

Synthesis and characterization of large stereoregular organosiloxane cycles

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Abstract

The large stereoregular phenyltrimethylsiloxysiloxane macrocycles of general formula $[\text{PhSi}(\text{OSiMe}_3)\text{O}]_n$ ($n = 6$ and 12) have been selectively obtained with high yields by trimethylsilylation of cage-like oligophenylmetallasiloxanes (OPMS) which we described earlier. The compounds **3** ($n = 6$) and **4** ($n = 12$) have been characterized by NMR-spectroscopy method and by single crystal X-ray analysis. This investigation showed unambiguously that the siloxane macrocycles keep their size and configuration (the same as in the initial OPMS) during the trimethylsilylation. Thus a synthetic route for obtaining large stereoregular siloxane macrocycles has been developed. © 1998 Elsevier Science S.A. All rights reserved.

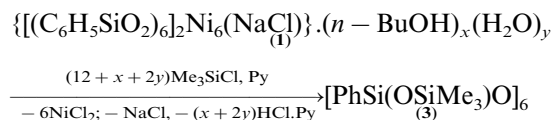
Keywords: Oligophenylmetallasiloxanes (OPMS); Stereoregular siloxane macrocycles; Trimethylsilylation; Single crystal X-ray analysis

1. Introduction

Earlier we obtained the new type of metal-oligo(phenylsiloxanolate)—cage-like oligophenylmetallasiloxanes (OPMS) via treatment of sodium phenylsiloxanolate with divalent metal chlorides (Mn, Ni, Co, Cu) [1–4]. The OPMS known (Figs. 1 and 2) contain two types of highly symmetrical stereoregular macrocyclic organosiloxanolate ligands: $[\text{PhSi}(\text{O}^-)\text{O}]_n$, with $n = 6$ or 12 . It has been very attractive to utilize these compounds as a source for large stereoregular organosiloxane cycles. As a part of our general study in this direction, we have examined the reaction of some of the OPMS with trimethylchlorosilane. Here we report our findings on this reaction.

2. Results and discussion

Nickel-containing OPMS (**1**) (Fig. 1) has a sandwich-like structure with two all-*cis* six-membered hexaphenylcyclohexasiloxanehexaolate ligands coordinating the metal cationic core [1]. Treatment with Me_3SiCl gives a white crystalline product **3** (m.p. 410°C ; $M = 1268$) with high yield (70.9%), according to the following scheme:

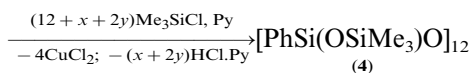
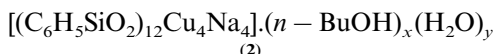


The $^1\text{H-NMR}$ spectrum of **3** contains only one singlet with a chemical shift of 0.15 ppm for the methyl groups (the ratio of integrated intensities of phenyl and methyl protons comes to 5:9). The silicon NMR spectrum has two signals: one with a chemical shift of 9.77 ppm corresponding to the OSiMe_3 groups and the other at -80.97 ppm (O_3SiPh groups). On the basis of all

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this data, we supposed the formation of the twelve-membered cyclosiloxane derivative ($M_{\text{theor.}} = 1262.28$). The single crystal X-ray analysis has corroborated this supposition: the compound **3** turned out to be the *symm-cis*-hexaphenylhexakis(trimethylsiloxy)cyclohexasiloxane (Fig. 3).

Similar destruction of the copper/sodium-containing OPMS (**2**; Fig. 2), which is based on a dodecaphenylcyclododecasiloxanedodecaolate ligand with *tris-cis-trans*-configuration, leads with 77.9% yield to a crystalline dodecamerous product of trimethylsilylation **4** (m.p. 362°C, $M = 2522$) according to the scheme:



The (*tris-cis*)-*trans*-(*tris-cis*)-*trans*-(*tris-cis*)-*trans*-(*tris-cis*)-*trans*-configuration of **4** (as in the initial OPMS **2**) might be expected. Indeed, it is confirmed by the ¹H-NMR spectrum of **4** which shows two non-equivalent types of Me groups—two singlets at -0.10 ppm (*cis/cis*-SiMe₃) and -0.33 ppm (*cis/trans*-SiMe₃)—with the ratio of integrated intensities 1:2. The ratio of integrated intensities of the phenyl region (6.5–7.5 ppm) to that of both methyl signals is 5:9. In the ²⁹Si-NMR spectrum, three signals with chemical shifts of 8.84 ppm (*cis/cis*-OSiMe₃), 9.83 ppm (*cis/trans*-OSiMe₃) and -80.73 ppm (O₃SiPh) were registered. The final evidence was obtained from single crystal X-ray structural data: the compound **4** is the *symm*-(*tris-cis*)-*trans*-(*tris-cis*)-*trans*-(*tris-cis*)-*trans*-(*tris-cis*)-*trans*-dodecaphenyl-dodecakis(trimethylsiloxy)cyclododecasiloxane (Fig. 4).

The conformations of the siloxane macrocycles in **3** and **4** are most interesting. In the initial compounds those are highly symmetrical: a ‘crown’ conformation of 6 mm symmetry in **1** [4] and a ‘horse-saddle’ or a

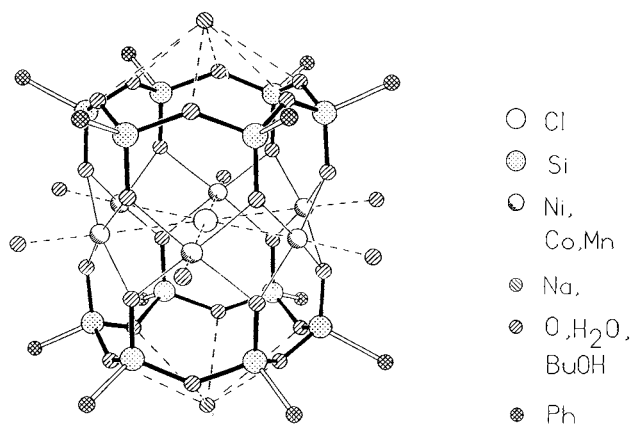


Fig. 1. A general view of molecular structure of the OPMS based on bivalent ions of transition metals and six-membered phenylsiloxanolate ligands (**1**).

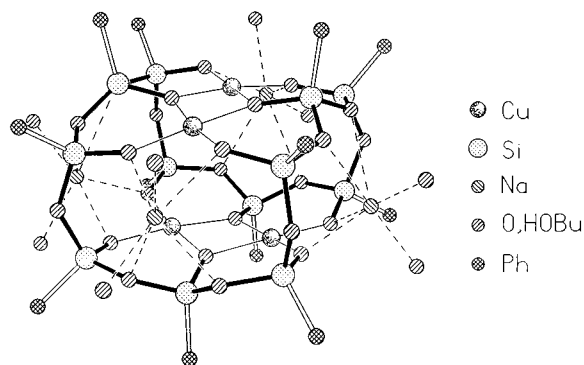


Fig. 2. The molecular structure of the OPMS based on copper(II) ions and a 12-membered phenylsiloxanolate ligand (**2**).

‘tennis-ball furrow’ conformation of **2** [3]. In the molecules of **3** and **4** these macrocycles have more complicated, less symmetrical shape (Tables 1 and 2; Figs. 3 and 4) which is difficult to describe traditional way.

Nevertheless, the conformation of the siloxane cycle in **3** may be described qualitatively as a convex gross chair: three endocyclic silicon atoms are positioned above and three—below their mean plane. Then three Ph groups (at Si(1), Si(3) and Si(5)) are oriented quasi-axial and other three—quasi-equatorial.

The conformation of the siloxane macrocycle in **4** is, on the contrary, concave: the Si(2) atom is pushed by its substituents towards the center of the cycle, possibly to fill its inner cavity. A solvate toluene molecule is situated outside the cycle and does not take part in the filling of the inner cavity of the macrocycle.

In the molecule **3**, endocyclic bonds Si–O are slightly shorter (1.606–1.622(2) Å, av. 1.615 Å; Table 3) than a standard value of 1.631 Å [5], perhaps as a result of a tiny disorder or a residual exceed thermal motion of the atoms (siloxane chains are well known as extremely conformationally flexible [6]). An additional shortening of exocyclic Si–OSiMe₃ bonds in **3** (1.595–1.616(2–3) Å, av. 1.608 Å) as well as even more pronounced effective shortening both of endocyclic (1.581–1.624(5–6) Å, av. 1.604 Å; Table 4) and exocyclic (1.555–1.597(6–8) Å, av. 1.580 Å) Si–O bonds in the less ordered structure **4** corroborates this supposition. Furthermore the structure determination of **4** has been carried out at a higher temperature.

Apparently, because of the same reasons, bonds Si–C(Ph) (1.845–1.860(3) Å, av. 1.853 Å in **3**; 1.81–1.86(1) Å, av. 1.830 Å with exception of a disordered group in **4**) and Si–C(Me) (1.844–1.860(3–5) Å, av. 1.851 Å in **3**; 1.78–1.87(1–2) Å, av. 1.831 Å in **4**; both—with exception of disordered groups) display also the tendency to be effectively shortened in comparison with standard values 1.868 and 1.857 Å [5], respectively.

However, instead of a larger thermal motion, the ‘terminal’ O–SiMe₃ bonds are systematically lengthened as

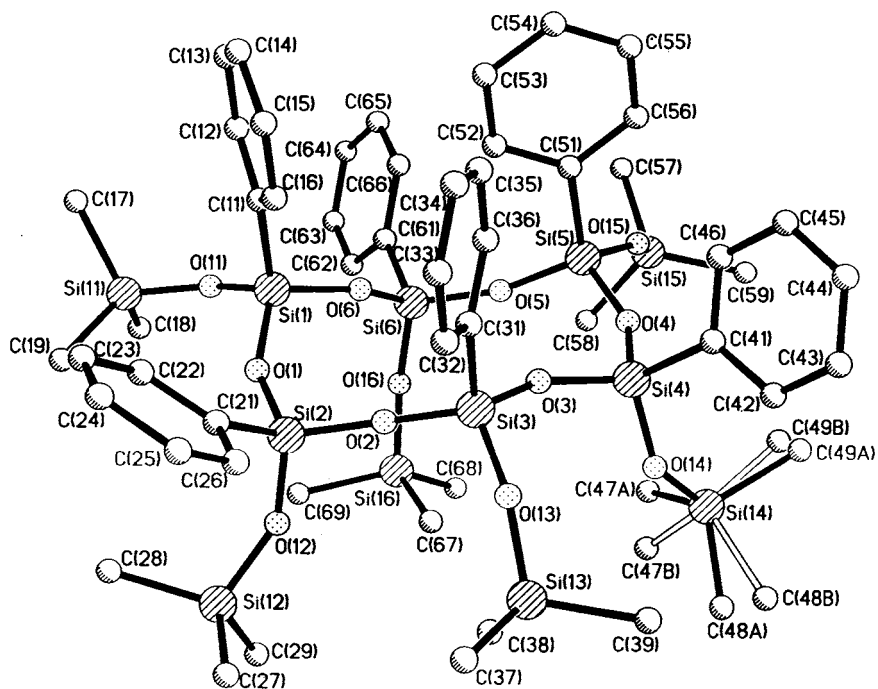


Fig. 3. The molecular structure of 3. Atom numbers are given. An alternative position of a disordered trimethylsilyloxy group is shown by open lines.

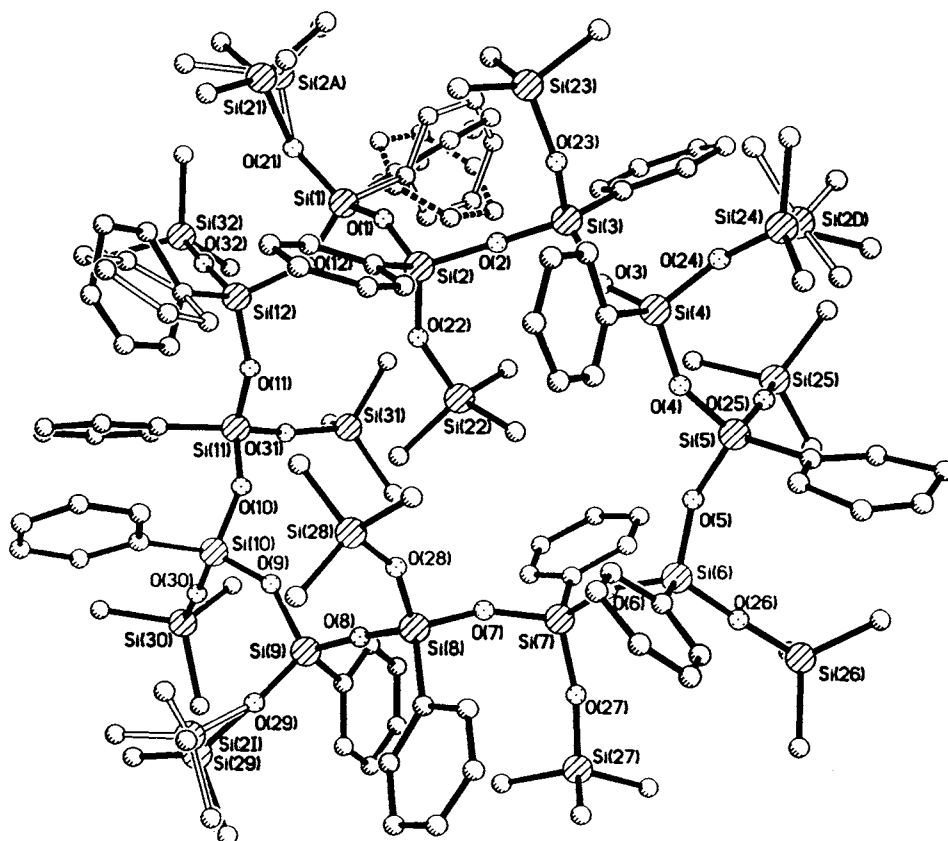


Fig. 4. The molecular structure of 4. Silicon and oxygen atom numbers are given. Alternative positions of disordered groups are shown by open and (for a Ph group disordered in three positions) by dashed solid lines.

Table 1
Selected torsion angles (φ , °) for **3**

Angle	φ	Angle	φ
Siloxane macrocycle			
O(6)–Si(1)–O(1)–Si(2)	52.7(3)	O(3)–Si(4)–O(4)–Si(5)	13.3(3)
Si(1)–O(1)–Si(2)–O(2)	–18.5(3)	Si(4)–O(4)–Si(5)–O(5)	–60.3(3)
O(1)–Si(2)–O(2)–Si(3)	130.3(6)	O(4)–Si(5)–O(5)–Si(6)	126.3(6)
Si(2)–O(2)–Si(3)–O(3)	–167.8(6)	Si(5)–O(5)–Si(6)–O(6)	–50.8(7)
O(2)–Si(3)–O(3)–Si(4)	–151.3(3)	O(5)–Si(6)–O(6)–Si(1)	–177.1(3)
Si(3)–O(3)–Si(4)–O(4)	–169.7(3)	Si(6)–O(6)–Si(1)–O(1)	100.7(3)
Trimethylsilyl substituents			
O(1)–Si(1)–O(11)–Si(11)	47.3(4)	O(3)–Si(4)–O(14)–Si(14)	150.1(2)
O(6)–Si(1)–O(11)–Si(11)	166.6(4)	O(4)–Si(4)–O(14)–Si(14)	32.3(3)
C(11)–Si(1)–O(11)–Si(11)	–74.5(4)	C(41)–Si(4)–O(14)–Si(14)	–87.9(3)
O(1)–Si(2)–O(12)–Si(12)	–96.8(3)	O(4)–Si(5)–O(15)–Si(15)	111.5(3)
O(2)–Si(2)–O(12)–Si(12)	144.6(3)	O(5)–Si(5)–O(15)–Si(15)	–7.0(4)
C(21)–Si(2)–O(12)–Si(12)	22.4(3)	C(51)–Si(5)–O(15)–Si(15)	–129.6(3)
O(2)–Si(3)–O(13)–Si(13)	49.9(5)	O(5)–Si(6)–O(16)–Si(16)	56.9(8)
O(3)–Si(3)–O(13)–Si(13)	–67.8(5)	O(6)–Si(6)–O(16)–Si(16)	–60.1(8)
C(31)–Si(3)–O(13)–Si(13)	171.0(4)	C(61)–Si(6)–O(16)–Si(16)	177.4(8)
Phenyl substituents			
O(1)–Si(1)–C(11)–C(12)	–154.2(3)	O(3)–Si(4)–C(41)–C(42)	104.1(3)
O(6)–Si(1)–C(11)–C(12)	85.0(3)	O(4)–Si(4)–C(41)–C(42)	–136.7(3)
O(11)–Si(1)–C(11)–C(12)	–33.5(3)	O(14)–Si(4)–C(41)–C(42)	–16.5(3)
O(1)–Si(2)–C(21)–C(22)	12.1(3)	O(4)–Si(5)–C(51)–C(52)	–101.7(3)
O(2)–Si(2)–C(21)–C(22)	132.2(3)	O(5)–Si(5)–C(51)–C(52)	18.6(3)
O(12)–Si(2)–C(21)–C(22)	–107.8(3)	O(15)–Si(5)–C(51)–C(52)	140.7(3)
O(2)–Si(3)–C(31)–C(32)	88.5(3)	O(5)–Si(6)–C(61)–C(62)	129.4(3)
O(3)–Si(3)–C(31)–C(32)	–154.7(3)	O(6)–Si(6)–C(61)–C(62)	–112.9(3)
O(13)–Si(3)–C(31)–C(32)	–32.6(3)	O(16)–Si(6)–C(61)–C(62)	9.0(3)

compared with the ‘internal’ Si–O bonds (1.623–1.646(2–3) Å, av. 1.637 Å in **3**; 1.564–1.630(6–8) Å, av. 1.607 Å with exception of disordered groups in **4**) evidently due to a large positive inductive effect of the Me groups.

In both compounds studied, a tetrahedral coordination geometry of Si atoms is practically undistorted, although endocyclic O–Si–O bond angles seem to be, in general, slightly reduced (106.0–109.7(1)°, av. 108.1° in **3**, Table 3; 105.6–110.5(3–4)°, av. 107.8° in **4**, Table 4) as compared with exocyclic O–Si–O (107.1–111.3(1–2)°, av. 109.3° in **4**, 107.3–111.9(3–4)°, av. 109.8° in **4**) and O–Si–C bond angles (107.8–111.8(1–2)°, av. 110.1° in **3**, 108.3–112.3(4–7)°, av. 109.8° with exception of disordered groups in **4**).

Geometry of Ph substituents is close to ideal, too (of course, with exception of distortions followed by disorder for some groups). We can only mention a remarkable decrease of the *ipso*-angle C–C(–Si)–C up to 116.5–117.2(3)°, av. 117.0° in the molecule **3** (113–120(1–2)°, av. 115.7° in the less precise and less ordered structure **4**) caused by a lower electronegativity of the bonded Si atom.

Coordination geometry of O atoms is most flexible: both endocyclic and exocyclic Si–O–Si bond angles have values much larger than 120°: 139.3–164.8(2)° in **3**

and 141.2–177.9(3–7)° in **4**. This is quite usual for sterically hindered siloxane molecules [6] and displays a large contribution of a *sp*-hybrid state (instead of *sp*²-hybrid) in the electron structure of siloxane oxygens. However, we could not establish any effect of the values of Si–O–Si bond angles on the corresponding Si–O bond lengths as well as any direct dependence of these angles on conformational parameters.

3. Experimental part

The ¹H- and ²⁹Si-NMR spectra were recorded with a Bruker WP-SY200 spectrometer (200.13 MHz for ¹H, 39.76 MHz for ²⁹Si) at 20°C in CCl₄ solution with TMS as an internal reference standard.

Chemical grade solvents were purified using standard procedures.

Molecular weights were determined by ebullioscopy in acetone on EP-75 Precision ebulliograph according to the method described in [7] at the laboratory for Physical Chemistry of Polymers in INEOS RAS.

Melting points were measured in sealed capillaries with a melting points apparatus and are uncorrected.

X-ray diffraction experiments were carried out with a Siemens P3/PC diffractometer. Main details of the data

Table 2
Selected torsion angles (φ , °) for 4

Angle	φ	Angle	φ
Siloxane macrocycle			
O(12)–Si(1)–O(1)–Si(2)	18.1(1.1)	O(6)–Si(7)–O(7)–Si(8)	–82.8(1.1)
Si(1)–O(1)–Si(2)–O(2)	128.9(9)	Si(7)–O(7)–Si(8)–O(8)	–121.6(1.1)
O(1)–Si(2)–O(2)–Si(3)	130.1(1.2)	O(7)–Si(8)–O(8)–Si(9)	114.0(5.9)
Si(2)–O(2)–Si(3)–O(3)	67.8(1.3)	Si(8)–O(8)–Si(9)–O(9)	157.7(5.9)
O(2)–Si(3)–O(3)–Si(4)	–150.7(7)	O(8)–Si(9)–O(9)–Si(10)	–173.2(6)
Si(3)–O(3)–Si(4)–O(4)	–160.6(7)	Si(9)–O(9)–Si(10)–O(10)	–147.1(6)
O(3)–Si(4)–O(4)–Si(5)	96.6(9)	O(9)–Si(10)–O(10)–Si(11)	167.7(7)
Si(4)–O(4)–Si(5)–O(5)	–158.4(9)	Si(10)–O(10)–Si(11)–O(11)	135.8(7)
O(4)–Si(5)–O(5)–Si(6)	–110.0(9)	O(10)–Si(11)–O(11)–Si(12)	–139.1(9)
Si(5)–O(5)–Si(6)–O(6)	166.6(9)	Si(11)–O(11)–Si(12)–O(12)	144.1(9)
O(5)–Si(6)–O(6)–Si(7)	127.5(1.1)	O(11)–Si(12)–O(12)–Si(1)	–170.2(7)
Si(6)–O(6)–Si(7)–O(7)	153.7(1.1)	Si(12)–O(12)–Si(1)–O(1)	114.0(8)
Trimethylsilyl substituents			
O(1)–Si(1)–O(21)–Si(21)	25.5(1.6)	O(5)–Si(6)–O(26)–Si(26)	–0.1(12.3)
O(12)–Si(1)–O(21)–Si(21)	146.0(1.4)	O(6)–Si(6)–O(26)–Si(26)	117.1(12.1)
C(11)–Si(1)–O(21)–Si(21)	–92.7(1.6)	C(61)–Si(6)–O(26)–Si(26)	–122.6(12.1)
C(11A)–Si(1)–O(21)–Si(21)	–85.7(1.6)	O(6)–Si(7)–O(27)–Si(27)	152.1(2.8)
C(11B)–Si(1)–O(21)–Si(21)	–98.7(1.5)	O(7)–Si(7)–O(27)–Si(27)	33.52(3.0)
O(1)–Si(1)–O(21)–Si(2A)	85.1(1.3)	C(71)–Si(7)–O(27)–Si(27)	–87.9(2.9)
O(12)–Si(1)–O(21)–Si(2A)	–154.4(1.2)	O(7)–Si(8)–O(28)–Si(28)	–167.0(9)
C(11)–Si(1)–O(21)–Si(2A)	–33.1(1.5)	O(8)–Si(8)–O(28)–Si(28)	74.6(1.0)
C(11A)–Si(1)–O(21)–Si(2A)	–26.1(1.4)	C(81)–Si(8)–O(28)–Si(28)	–47.2(1.1)
C(11B)–Si(1)–O(21)–Si(2A)	–39.1(1.4)	O(8)–Si(9)–O(29)–Si(29)	–178.8(3.4)
O(1)–Si(2)–O(22)–Si(22)	118.1(9)	O(9)–Si(9)–O(29)–Si(29)	62.9(3.4)
O(2)–Si(2)–O(22)–Si(22)	0.2(1.0)	C(91)–Si(9)–O(29)–Si(29)	–58.3(3.4)
C(21)–Si(2)–O(22)–Si(22)	–122.3(9)	O(8)–Si(9)–O(29)–Si(2I)	72.9(1.4)
O(2)–Si(3)–O(23)–Si(23)	–57.3(9)	O(9)–Si(9)–O(29)–Si(2I)	–45.5(1.5)
O(3)–Si(3)–O(23)–Si(23)	–177.1(8)	C(91)–Si(9)–O(29)–Si(2I)	–166.7(1.3)
C(31)–Si(3)–O(23)–Si(23)	63.5(1.0)	O(9)–Si(10)–O(30)–Si(30)	–127.9(2.0)
O(3)–Si(4)–O(24)–Si(24)	151.8(9)	O(10)–Si(10)–O(30)–Si(30)	–10.7(2.2)
O(4)–Si(4)–O(24)–Si(24)	–90.0(1.1)	C(101)–Si(10)–O(30)–Si(30)	111.2(2.1)
C(41)–Si(4)–O(24)–Si(24)	30.9(1.2)	O(10)–Si(11)–O(31)–Si(31)	–85.4(1.4)
O(3)–Si(4)–O(24)–Si(2D)	176.7(1.8)	O(11)–Si(11)–O(31)–Si(31)	32.4(1.5)
O(4)–Si(4)–O(24)–Si(2D)	–65.1(2.0)	C(111)–Si(11)–O(31)–Si(31)	155.2(1.3)
C(41)–Si(4)–O(24)–Si(2D)	55.8(2.0)	O(11)–Si(12)–O(32)–Si(32)	–47.2(3.2)
O(4)–Si(5)–O(25)–Si(25)	–98.5(1.9)	O(12)–Si(12)–O(32)–Si(32)	71.2(3.1)
O(5)–Si(5)–O(25)–Si(25)	19.6(2.0)	C(121)–Si(12)–O(32)–Si(32)	–167.7(3.0)
C(51)–Si(5)–O(25)–Si(25)	138.8(1.8)		
Phenyl substituents			
O(1)–Si(1)–C(11)–C(12)	150.3(1.0)	O(6)–Si(7)–C(71)–C(72)	–157.7(8)
O(12)–Si(1)–C(11)–C(12)	26.8(1.0)	O(7)–Si(7)–C(71)–C(72)	–39.2(1.0)
O(21)–Si(1)–C(11)–C(12)	–92.2(1.1)	O(27)–Si(7)–C(71)–C(72)	82.3(9)
O(1)–Si(1)–C(11A)–C(12A)	–78.4(1.0)	O(7)–Si(8)–C(81)–C(82)	–114.8(9)
O(12)–Si(1)–C(11A)–C(12A)	161.9(1.0)	O(8)–Si(8)–C(81)–C(82)	6.3(1.0)
O(21)–Si(1)–C(11A)–C(12A)	37.3(1.0)	O(28)–Si(8)–C(81)–C(82)	127.6(9)
O(1)–Si(1)–C(11B)–C(12B)	38.4(1.0)	O(8)–Si(9)–C(91)–C(92)	–81.3(8)
O(12)–Si(1)–C(11B)–C(12B)	–80.5(1.0)	O(9)–Si(9)–C(91)–C(92)	36.9(9)
O(21)–Si(1)–C(11B)–C(12B)	161.3(1.0)	O(29)–Si(9)–C(91)–C(92)	159.2(7)
O(1)–Si(2)–C(21)–C(22)	21.4(1.4)	O(9)–Si(10)–C(101)–C(102)	–131.9(9)
O(2)–Si(2)–C(21)–C(22)	140.2(1.3)	O(10)–Si(10)–C(101)–C(102)	112.1(1.0)
O(22)–Si(2)–C(21)–C(22)	–98.0(1.3)	O(30)–Si(10)–C(101)–C(102)	–10.9(1.1)
O(2)–Si(3)–C(31)–C(32)	179.5(8)	O(10)–Si(11)–C(111)–C(112)	58.9(8)
O(3)–Si(3)–C(31)–C(32)	–60.9(9)	O(11)–Si(11)–C(111)–C(112)	–60.3(9)
O(23)–Si(3)–C(31)–C(32)	57.4(1.0)	O(31)–Si(11)–C(111)–C(112)	178.6(7)
O(3)–Si(4)–C(41)–C(42)	–73.0(1.1)	O(11)–Si(12)–C(121)–C(122)	–163.8(1.3)
O(4)–Si(4)–C(41)–C(42)	170.1(1.0)	O(12)–Si(12)–C(121)–C(122)	77.7(1.4)
O(24)–Si(4)–C(41)–C(42)	47.4(1.2)	O(32)–Si(12)–C(121)–C(122)	–43.1(1.4)
O(4)–Si(5)–C(51)–C(52)	48.4(1.5)	O(11)–Si(12)–C(121)–C(127)	–126.2(1.7)
O(5)–Si(5)–C(51)–C(52)	–69.1(1.4)	O(12)–Si(12)–C(121)–C(127)	115.3(1.7)
O(25)–Si(5)–C(51)–C(52)	170.1(1.3)	O(32)–Si(12)–C(121)–C(127)	–5.5(1.8)
		O(5)–Si(6)–C(61)–C(62)	55.7(1.0)
		O(6)–Si(6)–C(61)–C(62)	–60.7(1.1)
		O(26)–Si(6)–C(61)–C(62)	177.6(9)

collection and structure refinement are given in Table 5. The structures of **3** and **4** were solved by direct method (SHELXS program [8]) and refined on F^2 (SHELXL program [9]) in anisotropic approximation for all non-hydrogen atoms.

Table 3
Selected bond lengths (d , Å) and angles (ω , °) for **3**

Bond	d	Angle	ω
Si(1)–O(1)	1.617(2)	O(1)–Si(1)–O(6)	109.7(1)
Si(1)–O(6)	1.618(2)	O(1)–Si(1)–O(11)	109.1(1)
Si(2)–O(1)	1.622(2)	O(6)–Si(1)–O(11)	108.3(1)
Si(2)–O(2)	1.606(2)	O(1)–Si(1)–C(11)	110.9(1)
Si(3)–O(2)	1.612(2)	O(6)–Si(1)–C(11)	108.9(1)
Si(3)–O(3)	1.617(2)	O(11)–Si(1)–C(11)	110.0(2)
Si(4)–O(3)	1.616(2)	O(1)–Si(2)–O(2)	109.5(1)
Si(4)–O(4)	1.619(2)	O(1)–Si(2)–O(12)	109.1(1)
Si(5)–O(4)	1.620(2)	O(2)–Si(2)–O(12)	107.4(1)
Si(5)–O(5)	1.611(2)	O(1)–Si(2)–C(21)	107.9(1)
Si(6)–O(5)	1.612(2)	O(2)–Si(2)–C(21)	111.2(1)
Si(6)–O(6)	1.613(2)	O(12)–Si(2)–C(21)	111.7(1)
Si(1)–O(11)	1.612(2)	O(2)–Si(3)–O(3)	106.2(1)
Si(2)–O(12)	1.604(2)	O(2)–Si(3)–O(13)	110.4(1)
Si(3)–O(13)	1.610(3)	O(3)–Si(3)–O(13)	111.3(2)
Si(4)–O(14)	1.616(2)	O(2)–Si(3)–C(31)	110.2(1)
Si(5)–O(15)	1.613(2)	O(3)–Si(3)–C(31)	110.0(1)
Si(6)–O(16)	1.595(3)	O(13)–Si(3)–C(31)	108.7(2)
Si(1)–C(11)	1.855(3)	O(3)–Si(4)–O(4)	108.0(1)
Si(2)–C(21)	1.858(3)	O(3)–Si(4)–O(14)	108.9(1)
Si(3)–C(31)	1.845(3)	O(4)–Si(4)–O(14)	109.3(1)
Si(4)–C(41)	1.860(3)	O(3)–Si(4)–C(41)	111.2(1)
Si(5)–C(51)	1.852(3)	O(4)–Si(4)–C(41)	109.5(1)
Si(6)–C(61)	1.849(3)	O(14)–Si(4)–C(41)	109.9(1)
Si(11)–O(11)	1.631(3)	O(4)–Si(5)–O(5)	109.2(1)
Si(12)–O(12)	1.645(2)	O(4)–Si(5)–O(15)	107.1(1)
Si(13)–O(13)	1.642(3)	O(5)–Si(5)–O(15)	110.0(1)
Si(14)–O(14)	1.646(2)	O(4)–Si(5)–C(51)	109.3(1)
Si(15)–O(15)	1.633(2)	O(5)–Si(5)–C(51)	110.7(1)
Si(16)–O(16)	1.623(3)	O(15)–Si(5)–C(51)	110.4(1)
Si(11)–C(17)	1.846(5)	O(5)–Si(6)–O(6)	106.0(1)
Si(11)–C(18)	1.853(5)	O(5)–Si(6)–O(16)	110.2(1)
Si(11)–C(19)	1.844(5)	O(6)–Si(6)–O(16)	110.8(2)
Si(12)–C(27)	1.853(4)	O(5)–Si(6)–C(61)	110.4(1)
Si(12)–C(28)	1.855(4)	O(6)–Si(6)–C(61)	111.8(1)
Si(12)–C(29)	1.847(3)	O(16)–Si(6)–C(61)	107.8(1)
Si(13)–C(37)	1.852(5)	Si(1)–O(1)–Si(2)	150.0(2)
Si(13)–C(38)	1.845(4)	Si(2)–O(2)–Si(3)	162.6(2)
Si(13)–C(39)	1.850(5)	Si(3)–O(3)–Si(4)	148.2(2)
Si(14)–C(47A)	1.955(9)	Si(4)–O(4)–Si(5)	150.2(2)
Si(14)–C(48A)	1.742(9)	Si(5)–O(5)–Si(6)	164.8(2)
Si(14)–C(49A)	1.873(8)	Si(1)–O(6)–Si(6)	147.3(2)
Si(14)–C(47B)	1.760(11)	Si(1)–O(11)–Si(11)	152.2(2)
Si(14)–C(48B)	1.988(9)	Si(2)–O(12)–Si(12)	145.6(2)
Si(14)–C(49B)	1.788(9)	Si(3)–O(13)–Si(13)	150.5(2)
Si(15)–C(57)	1.854(5)	Si(4)–O(14)–Si(14)	139.3(2)
Si(15)–C(58)	1.846(5)	Si(5)–O(15)–Si(15)	148.0(2)
Si(15)–C(59)	1.851(5)	Si(6)–O(16)–Si(16)	164.5(2)
Si(16)–C(67)	1.854(4)	C(16)–C(11)–C(12)	116.5(3)
Si(16)–C(68)	1.855(4)	C(26)–C(21)–C(22)	117.1(3)
Si(16)–C(69)	1.860(4)	C(36)–C(31)–C(32)	117.0(3)
		C(42)–C(41)–C(46)	117.1(3)
		C(52)–C(51)–C(56)	117.2(3)
		C(62)–C(61)–C(66)	116.9(3)

Table 4
Selected bond lengths (d , Å) and angles (ω , °) for **4**

Bond	d	Angle	ω
Si(1)–O(1)	1.602(6)	O(1)–Si(1)–O(12)	110.5(3)
Si(1)–O(12)	1.607(6)	O(1)–Si(1)–O(21)	108.8(4)
Si(2)–O(1)	1.606(5)	O(12)–Si(1)–O(21)	109.0(4)
Si(2)–O(2)	1.617(6)	O(1)–Si(1)–C(11)	109.9(6)
Si(3)–O(2)	1.593(6)	O(12)–Si(1)–C(11)	112.4(6)
Si(3)–O(3)	1.624(6)	O(21)–Si(1)–C(11)	106.1(4)
Si(4)–O(3)	1.609(6)	O(1)–Si(1)–C(11A)	101.8(4)
Si(4)–O(4)	1.615(6)	O(12)–Si(1)–C(11A)	115.4(7)
Si(5)–O(4)	1.592(6)	O(21)–Si(1)–C(11A)	111.0(6)
Si(5)–O(5)	1.582(6)	O(1)–Si(1)–C(11B)	111.2(6)
Si(6)–O(5)	1.610(6)	O(12)–Si(1)–C(11B)	104.0(4)
Si(6)–O(6)	1.602(6)	O(21)–Si(1)–C(11B)	113.3(7)
Si(7)–O(6)	1.588(6)	O(1)–Si(2)–O(2)	108.0(3)
Si(7)–O(7)	1.608(5)	O(1)–Si(2)–O(22)	108.7(3)
Si(8)–O(7)	1.591(6)	O(2)–Si(2)–O(22)	109.7(3)
Si(8)–O(8)	1.581(5)	O(1)–Si(2)–C(21)	109.1(5)
Si(9)–O(8)	1.598(5)	O(2)–Si(2)–C(21)	110.9(5)
Si(9)–O(9)	1.620(5)	O(22)–Si(2)–C(21)	110.3(4)
Si(10)–O(9)	1.617(5)	O(2)–Si(3)–O(3)	109.2(3)
Si(10)–O(10)	1.603(6)	O(2)–Si(3)–O(23)	111.3(3)
Si(11)–O(10)	1.607(5)	O(3)–Si(3)–O(23)	107.9(3)
Si(11)–O(11)	1.592(6)	O(2)–Si(3)–C(31)	109.1(5)
Si(12)–O(11)	1.615(6)	O(3)–Si(3)–C(31)	109.8(4)
Si(12)–O(12)	1.612(6)	O(23)–Si(3)–C(31)	109.5(4)
Si(1)–O(21)	1.590(6)	O(3)–Si(4)–O(4)	107.2(3)
Si(2)–O(22)	1.575(6)	O(3)–Si(4)–O(24)	108.9(4)
Si(3)–O(23)	1.584(6)	O(4)–Si(4)–O(24)	111.6(4)
Si(4)–O(24)	1.568(7)	O(3)–Si(4)–C(41)	109.9(4)
Si(5)–O(25)	1.555(8)	O(4)–Si(4)–C(41)	108.4(6)
Si(6)–O(26)	1.594(6)	O(24)–Si(4)–C(41)	110.7(6)
Si(7)–O(27)	1.589(6)	O(4)–Si(5)–O(5)	106.8(4)
Si(8)–O(28)	1.582(6)	O(4)–Si(5)–O(25)	110.2(4)
Si(9)–O(29)	1.569(5)	O(5)–Si(5)–O(25)	111.0(4)
Si(10)–O(30)	1.580(6)	O(4)–Si(5)–C(51)	111.7(6)
Si(11)–O(31)	1.578(6)	O(5)–Si(5)–C(51)	108.6(5)
Si(12)–O(32)	1.597(5)	O(25)–Si(5)–C(51)	108.6(7)
Si(1)–C(11)	1.85(3)	O(5)–Si(6)–O(6)	106.5(3)
Si(1)–C(11A)	1.87(4)	O(5)–Si(6)–O(26)	109.7(4)
Si(1)–C(11B)	1.83(3)	O(6)–Si(6)–O(26)	110.8(4)
Si(2)–C(21)	1.82(1)	O(5)–Si(6)–C(61)	110.6(4)
Si(3)–C(31)	1.84(1)	O(6)–Si(6)–C(61)	108.4(4)
Si(4)–C(41)	1.83(1)	O(26)–Si(6)–C(61)	110.8(4)
Si(5)–C(51)	1.86(1)	O(6)–Si(7)–O(7)	108.4(3)
Si(6)–C(61)	1.82(1)	O(6)–Si(7)–O(27)	108.9(4)
Si(7)–C(71)	1.81(1)	O(7)–Si(7)–O(27)	109.8(4)
Si(8)–C(81)	1.84(1)	O(6)–Si(7)–C(71)	108.9(4)
Si(9)–C(91)	1.83(1)	O(7)–Si(7)–C(71)	109.6(4)
Si(10)–C(101)	1.83(1)	O(27)–Si(7)–C(71)	111.1(4)
Si(11)–C(111)	1.833(9)	O(7)–Si(8)–O(8)	108.9(3)
Si(12)–C(121)	1.82(1)	O(7)–Si(8)–O(28)	107.3(4)
Si(21)–O(21)	1.77(1)	O(8)–Si(8)–O(28)	110.3(3)
Si(2A)–O(21)	1.55(1)	O(7)–Si(8)–C(81)	110.9(4)
Si(22)–O(22)	1.630(6)	O(8)–Si(8)–C(81)	111.0(4)
Si(23)–O(23)	1.628(6)	O(28)–Si(8)–C(81)	108.5(4)
Si(24)–O(24)	1.63(1)	O(8)–Si(9)–O(9)	107.3(3)
Si(2D)–O(24)	1.68(1)	O(8)–Si(9)–O(29)	109.0(3)
Si(25)–O(25)	1.599(8)	O(9)–Si(9)–O(29)	111.5(3)
Si(26)–O(26)	1.593(6)	O(8)–Si(9)–C(91)	110.5(3)
Si(27)–O(27)	1.564(6)	O(9)–Si(9)–C(91)	109.8(4)
Si(28)–O(28)	1.628(6)	O(29)–Si(9)–C(91)	108.7(4)
Si(29)–O(29)	1.575(8)	O(9)–Si(10)–O(10)	105.6(3)
Si(21)–O(29)	1.679(8)	O(9)–Si(10)–O(30)	110.4(3)

Table 4 (continued)

Bond	<i>d</i>	Angle	ω
Si(30)–O(30)	1.620(6)	O(10)–Si(10)–O(30)	111.9(3)
Si(31)–O(31)	1.618(6)	O(9)–Si(10)–C(101)	110.0(4)
Si(32)–O(32)	1.585(6)	O(10)–Si(10)–C(101)	110.2(4)
Si(21)–C(21A)	2.10(3)	O(30)–Si(10)–C(101)	108.8(5)
Si(21)–C(21B)	1.63(4)	O(10)–Si(11)–O(11)	107.4(3)
Si(21)–C(21C)	1.72(3)	O(10)–Si(11)–O(31)	109.9(3)
Si(2A)–C(21D)	1.92(3)	O(11)–Si(11)–O(31)	109.6(4)
Si(2A)–C(21E)	1.54(5)	O(10)–Si(11)–C(111)	109.4(4)
Si(2A)–C(21F)	2.04(3)	O(11)–Si(11)–C(111)	112.3(4)
Si(22)–C(22A)	1.84(1)	O(31)–Si(11)–C(111)	108.3(4)
Si(22)–C(22B)	1.849(9)	O(11)–Si(12)–O(12)	107.8(3)
Si(22)–C(22C)	1.83(1)	O(11)–Si(12)–O(32)	110.0(3)
Si(23)–C(23A)	1.78(1)	O(12)–Si(12)–O(32)	109.7(4)
Si(23)–C(23B)	1.84(2)	O(11)–Si(12)–C(121)	109.5(4)
Si(23)–C(23C)	1.79(1)	O(12)–Si(12)–C(121)	110.2(4)
Si(24)–C(24A)	1.80(3)	O(32)–Si(12)–C(121)	109.7(4)
Si(24)–C(24B)	1.74(3)	Si(1)–O(1)–Si(2)	154.6(4)
Si(24)–C(24C)	2.10(3)	Si(2)–O(2)–Si(3)	160.3(4)
Si(2D)–C(24D)	1.64(3)	Si(3)–O(3)–Si(4)	145.5(4)
Si(2D)–C(24E)	2.01(3)	Si(4)–O(4)–Si(5)	151.1(5)
Si(2D)–C(24F)	1.56(4)	Si(5)–O(5)–Si(6)	151.6(4)
Si(25)–C(25A)	1.82(1)	Si(6)–O(6)–Si(7)	158.7(4)
Si(25)–C(25B)	1.79(2)	Si(7)–O(7)–Si(8)	156.7(4)
Si(25)–C(25C)	1.86(2)	Si(8)–O(8)–Si(9)	175.9(4)
Si(26)–C(26A)	1.83(1)	Si(9)–O(9)–Si(10)	144.8(4)
Si(26)–C(26B)	1.85(1)	Si(10)–O(10)–Si(11)	149.8(3)
Si(26)–C(26C)	1.86(1)	Si(11)–O(11)–Si(12)	152.7(4)
Si(27)–C(27A)	1.79(1)	Si(1)–O(12)–Si(12)	147.7(4)
Si(27)–C(27B)	1.87(1)	Si(1)–O(21)–Si(21)	155.3(6)
Si(27)–C(27C)	1.85(1)	Si(1)–O(21)–Si(2A)	148.3(7)
Si(28)–C(28A)	1.82(1)	Si(2)–O(22)–Si(22)	148.7(5)
Si(28)–C(28B)	1.80(2)	Si(3)–O(23)–Si(23)	147.4(5)
Si(28)–C(28C)	1.85(1)	Si(4)–O(24)–Si(24)	141.2(7)
Si(29)–C(29A)	1.69(4)	Si(4)–O(24)–Si(2D)	158.9(7)
Si(29)–C(29B)	1.79(3)	Si(5)–O(25)–Si(25)	161.6(6)
Si(29)–C(29C)	1.73(2)	Si(6)–O(26)–Si(26)	177.9(5)
Si(21)–C(29D)	1.70(3)	Si(7)–O(27)–Si(27)	168.5(5)
Si(21)–C(29E)	1.81(2)	Si(8)–O(28)–Si(28)	151.1(5)
Si(21)–C(29F)	1.77(2)	Si(9)–O(29)–Si(29)	171.2(5)
Si(30)–C(30A)	1.86(1)	Si(9)–O(29)–Si(21)	159.9(5)
Si(30)–C(30B)	1.86(1)	Si(10)–O(30)–Si(30)	168.7(5)
Si(30)–C(30C)	1.85(1)	Si(11)–O(31)–Si(31)	160.7(5)
Si(31)–C(31A)	1.85(1)	Si(32)–O(32)–Si(12)	170.2(5)
Si(31)–C(31B)	1.81(1)	C(16)–C(11)–C(12)	121(5)
Si(31)–C(31C)	1.81(1)	C(12A)–C(11A)–C(16A)	124(4)
Si(32)–C(32A)	1.83(2)	C(12B)–C(11B)–C(16B)	119(4)
Si(32)–C(32B)	1.82(1)	C(22)–C(21)–C(26)	116(1)
Si(32)–C(32C)	1.83(2)	C(32)–C(31)–C(36)	116(1)
		C(42)–C(41)–C(46)	116(2)
		C(52)–C(51)–C(56)	120(2)
		C(62)–C(61)–C(66)	113(1)
		C(72)–C(71)–C(76)	114(1)
		C(82)–C(81)–C(86)	116(1)
		C(92)–C(91)–C(96)	116(1)
		C(102)–C(101)–C(106)	115(1)
		C(112)–C(111)–C(116)	115.4(9)
		C(122)–C(121)–C(126)	118(2)
		C(127)–C(121)–C(131)	118(2)

In the structure **3**, one of the SiMe₃ groups has been found to be disordered (rotation around the O(14)–Si(14) bond; Fig. 3). The two corresponding sets of

Table 5

Crystal data and structure refinement for **3** and **4**

	3	4
Empirical formula	C ₅₄ H ₈₄ O ₁₂ Si ₁₂	C ₁₀₈ H ₁₆₈ O ₂₄ Si ₂₄ · 1/4C ₇ H ₈
Formula weight	1262.28	2547.62
Temperature (K)	153(2)	193(2)
Wavelength (Å)	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
Unit cell dimensions		
<i>a</i> (Å)	20.247(7)	64.23(3)
<i>b</i> (Å)	17.772(5)	13.335(5)
<i>c</i> (Å)	39.755(12)	37.342(14)
β (°)	96.93(2)	106.16(2)
<i>V</i> (Å ³)	14 201(8)	30 721(22)
<i>Z</i>	8	8
<i>d</i> _{calc.} (g cm ⁻³)	1.181	1.102
μ (mm ⁻¹)	0.269	2.306
<i>F</i> (000)	5376	10 852
θ range for $\omega/2\theta$ -data collection (°)	2.03–27.54	2.46–55.06
Limiting indices	–24 < <i>h</i> < 24 –1 < <i>k</i> < 23 –51 < <i>l</i> < 51	0 < <i>h</i> < 68 0 < <i>k</i> < 14 –39 < <i>l</i> < 38
Reflections collected	14 215	19 521
Independent reflections	13 749	19 294
<i>R</i> _{int}	0.0444	0.0415
Data/restraints/parameters	13 688/0/733	19 273/54/1482
Weight scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$	a = 0.0582 b = 54.57	a = 0.0879 b = 102.81
Goodness-of-fit on <i>F</i> ²	1.049	1.075
Reflections observed (<i>I</i> > 2 σ (<i>I</i>))	10 355	8160
Final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))		
<i>R</i> ₁	0.0529	0.0944
<i>wR</i> ₂	0.1279	0.1845
<i>R</i> indices (all data)		
<i>R</i> ₁	0.0836	0.2546
<i>wR</i> ₂	0.1559	0.2543
Largest diff. Peak/hole (e Å ⁻³)	0.736/–0.556	0.319/–0.434

position of the Me group (C(47A)–C(49A) and C(47B)–C(49B)) were refined isotropically with equal occupancy factors *g* = 0.5.

The structure of **4** is less ordered (Fig. 4). A Ph group C(11)–C(16) bonded to Si(1) has two more alternative positions: C(11A)–C(16A) and C(11B)–C(16B), differing from each other by turns of ca. 60° around the Si–C(Ph) bond. The Si–C bond is oriented differently for these three positions of the benzene ring so that the positions of the *ipso*-atom (C(11), C(11A) and C(11B)) do not coincide. Carbon atoms of this disordered group were refined with occupancy factors *g* = 1/3 and with equal isotropic thermal parameters for the *ipso*-atom and for the rest, separately. The C–C bond lengths were put into refinement to be equal 1.38 Å, all Si(1)···*ortho*-C distances were fixed to be equal to 2.80

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (\AA^2 ; $\times 10^3$) for **3**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Si(1)	8696(1)	532(1)	5771(1)	26(1)
Si(2)	8279(1)	−951(1)	6113(1)	22(1)
Si(3)	6777(1)	−564(1)	6203(1)	25(1)
Si(4)	6216(1)	849(1)	6532(1)	23(1)
Si(5)	6869(1)	2289(1)	6261(1)	25(1)
Si(6)	8393(1)	1833(1)	6249(1)	24(1)
Si(11)	10226(1)	647(1)	5701(1)	32(1)
Si(12)	9205(1)	−1821(1)	6659(1)	26(1)
Si(13)	6600(1)	−1608(1)	6824(1)	39(1)
Si(14)	6350(1)	1105(1)	7298(1)	38(1)
Si(15)	7113(1)	3819(1)	6640(1)	34(1)
Si(16)	9061(1)	1154(1)	6951(1)	30(1)
O(1)	8687(1)	−278(1)	5955(1)	30(1)
O(2)	7566(1)	−644(1)	6189(1)	34(1)
O(3)	6658(1)	281(1)	6334(1)	30(1)
O(4)	6458(1)	1699(1)	6467(1)	29(1)
O(5)	7644(1)	2058(1)	6309(1)	32(1)
O(6)	8322(1)	1148(1)	5981(1)	35(1)
O(11)	9457(1)	797(1)	5767(1)	40(1)
O(12)	8677(1)	−1210(1)	6468(1)	30(1)
O(13)	6526(1)	−1181(2)	6455(1)	49(1)
O(14)	6344(1)	667(1)	6933(1)	29(1)
O(15)	6776(1)	3110(1)	6421(1)	38(1)
O(16)	8804(1)	1577(2)	6598(1)	48(1)
C(11)	8270(2)	484(2)	5331(1)	28(1)
C(12)	8434(2)	987(3)	5086(1)	53(1)
C(13)	8126(2)	978(3)	4759(1)	60(1)
C(14)	7643(2)	456(3)	4663(1)	51(1)
C(15)	7454(2)	−40(2)	4901(1)	57(1)
C(16)	7762(2)	−23(2)	5231(1)	45(1)
C(17)	10366(3)	976(3)	5275(1)	80(2)
C(18)	10768(2)	1205(3)	6017(1)	77(2)
C(19)	10410(3)	−367(3)	5747(2)	75(2)
C(21)	8189(2)	−1733(2)	5802(1)	29(1)
C(22)	8552(2)	−1741(2)	5525(1)	42(1)
C(23)	8480(2)	−2314(2)	5285(1)	56(1)
C(24)	8046(2)	−2888(2)	5319(1)	51(1)
C(25)	7685(2)	−2910(2)	5591(1)	51(1)
C(26)	7758(2)	−2330(2)	5831(1)	40(1)
C(27)	8761(2)	−2714(2)	6719(1)	44(1)
C(28)	9880(2)	−1986(2)	6391(1)	45(1)
C(29)	9527(2)	−1411(2)	7074(1)	38(1)
C(31)	6320(2)	−702(2)	5777(1)	28(1)
C(32)	6117(2)	−1421(2)	5659(1)	42(1)
C(33)	5786(2)	−1522(3)	5342(1)	59(1)
C(34)	5645(2)	−930(3)	5126(1)	64(1)
C(35)	5833(2)	−213(3)	5235(1)	64(1)
C(36)	6165(2)	−101(2)	5557(1)	45(1)
C(37)	6670(3)	−2629(2)	6743(1)	62(1)
C(38)	7345(2)	−1253(2)	7090(1)	49(1)
C(39)	5845(2)	−1413(3)	7030(1)	58(1)
C(41)	5316(2)	755(2)	6378(1)	26(1)
C(42)	4874(2)	377(2)	6563(1)	34(1)
C(43)	4202(2)	311(2)	6440(1)	42(1)
C(44)	3960(2)	634(2)	6135(1)	39(1)
C(45)	4381(2)	1015(2)	5948(1)	40(1)
C(46)	5054(2)	1067(2)	6068(1)	35(1)
C(47A) ^a	7163(4)	1706(5)	7368(2)	55(2) ^b
C(48A) ^a	6343(5)	467(5)	7630(2)	52(2) ^b
C(49A) ^a	5656(4)	1809(5)	7259(2)	38(2) ^b

Table 6 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(47B) ^a	7158(6)	1182(7)	7515(3)	80(3) ^b
C(48B) ^a	5880(5)	393(5)	7573(2)	56(2) ^b
C(49B) ^a	5875(5)	1954(5)	7242(2)	45(2) ^b
C(51)	6529(2)	2274(2)	5807(1)	26(1)
C(52)	6844(2)	1889(2)	5564(1)	33(1)
C(53)	6559(2)	1846(2)	5230(1)	39(1)
C(54)	5945(2)	2178(2)	5129(1)	39(1)
C(55)	5627(2)	2560(2)	5365(1)	40(1)
C(56)	5915(2)	2614(2)	5697(1)	34(1)
C(57)	7320(3)	4556(3)	6339(1)	79(2)
C(58)	7897(3)	3528(3)	6891(1)	74(2)
C(59)	6495(3)	4164(3)	6911(2)	82(2)
C(61)	8825(2)	2650(2)	6088(1)	25(1)
C(62)	9450(2)	2864(2)	6241(1)	41(1)
C(63)	9787(2)	3471(2)	6124(1)	54(1)
C(64)	9509(2)	3881(2)	5850(1)	39(1)
C(65)	8890(2)	3686(2)	5694(1)	37(1)
C(66)	8549(2)	3076(2)	5811(1)	34(1)
C(67)	8470(2)	388(2)	7019(1)	53(1)
C(68)	9102(2)	1873(2)	7292(1)	51(1)
C(69)	9902(2)	772(2)	6910(1)	51(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^a Atoms of the disordered SiMe_3 group; $g = 0.5$.

^b U_{iso} .

\AA and the geometry of the cycles (including the external Si atom) was set to be flat. A neighbouring C(121)–C(126) Ph group is rotationally disordered, too, but has only one alternative orientation (C(127)–C(131), the C(121)-*ipso*-atom position does not split). The C(122)–C(131) atom positions were refined isotropically with occupancy factors $g = 0.5$. Moreover, three of $-\text{SiMe}_3$ groups have turned out to be disordered in two positions (by rotation around both Si–O and O–Si bonds): $-\text{Si}(21)\text{C}(21\text{A}-\text{C})$ (an alternative position $-\text{Si}(2\text{A})\text{C}(21\text{D}-\text{F})$), $-\text{Si}(24)\text{C}(24\text{A}-\text{C})$ ($-\text{Si}(2\text{D})\text{C}(24\text{D}-\text{F})$) and $-\text{Si}(29)\text{C}(29\text{A}-\text{C})$ ($-\text{Si}(21)\text{C}(29\text{D}-\text{F})$). The Si and C atoms in both alternative positions were refined isotropically with occupancy factors $g = 0.5$.

In a difference Fourier map in the structure **4** some significant peaks were localized and identified as a solvate toluene molecule with a total population 0.5 and disordered by a two-fold axis. Corresponding atoms C(1T)–C(7T) were put into refinement with an occupancy factor $g = 0.25$ and with a common isotropic thermal parameter. Endocyclic bond lengths C–C were fixed to be equal to 1.38 \AA , exocyclic bond C–Me was taken equal to 1.51 \AA , 1,3-distances C···C in the cycle were leveled 2.39 \AA and external 1,3-distances Me···C were taken to be equal each other. The geometry of the molecule was set to be flat at the refinement.

Hydrogen atoms both in **3** and **4** structures were placed in geometrically calculated positions and put into refinement using the riding model with torsion angles OSiCH (CCCH in the toluene solvent molecule in the structure **4**) optimized for Me groups. Their

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (\AA^2 ; $\times 10^3$) for **4**

Atom	x	y	z	U_{eq}
Si(1)	977(1)	6812(2)	1272(1)	90(1)
Si(2)	853(1)	7819(2)	484(1)	79(1)
Si(3)	536(1)	6816(2)	-228(1)	80(1)
Si(4)	500(1)	7767(2)	-997(1)	94(1)
Si(5)	831(1)	7312(2)	-1444(1)	97(1)
Si(6)	1248(1)	8526(2)	-1399(1)	81(1)
Si(7)	1660(1)	8670(2)	-714(1)	76(1)
Si(8)	1671(1)	10530(2)	-197(1)	67(1)
Si(9)	2058(1)	10547(2)	550(1)	67(1)
Si(10)	2027(1)	10042(2)	1341(1)	71(1)
Si(11)	1855(1)	8212(2)	1683(1)	73(1)
Si(12)	1382(1)	7950(2)	1735(1)	81(1)
Si(21) ^a	601(1)	7439(7)	1674(2)	121(3) ^b
Si(2A) ^a	647(2)	6857(8)	1713(2)	142(3) ^b
Si(22)	1271(1)	7663(2)	234(1)	96(1)
Si(23)	110(1)	7170(3)	-20(1)	132(1)
Si(24) ^a	88(2)	7095(9)	-1559(3)	143(4) ^b
Si(2D) ^a	107(2)	6648(11)	-1572(3)	155(5) ^b
Si(25)	933(1)	5062(3)	-1250(1)	145(1)
Si(26)	1447(1)	7482(3)	-1998(1)	119(1)
Si(27)	2033(1)	9411(2)	-1042(1)	101(1)
Si(28)	1273(1)	11474(3)	-4(1)	127(1)
Si(29) ^a	2263(1)	12686(6)	726(2)	100(3) ^b
Si(2I) ^a	2161(1)	12873(5)	716(2)	77(2) ^b
Si(30)	2527(1)	9593(3)	1725(1)	111(1)
Si(31)	1979(1)	6112(2)	1414(1)	99(1)
Si(32)	1518(1)	6733(3)	2494(1)	135(1)
O(1)	860(1)	7264(4)	869(1)	86(2)
O(2)	713(1)	7132(4)	146(2)	99(2)
O(3)	595(1)	7333(4)	-582(2)	87(2)
O(4)	697(1)	7795(5)	-1187(2)	112(2)
O(5)	1065(1)	7802(5)	-1323(2)	97(2)
O(6)	1428(1)	8662(4)	-1008(1)	89(2)
O(7)	1657(1)	9460(4)	-390(1)	89(2)
O(8)	1859(1)	10510(4)	181(1)	79(2)
O(9)	1968(1)	10177(4)	893(1)	79(2)
O(10)	1897(1)	9067(4)	1408(1)	80(2)
O(11)	1599(1)	8099(4)	1603(1)	88(2)
O(12)	1217(1)	7265(5)	1428(2)	94(2)
O(21)	839(1)	7104(6)	1551(2)	143(3)
O(22)	1092(1)	7927(5)	454(2)	107(2)
O(23)	301(1)	7184(5)	-228(2)	104(2)
O(24)	312(1)	7068(6)	-1219(2)	131(3)
O(25)	845(1)	6155(6)	-1391(2)	157(3)
O(26)	1351(1)	8021(5)	-1698(2)	115(2)
O(27)	1835(1)	9003(6)	-919(2)	132(3)
O(28)	1445(1)	10729(5)	-117(2)	112(2)
O(29)	2147(1)	11647(4)	611(2)	94(2)
O(30)	2280(1)	9917(5)	1511(2)	98(2)
O(31)	1954(1)	7185(4)	1601(2)	106(2)
O(32)	1439(1)	7404(5)	2131(2)	108(2)
C(11) ^c	976(3)	5427(26)	1251(4)	113(4) ^b
C(12) ^c	1142(5)	4897(13)	1492(9)	188(4) ^b
C(13) ^c	1136(6)	3861(13)	1468(11)	188(4) ^b
C(14) ^c	967(5)	3384(41)	1208(9)	188(4) ^b
C(15) ^c	799(7)	3905(13)	963(10)	188(4) ^b
C(16) ^c	810(6)	4939(15)	994(9)	188(4) ^b
C(11A) ^c	962(3)	5432(26)	1177(3)	113(4) ^b
C(12A) ^c	769(6)	4945(15)	1146(7)	188(4) ^b
C(13A) ^c	767(7)	3926(18)	1076(7)	188(4) ^b
C(14A) ^c	955(6)	3474(37)	1040(6)	188(4) ^b

Table 7 (continued)

Atom	x	y	z	U_{eq}
C(15A) ^c	1153(8)	3939(15)	1069(7)	188(4) ^b
C(16A) ^c	1147(6)	4958(15)	1141(6)	188(4) ^b
C(11B) ^c	1021(2)	5458(24)	1248(5)	113(4) ^b
C(12B) ^c	1080(4)	5048(17)	951(9)	188(4) ^b
C(13B) ^c	1120(5)	4055(13)	886(11)	188(4) ^b
C(14B) ^c	1092(3)	3457(35)	1171(9)	188(4) ^b
C(15B) ^c	1033(4)	3822(19)	1475(12)	188(4) ^b
C(16B) ^c	995(4)	4827(11)	1525(10)	188(4) ^b
C(21)	730(2)	9048(8)	480(4)	102(3)
C(22)	720(3)	9522(12)	791(5)	220(9)
C(23)	633(5)	10477(18)	787(7)	303(16)
C(24)	557(3)	10952(16)	471(8)	208(10)
C(25)	552(3)	10534(15)	141(7)	182(7)
C(26)	643(2)	9558(11)	152(5)	144(5)
C(31)	536(2)	5442(8)	-276(4)	89(3)
C(32)	398(2)	4947(11)	-572(4)	134(4)
C(33)	398(3)	3902(13)	-602(5)	165(7)
C(34)	539(3)	3375(14)	-331(7)	162(7)
C(35)	672(3)	3800(17)	-38(6)	170(7)
C(36)	669(2)	4861(12)	-14(4)	131(4)
C(41)	402(2)	9050(10)	-978(3)	111(4)
C(42)	209(3)	9236(13)	-880(4)	185(7)
C(43)	129(3)	10236(18)	-889(5)	197(8)
C(44)	237(5)	11008(16)	-978(6)	208(10)
C(45)	406(4)	10824(20)	-1094(7)	238(11)
C(46)	495(3)	9828(15)	-1080(5)	184(7)
C(51)	705(2)	7589(16)	-1946(4)	141(5)
C(52)	645(3)	8554(20)	-2054(5)	209(9)
C(53)	556(4)	8826(25)	-2466(7)	292(17)
C(54)	562(8)	7924(41)	-2655(11)	327(39)
C(55)	567(9)	6967(41)	-2613(15)	380(37)
C(56)	677(3)	6847(22)	-2203(5)	271(14)
C(61)	1136(2)	9749(7)	-1558(3)	88(3)
C(62)	1032(2)	10320(10)	-1359(3)	138(5)
C(63)	941(3)	11264(12)	-1475(5)	170(6)
C(64)	952(3)	11611(12)	-1807(5)	188(7)
C(65)	1054(4)	11079(16)	-2005(5)	254(11)
C(66)	1140(3)	10177(12)	-1884(4)	192(7)
C(71)	1718(2)	7428(8)	-515(3)	80(3)
C(72)	1861(2)	7233(10)	-187(4)	124(4)
C(73)	1910(3)	6267(17)	-43(4)	145(6)
C(74)	1805(4)	5474(14)	-239(7)	158(7)
C(75)	1663(3)	5631(15)	-568(6)	206(9)
C(76)	1621(2)	6600(13)	-694(4)	161(6)
C(81)	1718(2)	11521(7)	-508(3)	81(3)
C(82)	1903(3)	12070(9)	-426(3)	139(5)
C(83)	1941(3)	12851(12)	-658(4)	179(7)
C(84)	1779(5)	13033(13)	-973(6)	187(11)
C(85)	1597(4)	12524(15)	-1068(5)	174(8)
C(86)	1563(2)	11760(10)	-839(3)	128(4)
C(91)	2275(2)	9718(9)	504(2)	76(3)
C(92)	2269(2)	8711(11)	566(3)	110(4)
C(93)	2428(3)	8065(11)	528(4)	144(5)
C(94)	2600(3)	8415(16)	436(4)	156(6)
C(95)	2617(2)	9418(16)	380(4)	160(6)
C(96)	2457(2)	10068(10)	408(3)	129(4)
C(101)	1938(2)	11140(8)	1551(3)	95(3)
C(102)	2062(3)	11631(10)	1846(4)	141(5)
C(103)	1991(4)	12461(14)	2015(6)	182(8)
C(104)	1797(5)	12796(20)	1872(8)	223(14)
C(105)	1670(4)	12345(23)	1594(9)	348(20)
C(106)	1741(3)	11486(14)	1428(5)	235(10)
C(111)	1987(2)	8568(8)	2167(2)	75(3)

Table 7 (continued)

Atom	x	y	z	U_{eq}
C(112)	1936(2)	9458(8)	2320(3)	96(3)
C(113)	2050(2)	9763(10)	2677(4)	127(4)
C(114)	2213(2)	9179(13)	2888(3)	134(5)
C(115)	2266(2)	8306(12)	2749(3)	136(5)
C(116)	2154(2)	8024(8)	2392(3)	105(3)
C(121)	1261(2)	9166(7)	1768(3)	90(3)
C(122) ^a	1097(4)	9282(19)	1973(6)	107(8) ^b
C(123) ^a	994(5)	10208(22)	1992(8)	122(10) ^b
C(124) ^a	1111(5)	11068(24)	1835(9)	127(11) ^b
C(125) ^a	1234(5)	10976(22)	1642(8)	150(10) ^b
C(126) ^a	1327(4)	10023(21)	1621(7)	123(8) ^b
C(127) ^a	1211(4)	9504(19)	2058(7)	107(8) ^b
C(128) ^a	1104(5)	10475(23)	2062(7)	120(9) ^b
C(129) ^a	1003(5)	10968(23)	1753(8)	127(11) ^b
C(130) ^a	1077(5)	10659(21)	1428(8)	149(9) ^b
C(131) ^a	1193(4)	9755(17)	1419(6)	109(7) ^b
C(21A) ^a	694(5)	6654(27)	2180(8)	210(13) ^b
C(21B) ^a	572(6)	8644(27)	1715(12)	285(20) ^b
C(21C) ^a	398(5)	6635(27)	1446(8)	202(13) ^b
C(21D) ^a	676(5)	7701(25)	2141(8)	188(12) ^b
C(21E) ^a	562(10)	5775(40)	1714(17)	485(45) ^b
C(21F) ^a	422(5)	7816(29)	1400(9)	225(15) ^b
C(22A)	1299(2)	6290(9)	235(4)	171(5)
C(22B)	1172(2)	8132(10)	-250(2)	139(5)
C(22C)	1525(2)	8257(9)	491(3)	136(4)
C(23A)	66(2)	8414(12)	117(5)	245(9)
C(23B)	209(3)	6387(15)	400(4)	272(11)
C(23C)	-130(2)	6671(12)	-334(4)	203(7)
C(24A) ^a	60(5)	8112(21)	-1885(7)	160(11) ^b
C(24B) ^a	-111(5)	6414(25)	-1432(8)	167(11) ^b
C(24C) ^a	157(5)	5903(24)	-1876(9)	199(12) ^b
C(24D) ^a	102(5)	7285(26)	-1949(8)	191(13) ^b
C(24E) ^a	-132(5)	7226(27)	-1385(9)	202(14) ^b
C(24F) ^a	65(6)	5496(29)	-1570(12)	287(21) ^b
C(25A)	1144(2)	4751(12)	-1470(4)	217(7)
C(25B)	711(3)	4191(11)	-1379(6)	286(11)
C(25C)	1042(3)	5083(13)	-735(4)	250(9)
C(26A)	1223(2)	6941(11)	-2359(3)	191(6)
C(26B)	1641(2)	6504(11)	-1759(4)	201(7)
C(26C)	1588(2)	8444(13)	-2206(4)	216(8)
C(27A)	1950(3)	10527(10)	-1312(4)	237(9)
C(27B)	2246(2)	9662(12)	-596(5)	244(9)
C(27C)	2130(2)	8444(9)	-1313(3)	160(5)
C(28A)	1018(2)	11361(14)	-368(4)	232(9)
C(28B)	1362(3)	12755(12)	13(6)	292(12)
C(28C)	1233(2)	11061(13)	446(3)	215(7)
C(29A) ^a	2044(8)	13430(39)	574(13)	375(35) ^b
C(29B) ^a	2399(5)	13119(24)	396(8)	194(13) ^b
C(29C) ^a	2449(4)	12749(20)	1162(6)	145(11) ^b
C(29D) ^a	1920(5)	13381(25)	724(9)	193(15) ^b
C(29E) ^a	2251(4)	13583(16)	374(5)	102(7) ^b
C(29F) ^a	2319(4)	13078(17)	1181(6)	118(8) ^b
C(30A)	2716(2)	10087(14)	1470(4)	220(8)
C(30B)	2542(2)	8203(10)	1740(4)	178(6)
C(30C)	2597(2)	10107(11)	2204(3)	174(6)
C(31A)	2079(3)	6344(10)	1004(3)	201(7)
C(31B)	1713(2)	5532(10)	1267(4)	207(7)
C(31C)	2165(3)	5347(9)	1756(3)	206(7)
C(32A)	1701(3)	5770(13)	2403(5)	282(11)
C(32B)	1281(3)	6232(12)	2606(4)	224(8)
C(32C)	1662(3)	7542(17)	2878(3)	332(15)
C(1T) ^d	-12(6)	8673(28)	2588(12)	541(34) ^b
C(2T) ^d	-146(6)	8393(32)	2245(12)	541(34) ^b

Table 7 (continued)

Atom	x	y	z	U_{eq}
C(3T) ^d	-129(10)	7443(36)	2108(15)	541(34) ^b
C(4T) ^d	20(12)	6774(27)	2315(22)	541(34) ^b
C(5T) ^d	153(10)	7054(37)	2658(22)	541(34) ^b
C(6T) ^d	137(8)	8004(41)	2795(15)	541(34) ^b
C(7T) ^d	-30(11)	9712(36)	2737(19)	541(34) ^b

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^a Atoms of the disordered groups; $g = 0.5$.

^b U_{iso} .

^c Atoms of a disordered Ph group; $g = 0.33$.

^d Atoms of the disordered solvate toluene molecule with partial population 1/2; $g = 0.25$.

isotropic thermal parameters were refined by groups: in both structures they were taken to be equal for all hydrogens belonging to the same Ph group and to the same -SiMe₃ (in the structure **3**) or Me group (in the structure **4**). In the disordered groups they were taken equal for both components. In the toluene solvent molecule in the structure **4** U_{iso} was fixed at 0.5 Å² for all H atoms.

Final coordinates and thermal displacement parameters of non-hydrogen atoms are listed in Table 6 (structure **3**) and Table 7 (structure **4**).

3.1. Preparation of polyphenylsiloxane resin

A solution of 100 ml ($d_4^{20} = 1.321$, 0.624 mol) of phenyltrichlorosilane in 100 ml of anhydrous toluene was added dropwise under vigorous stirring into a mixture of ice (300 g), water (100 ml) and toluene (150 ml). The stirring was continued for 30 min after the addition of the PhSiCl₃ solution. The organic phase was washed with water in separatory funnel till neutral reaction, then the solvent was evaporated and the residue was dried at 130–150°C for 4–6 h.

The solid resin (PhSiO_{1.5})_n obtained (76.2 g) contains a rest of the solvent so a determination of the Si content is required. It was found to be 20.56%.

3.2. Synthesis of nickel-containing OPMS **1**

13.66 g (0.1 m, counting on Si) of polyphenylsilsesquioxane and 2 g (0.05 m) of NaOH in *n*-butanol (300 ml) were refluxed with stirring till complete dissolution. Then 1.15 g (0.05 m) of Na were added at a temperature at 50–60°C. The solution was heated to reflux and finally 11.59 g (0.05 m) of hexaammoniate nickel(II) chloride, [Ni(NH₃)₆]Cl₂, were added. After vigorous evolution of ammonia the reaction mixture was refluxed for another 2 h and the hot solution was filtered to eliminate the NaCl precipitate. Half of the solvent (butanol) was distilled off from the filtrate, the rest was diluted with hexane to induce crystallization. The yellow crystals were isolated and then dried under

reduced pressure at 80–90°C to give yellow powder (14.6 g, yield 68%).

Analyses: $\{[(C_6H_5SiO_2)_6]_2Ni_6(NaCl)\} \cdot (n-BuOH)_5(H_2O)_6$. Found: C, 42.80; H, 4.28; Si, 13.19; Ni, 13.33; Na, 0.80; Cl, 1.23%. $C_{92}H_{122}ClNaNi_6O_{35}Si_{12}$. Calc.: C, 43.58; H, 4.85; Si, 13.29; Ni, 13.89; Na, 0.91; Cl, 1.40%.

3.3. Synthesis of copper/sodium-containing OPMS 2

This compound was obtained as above (**1**) from 16.39 g (0.12 Si g-at) of polyphenylsilsesquioxane, 2.40 g (0.06 m) of NaOH, 1.38 g (0.06 m) of Na and 5.38 g (0.04 m) of $CuCl_2$ in *n*-butanol (400 ml). The copper chloride itself was dissolved in 160 ml of *n*-butanol. Blue crystals, which fell from the filtrate after partial elimination of the *n*-butanol, were recrystallized from *n*-butanol and dried at 80–90°C. Yield: 16.02 g (70%).

Analysis: $[(C_6H_5SiO_2)_{12}Cu_4Na_4] \cdot (n-BuOH)_2(H_2O)_5$. Found: C, 43.00; H, 4.02; Cu, 11.24; Na, 4.72; Si, 14.84%. $C_{80}H_{90}Cu_4Na_4O_{31}Si_{12}$. Calc.: C, 43.07; H, 4.07; Cu, 11.39; Na, 4.12; Si, 15.11%.

3.4. Synthesis of symm-cis-hexaphenylhexakis-(trimethylsiloxy)cyclohexasiloxane $[PhSi(OSiMe_3)O]_6$ (**3**)

A flask was charged with 5.10 g (0.002 m) of **1** and 2.69 g (0.034 m) of pyridine. The mixture was stirred when Me_3SiCl (6.30 g, 0.058 m) was added dropwise. The resulting mixture was stirred for another 20 min, then 50 ml of toluene were added and the reaction mixture was refluxed for 1 h. After cooling to room temperature the precipitate was filtered off. The toluene filtrate was washed free of chloride by water and then dried over sodium sulfate. The toluene was removed in vacuo, and the residue was recrystallized from hot ethanol to afford 3.58 g (71%) of white crystals with m.p. 410°C and mol. weight 1268.

Analysis: $[PhSi(OSiMe_3)O]_6$. Found: C, 51.28; H, 6.78; Si, 26.19%. $C_{54}H_{84}O_{12}Si_{12}$. Mol. weight 1268. Calc: C, 51.38; H, 6.71; Si 26.70%. Mol. weight 1262.

3.5. Synthesis of symm-(tris-cis)-trans-(tris-cis)-trans-(tris-cis)-trans-do-decaphenyldodecakis(trimethylsiloxy)cyclodo-decasiloxane $[PhSi(OSiMe_3)O]_{12}$ (**4**)

5.51 g (78%) of white crystals with m.p. 362°C and mol.wt. 2522 was obtained from 6.25 g (0.028 m) of **2**

and 7.29 g (0.0672 m) of Me_3SiCl in toluene (80 ml) in presence of pyridine (2.66 g, 0.0336 mol) by the same way as **3**.

Analysis: $[PhSi(OSiMe_3)O]_{12}$. Found: C, 51.88; H 6.87; Si 26.50%. $C_{108}H_{168}O_{12}Si_{12}$. Mol. weight 2522. Calc.: C, 51.38; H, 6.71; Si, 26.70%. Mol. weight 2525.

4. Conclusions

This paper describes our first attempts to utilize OPMS as a source for large stereoregular siloxane cycles.

The metallasiloxane cores of the cage-like OPMS based on 6- and 12-membered stereoregular siloxane macrocycles do not undergo any dissociation in solution [10] and their decomposition by treatment with Me_3SiCl allowed us to obtain stereoregular siloxane cycles in high yields without changing of their size and configuration.

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