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Synthesis and Properties of Stereoregular Cyclic Polysilanols: *cis*-$[PhSi(O)OH]_4$, *cis*-$[PhSi(O)OH]_6$, and Tris-*cis*-tris-*trans*-$[PhSi(O)OH]_{12}$

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New stereoregular cyclic polysilanols of the general formula $[PhSi(O)OH]n$ ($n = 6$ and 12) have been selectively obtained in high yields by the reaction of cagelike oligophenylmetallasiloxanes with dilute solutions of hydrochloric acid at low temperatures. An alternative method was used to prepare *cis*-$[PhSi(O)OH]_4$ from sodium phenylsiloxanolate, *cis*-$\{(Na^+)_4[PhSi(O)O^-]_4\}\cdot(1\text{-butanol})_x$. All compounds were fully characterized by NMR and IR spectroscopy and molecular weight determinations. The structure of *cis*-$[PhSi(O)OH]_6$ was confirmed by single-crystal X-ray analysis. Furthermore, a series of stereoregular cyclosiloxanes containing triorganylsiloxy groups at each silicon atom was prepared by the reactions of the cyclic polysilanols with triorganylchlorosilanes Me_3SiCl, $Me_2ViSiCl$, and $Me_2(CH_2Cl)SiCl$.

Introduction

Cagelike oligophenylmetallasiloxanes (abbreviated herein as OPMS) are crystalline compounds most commonly consisting of stereoregular phenylsiloxane macrocycles coordinated to alkaline and/or transition metals (e.g., Mn, Co, Ni, Cu, and trivalent lanthanide metals).[1−4] We reported the first examples of these compounds in the early 1990s.[1,2a] The general method for their synthesis is a three-step process, shown in Scheme 1. Phenyltrichlorosilane is hydrolyzed in an aromatic solvent (eq 1), and then the resulting phenylsilsesquioxane resin (of low molecular weight) is depolymerized with an equimolar amount of sodium or potassium hydroxide in 1-butanol (eq 2), and the alkaline metal phenylsiloxanolate solution is subsequently reacted with an anhydrous metal chloride (in equimolar ratio or less) to produce the cagelike oligophenylmetallasiloxane (eq 3).

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10.1021/ic020546h CCC: $22.00

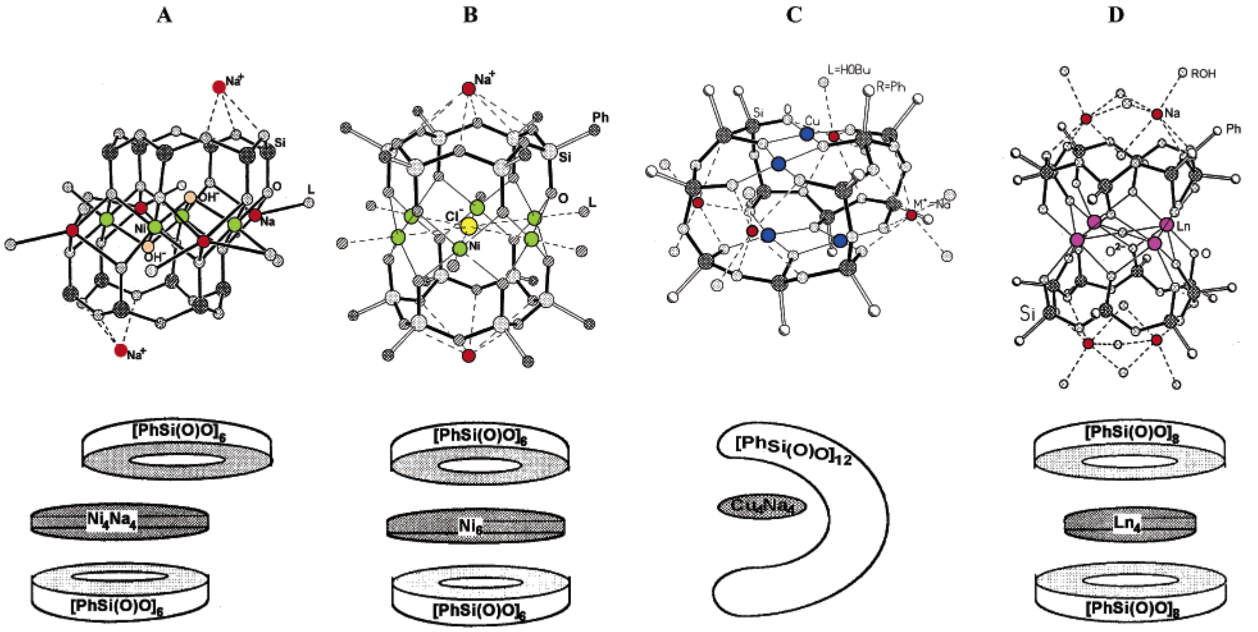


Figure 1. General view of molecular structures of cagelike metallasiloxanes: (A) $Na_2[(PhSiO_2)_6Ni_4Na_4(\mu_3\text{-}OH)_2(PhSiO_2)_6]\}\cdot L_n$, (B) $[(PhSiO_2)_6Ni_6(\mu_6\text{-}Cl)(PhSiO_2)_6]\cdot L_n$,, (C) $Na_4\{[PhSiO_2]_{12}Cu_4\}\cdot L_n$, (D) $Na_6\{[(PhSiO_2)_8]_2Ln_4(\mu_4\text{-}O)\}\cdot L_n$, (L = ROH, R = *n*-Bu, Et, H) and their schematic depiction. The phenyl rings of the cyclohexasiloxanolate fragments and the alkyl chains of the ligands are omitted for clarity.

Scheme 1

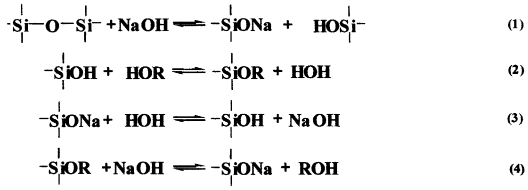
$$n\mathrm{PhSiCl_3} \rightarrow \{[\mathrm{PhSiO_{1.5}}]_n(\mathrm{OH})_x\} \qquad (1)$$

$$m/n\{[\mathrm{PhSiO_{1.5}}]_n(\mathrm{OH})_x\} + m\mathrm{NaOH} \xrightarrow{\text{1-butanol}} [\mathrm{PhSi(O)ONa}]_m + (m + x)/2\mathrm{H_2O} \qquad (2)$$

$$x/m[\mathrm{PhSi(O)ONa}]_m + \mathrm{MCl}_x \xrightarrow{\text{1-butanol}} \{[\mathrm{PhSiO_{1.5}}]_x(\mathrm{M}_{2/x}\mathrm{O}_{x/2})_y\}\cdot\mathrm{L}_z \qquad (3)$$

$$\mathrm{L} = \text{1-butanol, } \mathrm{H_2O}$$

Scheme 2



$$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}- + \mathrm{NaOH} \rightleftharpoons -\mathrm{SiONa} + \mathrm{HOSi}- \qquad (1)$$

$$-\mathrm{SiOH} + \mathrm{HOR} \rightleftharpoons -\mathrm{SiOR} + \mathrm{HOH} \qquad (2)$$

$$-\mathrm{SiONa} + \mathrm{HOH} \rightleftharpoons -\mathrm{SiOH} + \mathrm{NaOH} \qquad (3)$$

$$-\mathrm{SiOR} + \mathrm{NaOH} \rightleftharpoons -\mathrm{SiONa} + \mathrm{ROH} \qquad (4)$$

X-ray crystallography of the crystalline metallasiloxanes showed that the molecules are based on one or two stereoregular macrocycles $[(\mathrm{PhSi(O)O})^-]_n$ (n = 6, 8, 12), which surround up to six transition metal atoms to form cagelike structures (Figure 1, compounds A−D). The structural organization of these molecules falls into two principal types: (i) compounds in which the metal atoms are positioned in planes between two layers of cyclosiloxanolate fragments (sandwich type; compounds A, B, and D) or (ii) a second type in which the metal atom assembly is folded into one cyclosiloxanolate envelope (compound C). In general, molecules that contain bivalent ions of transition metals (e.g., nickel ions) adopt the sandwich structure shown in Figure 1 with two 12-member siloxane cycles and four nickel and four sodium atoms (A) or six nickel atoms in a metal interface (B). The OPMS that contains two different transition metal atoms (such as Ni and Co, Ni and Cu, and Ni and Fe) also adopts structures of the B type.[4a−c] Molecules with lanthanide atoms (La, Dy, Gd, and Nd) consist of two 16-member siloxane cycles with four metal atoms in a square interface layer (compound D). Bridging anions such as Cl^-, OH^-, or O^{2-} are also included as part of the sandwich-type structures of many OPMS molecules. Compound C consists of one 24-member phenylsiloxanolate ligand, which forms a globulelike structure with four copper atoms in a tetrahedral interface. The additional presence of Na^+ or K^+ cations provides for the electroneutrality of the cagelike metallasiloxane anions.

Of particular interest is the fact that depending on the transition metal chloride used, large 12-, 16-, and 24-member siloxane rings have been generated with high selectivity. Such selectivity had not been observed before in traditional siloxane polymer chemistry[5] and could be due to a directive effect by the transition metal atoms on a silicon−oxygen-containing alkaline intermediate, which is generated in the course of the alkaline splitting of oligophenylsilsesquioxane resin and is able to organize around the metal centers.

Since the alkaline depolymerization of the phenylsilsesquioxane resins is performed in an alcohol media, at least four coupled equilibrium reactions (Scheme 2, eqs 1−4) must take place: (1) splitting of siloxane bonds by MOH (M = Na^+ or K^+); (2) etherification of silanol units by alcohol solvent and liberation of reaction water; (3) hydrolysis of metal silanolate units by the produced water; and (4) substitution of alkoxy groups by the alkaline metal cations. As a consequence of these possible reactions and a rapid proton−cation exchange between protons of OH and M (most frequently Na) groups,[6] an equilibrium labile reacting

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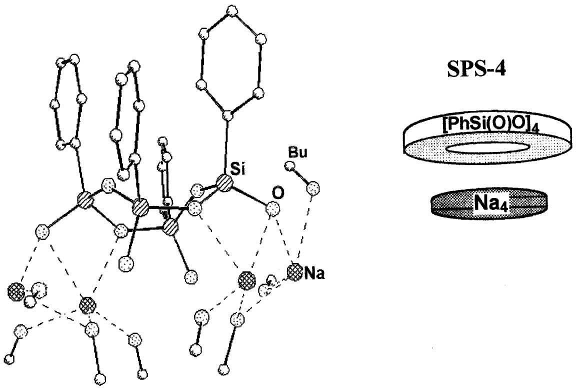

Figure 2. General view of the molecular structure of sodium phenylsiloxanolate *cis*-$\{(Na^+)_4[PhSi(O)O^-]_4\}\cdot$(1-butanol)$_x$ (SPS-4) and its schematic depiction.

unit such as Ph(OR)Si(OH)ONa (R = alkyl, H) is quite plausible.

Indirect evidence for the existence of Ph(OR)Si(OH)ONa (R = alkyl, H) was gathered through the following two parallel experiments: (i) a sodium hydroxide reaction of oligophenylsilsesquioxane in 1-butanol and (ii) a hydrolysis of phenyltri(*n*-butoxy)silane in 1-butanol in the presence of an equimolar amount of NaOH.[7] We considered that in the latter case the same coupled equilibria reactions would take place in reverse order, resulting in a generation of the same alkaline silicon−oxygen-containing intermediate, and as a result both reactions should lead to the formation of only one identical product. As it was expected, crystalline *sym-cis*-$\{(Na^+)_4[PhSi(O)O^-]_4\}\cdot$8(1-butanol) (SPS-4) (Figure 2) was the sole product isolated in high yield from both reactions. At the same time, we found that under anhydrous conditions $PhSi(OBu^n)_3$ and NaOH react to give only monomeric sodium phenyl(di-*n*-butoxy)silanolate, $PhSi(ONa)(OBu^n)_2$.

These data suggested that cagelike metallasiloxanes could also be prepared from monomeric alkoxysilanes. We pursued this synthetic route, and indeed we prepared and characterized several cagelike copper/sodium metallasiloxanes, $\{Na_4[(RSiO_2)_{12}Cu_4](R'OH)_n\}$ (R = Ph, Vi; R′ = *n*-Bu; R = Ph; R′ = Me; R = Vi; R′ = Me) from the individual alkoxysilanes, $PhSi(OBu^n)_3$, $PhSi(OMe)_3$, and $ViSi(OMe)_3$.[8] The advantage of this approach over that of the alkaline depolymerization of silsesquioxane resins is the use of well-defined starting materials (that of alkoxysilanes) rather than the ill-defined networks of silsesesquioxane polymers. We consider this route as a self-assembly of cagelike metallasiloxanes in good yields from trialkoxysilanes and alkaline and transition metal atoms.[9,10]

The method was investigated mostly for the hydrolysis of phenyltrialkoxysilanes in alkaline media (Si/Na (or K)) with the in situ generation of an alkaline intermediate (postulated to be [PhSi(OM)(OH)(OR)]), which subsequently undergoes exchange reactions with transition metal chlorides. We postulate that because of the directing influence of alkaline or transition metal ions, such intermediates are able to self-organize during crystallization. As a result, the oligocyclization occurs, generating stereoregular 6-, 8-, 12-, 16-, and 24-member siloxanes fixed on a complex metal/halide/oxide substrate. The structures and yields of these compounds depend upon the nature of the alkaline metal or transition metal ions. In addition, the reactivity of alkoxy groups, the amount of water and the nature of the solvent also influence the yield and in some cases the structure of metallasiloxanes.[11] The new method opens the possibility to produce cagelike metallasiloxanes even with small substituents at silicon atoms such as vinyl or methyl.[8,12]

A significant feature of the metallasiloxane complexes is that they are precursors of stereoregular organocyclosiloxanes. We have recently shown that the appropriate cycles with trimethylsiloxy groups attached at each silicon atom, *cis*-$[PhSi(O)(OSiMe_3)]_4$, *cis*-$[PhSi(O)(OSiMe_3)]_6$, and tris-*cis*-tris-*trans*-$[PhSi(O)(OSiMe_3)]_{12}$, can be synthesized by cleaving off the metal centers from the cagelike metallasiloxanes with trimethylchlorosilane in the presence of pyridine,[7,13] forming cyclic siloxanes and the corresponding metal chlorides.

For further use of the siloxane cycles in chemical transformations or follow-up reactions, the stereoregular siloxane building blocks with functional groups (such as hydroxyl) at the silicon atoms are preferred; therefore, their synthesis is of greatest interest. These model compounds with well-defined structures can be utilized as precursors for new silsesquioxane-based materials with various tailor-made properties. In this paper we describe the preparation and characterization of three stereoregular cyclic polysilanols, *cis*-$[PhSi(O)OH]_6$, tris-*cis*-tris-*trans*-$[PhSi(O)OH]_{12}$, and *cis*-$[PhSi(O)OH]_4$, that were produced from compounds A, C, and SPS-4, respectively.

Experimental Section

The ^1H and ^{29}Si NMR spectra were obtained on a Bruker DRX-500 spectrometer operating at 500.12 MHz for ^1H and 99.325 MHz for ^{29}Si and a Bruker-AMX spectrometer (400.13 MHz for ^1H and

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Table 1. ^{1}H and ^{29}Si NMR Data for Cyclic Polysilanols

compound	^{1}H (δ, ppm)				^{29}Si (δ, ppm)
	Ph			OH	PhSi(O)OH
	o-H (d, 2H)	*p*-H (t, 1H)	*m*-H (t, 2H)		
cis-[PhSi(O)OH]$_4$[a]	7.503	7.327	7.189	6.260	−69.68
cis-[PhSi(O)OH]$_6$	7.588	7.312	7.146	6.470	−70.55
tris-*cis*-tris-*trans*-[PhSi(O)OH]$_{12}$	two doublets 7.696 7.565	7.342[b]	7.148[b]	6.850 6.798	−70.80

[a] ^{1}H NMR (500.1 MHz, CD_3CN, ppm) δ: 7.45 (m, 2H, *o*-C_6H_5), 7.35 (m, 1H, *p*-C_6H_5), 7.22 (m, 2H, *m*-C_6H_5). ^{29}Si NMR (Et_2O, ppm) δ: −69.84.[19]
[b] Two triplets overlapped.

Table 2. Crystal Data, Data Collection, and Structure Refinement Parameters for **1**

complex	**1**
formula	$C_{36}H_{36}O_{12}Si_6 \cdot 3/2((CH_3)_2CO)$
mol wt	916.30
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	11.3234(8)
b, Å	14.258(1)
c, Å	15.244(1)
α, deg	112.946(1)
β, deg	91.301(1)
γ, deg	100.317(1)
V, Å^3	2218.1(3)
Z	2
d_{calcd}, g cm^{-3}	1.372
μ (Mo Kα), cm^{-1}	2.52
diffractometer	SMART 1000 CCD
T, K	110.0(2)
scan mode	ω-scan (with 0.3° step and 10 s per frame exposure)
θ_{max}, deg	25
absorption correction	multiscan (Sadabs)
transm factors, min/max	0.579/0.928
no. collected reflns	15250
no. unique reflns (R_{int})	7742 (0.0233)
no. obs reflns ($I > 2\sigma(I)$)	6835
no. params	764
R_1 (on F for obs reflns)[a]	0.0743
wR_2 (on F^2 for all reflns)[b]	0.1729
weighing scheme	$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = (F_o^2 + 2F_c^2)/3$
GOF on F^2	1.144

[a] $R_1 = \Sigma|F_o - |F_c||/\Sigma(F_o)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

79.495 MHz for ^{29}Si) at 20 °C in $(CD_3)_2CO$ as solvent for polysilanols and in $CDCl_3$ or C_6D_6 for their triorganylsiloxy-substituted derivatives. Chemical shifts are given relative to TMS.

Single-Crystal X-ray Diffraction Analysis. Details of crystal data, data collection, and structure refinement parameters for structure **1** (*cis*-[PhSi(O)OH]$_6$) are given in Table 2. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 with the anisotropic temperature factors for all non-hydrogen atoms. The analysis of the difference Fourier synthesis revealed that two phenyl rings (C(10)−C(15) and C(40)−C(45)) as well as two solvate acetone molecules were disordered by two positions. The refinement of the atom occupancies in all cases has shown that they were equal. The positions of the hydrogen atoms were calculated from the geometrical point of view for the disordered groups, and the rest of the hydrogen atoms were located from the difference Fourier synthesis. The positions of the hydroxyl hydrogen atoms linked to the O(1) and O(7) atoms were not found most probably because of statistical disorder. Data reduction and further calculations were performed using SAINT[14] and SHELXTL-97[15] on IBM PC AT.

IR spectra in the region of 1500−3700 cm^{-1} were recorded using a computerized Carl Zeiss M-82 spectrophotometer. Solid substances were deposited on CaF_2 supports in various ways (see text). Because of hydrogen bonding, the νOH band displacement is used as a tool to measure the strength of the H-bond. To estimate $\Delta\nu$OH, the position of the center of gravity of the broad band in the region of 3200−3300 cm^{-1} was determined.

Molecular weights were determined by vapor pressure osmometry (VPO) on Wescon (solvent: acetone, 25 °C) according to the method described previously.[16]

Synthesis of Nickel/Sodium-Containing OPMS (A). Phenyltri(*n*-butoxy)silane (12.80 g, 39 mmol) and NaOH (1.80 g, 45 mmol) were heated for 1 h under reflux in 130 mL of 1-butanol containing 0.70 mL of water. $[Ni(NH_3)_6]Cl_2$ (3.01 g, 13 mmol) was added to the reaction mixture, which was refluxed for another 2 h, and the hot solution was filtered to remove NaCl. Orange crystals precipitated after partial elimination of 1-butanol and overnight storage at room temperature. After separation they were dried in a vacuum at 80−90 °C. Yield: 5.44 g (71.8%). Anal. Calcd for $\{[(C_6H_5SiO_2)_6]_2Ni_4Na_4(NaOH)_2\}(n\text{-}C_4H_9OH)_3(H_2O)_3$; $C_{84}H_{98}Na_6Ni_4O_{32}Si_{12}$: C, 43.31; H, 4.24; Si, 14.47; Ni, 10.08; Na, 5.92. Found: C, 43.98; H, 4.44; Si, 14.89; Ni, 9.46; Na, 5.45.

Synthesis of Copper/Sodium-Containing OPMS (C). A mixture of 1-butanol (120 mL), 14.60 g (45 mmol) of phenyltri(*n*-butoxy)silane, water (0.81 mL), and 1.80 g (45 mmol) of sodium hydroxide was stirred and refluxed for 1 h. Then a solution of anhydrous copper chloride (2.01 g, 15 mmol) in 30 mL of 1-butanol was added dropwise to the reaction mixture. After completion, the reaction mixture was refluxed for an additional 30 min. The hot solution was filtered to remove NaCl. The filtrate was evaporated to half the volume under vacuum. Precipitated blue crystals were filtered and dried at reduced pressure (90°, 1 mmHg). Yield: 1.92 g (73.8%). Anal. Calcd for $[(C_6H_5SiO_2)_{12}Cu_4Na_4](n\text{-}C_4H_9OH)_2(H_2O)_5$; $C_{80}H_{90}Cu_4Na_4O_{31}Si_{12}$: C, 43.07; H, 4.07; Cu, 11.39; Na, 4.12; Si, 15.11. Found: C, 43.00; H, 4.02; Cu, 11.24; Na, 4.72; Si, 14.84.

Synthesis of *cis*-Hexa[(phenyl)(hydroxy)]cyclohexasiloxane (1) from A. A solution of nickel/sodium-containing OPMS (A) (5.60 g, 2.4 mmol) in a benzene/ethanol (100:50 mL) mixture was added dropwise to the mixture of water and hydrochloric acid (concentrated) (60:15 mL) at ∼5 °C. After 2−5 min of being stirred, the organic layer was separated and added to 300 mL of water. The resulting white crystalline product was filtered, washed with water until neutral reaction to Cl$^-$ ion, and dried in a vacuum over $CaCl_2$ at room temperature for a few days. Yield: 3.21 g (80.6%). Anal. Calcd for $[C_6H_5Si(O)OH]_6$; $C_{36}H_{36}Si_6O_{12}$: C, 52.14; H, 4.38; Si, 20.33. Found: C, 52.23; H, 4.23; Si, 20.31. ^{1}H NMR (δ (ppm),

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(16) Bakeev, K. A.; Chugunov, S. A.; Larina, T. V.; Macnight, V. G.; Zezin, A. B.; Kabanov, V. A. *Visokomol. Soedineniya* **1994**, *36*, 247−256.

acetone-d_6): 7.588 (d, 2H, *o*-Ph), 7.312 (t, 1H, *p*-Ph), 7.146 (t, 2H, *m*-Ph), 6.470 (s, 1H, SiOH). ^{29}Si NMR (δ (ppm), acetone-d_6): −70.55 (s).

Synthesis of Tris-*cis*-tris-*trans*-dodeca[(phenyl)(hydroxy)]cyclododecasiloxane (2). A toluene/ethanol (200:50 mL) solution of 8.4 g (3.77 mmol) of Cu/Na-containing OPMS (C) was added dropwise under vigorous stirring to a mixture of 100 mL of water and 30 mL of concentrated hydrochloric acid. The reaction mixture was stirred for 2−3 min and filtered. The white crystalline product obtained was washed with water until neutral reaction to Cl^- ion and dried in a vacuum (1 mmHg) over $CaCl_2$ at room temperature. A white crystalline product was obtained (5.62 g, 90.0%). Anal. Calcd for $[C_6H_5Si(O)OH]_{12}$; $C_{72}H_{72}Si_{12}O_{24}$: C, 52.14; H, 4.38; Si, 20.33. Found: C, 52.87; H, 4.58; Si, 19.95. ^{1}H NMR (δ (ppm), acetone-d_6): 7.696 (d, 2H, *o*-Ph, *cis-cis*-Ph), 7.565 (d, 2H, *o*-Ph, *cis-trans*-Ph), 7.342 (m, 1H, *p*-Ph), 7.148 (m, 2H, *m*-Ph), 6.850 (s, 1H, *cis-trans*-OH), 6.798 (s, 1H, *cis-cis*-OH). ^{29}Si NMR (δ (ppm), acetone-d_6): −70.80 (s).

Synthesis of *cis*-Hexa[(phenyl)(trimethylsiloxy)]cyclohexasiloxane (D_6a). A total of 4.4 g (5.3 mmol) of $[PhSi(O)OH]_6$ was added to a mixture of toluene (70 mL), Me_3SiCl (17.3 g, 160 mmol), and pyridine (12.59 g, 160 mmol). The reaction mixture was refluxed for 30 min. After being cooled to room temperature, the precipitate was filtered off. The toluene filtrate was washed chloride-free with water and then dried over sodium sulfate. Toluene was removed in a vacuum to afford 5.6 g (83.4%) of a white waxlike product. Anal. Calcd for $[C_6H_5Si(O)OSi(CH_3)_3]_6$; $C_{54}H_{84}Si_{12}O_{12}$: C, 51.38; H, 6.71; Si, 26.70. Found: C, 51.28; H, 6.78; Si, 26.19. ^{1}H NMR (δ (ppm), $CDCl_3$): 6.93−6.51 (m, 5H, Ph), 0.22 (s, 9H, Me). ^{29}Si NMR (δ (ppm), $CDCl_3$): 9.59 (s, $OSiMe_3$), −81.60 (s, O_3SiPh).

Synthesis of *cis*-Hexa[(phenyl)(dimethylvinylsiloxy)]cyclohexasiloxane (D_6b). A total of 4.9 g (81.7%) of the product was obtained from 4 g (4.5 mmol) of *cis*-hexol and 4.85 g (40 mmol) of $Me_2ViSiCl$ in toluene (60 mL) in the presence of 3.16 g (40 mmol) of pyridine similar to the synthesis of **D_6a**. Anal. Calcd for $[C_6H_5Si(O)OSi(CH_3)_2CH{=}CH_2]_6$; $C_{60}H_{84}Si_{12}O_{12}$: C, 53.98; H, 6.34; Si, 25.27. Found: C, 54.49; H, 6.46; Si, 24.93. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.030−7.368 (m, 5H, Ph), 5.883−6.382 (m, 3H, Vi), 0.397 (s, 6H, Me). ^{29}Si NMR (δ (ppm), $CDCl_3$): −1.50 (s, $OSiMe_2Vi$), −80.448 (s, O_3SiPh).

Synthesis of *cis*-Hexa[(phenyl)(dimethylchloromethylsiloxy)]-cyclohexasiloxane (D_6c). A total of 8.35 g (92.16%) of crude product was obtained from 5.55 g (62 mmol) of *cis*-hexol and 13.31 g (93 mmol) of $Me_2(CH_2Cl)SiCl$ in 70 mL of toluene in the presence of pyridine (7.36 g, 98 mmol). Crystallization of the crude solid from methanol gave 5.57 g (61.48%) of the product. Anal. Calcd for $[C_6H_5Si(O)OSi(CH_3)_2CH_2Cl]_6$; $C_{54}H_{78}Si_{12}Cl_6O_{12}$: C, 44.12; H, 5.35; Si, 22.94; Cl, 14.50. Found: C, 45.11; H, 5.80; Si, 22.33; Cl, 14.22. ^{1}H NMR (δ (ppm), $CDCl_3$): 6.995−7.297 (m, 5H, Ph), 2.840 (s, 2H, CH_2Cl), 0.366 (s, 6H, Me). ^{29}Si NMR (δ (ppm), $CDCl_3$): 4.95 (s, $OSiMe_2CH_2Cl$), −80.57 (s, O_3SiPh).

Synthesis of Tris-*cis*-tris-*trans*-dodeca[(phenyl)(trimethylsiloxy)]cyclododecasiloxane (D_{12}a). A total of 5.7 g (3.4 mmol) of $[PhSi(O)OH]_{12}$ was added at once to a mixture of 100 mL of benzene, 22.42 g (210 mmol) of Me_3SiCl, and 16.31 g (210 mmol) of pyridine. The reaction mixture was refluxed for 1 h, then cooled to room temperature, filtered from a precipitate, and washed with water until neutral reaction to Cl^- ion. After removal of the solvent, the product was dried in a vacuum (1 mmHg at 80−90 °C for 1 h). A total of 5.7 g (66%) of white crystalline $[PhSi(O)OSiMe_3]_{12}$ was obtained. Anal. Calcd for $[C_6H_5Si\ (O)OSi(CH_3)_3]_{12}$; $C_{108}H_{168}Si_{24}O_{24}$: C, 51.38; H, 6.71; Si, 26.70. Found: C, 51.17; H, 6.44; Si, 25.02. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.097−7.505 (m, 5H, Ph), −0.071 (s, 9H, CH_3, *cis-cis*-$OSiMe_3$), −0.292 (s, 9H, CH_3, *cis-trans*-$OSiMe_3$). ^{29}Si NMR (δ (ppm), $CDCl_3$): 9.52 (s, *cis-cis*-$OSiMe_3$), 8.51 (s, *cis-trans*-$OSiMe_3$), −81.19 (s, O_3SiPh).

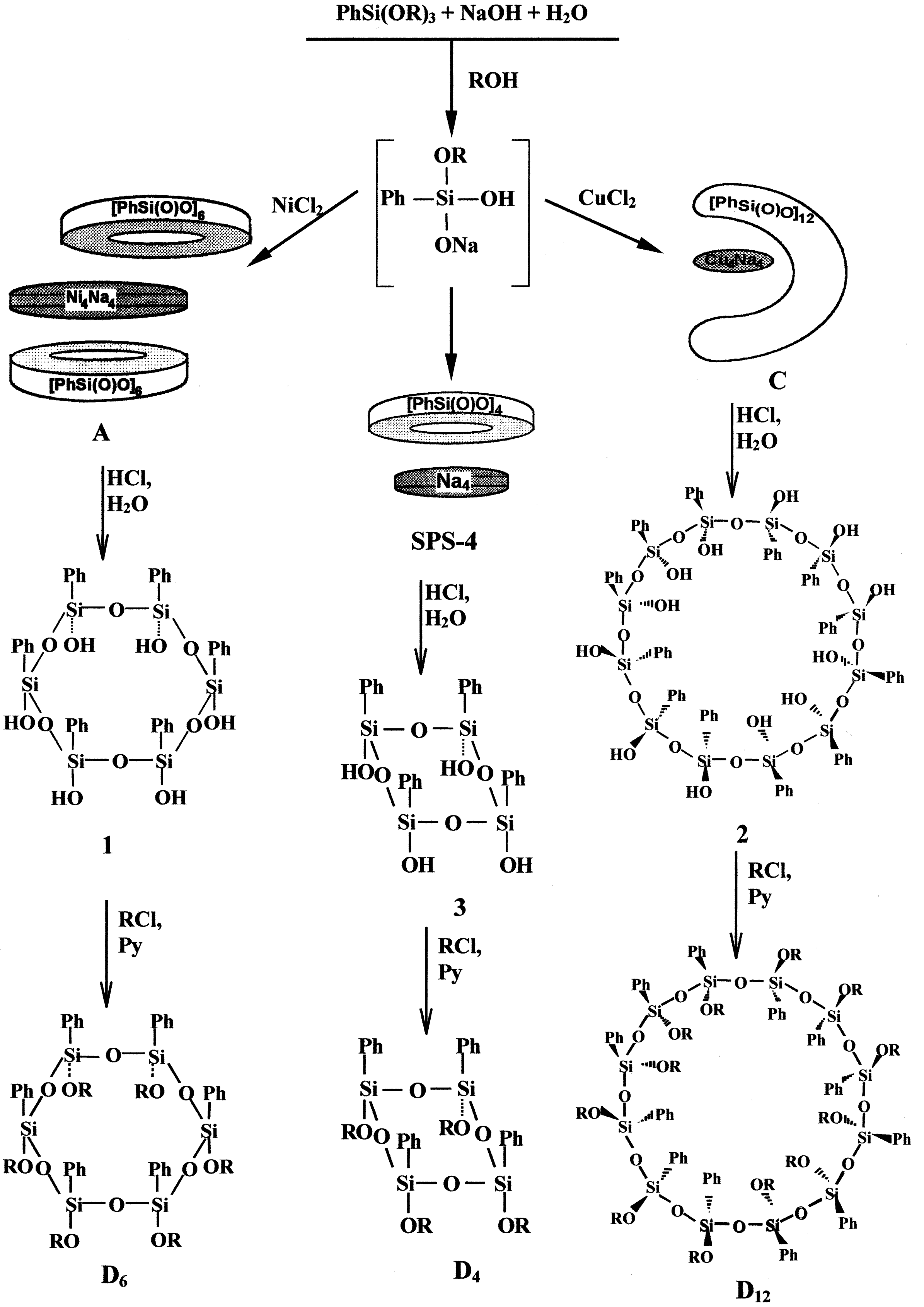
Synthesis of Tris-*cis*-tris-*trans*-dodeca[(phenyl)(dimethylvinylsiloxy)]cyclododecasiloxane (D_{12}b). A total of 2 g (14.5 mmol) of $[PhSi(O)OH]_{12}$ dissolved in 6.87 g (87 mmol) of pyridine was added to 10.48 g (87 mmol) of $ViMe_2SiCl$ at room temperature and under vigorous stirring. The mixture was refluxed for 1 h, then 65 mL of toluene was added to the cooled mass, and the solution was refluxed for another 1 h. Then the reacting mixture was cooled to room temperature, washed with water to remove Cl^-, dried over Na_2SO_4, and the solvent was evaporated. A total of 2.85 g (87.6%) of white solid $[PhSi(O)OSiMe_2Vi]_{12}$ was obtained after drying in a vacuum (1 mmHg/150 °C/15 min) and recrystallized from hot EtOH. Anal. Calcd for $[C_6H_5Si(O)OSi(CH_3)_2CH{=}CH_2]_{12}$; $C_{120}H_{168}Si_{24}O_{24}$: C, 53.98; H, 6.34; Si, 25.27. Found: C, 53.81; H, 6.38; Si, 25.11. ^{1}H (δ (ppm), $CDCl_3$): 7.126−7.314 (m, 5H, Ph), 5.375−6.006 (m, 3H, Vi), −0.04 (s, 6H, CH_3, *cis-cis*-$OSiMe_2Vi$), −0.24 (s, 6H, CH_3, *cis-trans*-$OSiMe_2Vi$), −0.25 (s, 6H, CH_3, *cis-trans*-$OSiMe_2Vi$). ^{29}Si (δ (ppm), $CDCl_3$): −1.73 (*cis-cis*-$OSiMe_2Vi$), −2.62 (*cis-trans*-$OSiMe_2Vi$), −80.93 (*cis-cis*-O_3SiPh), −80.98 (*cis-trans*-O_3SiPh).

Synthesis of Tris-*cis*-tris-*trans*-dodeca[(phenyl)(dimethylchloromethylsiloxy)]cyclododecasiloxane (D_{12}c). Analogous to the synthesis of **D_{12}b**, 2.66 g (75%) of **D_{12}c** was obtained from 2 g (14.5 mmol) of $[PhSi(O)OH]_{12}$ and 12.43 g (87 mmol) of $ClCH_2Me_2SiCl$ in the presence of 6.87 g (87 mmol) of pyridine and recrystallized from hot EtOH. Anal. Calcd for $[C_6H_5Si(O)OSi(CH_3)_2CH_2Cl]_{12}$; $C_{108}H_{156}Si_{24}O_{24}Cl_{12}$: C, 44.12; H, 5.35; Si, 22.94; Cl, 14.50. Found: C, 43.18; H, 5.71; Si, 22.71; Cl, 14.22. ^{1}H (δ (ppm), $CDCl_3$): 7.236−7.477 (m, 5H, Ph), 2.49 (s, 2H, CH_2Cl, *cis-cis*-$OSiMe_2CH_2Cl$), 2.01 (AB-system, 2H, CH_2Cl, *cis-trans*-$OSiMe_2CH_2Cl$), 0.09 (s, 6H, CH_3, *cis-cis*-$OSiMe_2CH_2Cl$), −0.19 (s, 6H, CH_3, *cis-trans*-$OSiMe_2CH_2Cl$), −0.20 (s, 6H, CH_3, *cis-trans*-$OSiMe_2CH_2Cl$). ^{29}Si NMR (δ (ppm), $CDCl_3$): 4.74 (*cis-cis*-$OSiMe_2CH_2Cl$), 3.95 (*cis-trans*-$OSiMe_2CH_2Cl$), −80.26 (*cis-cis*-O_3SiPh), −80.31 (*cis-trans*-O_3SiPh).

Synthesis of *cis*-Tetra[(phenyl)(hydroxy)]cyclotetrasiloxane (3). (**a**) A mixture of 12.56 g (38.7 mmol) of PhSi(On-Bu)$_3$, 1.55 g (38.7 mmol) of NaOH, and 0.7 mL (38.7 mmol) of H_2O was refluxed in 1-butanol (60 mL) for 1 h. White needlelike crystals precipitated after the solution was cooled to room temperature and overnight storage. A total of 10.9 g (8.52 Si%) of wet crystals of SPS-4 was obtained upon filtration over a Schott filter. Yield: 85.4% based on Si. (**b**) A total of 9.5 g (0.0288 g-atom Si) of wet SPS-4 (Si: 8.52%) was dissolved in a toluene/ethanol (60:35 mL) mixture and added dropwise to a solution of 500 mL of water containing 9 mL of hydrochloric acid at 3−5 °C under vigorous stirring. After 2−3 min, the white precipitate formed during the reaction was separated via filtration and washed with water until neutral reaction to Cl^- ion. It was then washed with toluene and dried in a vacuum over $CaCl_2$ for a few days. Yield: 3.2 g (80.4%). Anal. Calcd for $[C_6H_5Si(O)OH]_4$; $C_{24}H_{24}Si_4O_8$: C, 52.14; H, 4.38; Si, 20.33. Found: C, 52.29; H, 4.11; Si, 20.19. ^{1}H NMR (δ (ppm), acetone-d_6): 7.503 (d, 2H, *o*-Ph), 7.327 (t, 1H, *p*-Ph), 7.189 (t, 2H, *m*-Ph), 6.260 (s, 1H, SiOH). ^{29}Si NMR (δ (ppm), acetone-d_6): −69.68 (s).

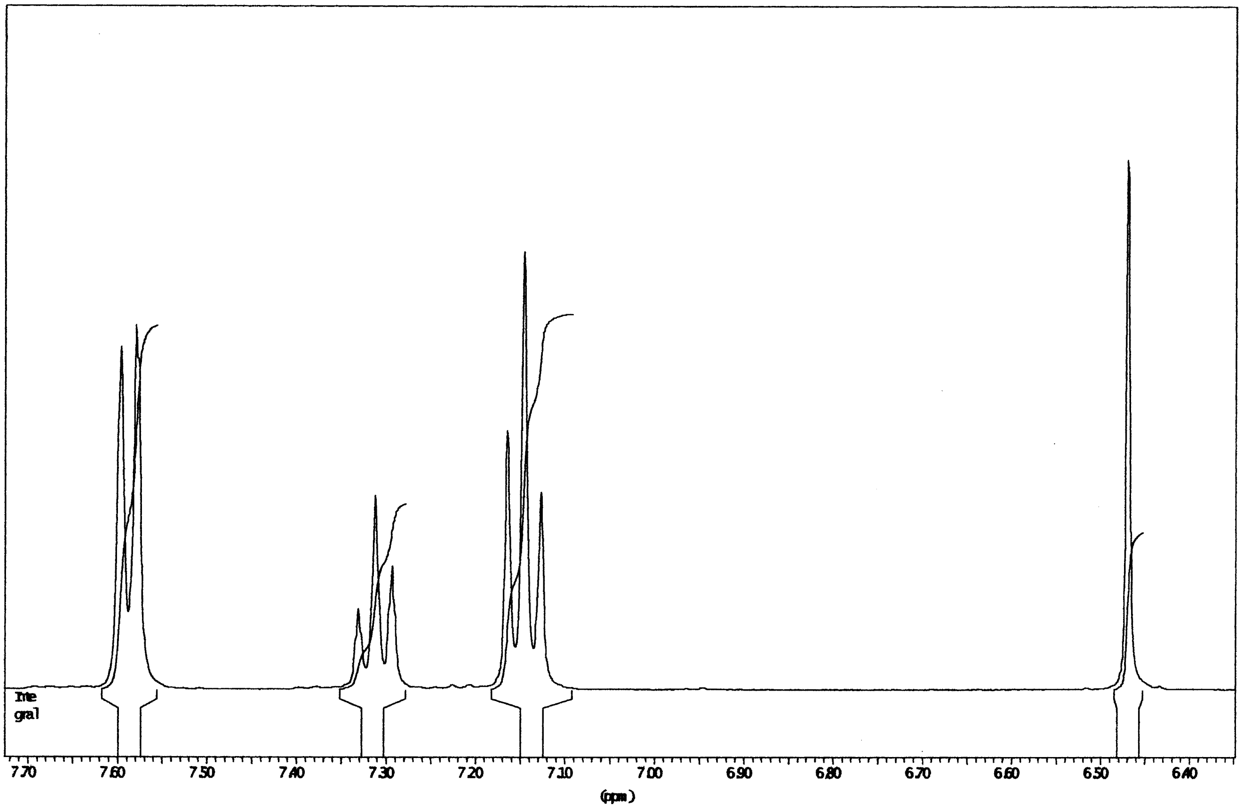
Synthesis of *cis*-Tetra[(phenyl)(trimethylsiloxy)]cyclotetrasiloxane (D_4a). According to the procedure described for **D_6a**, 0.60 g (1.1 mmol) of tetrol was treated with 1.92 g (18 mmol) of Me_3SiCl in the presence of pyridine (0.36 g, 4.6 mmol) in 15 mL of

Scheme 3. General Scheme of the Synthesis of Metallasiloxanes (A, C, and SPS-4), Cyclosilanols (1−3), and Their Triorganylsiloxy Derivatives[a]



[a] (a) D_4, D_6, D_{12}, R = $OSiMe_3$, (b) $OSi(Me)_2CH{=}CH_2$, and (c) $OSi(Me)_2CH_2Cl$.

toluene. Crystalline $[PhSi(O)(OSiMe_3)]_4$ was obtained with a 71% (0.65 g) yield after crystallization from hot ethanol. Anal. Calcd for $[C_6H_5Si(O)OSi(CH_3)_3]_4$; $C_{36}H_{56}O_8Si_8$: C, 51.38; H, 6.71; Si, 26.70. Found: C, 50.93; H, 6.68; Si, 26.11. ^1H NMR (δ (ppm), C_6D_6): 7.45−7.80 (m, 5H, Ph), 0.19 (s, 3H, Me). ^{29}Si NMR (δ (ppm), C_6D_6): 10.49 (s, $OSiMe_3$), −79.02 (s, O_3SiPh).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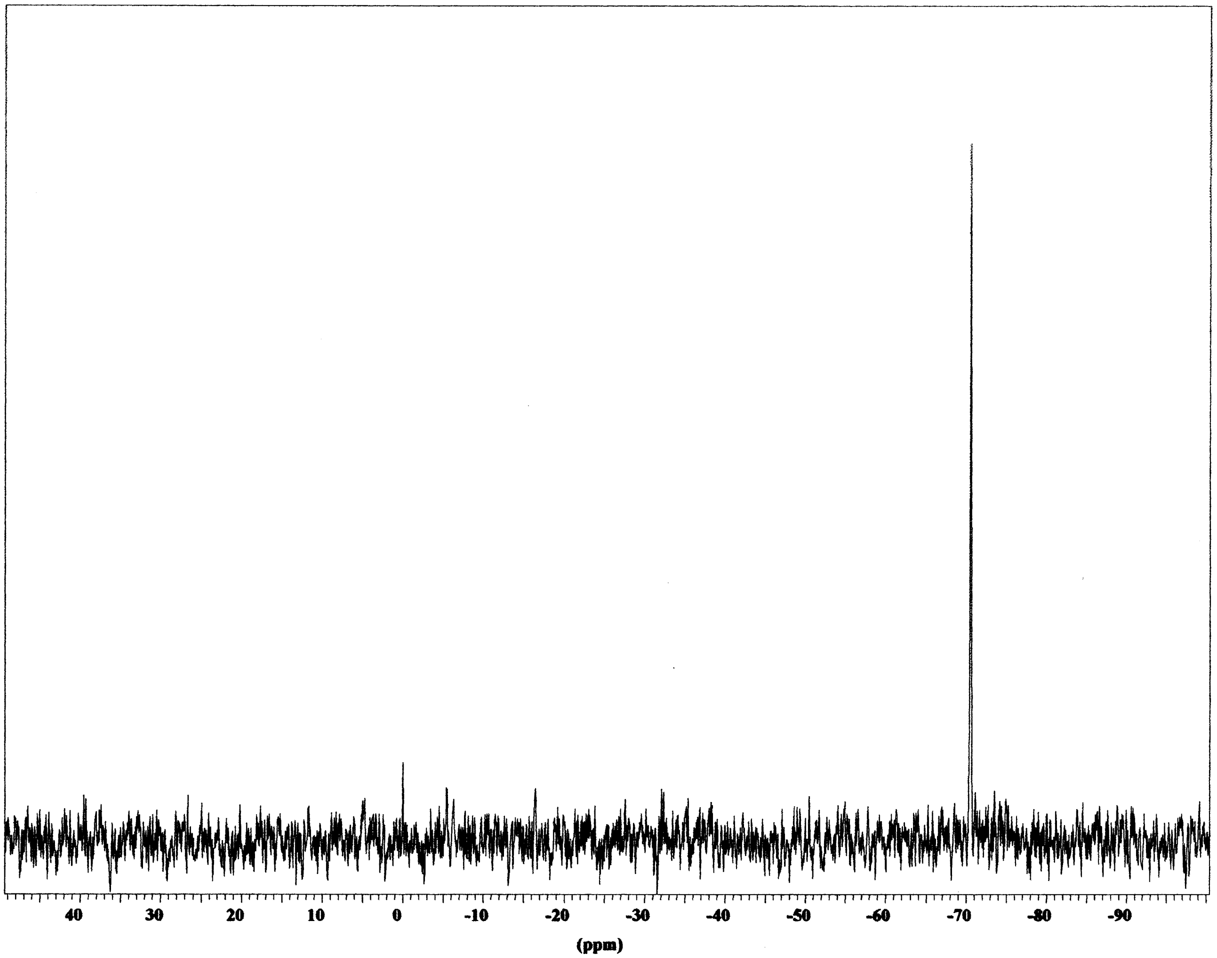
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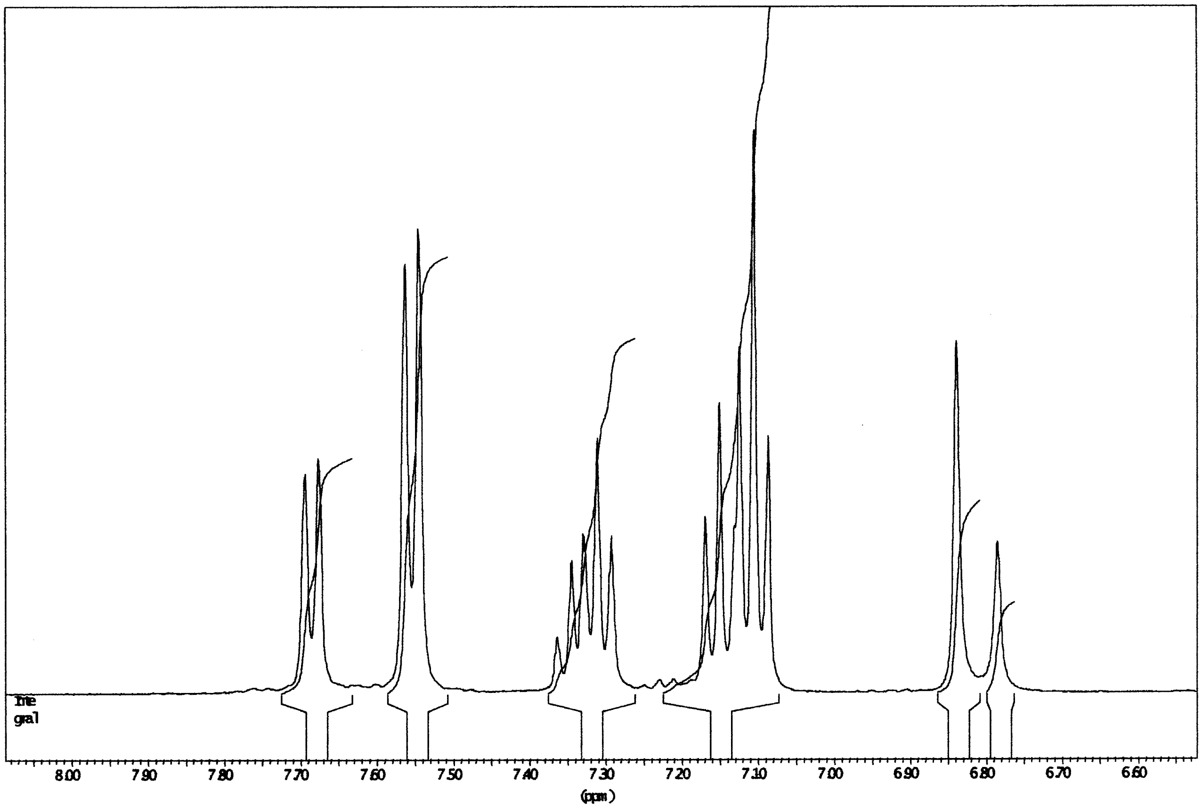
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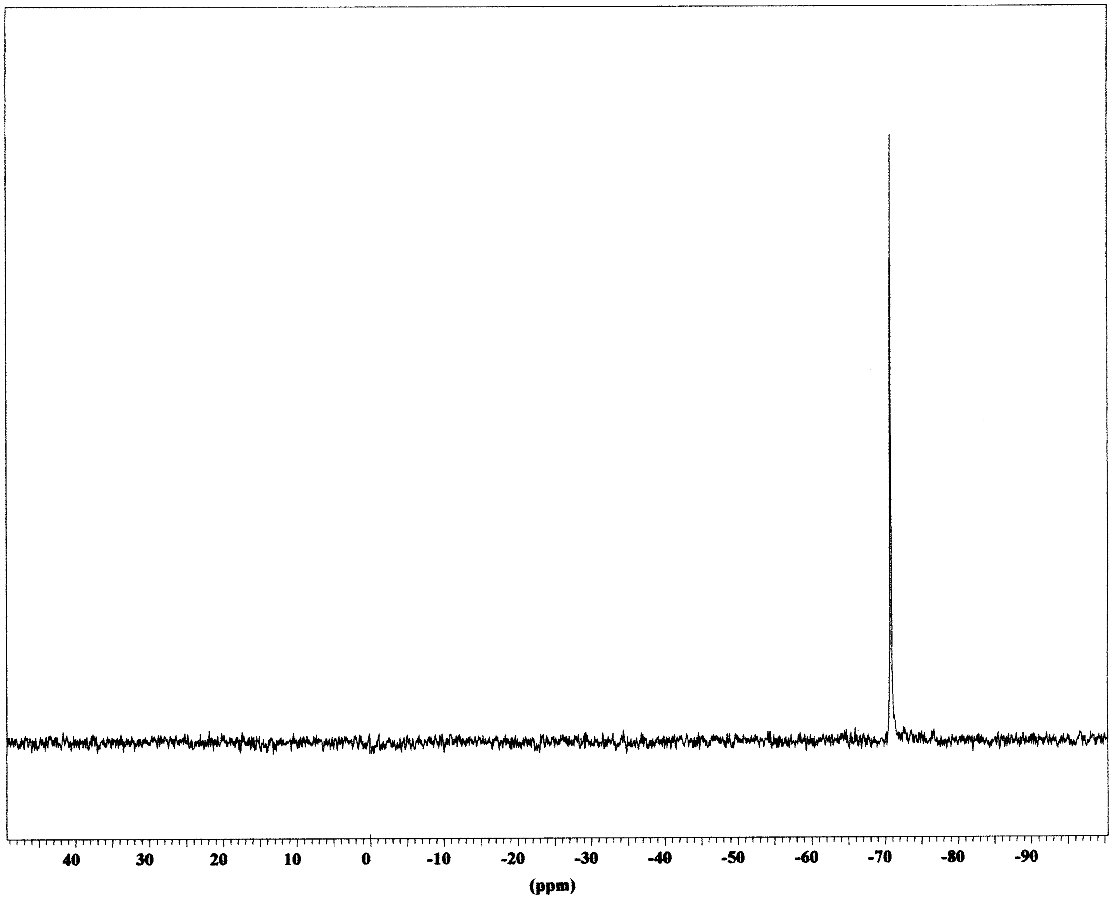
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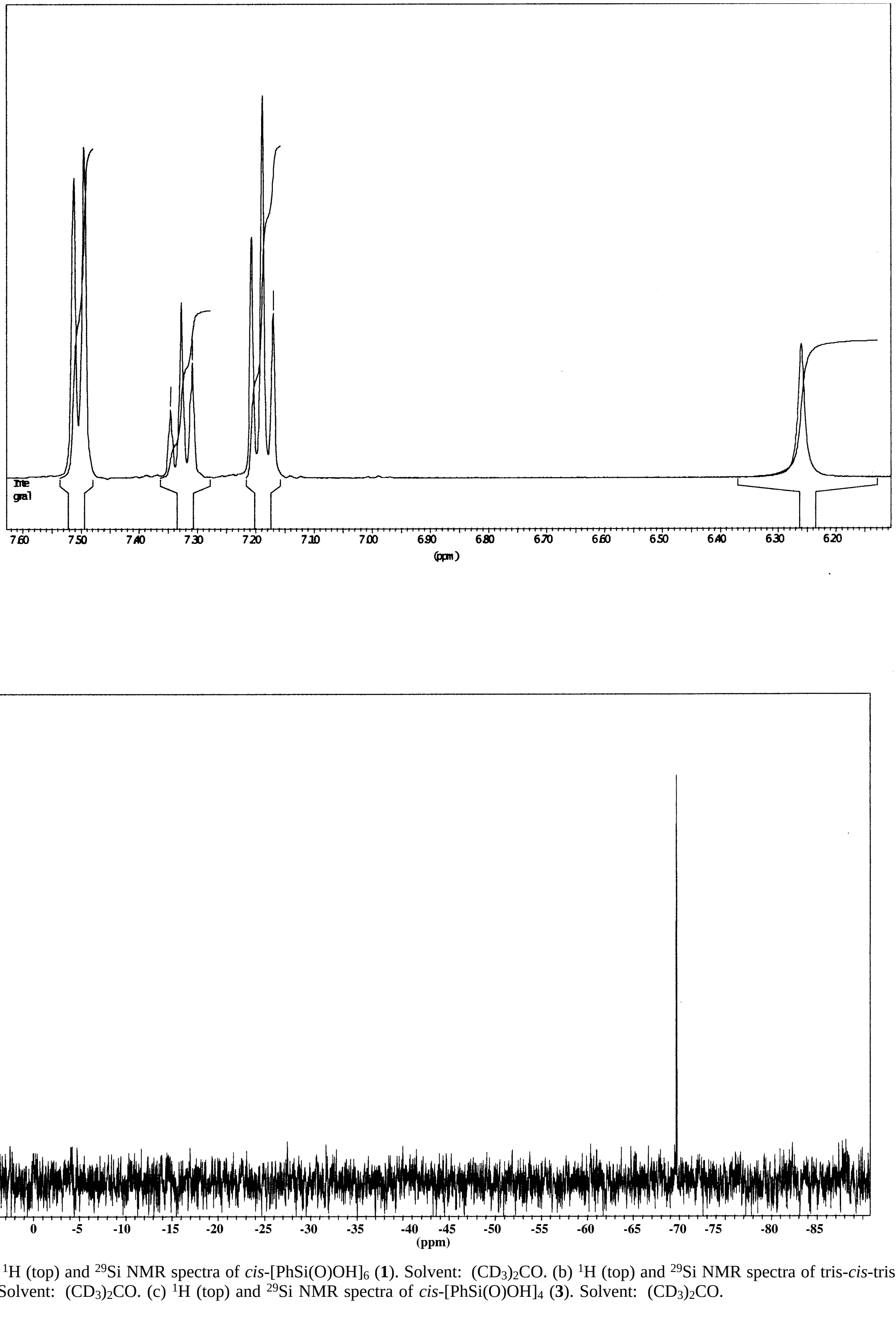

Figure 3. (a) ^{1}H (top) and ^{29}Si NMR spectra of *cis*-[PhSi(O)OH]$_6$ (**1**). Solvent: $(CD_3)_2CO$. (b) ^{1}H (top) and ^{29}Si NMR spectra of tris-*cis*-tris-*trans*-[PhSi(O)OH]$_{12}$ (**2**). Solvent: $(CD_3)_2CO$. (c) ^{1}H (top) and ^{29}Si NMR spectra of *cis*-[PhSi(O)OH]$_4$ (**3**). Solvent: $(CD_3)_2CO$.

Synthesis of *cis*-Tetra[(phenyl)(dimethylvinylsiloxy)]cyclotetrasiloxane (D$_4$b). A total of 3.00 g (97%) of *cis*-[PhSi(O)OSiMe$_2$-Vi]$_4$ was obtained similarly from 2.07 g (3.5 mmol) of tetrol and 3.35 g (27.7 mmol) of Me$_2$ViSiCl in the presence of pyridine (2.19 g, 27.7 mmol) in 30 mL of toluene. Anal. Calcd for [$C_6H_5Si(O)OSi(CH_3)_2CH{=}CH_2$]$_4$; $C_{40}H_{56}O_8Si_8$: C, 53.98; H, 6.34; Si, 25.27. Found: C, 54.35; H, 6.56; Si, 25.06. ^{1}H NMR (δ (ppm), C_6D_6): 7.00−7.40 (m, 5H, Ph), 5.75−6.30 (m, 3H, Vi), 0.26 (s, 6H, Me). ^{29}Si NMR (δ (ppm), C_6D_6): −0.921 (s, OSiMe$_2$Vi), −78.83 (s, O$_3$-SiPh).

Synthesis of *cis*-Tetra[(phenyl)(dimethylchloromethylsiloxy)]-cyclotetrasiloxane (D$_4$c). A total of 3.68 g (86%) of *cis*-[PhSi(O)OSi(CH$_3$)$_2$CH$_2$Cl]}$_4$ was obtained from 2.60 g (4.4 mmol) of tetrol and 7.48 g (52 mmol) of chloromethyldimethylchlorosilane

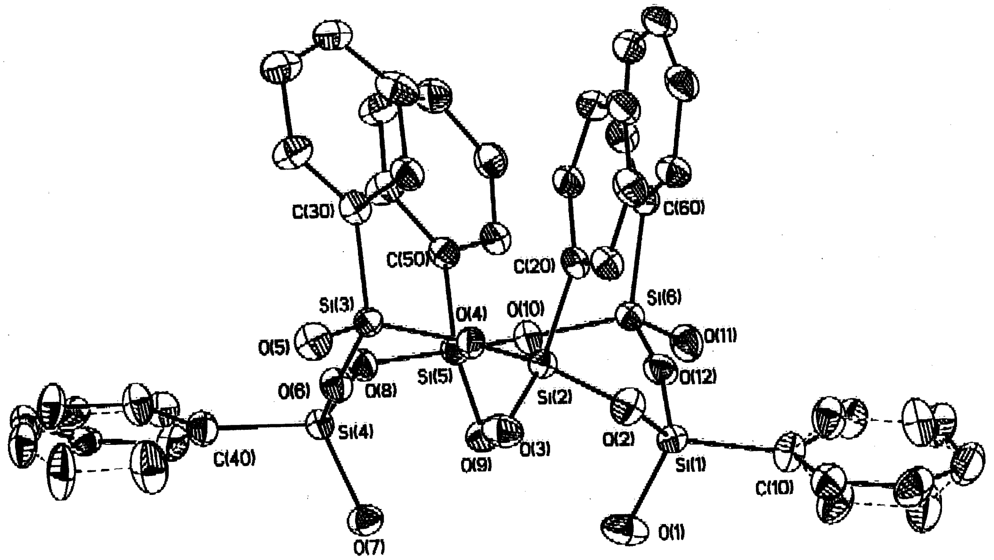

Figure 4. General view of **1** with numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

in 50 mL of benzene in the presence of pyridine (4.11 g, 52 mmol). The product was purified by sublimation (250−280 °C, 1 mm Hg). Anal. Calcd for $[C_6H_5Si(O)OSi(CH_3)_2CH_2Cl]_4$; $C_{36}H_{52}Cl_1O_8Si_8$: C, 44.14; H, 5.35; Si, 22.94; Cl, 14.50. Found: C, 45.02; H, 5.60; Si, 22.73; Cl, 14.28. ^{1}H NMR (δ (ppm), $CDCl_3$): 7.09−7.32 (m, 5H, Ph), 2.81 (s, 2H, CH_2Cl), 0.33 (s, 6H, Me). ^{29}Si NMR (δ (ppm), C_6D_6): 5.940 (s, OMe_2CH_2Cl), −78.13 (s, O_3SiPh).

Results and Discussion

Synthesis of Polysilanols. It is well-documented that the synthesis of hydroxyl-containing silanes and siloxanes is experimentally complicated as these compounds undergo self-condensation, especially in the presence of ionic agents.[17] Experience has shown that great care must be exercised to isolate pure compounds and to minimize the contact of silanols and ionic agents (acids or bases). High dilution reaction conditions and low temperatures are required for these reactions. The presence of bulky substituents at the silicon centers also inhibits the condensation reactions. Thus, dilute solutions of hydrochloric acid were used to split the cagelike metallasiloxanes, $Na_2\{[(PhSiO_2)_6Ni_4Na_4(\mu_3\text{-}OH)_2(PhSiO_2)_6]\}\cdot L_n$ (A), $Na_4\{[PhSiO_2]_{12}Cu_4\}\cdot L_n$ (C), and *cis*-$\{(Na^+)_4[PhSi(O)O^-]_4\}\cdot$(1-butanol)$_x$ (SPS-4), at low temperatures and low concentrations. The parent compounds were prepared via hydrolysis of phenyltri(*n*-butoxy)silane in the presence of sodium and nickel or sodium and copper ions according to Scheme 3. This scheme presents a general method of the preparation of the initial metallasiloxanes $Na_2\{[(PhSiO_2)_6Ni_4Na_4\ (\mu_3\text{-}OH)_2(PhSiO_2)_6]\}\cdot L_n$ (A), $Na_4\{[PhSiO_2]_{12}Cu_4\}\cdot L_n$ (C), and *cis*-$\{(Na^+)_4[PhSi(O)O^-]_4\}\cdot$(1-butanol)$_x$ (SPS-4) as well as polysilanols and their triorganylsiloxy-substituted derivatives. Besides metal chloride formation, under these conditions we obtained high yields of stereoregularly formed oligo(phenyl)(hydroxy)cyclosiloxanes containing a hydroxyl group attached to each silicon atom. Their structures, stereoregularities, and compositions were confirmed by ^{1}H and ^{29}Si NMR data, elemental analysis, and molecular weight determinations by VPO in acetone. Furthermore, the structure of *cis*-$[PhSi(O)OH]_6$ was confirmed by single-crystal X-ray analysis.

cis-Hexa[(phenyl)(hydroxy)]cyclohexasiloxane (**1**) was obtained from nickel/sodium-OPMS (A) (Scheme 3). The ^{1}H and ^{29}Si NMR data are summarized in Table 1 and Figure 3a and are consistent with the formula *cis*-$[PhSi(O)OH]_6$. The molecular weight obtained is equal to 800 (mol wt calcd = 829).

Tris-*cis*-tris-*trans*-dodeca[(phenyl)(hydroxy)]cyclododecasiloxane (**3**) was prepared by reaction of dilute aqueous HCl with copper/sodium-containing OPMS (C) (Scheme 3). The ^{1}H NMR spectrum of **2** shows two OH signals at δ = 6.798 and 6.850 ppm of two nonequivalent protons with relative intensities of 1:2 (Table 1, Figure 3b). The magnetic nonequivalence of OH protons is a result of their different environment because of the fact that one hydroxyl group has two other OH groups as neighbors in a cis−cis-position, whereas these others are surrounded by one OH and one Ph group in a cis−trans-position. The magnetic nonequivalence is also observed for protons of phenyl groups. In particular, there are two doublets of *o*-protons at δ = 7.696 and 7.565 ppm with the same relative intensities of 1:2. The intensity of phenyl protons relative to the OH protons is 5:1. The molecular weight determined by VPO was 1600 (mol wt calcd = 1658). These data are consistent with the assigned tris-*cis*-tris-*trans*-$[PhSi(O)OH]_{12}$ structure.

The reaction of dilute HCl solution with crystalline sodium phenylsiloxanolate, *cis*-$\{(Na^+)_4[PhSi(O)O^-]_4\}\cdot$(1-butanol)$_x$ (SPS-4)[7] (Scheme 3), gives *cis*-tetra[(phenyl)(hydroxy)]cyclotetrasiloxane (**3**) in more than 80% yield. The NMR data of **3** are summarized in Table 1 and Figure 3c. The VPO-determined molecular weight was equal to 540 (mol wt calcd = 552.9). Earlier, *cis*-tetrol (**3**) was isolated by Brown from the hydrolysis of phenyltrichlorosilane in aqueous acetone.[18] Subsequently, Feher et al. confirmed its

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(17) (a) Lickiss, P. D. *Adv. Inorg. Chem.* **1995**, *42*, 147−262. (b) Lickiss, P. D. In *Tailor-made Silicon−Oxygen Compound: From Molecules to Materials*; Corriu, R., Jutzi, P., Eds.; Friedr. Vieweg & Son: Braunschweig/Wiesbaden, Germany, 1996; 47−69.

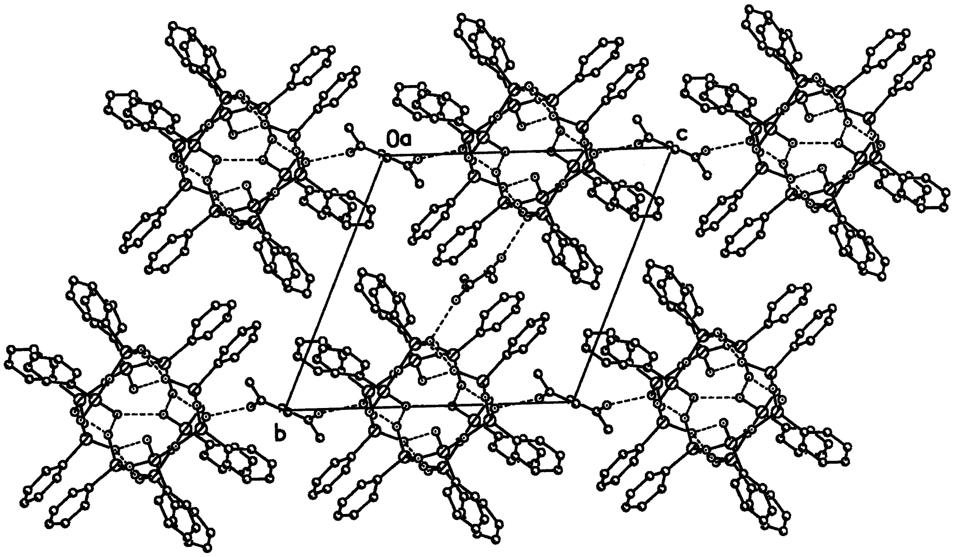

Figure 5. Crystal packing of **1**.

structure by single-crystal X-ray analysis.[19] In comparison to the published methods, the current reaction takes just a few minutes and produces *cis*-tetrol with a higher yield.

X-ray Analysis of *cis*-Hexa[(phenyl)(hydroxy)]cyclohexasiloxane (1). The X-ray analysis of **1** revealed that the conformation of the 12-membered cycle is best described as a boatlike structure, with a deviation of the Si(1) and Si(4) atoms by approximately 1.5 Å from the Si(2)Si(3)Si(5)Si(6) plane (the mean deviation is 0.29 Å) (Figure 4). Noteworthy, the hydroxyl groups linked to the Si(1) and Si(4) atoms are located at the pseudoaxial positions of the boat while all other OH groups are pseudoequatorial.

The geometry of **1** (Table 3) is similar to its trimethylsiloxy-substituted derivative, $[PhSi(O)(OSiMe_3)]_6$, reported earlier.[13] The silicon atoms are characterized by an almost undistorted tetrahedral coordination, with the O−Si−O and O−Si−C angles varying in the narrow ranges of 106.6(2)−111.7(2)° and 107.3(2)−112.9(2)°, respectively. In contrast, the coordination geometry of the oxygen atoms is much more flexible. The exo- as well as the endocyclic oxygen atoms in **1** are characterized by the Si−O−Si bond angles (140.5(2)−165.5(2)°) significantly exceeding the standard value (120°). Such behavior is quite usual for the sterically hindered siloxane moiety.[17]

The values of the Si−O bonds in **1** (1.602(4)−1.640(5) Å) are in general slightly shortened as compared with the standard value for a Si−O bond (1.631 Å).[20] Remarkably, the most elongated Si−O bonds are observed for the exocyclic Si−OH groups, which are located in the pseudoequatorial positions. The Si−C(Ph) bonds (average 1.852 Å), with exception of the disordered Ph groups, exhibit the normal values.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in **1**

Bond Lengths			
Si(1)−O(1)	1.640(4)	Si(4)−O(6)	1.602(4)
Si(1)−O(2)	1.616(4)	Si(4)−O(7)	1.633(3)
Si(1)−O(12)	1.602(4)	Si(4)−O(8)	1.622(3)
Si(1)−C(10)	1.853(5)	Si(4)−C(40)	1.839(5)
Si(2)−O(2)	1.619(4)	Si(5)−O(8)	1.617(3)
Si(2)−O(3)	1.619(4)	Si(5)−O(9)	1.630(3)
Si(2)−O(4)	1.616(3)	Si(5)−O(10)	1.624(3)
Si(2)−C(20)	1.851(5)	Si(5)−C(50)	1.850(5)
Si(3)−O(4)	1.623(3)	Si(6)−O(10)	1.616(3)
Si(3)−O(5)	1.608(4)	Si(6)−O(11)	1.619(4)
Si(3)−O(6)	1.617(3)	Si(6)−O(12)	1.615(4)
Si(3)−C(30)	1.857(5)	Si(6)−C(60)	1.854(5)

Bond Angles			
O(12)−Si(1)−O(2)	111.7(2)	O(6)−Si(4)−C(40)	109.7(2)
O(12)−Si(1)−O(1)	108.1(2)	O(8)−Si(4)−C(40)	107.3(2)
O(2)−Si(1)−O(1)	108.6(2)	O(7)−Si(4)−C(40)	112.7(2)
O(12)−Si(1)−C(10)	107.0(2)	O(8)−Si(5)−O(10)	107.3(2)
O(2)−Si(1)−C(10)	108.7(2)	O(8)−Si(5)−O(9)	111.8(2)
O(1)−Si(1)−C(10)	112.9(2)	O(10)−Si(5)−O(9)	106.0(2)
O(4)−Si(2)−O(2)	109.3(2)	O(8)−Si(5)−C(50)	107.8(2)
O(4)−Si(2)−O(3)	108.8(2)	O(10)−Si(5)−C(50)	111.6(2)
O(2)−Si(2)−O(3)	109.4(2)	O(9)−Si(5)−C(50)	112.3(2)
O(4)−Si(2)−C(20)	110.4(2)	O(12)−Si(6)−O(10)	107.7(2)
O(2)−Si(2)−C(20)	108.4(2)	O(12)−Si(6)−O(11)	111.0(2)
O(3)−Si(2)−C(20)	110.5(2)	O(10)−Si(6)−O(11)	110.3(2)
O(5)−Si(3)−O(6)	109.6(2)	O(12)−Si(6)−C(60)	107.7(2)
O(5)−Si(3)−O(4)	110.1(2)	O(10)−Si(6)−C(60)	110.3(2)
O(6)−Si(3)−O(4)	107.1(2)	O(11)−Si(6)−C(60)	109.8(2)
O(5)−Si(3)−C(30)	110.3(2)	Si(1)−O(2)−Si(2)	146.5(2)
O(6)−Si(3)−C(30)	109.9(2)	Si(2)−O(4)−Si(3)	144.2(2)
O(4)−Si(3)−C(30)	109.7(2)	Si(4)−O(6)−Si(3)	161.4(2)
O(6)−Si(4)−O(8)	111.6(2)	Si(5)−O(8)−Si(4)	140.5(2)
O(6)−Si(4)−O(7)	106.6(2)	Si(6)−O(10)−Si(5)	144.4(2)
O(8)−Si(4)−O(7)	109.0(2)	Si(1)−O(12)−Si(6)	165.5(2)

Because of the presence of numerous active hydrogen and oxygen atoms, which can participate in the formation of bridging H-bonds, most interest focused on the crystal packing of **1**. The analysis of the crystal structure revealed that the single molecules in the unit cell are assembled by the Si−OH···O(H)−Si H-bonds into the infinite hydrophobic coated (by the Ph groups) tubes, directed along the crystallographic axes *a* (Figure 5). Solvate acetone molecules are located in the cavities formed by the Ph groups and are linked to the tubes by the C═O···HO−Si H-bonds.

The complex system of H-bonds in the crystal structure of **1** is shown in Figure 6. Each siloxane cycle forms H-bonds

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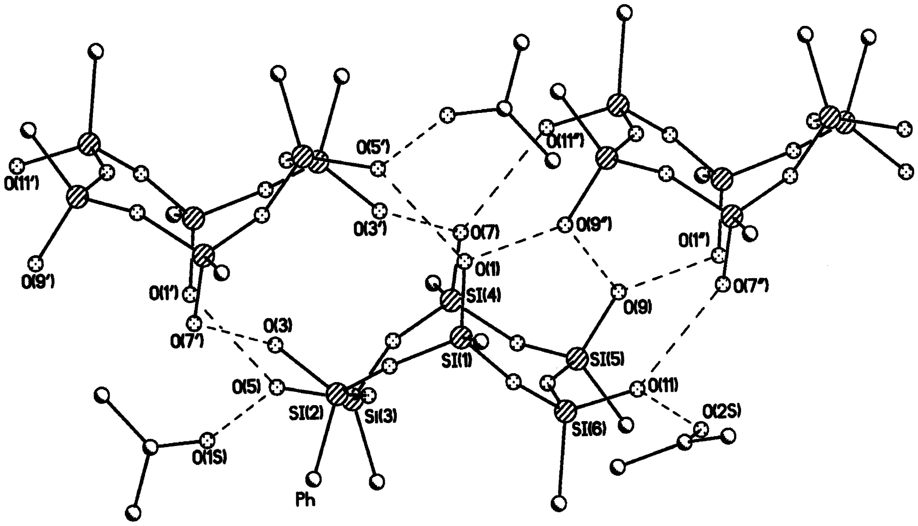

Figure 6. H-bonded tube formation in **1**; the Ph groups are omitted for clarity.

with two siloxane molecules and in addition with two solvate molecules of acetone. Unfortunately, the possibility of bifurcate H-bond formation between the Si−OH groups as well as the participation of the disordered solvate acetone molecules prevents a clear description of the H-bonds in **1**. Thus, the only available information concerning the H-bond system is limited to the O···O distances, which vary from 2.684(5) up to 2.964(5) Å, indicating Si−OH···O(H)−Si bonds. The corresponding values for the C═O···HO−Si bonds are approximately 2.64 Å (because of disorder). The determination of intra- and intermolecular Si−OH···Ph distances in the acetone-containing crystal structure of **1** revealed that H-bonds of the Si−OH···Ph type are absent.

IR Spectroscopy of Compounds 1−3. As expected, the IR spectra of **1**−**3** in the region of the OH groups' stretching vibrations did not exhibit any sharp narrow bands characteristic of free silanol groups. In the spectra of the phenyl-substituted silanols containing one OH group attached to Si, νOH is expected to appear at 3680−3690 $\mathrm{cm^{-1}}$.[17,21−24] For the silanol groups in solid **1**−**3**, a broad intense band with complicated contour is observed, whose center of gravity lies in the region of about 3200 $\mathrm{cm^{-1}}$ (Figure 7). This indicates a strong intermolecular H-bond of the OH···O type; the silanol groups in the solids are associated.

Reactivity of Polysilanols. According to Scheme 1, the reactivity of the polysilanols **1**−**3** was investigated performing their reactions with triorganylchlorosilane, $Me_2(R)SiCl$ (R = Me, CH_2Cl, $CH{=}CH_2$), in the presence of pyridine as an acceptor of HCl. The corresponding triorganylsiloxy-substituted derivatives were obtained in high yields. According to NMR and GPC data, the reaction of the silanols with trimethylchlorosilane occurred without change of the size and stereoregularity of the siloxane cycles.

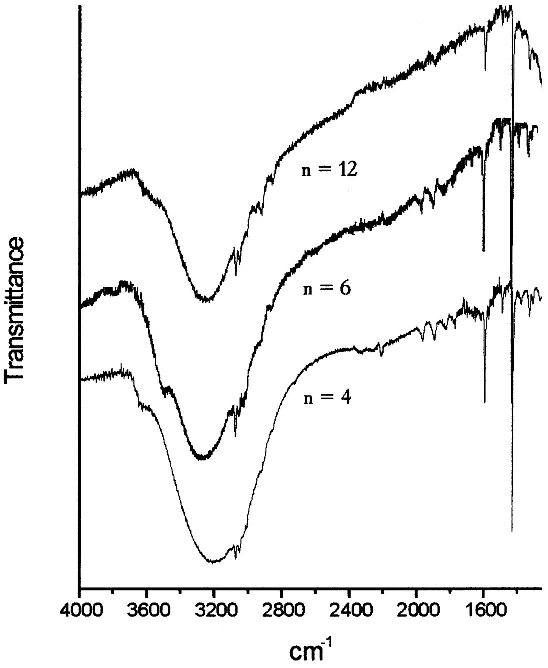

Figure 7. IR spectra in the region 4000−1500 $\mathrm{cm^{-1}}$ of solids **1**−**3.** The samples were prepared by spreading the substances between two CaF_2 plates with subsequent grinding by rotating the plates relative to each other.

However, it is necessary to note that the complete replacement of all hydroxyl by triorganylsiloxy groups requires a sufficient surplus of triorganylchlorosilane and elevated temperatures. A similar result was reported earlier describing the synthesis of $[PhSi(O)(OSiMe_3)]_4$ from *cis*-$[PhSi(O)OH]_4$ that was obtained by hydrolysis of phenyltrichlorosilane.[19,25]

According to differential scanning calorimetry, wide-angle X-ray scattering, and optical polarizing microscopy data, all stereoregular cycles described in this paper exhibited mesomorphic behavior, some in a large temperature region. The results of these investigations will be published elsewhere.

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Conclusion

In this paper we report a unique experimental approach to produce polyfunctional hydroxyl-containing cyclosiloxanes. Using the metal template effect for the synthesis of metallasiloxanes in a preliminary step, stereoregularly formed siloxane cycles are subsequently released under controlled conditions by the reaction with aqueous solutions of hydrochloric acid. In each case, this reaction gives only one cyclosiloxane selectively and with high yields. Such discrete molecules can be regarded as predetermined building blocks for the preparation of well-defined discrete supramolecular architectures, which we are currently pursuing.

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