatives. Model Compounds for Diphenylsiloxane Polymer†

Jens Beckmann,‡ Klaus Jurkschat,*,‡ Dirk Müller,§ Stephanie Rabe,‡ and
Markus Schürmann‡

*Lehrstuhl für Anorganische Chemie II, Fachbereich Chemie der Universität Dortmund,
D-44221 Dortmund, Germany, and Institut für Angewandte Chemie,
Rudower Chaussee 5, D-12484 Berlin, Germany*

Received February 17, 1999

The hydrolysis of the spirotitanasiloxane $Ti[(OSiPh_2)_4O]_2$ provides 1,1,3,3,5,5,7,7-octaphenyl-1,3,5,7-tetrasiloxane-1,7-diol, $H(OSiPh_2)_4OH$ (**1**), in high yield. The reaction of **1** with tricyclohexyltin hydroxide, *cyclo*-Hex_3SnOH, and di-*tert*-butyltin oxide, *cyclo*-(*t*-$Bu_2SnO)_3$, respectively, gives 1,1,3,3,5,5,7,7-octaphenyl-1,7-tricyclohexylstannyl-1,3,5,7-tetrasiloxane, (*cyclo*-$Hex_3SnOSiPh_2OSiPh_2)_2O$ (**2**), and 1,1-di-*tert-(*butyl-3,5,7,9-octaphenyl-2,4,6,8,10-pentaoxa-,3,5,7,9-tetrasila-1-stannacyclododecane, *cyclo*-*t*-$Bu_2Sn(OSiPh_2OSiPh_2)_2O$ (**3**). The molecular structures of **1** and **2** were determined by X-ray diffraction. In both compounds the central Si−O−Si angle amounts to 180°. Remarkably, no hydrogen bonding is observed for **1**.

Introduction

The hydrolysis of organochlorosilanes gives either organosiloxanes or organosil(ox)anols. Which of these products is obtained depends on the reaction conditions applied and/or on the steric bulk of the organic substituents.[1]

The hydrolysis of diphenyldichlorosilane Ph_2SiCl_2 leads to oligomeric diphenylsiloxanes of the type *cyclo*-$(Ph_2SiO)_n$ ($n = 3, 4$)[2] or diphenylsil(ox)anols of the type $HO(Ph_2SiO)_nH$ ($n = 1-3$).[2,3] The hydrolysis of *cyclo*-$(Ph_2SiO)_4$ was reported to give $HO(Ph_2SiO)_4H$ in rather low yield.[2c]

Polymeric diphenylsiloxane, hereafter referred to as PDPhS, is prepared either by ring-opening polymerization (ROP) under nonequilibrium conditions of the six-membered ring $(Ph_2SiO)_3$[4] or by condensation of oligodiphenylsiloxanols with diorganochlorosilanes.[2j] Because of their excellent thermal and chemical stability, there is a variety of applications for poly(dimethyl)-, poly(methyl/trifluoropropyl)-, and poly(methyl/phenyl)siloxane.[5] In contrast to these polysiloxanes which show a high flexibility, the steric hindrance of the phenyl groups in poly(diphenyl)siloxane causes a certain ridgidity which is responsible for the high crystallinity of this polymer. Above its melting point of 260 °C a transition into a mesomorphic liquid crystalline phase takes place.[6] The major advantage over other liquid crystals is that PDPhS can be obtained with almost any chain length by using anionic polymerization techniques.[5b] However, the conformational analysis of PDPhS was the subject of controversal discussions,[7] and consequently, molecular structures of any model compounds resembling PDPhS are welcome.[8]

For some time we have been interested in the chemistry of stannasiloxanes, and recently we reported [O*t*-$Bu_2SnOSiPh_2OSiPh_2O]_n$, which is the first well-defined polystannasiloxane in the solid state.[9] However, in solution this polymer reversibly turns into the corresponding six-membered stannasiloxane ring *cyclo*-(*t*-Bu_2-

---

† Dedicated to Professor Friedo Huber on the occasion of his 70th birthday. This paper contains part of the intended Ph.D. Thesis of Stephanie Rabe.

‡ Dortmund University.

§ Institut für Angewandte Chemie.

(1) *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: Berlin, 1958; Part 15C.

(2) (a) Dilthey, W. *Ber.* **1905**, 4132. (b) Kipping, F. S. *J. Chem. Soc.* **1912**, *101*, 2125. (c) Kipping, F. S.; Robinson, R. *J. Chem. Soc.* **1914**, *105*, 484. (d) Kipping, F. S. *J. Chem. Soc.* **1927**, 2728. (e) Burkhard, C. A. *J. Am. Chem. Soc.* **1945**, *67*, 2173. (f) Hyde, J. F.; Frevel, L. K.; Nutting, H. S.; Petrie, P. S.; Purcel, M. A. *J. Am. Chem. Soc.* **1947**, *69*, 488. (g) Young, C. W.; Servais, P. C.; Currie, C. C.; Hunter, M. J. *J. Am. Chem. Soc.* **1948**, *70*, 3758. (h) Braga, D.; Zanotti, G. *Acta Crystallogr.* **1980**, *B36*, 950. (i) Tomlins, P. E.; Lydon, J. E.; Akrogg, D.; Sheldrick, B. *Acta Crystallogr.* **1985**, *C41*, 292. (j) Harkness, B. H.; Tachikawa, M. *Chem. Mater.* **1998**, *10*, 1706.

(3) (a) Fawcett, J. K.; Camerman, N.; Camerman, A. *Can. J. Chem.* **1977**, *55*, 3631. (b) Párkányi, L.; Bocelli, G. *Cryst. Struct. Commun.* **1978**, *7*, 335. (c) Hossain, M. A., Hursthouse, M. B. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 227. (d) Behbehani, H.; Brisdon, B. J.; Mahon, M. F.; Molloy, K. C. *J. Organomet. Chem.* **1993**, *463*, 41.

(4) (a) Buzin, M. I.; Gerasimov, M. V.; Obolonkova, E. S.; Papkov, V. S. *J. Polym. Sci. Part A, Polym. Chem.* **1997**, *35*, 1973. (b) Harkness, B. H.; Tachikawa, M.; Yue, H.; Mita, I. *Chem. Mater.* **1998**, *10*, 1700.

(5) (a) Lee, M. K.; Meier, D. J. *Polymer* **1993**, *34*, 4882. (b) Lee, M. K.; Meier, D. J. *Polymer* **1993**, *35*, 3282. (c) Chou, C.; Yang, M. H. *J. Therm. Anal.* **1993**, *40*, 657.

(6) (a) Harkness, B.; Tachikawa, M.; Mita, I. *Macromolecules* **1995**, *28*, 1323. (b) Harkness, B. R.; Tachikawa, M.; Mita, I. *Macromolecules* **1995**, *28*, 8136. (c) Li, L. J.; Yang, M. H. *Polymer* **1998**, *39*, 689.

(7) (a) Dubchak, I. L.; Babchinister, T. M.; Kazaryan, L. G.; Tartakovskaya, L. M.; Vasilenko, N. G.; Zhdanov, A. A.; Korshak, V. V. *Polym. Sci. USSR (Engl. Transl.)* **1989**, *31*, 70. (b) Grigoras, S.; Qian, C.; Crowder, C.; Harkness, B.; Mita, I. *Macromolecules* **1995**, *28*, 7370. (c) Papkov, V. S., Gerasimov, M. V.; Buzin, M. I.; Il'ina, M. N.; Kazaryan, L. G. *Polym. Sci. Ser. A* **1996**, *38*, 1097.

(8) Brisdon, B. J.; Mahon, M. F.; Molloy, K. C.; Schofield, P. J. *J. Organomet. Chem.* **1994**, *465*, 145.

(9) (a) Beckmann, J.; Jurkschat, K.; Schollmeyer, D.; Schürmann, M. *J. Organomet. Chem.* **1997**, *543*, 229. (b) Beckmann, J.; Mahieu, B.; Nigge, W.; Schollmeyer, D.; Schürmann, M.; Jurkschat, K. *Organometallics* **1998**, *17*, 5697.

10.1021/om990107z CCC: $18.00
Publication on Web 05/20/1999

$SnOSiPh_2)_2O$. In comparison to its parent system $(Ph_2SiO)_n$, the formal replacement of one Ph_2SiO group by a *t*-Bu_2SnO group decreases the barrier between the six-membered ring and its polymer and allows the study of the interplay of ring strain on one hand and entropic favor of various species in solution on the other hand. Characteristic features of the polymer are the zigzag chain conformation and the Si−O−Si angle of 180°.

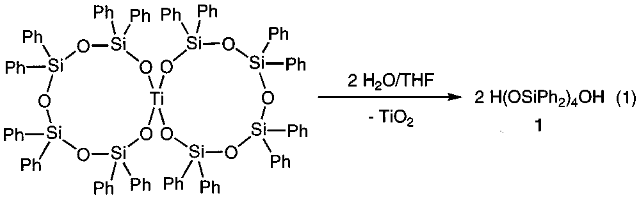
The template-driven synthesis of the spirotitanasiloxane $Ti[(OSiPh_2)_4O]_2$ from $Ph_2Si(OH)_2$ and Ti(*i*-OPr)$_4$ was first reported by Zeitler and Brown in 1957.[10a] Its molecular structure was established more recently by Hursthouse and Hossain.[10b]

Here we describe the hydrolysis of $Ti[(OSiPh_2)_4O]_2$ to give 1,1,3,3,5,5,7,7-octaphenyltetrasiloxy-1,7-diol, $H(OSiPh_2)_4OH$ (**1**). Former investigations concerning the hydrolysis of spirotitanasiloxanes concentrated mainly on kinetic aspects.[11]

Organosil(ox)anols are useful building blocks for the synthesis of metallasiloxanes, the chemistry of which has been reviewed recently.[12] The reaction of **1** with tricyclohexyltin hydroxide and di-*tert*-butyltin oxide, respectively, gives the open-chain and cyclic stannasiloxanes **2** and **3**. Stannasiloxane **2** and the diol **1** can be regarded as model compounds for polydiphenylsiloxanes.

Results and Discussion

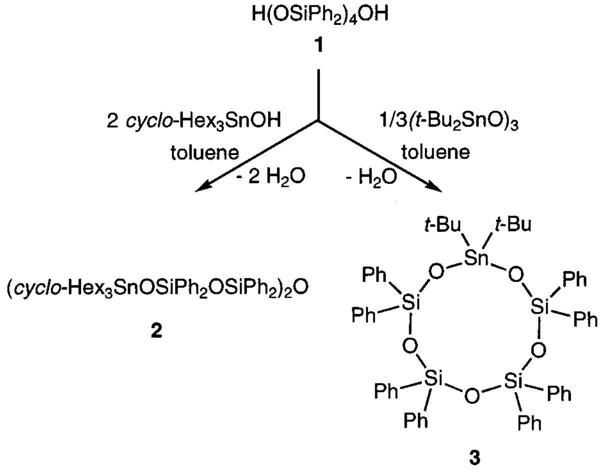
1,1,3,3,5,5,7,7-Octaphenyltetrasiloxy-1,7-diol, $H(OSiPh_2)_4OH$ (**1**), was obtained in high yield by the hydrolysis of *spiro*-$Ti[(OSiPh_2)_4O]_2$ in THF/H_2O (eq 1).



The reaction of the organosil(ox)anol **1** with tricyclohexyltin hydroxide, *cyclo*-Hex_3SnOH, and di-*tert*-butyltin oxide, *cyclo*-(*t*-$Bu_2SnO)_3$, respectively, afforded 1,1,3,3,5,5,7,7-octaphenyl-1,7-tricyclohexylstannyl-1,3,5,7-tetrasiloxane, (*cyclo*-$Hex_3SnOSiPh_2OSiPh_2)_2O$ (**2**), and 1,1-di-*tert*-butyl-3,5,7,9-octaphenyl-2,4,6,8,10-pentaoxa-3,5,7,9-tetrasila-1-stannacyclododecane, *cyclo*-*t*-$Bu_2Sn(OSiPh_2OSiPh_2)_2O$ (**3**), in good yields (Scheme 1).

The organosil(ox)anol **1** as well as the stannasiloxanes **2** and **3** are colorless, sharp melting solids and well soluble in common organic solvents, such as CH_2Cl_2, toluene, and thf. Compound **3** is even soluble in *n*-hexane.

Scheme 1



The identity in solution of compounds **1**−**3** was confirmed by NMR spectroscopy and molecular weight determinations. The ^{29}Si NMR ($CDCl_3$) spectrum of **1** shows two equally intense signals at −36.9 and −45.3 ppm, respectively, which are in the expected region as compared to $Ph_2Si(OH)_2$ (δ −32.4 ppm),[13] $H(OSiPh_2)_2OH$ (δ −36.0 ppm),[3d] and $H(OSiPh_2)_3OH$ (δ −36.5, −44.0 ppm; 2:1).[3d] The ^{29}Si MAS NMR chemical shifts of −39.7 and −47.8 ppm are very similar to those in solution. Thermally equilibrated PDPhS shows ^{29}Si MAS NMR chemical shifts of −43.6, −46.0, −46.6, and −47.7 ppm, whereas pure $(Ph_2SiO)_3$ and $(Ph_2SiO)_4$ show signals at −33.8 and −42.7 ppm, respectivly.[4b] The replacement of the two hydroxy protons in the siloxanol **1** by tricyclohexyltin moieties in compound **2** and the di-*tert*-butyltin fragment in the 10-membered stannasiloxane ring **3** results in low-frequency shifts of the ^{29}Si NMR resonances of the adjacent silicon atoms, whereas the chemical shifts of the two other silicon atoms are not affected (**2**, δ ^{29}Si −45.8 ($^2J(^{29}Si{-}O{-}^{117/119}Sn)$ 70 Hz, *Si*−O−Sn), −47.7 (*Si*−O−Si); **3**, δ ^{29}Si −44.9 ($^2J(^{29}Si{-}O{-}^{117/119}Sn)$ 69 Hz, *Si*−O−Sn), −47.4 (*Si*−O−Si)). The resonances observed for 10-membered stannasiloxane ring **3** are close to the values measured for the related eight-membered stannasiloxane ring *cyclo*-*t*-$Bu_2Sn(OSiPh_2O)_2SiPh_2$ (δ ^{29}Si −43.2, −45.8).[9b] The ^{29}Si MAS NMR spectrum of the stannasiloxane **2** shows two signals at −46.2 and −46.8 ppm, being comparable with the chemical shifts found in solution. The ^{29}Si MAS NMR spectrum of the 10-membered cyclostannasiloxane **3** shows four signals at −44.7, −47.4, −49.1, and −50.2 ppm, respectively, which hints at four crystallographically inequivalent silicon atoms in the solid state.

The molecular structures of compounds **1** and **2** are shown in Figures 1 and 2, respectively. Selected bond lengths and bond angles are given in Table 1.

The most important features to be noticed are (i) the absence of any Si−O···H···O hydrogen bridges in the 1,3,5,7-tetrasiloxane-1,7-diol derivative **1**, which is in sharp contrast to any other structurally characterized organosilanol and organosil(ox)anol, respectively[14a−c] and which illustrates the qualitative change in the structures of $Ph_2(OH)Si(OSiPh_2O)_nSi(OH)Ph_2$ on going from $n = 1$[3d] to $n = 2$, and (ii) the Si(1)−O−Si(1a) angles of 180° in both **1** and its tricyclohexyltin derivative **2**.

---

(10) (a) Zeitler, V. A.; Brown, C. A. *J. Am. Chem. Soc.* **1957**, *79*, 4618. (b) Hursthouse, M. B.; Hossain, M. A. *Polyhedron* **1984**, *3*, 95.

(11) (a) Hoebbel, D.; Reinert, T.; Schmidt, H. *J. Sol−Gel Sci. Technol.* **1996**, *6*, 139. (b) Hoebbel, D.; Nacken, M.; Schmidt, H.; Huch, V.; Veith, M. *J. Mater. Chem.* **1998**, *8*, 171.

(12) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205.

(13) Marsmann, H. C. NMR Principles and Progress 17, ^{29}Si *NMR Spectroscopic Results*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1981.

(14) (a) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147. (b) Unno, M.; Takada, K.; Matsumoto, H. *Chem. Lett.* **1998**, 489. (c) Minkwitz, R.; Schneider, S. *Z. Naturforsch.* **1998**, *53b*, 426. (d) Jarvie, A. W.; Holt, A.; Thompson, J. *J. Organomet. Chem.* **1968**, *11*, 623.

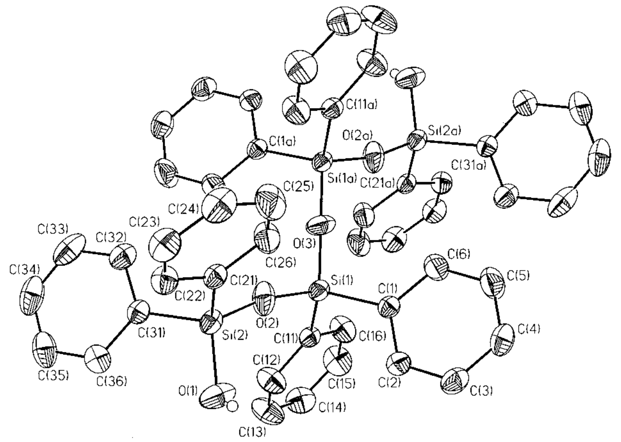


Figure 1. General view (SHELXTL-PLUS) of a molecule of **1** showing 30% probability displacement ellipsoids and the atom-numbering scheme (symmetry transformation used to generate equivalent atoms: $a = -x+1, -y+1, -z$).

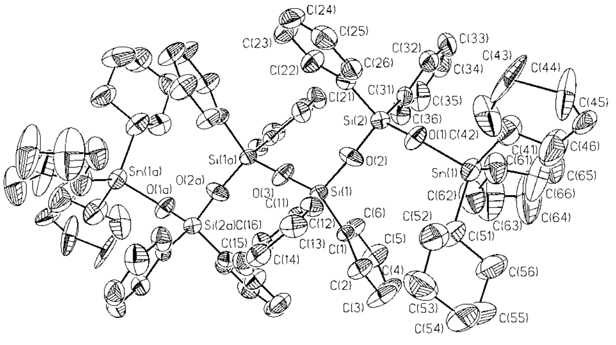


Figure 2. General view (SHELXTL-PLUS) of a molecule of **2** showing 30% probability displacement ellipsoids and the atom-numbering scheme (symmetry transformation used to generate equivalent atoms: $a = -x, -y, -z$).

Both features make compounds **1** and **2** the first true subunits[9a] showing the structural characteristics of PDPhS and of $[Ot\text{-}Bu_2SnOSiPh_2OSiPh_2O]_n$. In analogy to previously reported $(Ph_3SnO)Ph_2SiOSiPh_2(OSnPh_3)$,[8] compounds **1** and **2** adopt a staggered configuration about the vector joining Si(1)−Si(1a), as is illustrated by the corresponding dihedral angles across this vector, i.e., C(1)−Si(1)−Si(1a)−C(1a) (**1**)/(**2**), C(11)−Si(1)−Si(1a)−C(11a) (**1**)/(**2**), O(2)−Si(1)−Si(1a)−O(2a) (**1**)/(**2**) of 180°.

The molecular structure of the 1,3,5,7-tetrasiloxane-1,7-diol derivative **1** shows the O(1)-bonded hydrogen to point in the direction of the carbon atom C(21) (H(1)···C(21) 2.85(5) Å, H(1)−O(1)−Si(2)−C(21) −23.4(7)°), which probably indicates weak hydrogen interaction with the corresponding phenyl group and explains the infrared spectrum of compound **1**, as it was reported in 1968.[14d]

Recently it was suggested that PDPhS realizes zigzag chains in the solid state[7] rather than a helical structure. This view is supported by the structures of the 1,3,5,7-tetrasiloxane-1,7-diol derivative **1** (Figure 3), of its tricyclohexyltin derivative **2**, and of the polystannasiloxane $[Ot\text{-}Bu_2SnOSiPh_2OSiPh_2O]_n$.[9]

The ready commercial availability of $Ti(OPr^i)_4$ and $Ph_2Si(OH)_2$ and their simple conversion into TiO_2 and the organosiloxanol **1** make the latter compound a potential precursor for further tailor-made polydiphenylsiloxane derivatives.

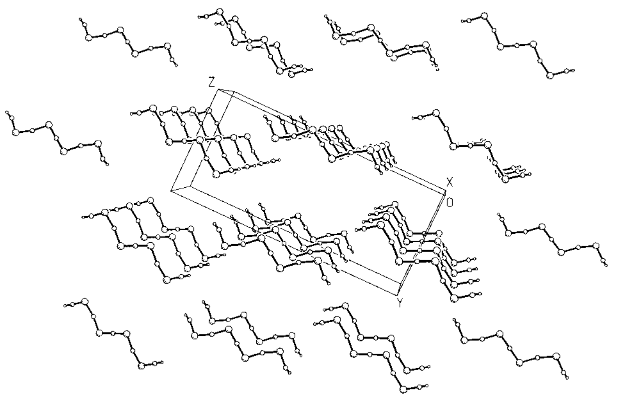


Figure 3. Side view (SHELXTL-PLUS) of the unit cell of **1** (all phenyl groups were omitted for clarity).

Table 1. Crystallographic Data of 1 and 2

	1	2
formula	$C_{48}H_{42}O_5Si_4$	$C_{84}H_{106}O_5Si_4Sn_2$
fw, g/mol	811.18	1545.43
cryst syst	monoclinic	triclinic
cryst size, mm	0.40 × 0.20 × 0.20	0.20 × 0.20 × 0.20
space group	$P2_1/n$	$P\bar{1}$
a, Å	10.150(1)	10.247(1)
b, Å	9.729(1)	10.413(1)
c, Å	21.643(1)	19.791(1)
α, deg	90	76.756(1)
β, deg	94.967(1)	79.305(1)
γ, deg	90	86.038(1)
V, Å^3	2129.2(3)	2019.1(3)
Z	2	1
ρ_{calcd}, Mg/m^3	1.265	1.271
ρ_{meas}, Mg/m^3	1.256(1)	1.275(2)
μ, mm^{-1}	0.186	0.726
F(000)	852	806
θ range, deg	4.18−25.67	4.09−25.88
index ranges	$-10 \le h \le 10$ $-11 \le k \le 11$ $-26 \le l \le 26$	$-12 \le h \le 12$ $-10 \le k \le 11$ $-23 \le l \le 24$
no. of reflns collcd	28415	23692
completeness to θ_{max}	92.6	91.4
no. of indep reflns/R_{int}	3743/0.024	7173/0.042
no. of reflns obsd with ($I > 2\sigma(I)$)	2640	2720
no. of refined params	343	476
GoF (F^2)	1.015	0.804
$R1$ (F) ($I > 2\sigma(I)$)	0.0380	0.0457
$wR2$ (F^2) (all data)	0.1026	0.1045
$(\Delta/\sigma)_{max}$	<0.001	<0.001
largest diff peak/hole, e/Å^3	0.380/−0.298	0.237/−0.272

Experimental Section

General Data. All solvents were dried according to standard procedures and freshly distilled prior to use. *spiro*-Ti-$[(OSiPh_2)_4O]_2$,[10a] *cyclo*-$(t\text{-}Bu_2SnO)_3$,[15a] and *cyclo*-Hex_3SnOH[15b] were synthesized according to literature procedures. Solution ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were recorded on a Bruker DRX 400 spectrometer and were referenced to $SiMe_4$ (^{1}H, ^{13}C, ^{29}Si) or $SnMe_4$ (^{119}Sn) in chloroform. ^{119}Sn MAS NMR spectra were obtained from a Bruker MSL 400 spectrometer using cross-polarization and high-power proton decoupling. Chemical shifts (δ) are given in ppm. Tetracyclohexyltin, *cyclo*-Hex_4Sn, was used as a second reference (δ −97.35 ppm) and to optimize Hartmann−Hahn CP matching conditions. ^{29}Si MAS NMR spectra were recorded on a UNITYplus-500 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 spec-

---

[15] (a) Puff, H.; Schuh, W.; Sievers, R.; Wald, W.; Zimmer, R. *J. Organomet. Chem.* **1984**, *260*, 271. (b) *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: Berlin, 1986; Part 13, p 10.

trometer. Ions showed the expected isotopic pattern. The elemental analyses were performed on an instrument from Carlo Erba Strumentazione (model 1106). The densities of single crystals were determined using a Micromeritics Accu Pyc 1330. The molecular weight measurements were performed on a Knaur osmometer.

1,1,3,3,5,5,7,7-Octaphenyl-1,3,5,7-tetrasiloxane-1,7-diol (1). *spiro*-Ti[(OSiPh_2)$_4$O]$_2$ (10.0 g, 6.0 mmol) was dissolved in 250 mL of THF, and H_2O (1.10 g, 60 mmol) was added. After stirring for 6 h the layers were separated and the organic layer was removed in vacuo. The solid residue was recrystallized from toluene, resulting in 4.2 g (86%) of **1** as colorless crystalline solid, mp 132 °C. ^{1}H NMR δ: 7.38 (complex pattern, *Ph*), 7,26 (complex pattern, *Ph*), 7.10 (complex pattern, *Ph*). ^{13}C{^{1}H} NMR δ: 134.5 (C_i), 134.4 (C_o), 134.3 (C_i, C_o superimposed), 130.1 (C_p), 130.08 (C_p), 127.7 (C_m). ^{29}Si{^{1}H} NMR δ: −36.9 (O*Si*(OH)Ph_2), −45.3 (O*Si*Ph_2O). ^{29}Si{^{1}H} MAS NMR δ: −39.7 (O*Si*(OH)Ph_2), −47.8 (O*Si*Ph_2O). MS *m*/*z* (%): 791 (25) [M^+], 714 (27) [M^+ − Ph], 636 (65) [M^+ − 2 Ph], 593 (38) [M^+ − OSiPh_2], 558 (94) [M^+ − 3 Ph]. Anal. Calcd for $C_{48}H_{42}O_4Si_4$ (795.21): C, 72.50; H, 5.32. Found: C, 70.97; H, 5.34. IR (KBr): 3591 (m, ν_{OH}), 3070 (m), 3020 (m), 1958 (m), 1899 (m), 1827 (m), 1590 (s), 1486 (s), 1428 (s), 1309 (w), 1264 (w).

1,1,3,3,5,5,7,7−Octaphenyl-1,7-tricyclohexylstannyl-1,3,5,7-tetrasiloxane (2). H(OSiPh_2)$_4$OH (**1**) (0.5 g, 0.62 mmol) was dissolved in 60 mL of toluene, and *cyclo*-Hex$_3$SnOH (0.47 g, 1.23 mmol) was added. After heating at a Dean and Stark condenser for 8 h, the solvent was evaporated. Recrystallization of the residue from CH_2Cl_2/hexane provided 0.62 g (87%) of **2** as a colorless crystalline solid, mp 156 °C. ^{1}H NMR δ: 7.33 (complex pattern, *Ph*), 7.15 (complex pattern, *Ph*), 6.98 (complex pattern, *Ph*), 1.30 (complex pattern, *cyclo-Hex*). ^{13}C{^{1}H} NMR δ: 138.5 (C_i), 135.7 (C_i), 134.7 (C_o), 134.6 (C_o), 129.2 (C_p), 128.7 (C_p), 127.1 (C_m), 127.08 (C_m), 33.0 (^1J(^{13}C−^{119}Sn) 342 Hz, Sn−*C*H), 30.9 (^2J(^{13}C−$^{117/119}$Sn) 14 Hz, CH*C*H_2), 28.8 (^3J(^{13}C−$^{117/119}$Sn) 64 Hz CHCH_2*C*H_2), 26.8. ^{29}Si{^{1}H} NMR δ: −45.8 (^2J(^{29}Si−O−^{119}Sn 70 Hz, *Si*−O−Sn), −47.7 (O*Si*Ph_2O). ^{119}Sn{^{1}H} NMR δ: −7.9. ^{29}Si{^{1}H} MAS NMR δ: −46.2 (*Si*−O−Sn), −46.8 (O*Si*Ph_2O).

MS *m*/*z* (%): 867 (23) [M^+ − 4 Ph, −Sn−*cyclo*-Hex$_3$], 714 (16) [M^+ − 6 Ph, −Sn−*cyclo*-Hex$_3$], 653 (30) [M^+ − 4 Ph, −Sn−*cyclo*-Hex$_3$, −OSiPh_2], 637 (36) [M^+ − 4 Ph, −Sn−*cyclo*-Hex$_3$, −O_2SiPh_2], 594 (40) [M^+ − 2 Ph, −Sn−*cyclo*-Hex$_3$, −O_2SiPh_2, −OSiPh_2]. Anal. Calcd for $C_{84}H_{106}O_5Si_4Sn_2$ (1545.58): C, 65.28; H, 6.91. Found: C, 64.98; H, 7.11. IR (KBr): 3067 (m), 3049 (m), 3021 (m), 2916 (s), 2845 (s), 1591 (m), 1487 (w), 1445 (s), 1428 (s), 1262(m), 1127 (s), 1073 (s), 984 (s), 877 (m), 840 (m), 803 (m), 740 (s), 716 (s), 698 (s), 519 (s), 485 (s), 418 (m) cm^{-1}.

1,1-Di-*tert*-butyl-3,5,7,9-octaphenyl-2,4,6,8,10-pentaoxa-3,5,7,9-tetrasila-1-stannacyclododecane, *cyclo*-*t*-Bu$_2$Sn(OSiPh$_2$OSiPh$_2$)$_2$O (3). H(OSiPh_2)$_4$OH (**1**) (1.25 g, 1.50 mmol) and (*t*-Bu$_2$SnO)$_3$ (0.38 g, 1.50 mmol) were dissolved in 100 mL of $CHCl_3$. The reaction mixture was heated at reflux for 4 h. Evaporation of the solvent provided 1.19 g (74%) of **3** as a colorless amorphous solid, mp >250 °C. ^{1}H NMR δ: 0.96 (3*J*(^{1}H−^{119}Sn) 104 Hz, CCH_3), 7.05 (complex pattern, *Ph*), 7.21 (complex pattern, *Ph*), 7.34 (complex pattern, *Ph*), 7.44 (complex pattern, *Ph*). ^{13}C{^{1}H} NMR δ: −29.2 (C*C*H_3), −39.9 (^1J(^{13}C−^{119}Sn) 499 Hz, *C*CH_3), 137.8 (C_i), 135.4 (C_i) 134.6 (C_o), 129.5 (C_p), 129.2 (C_p), 127.4 (C_m). ^{29}Si{^{1}H} NMR δ: −44.9 (^2J(^{29}Si−$^{117/119}$Sn) 69 Hz, OPh$_2$*Si*−O−Sn), −47.4 (OPh$_2$*Si*−O−Si). ^{119}Sn{^{1}H} NMR δ: −158.0 (^2J(^{119}Sn−O-^{29}Si) 69 Hz. ^{29}Si{^{1}H} MAS NMR δ: −44.7, −47.4, −49.1−50.2. ^{119}Sn{^{1}H} MAS NMR δ: −141.2. MS *m*/*z* (%): 850 (55) [M^+ − 2 *t*-Bu, −Ph], 653 (56) (M^+ − 2 *t*-Bu, −Ph, −OSiPh_2], 637 (10) [M^+ − 2 *t*-Bu, −Ph, −O_2SiPh_2], 533 (32) [M^+ − Sn*t*-Bu$_2$, −OSiPh_2, −2 Ph], 455 (72) [M^+ − 2 *t*-Bu, −Ph, −2 OSiPh_2]. Anal. Calcd for $C_{56}H_{58}O_5Si_4Sn$ (1042.16): C, 64.54; H, 5.61. Found: C,64.08; H, 5.71. IR (KBr): 3068 (m), 3047 (m), 2921 (w), 2850 (m), 2361 (w), 2338 (w), 1591 (w), 1466 (w), 1429 (s), 1124 (s), 966 (s), 741 (m), 715 (s), 698 (s), 523 (s), 508 (s), 384 (m) cm^{-1}. MW (10 mg/mL in $CHCl_3$): 940 g/mol.

Table 2. Selected Bond Lengths [Å], Angles [deg], and Torsion Angles [deg] for 1 and 2

	1 (X = H)[a]	**2** (X = Sn)[b]
Si(1)−O(3)	1.6064(6)	1.602(1)
Si(1)−O(2)	1.609(2)	1.598(3)
Si(1)−C(1)	1.853(2)	1.845(4)
Si(1)−C(11)	1.853(2)	1.835(4)
Si(2)−O(2)	1.609(2)	1.603(3)
Si(2)−O(1)	1.627(2)	1.591(3)
Si(2)−C(21)	1.854(2)	1.851(5)
Si(2)−C(31)	1.856(2)	1.861(5)
O(1)−X(1)	0.70(4)	1.970(3)
Sn(1)−C(41)		2.129(6)
Sn(1)−C(51)		2.116(6)
Sn(1)−C(61)		2.130(7)
O(3)−Si(1)−O(2)	109.07(7)	108.8(1)
O(3)−Si(1)−C(1)	108.80(7)	109.9(2)
O(2)−Si(1)−C(1)	109.96(9)	107.7(2)
O(3)−Si(1)−C(11)	108.41(7)	109.0(2)
O(2)−Si(1)−C(11)	109.37(9)	111.3(2)
C(1)−Si(1)−C(11)	111.18(9)	110.9(2)
O(2)−Si(2)−O(1)	111.0(1)	112.0(2)
O(2)−Si(2)−C(21)	108.34(9)	108.7(2)
O(1)−Si(2)−C(21)	110.5(1)	108.1(2)
O(2)−Si(2)−C(31)	108.71(9)	105.1(2)
O(1)−Si(2)−C(31)	106.0(1)	111.7(2)
C(21)−Si(2)−C(31)	112.35(9)	111.3(2)
Si(1)−O(2)−Si(2)	167.6(1)	166.1(2)
Si(1a)−O(3)−Si(1)	180.00(3)	180.00(7)
Si(2)−O(1)−X(1)	117(3)	145.6(2)
O(1)−Sn(1)−C(51)		103.4(2)
O(1)−Sn(1)−C(41)		101.6(2)
C(51)−Sn(1)−C(41)		117.0(4)
O(1)−Sn(1)−C(61)		106.2(2)
C(51)−Sn(1)−C(61)		113.9(3)
C(41)−Sn(1)−C(61)		112.8(4)
O(1)−Si(2)−O(2)−Si(1)	−7.9(5)	69.7(10)
O(3)−Si(1)−O(2)−Si(2)	−174.9(5)	107.6(10)
O(2)−Si(1)−O(3)−Si(1a)	63(13)	−86(17)
O(2)−Si(2)−O(1)−Sn(1)		74.5(4)

[a] *a* = −*x*+1, -*y*+1, -*z* (**1**). [b] *a* = −*x*,-*y*, -*z* (**2**).

Crystallography. Crystals of H(OSiPh_2)$_4$OH (**1**) and (*cyclo*-Hex$_3$SnOSiPh_2OSiPh_2)$_2$O (**2**) were grown from a CH_2Cl_2/hexane solution. Intensity data for the colorless crystals were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα radiation at 291 K. The data collections covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at two times 20 s (**1**, **2**) per frame. The crystal-to-detector distance was 2.7 cm (**1**) and 2.9 cm (**2**). Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections, there was no indication for any decay (**1**, **2**). The data were not corrected for absorption effects. The structures were solved by direct methods SHELXS97[16a] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods with SHELXL97.[16b]

H atoms for **1** were located in the difference Fourier map and refined isotropically. The H atoms for **2** were placed in geometrically calculated positions using a riding model. For the phenyl groups they were refined with a common isotropic temperature factor (H_{aryl} C−H 0.93 Å, U_{iso} 0.110(4) Å^2), and for the cyclohexyl groups the atomic displacement parameters were fixed to 1.5 times those of the C atoms (C−H_{sec} 0.97 Å).

Disordered cyclohexyl groups were found for **2** (C(42), C(43), C(44), C(45), C(66), C(42′), C(43′), C(44′), C(45′), C(66′) (sof 0,5)).

---

(16) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990** *A46*, 467−473. (b) Sheldrick, G. M. University of Göttingen, 1997. (c) *International Tables for Crystallography*, Kluwer Academic Publishers: Dordrecht, 1992; Vol. C. (d) Sheldrick, G. M. *SHELXTL-Plus*, Release 4.1; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1991.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from reference[16c]. Figures were created by SHELXTL-Plus.[16d] Crystallographic data are given in Table 1; selected bond lengths [Å] and angles [deg] are listed in Table 2.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990107Z