Alkali-Metal-Directed Hydrolytic Condensation of Trifunctional Phenylalkoxysilanes

Yulia A. Pozdniakova,[a] Konstantin A. Lyssenko,[a] Alexandr A. Korlyukov,[a]
Inessa V. Blagodatskikh,[a] Norbert Auner,[b] Dimitris Katsoulis,[c] and
Olga I. Shchegolikhina*[a]

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The alkali-metal-directed hydrolysis of phenyltrialkoxysilanes, $PhSi(OR)_3$ (R = Me, Et, *n*Bu), was performed under various reaction conditions. The alkali metal ions were used both as templating entities and as structural elements. The crystalline sodium and potassium phenylsiloxanolates (Na-PhS and K-PhS) were obtained in two different molecular compositions based on a *cis*-tetraphenylcyclotetrasiloxanolate, *cis*-$[PhSi(O)O^-]_4$, or on a *cis*-triphenylcyclotrisiloxanolate, *cis*-$[PhSi(O)O^-]_3$, anions assembled into a chain or double-layer supramolecular structure through coordination with alkali cations and hydrogen-bonding contacts. Conditions for selective preparation of crystalline Na-PhS or K-PhS of both structural types were identified. The molecular and crystal structures of $[(Na^+)_3\{PhSi(O)O^-\}_3]\cdot 8H_2O$ (**2**), $[(Na^+)_3\{PhSi(O)O^-\}_3]\cdot 4H_2O\cdot 1EtOH$ (**3**) and $[(K^+)_3\{PhSi(O)O^-\}_3]_2\cdot 7H_2O\cdot 3MeOH$ (**4**) were determined by single-crystal X-ray analysis.

Introduction

The hydrolytic condensation of trifunctional organosilanes [e.g. $RSiCl_3$ or $RSi(OR)_3$], generally used for the preparation of silsesquioxane materials, is a multistep and rather complicated process. Due to a statistical distribution of intermediate components the process is very sensitive to a combination of experimental factors and usually produces a wide range of products, from small oligomers and polyhedral silsesquioxanes to mixtures of resin materials and gels.[1] The purpose of our investigations is to direct a hydrolytic condensation process to the formation of only one desired compound, with a well-defined structure, using a template. The proposed method includes the assembling of silicon-containing species on the template through non-covalent bonding, thus bringing the functional groups attached at the silicon atom into close contact. Such a mutual arrangement will favor the cyclocondensation and, finally, the formation of well-organized architecture. Subsequent removal of the template will give an individual siloxane molecule with a well-defined structure.

At present the template and self-assembly approach to the design of metal-based molecules and supramolecules from oligodentate ligands and appropriate metal ions is one of the most popular and fastest growing areas of experimental chemistry that offers an alternative to the classical organic route. The effectiveness of metal-mediated self-assembly for the construction of one-, two- and three-dimensional structures has been demonstrated in an enormous number of examples published in various articles, reviews and books.[2] As an alternative to the traditional approaches used in siloxane chemistry we have taken advantage of a metal-directed self-assembly strategy to selectively create metallasiloxane molecules with well-defined architectures by hydrolysis of various trifunctional alkoxysilanes in the presence of alkaline and/or transition and lanthanide metal ions.[3]

The focus of our present work is a study of the alkali-metal-directed hydrolytic condensation of phenyltrialkoxysilanes under a wide variety of different experimental conditions. The alkali metal ions were used both as templating entities and as structural elements.

Literature data on the synthesis and structure of alkali metal organosiloxanolates are presented in details in our previous publication[4] and references cited therein.

Results

Reactions of phenyltrialkoxysilanes $PhSi(OR)_3$ (R = *n*Bu, Et, Me) with NaOH or KOH [Si/Na(K) = 1:1] were

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[a] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
Vavilova 28, 119991 Moscow, Russian Federation
E-mail: olga@ineos.ac.ru
[b] Chemistry Department, Goethe University of Frankfurt,
Marie Curie Strasse 11, 60439 Frankfurt, Germany
[c] Dow Corning Corporation,
Midland, MI 48686, USA

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performed in the presence of water according to Scheme 1 and the description given in the Exp. Sect. The H_2O/Si ratio was varied within the range 1−12:1. Alcohols (*n*BuOH, EtOH, MeOH) or their mixtures with either aromatic solvents (xylene, toluene, benzene) or with hexane, were used as solvents.

$$PhSi(OR)_3 + MOH + x\,H_2O \xrightarrow{\text{solvent}} [PhSi(O)OM]_n{\cdot}L$$

$$R = Me, Et, nBu;\ M = Na, K;\ x = 1\text{–}12,\ n = 3, 4;\ L = ROH, H_2O$$

Scheme 1

From some reaction solutions suitable single crystals were isolated and their molecular and crystal structures were determined by X-ray analysis. Trapping reactions of the bulk samples with Me_3SiCl were used in order to establish a correspondence between one element in the crystal structure (namely the size of the siloxanolate cycle) and the overall crystalline mass composition (Scheme 2). The corresponding trimethylsiloxy-substituted derivatives of alkali metal phenylsiloxanolates were analyzed by NMR spectroscopy and GPC.

$$[PhSi(O)OM]_n{\cdot}L + x\,Me_3SiCl \xrightarrow[-\,n\,MCl,\ -\,py{\cdot}HCl]{\text{solvent, py}} [PhSi(O)OSiMe_3]_n$$

$$M = Na, K;\ n = 3, 4$$

Scheme 2

The analytical data obtained from the above combination of physical methods proved unambiguously that crystalline sodium phenylsiloxanolates (Na-PhS) as well as potassium phenylsiloxanolates (K-PhS) are compounds that contain cyclic phenylsiloxanolate fragments, *cis*-$[PhSi(O)O^-]_n$, surrounded by sodium or potassium ions. Two different molecular structures can be generated based on either a *cis*-tetraphenylcyclotetrasiloxanolate (Figure 1) or on a *cis*-triphenylcyclotrisiloxanolate fragment (Figures 2−4); their specific formation depends on the reaction conditions (see below).

Sodium phenylsiloxanolates of both types crystallize in good yields over a wide range of different reaction conditions (Table 1). Crystalline sodium phenylsiloxanolate, based on a *cis*-tetraphenylcyclotetrasiloxanolate fragment (Na-PhS-4), was selectively produced from the reaction of $PhSi(OnBu)_3$ [4] with sodium hydroxide in *n*BuOH, in the presence of an equimolecular amount of water (molar ratio H_2O/Si = 1:1). Crystalline Na-PhS-4 was isolated in about 80% yield under similar conditions from the reaction of $PhSi(OEt)_3$ in ethanol. A single crystal of *cis*-$[(Na^+)_4\{PhSi(O)O^-\}_4]{\cdot}8nBuOH$ (**1**; Figure 1), obtained from $PhSi(OnBu)_3$, was characterized by X-ray crystallography.[4] Treatment of both crystalline bulks with Me_3SiCl yielded *cis*-$[PhSi(O)OSiMe_3]_4$ exclusively.

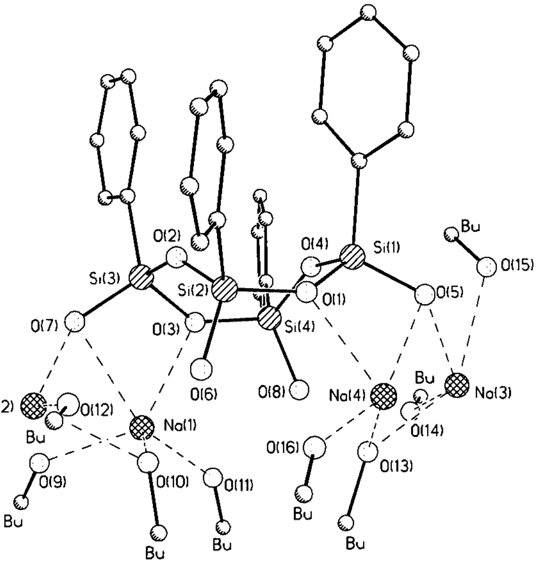


Figure 1. General view of the molecular structure of sodium phenylsiloxanolate **1**[4]

Crystalline sodium phenylsiloxanolate based on a *cis*-triphenylcyclotrisiloxanolate fragment (Na-Ph-3) was synthesized from $PhSi(OEt)_3$ under different reaction conditions. A summary of reactions performed with $PhSi(OEt)_3$ under different conditions is given in Table 1. The formation of the six-membered cycle was promoted by an increase of the H_2O/Si ratio and/or by the addition of a strongly hydrophobic solvent (hexane) to the reaction medium. Reactions performed in pure ethanol solution with a high excess of water (H_2O/Si = 4−12:1; Table 1, Entries 2 and 3) led to the selective formation of Na-PhS-3 as the only crystalline product in yields up to 63%. A single crystal (Table 1, Entry 3; H_2O/Si = 12:1) was characterized as *cis*-$[(Na^+)_3\{PhSi(O)O^-\}_3]{\cdot}8H_2O$ (**2**) by X-ray analysis (Figure 2). The use of an ethanol/hexane mixture as reaction

Table 1. Formation of Na-PhS-3 and/or Na-PhS-4 from $PhSi(OEt)_3$ under different experimental conditions

Entry	H_2O/Si ratio	Solvent	Yield of crystalline Na-PhS[a] (%)	Na-PhS-3/Na-PhS-4 ratio
1	1:1	ethanol	83	−:1
2	4:1	ethanol	42	1:−
3	12:1	ethanol	63	1:−
4	1:1	ethanol/hexane	95	1:1
5	2:1	ethanol/hexane	95	1:−

[a] Amorphous, powder-like by-products add to 100%; their trimethylsiloxy derivatives are the set of oligomers.

medium resulted in the selective formation of Na-PhS-3 in yields up to 95% even at molar H_2O/Si ratios of about 2:1 (Table 1, Entry 5). Derivatization of the crystalline bulk materials (Table 1, Entries 2, 3 and 5) with Me_3SiCl afforded the quantitative formation of *cis*-$[PhSi(O)OSiMe_3]_3$ in all cases.

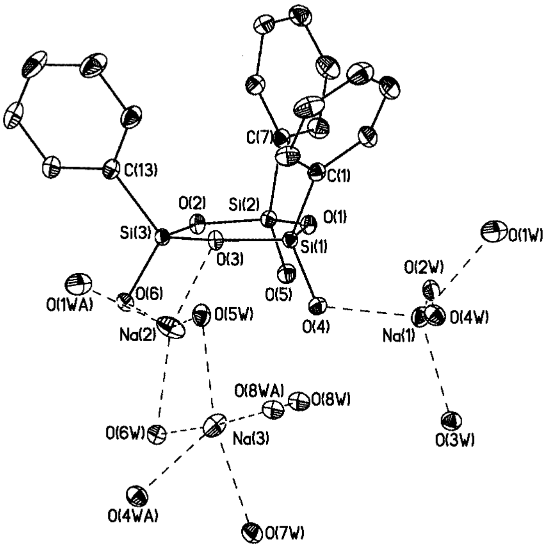


Figure 2. General view of **2** with thermal ellipsoids at 50% probability level

X-ray structure analysis of a single crystal isolated from the hydrolysis of $PhSi(OEt)_3$ in EtOH/hexane solution (molar ratio H_2O/Si = 1:1; Table 1, Entry 4) documents the formation of $[(Na^+)_3\{PhSi(O)O^-\}_3]\cdot 4H_2O\cdot 1EtOH$ (**3**; Figure 3). The molecular structure of **3** differs from that of compound **2** with respect to the coordination sphere of the sodium cations. In **3** one solvate molecule of ethanol replaces four water molecules in the molecular unit. Although the molecular structure of Na-PhS-3 is based on a trisiloxanolate cycle as the main fragment, the trapping reaction of the whole crystalline bulk with Me_3SiCl yielded a mixture of $[PhSi(O)OSiMe_3]_3$ and $[PhSi(O)OSiMe_3]_4$ in a molar ratio of 1:1. Thus, the formation of both structural types occurs under these reaction conditions.

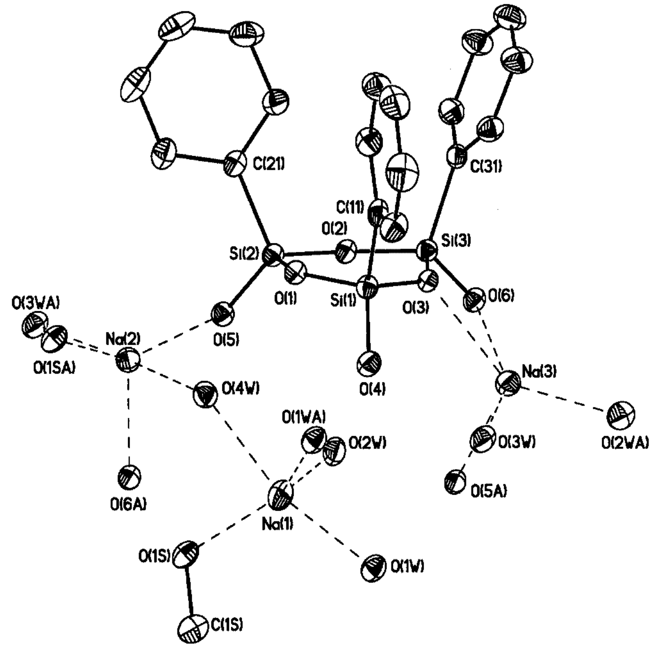


Figure 3. General view of **3** with thermal ellipsoids at 50% probability level

No crystalline products could be isolated from reactions of $PhSi(OMe)_3$ with NaOH in the presence of different amounts of water (H_2O/Si = 1−10:1) and in different solvents (MeOH, MeOH/benzene, MeOH/toluene, MeOH/hexane). The derivatization of the products obtained with Me_3SiCl gave a mixture of oligomers, as proven by GPC analytical methods.

Crystallization of potassium phenylsiloxanolate, unlike the corresponding sodium salt, occurs only under a narrow range of conditions, probably due to a higher solubility of the potassium siloxanolate intermediate compared to its sodium analogue. Thus, the use of a high dielectric constant medium (neat alcohol, excess of water) results in a low yield

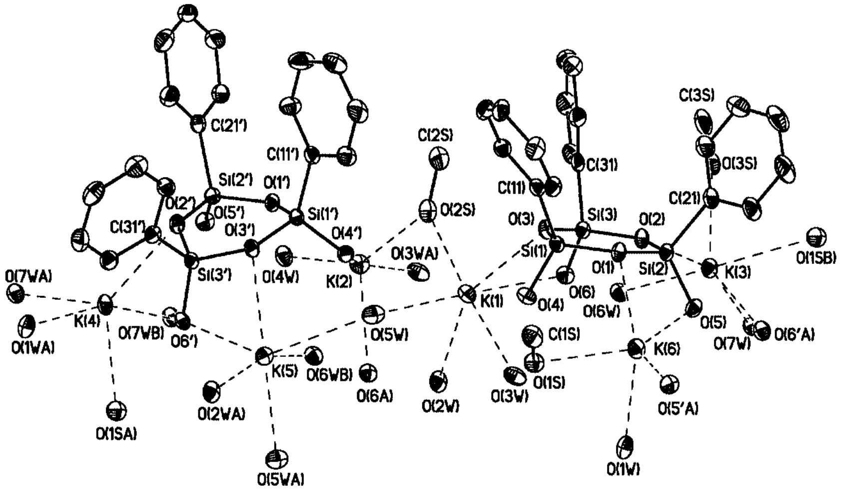


Figure 4. General view of **4** with thermal ellipsoids at 50% probability level

of crystalline material or even prevents crystallization. A defined molar ratio of H_2O/Si from 1:1 to 1.5:1 is required for a successful crystallization.

The reaction of $PhSi(OMe)_3$ with KOH, even in an equimolar ratio of H_2O/Si in neat MeOH, did not yield any crystalline material. In contrast, reactions of $PhSi(O\textit{n}Bu)_3$ and of $PhSi(OEt)_3$ with KOH using an equimolar ratio of H_2O/Si in pure *n*BuOH or EtOH, respectively, gave crystalline potassium phenylsiloxanolate with a tetraphenylcyclotetrasiloxanolate fragment (K-PhS-4), but only in low yields ranging from 10 to 28%. Although we failed to grow suitable single crystals for X-ray analysis, reactions of the crystalline bulk with Me_3SiCl yielded $[PhSi(O)OSiMe_3]_4$ selectively, proving the formation of a potassium salt based on a tetrasiloxanolate cyclic fragment.

Decreasing the dielectric constant of the reaction medium by addition of non-polar solvent supports the bulk crystallization of potassium triphenylcyclotrisiloxanolate (K-PhS-3). Crystalline materials in high yields (up to 95%) were isolated from phenyltrialkoxysilanes $PhSi(OR)_3$ (R = Me, Et, *n*Bu) used for KOH treatment in mixtures of MeOH/benzene, EtOH/toluene, and of *n*BuOH/xylene. In all cases the derivatization of the crystalline bulk with Me_3SiCl gave exclusively $[PhSi(O)OSiMe_3]_3$. A single crystal suitable for X-ray analysis was obtained from the reaction of $PhSi(OMe)_3$. The molecular structure is shown in Figure 4 and proves the formation of $[(K^+)_3\{PhSi(O)O^-\}_3]_2\cdot 7H_2O\cdot 3MeOH$ (**4**).

Molecular Structures of 2, 3, and 4

The single-crystal X-ray investigations revealed that the independent unit cells of compounds **2** and **3** contain one triphenylcyclotrisiloxanolate anion, three sodium cations and water (**2**) or water and alcohol molecules (**3**) (Figures 2 and 3, respectively). The peculiarity of the crystal structure of the potassium salt **4** is the presence of two independent siloxanolate anions and, consequently, of six potassium cations (see Table 2, Figure 4) in the unit cell. In all molecular structures the geometry of the siloxanolate anions is characterized by typical bond lengths and angles usually observed for this class of compounds (Tables 3 and 4).[5,6] Thus, the Si−C bonds of the Si−Ph groups are equal to 1.862(2) Å (average value), the cyclic Si−O bonds are significantly elongated [1.639(2)−1.661(1) Å] compared to terminal analogues [1.577(2)−1.596(1) Å]. The six-membered Si−O cycles exhibit an all-*cis* arrangement of the phenyl substituents. Their conformations vary from an approximately planar one in **2** and in **4** (in one of the two independent molecules) to an envelope conformation in **3** [deviation of Si(3) atom], and a distorted boat conformation [deviation of Si(3′) and O(1′) atoms] for the second independent molecule in **4**. This variation of the siloxanolate ring conformations is in line with the high flexibility of the siloxanolate rings.

The coordination sphere of the alkali cations is predominantly determined and formed by the negatively charged siloxanolates oxygen atoms and water (in **2**), and the sur-

Table 2. Crystallographic data and parameters of refinement for **2−4**

	2	**3**	**4**
Empirical formula	$C_{18}H_{31}Na_3O_{14}Si_3$	$C_{20}H_{29}Na_3O_{11}Si_3$	$C_{19.5}H_{28}K_3O_{11}Si_3$
Formula mass	624.67	598.67	1279.98
Crystal system	triclinic	monoclinic	triclinic
T [K]	110	110	110
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Radiation	Mo-K_α (λ = 0.71072 Å)		
Scan type	ω-scan with 0.3 step and 10 s exposure per frame		
Diffractometer	Smart 1000 K CCD		
a [Å]	9.2873(5)	16.803(4)	10.569(3)
b [Å]	9.3329(5)	9.761(2)	16.387(5)
c [Å]	17.7565(9)	17.177(4)	16.658(4)
α [°]	79.822(1)	90	101.352(6)
β [°]	83.524(1)	103.979(5)	97.692(6)
γ [°]	63.844(1)	90	92.636(6)
V [Å^3]	1358.7(1)	2734(1)	2795(1)
Z	2	4	4
μ [cm^{-1}]	2.88	2.76	6.70
$D_{calcd.}$ [g·cm^{-3}]	1.527	1.454	1.521
$2\theta_{max}$ [°]	60	54	60
Total number of reflections	10451	11641	23178
Independent reflections [R(int)]	74550 (0.0152)	5582 (0.0519)	15938 (0.0315)
$R1$ for refl.with $I > 2\sigma(I)$	0.0351 (for 6564 refl.)	0.0464 (for 3136 refl.)	0.0591 (for 10645 refl.)
$wR2$ for all reflections	0.0978 (for 7455 refl.)	0.0929 (for 5582 refl.)	0.1482 (for 15938 refl.)
GOF	1.052	0.96	1.065

Table 3. Selected bond lengths [Å] and angles [°] in **2** and **3**

	2	**3**
Bond lengths:		
Si(1)−O(1)	1.652(1)	1.645(2)
Si(1)−O(3)	1.652(1)	1.659(2)
Si(1)−O(4)	1.584(1)	1.576(2)
Si(1)−C(11)	1.861(1)	1.864(3)
Si(2)−O(1)	1.6533(9)	1.648(2)
Si(2)−O(2)	1.643(1)	1.669(2)
Si(2)−O(5)	1.594(1)	1.576(2)
Si(2)−C(21)	1.864(1)	1.864(3)
Si(3)−O(2)	1.638(1)	1.660(2)
Si(3)−O(3)	1.6529(9)	1.650(2)
Si(3)−O(6)	1.596(1)	1.580(2)
Si(3)−C(31)	1.857(1)	1.864(3)
Bond angles:		
O(1)−Si(1)−O(3)	107.38(5)	105.5(1)
O(1)−Si(1)−O(4)	110.01(5)	111.2(1)
O(3)−Si(1)−O(4)	107.38(5)	109.2(1)
O(1)−Si(1)−C(11)	107.67(6)	107.1(1)
O(3)−Si(1)−C(11)	106.70(5)	109.3(1)
O(4)−Si(1)−C(11)	113.81(5)	114.0(1)
O(1)−Si(2)−O(2)	105.23(5)	105.2(1)
O(1)−Si(2)−O(5)	110.87(5)	111.3(1)
O(2)−Si(2)−O(5)	112.10(5)	112.2(1)
O(1)−Si(2)−C(21)	107.26(5)	107.3(1)
O(2)−Si(2)−C(21)	108.20(5)	107.1(1)
O(5)−Si(2)−C(21)	112.78(6)	113.1(1)
O(2)−Si(3)−O(3)	106.74(5)	106.7(1)
O(2)−Si(3)−O(6)	112.21(5)	112.6(1)
O(3)−Si(3)−O(6)	108.99(5)	109.2(1)
O(2)−Si(3)−C(31)	109.31(6)	108.1(1)
O(3)−Si(3)−C(31)	108.02(5)	108.0(1)
O(6)−Si(3)−C(31)	111.37(6)	112.0(1)
Si(1)−O(1)−Si(2)	133.31(6)	135.6(1)
Si(3)−O(2)−Si(2)	135.02(6)	131.9(1)
Si(3)−O(3)−Si(1)	131.67(6)	132.1(1)

Table 4. Selected bond lengths [Å] and angles [°] for two independent molecules in **4**

	4A	**4B**
Bond lengths:		
Si(1)−O(1)	1.638(2)	1.645(2)
Si(1)−O(3)	1.641(2)	1.648(2)
Si(1)−O(4)	1.590(2)	1.591(2)
Si(1)−C(11)	1.857(3)	1.859(3)
Si(2)−O(1)	1.652(2)	1.660(2)
Si(2)−O(2)	1.649(2)	1.642(2)
Si(2)−O(5)	1.579(2)	1.576(2)
Si(2)−C(21)	1.858(3)	1.861(3)
Si(3)−O(2)	1.653(2)	1.654(2)
Si(3)−O(3)	1.648(2)	1.649(2)
Si(3)−O(6)	1.591(2)	1.579(2)
Si(3)−C(31)	1.863(3)	1.860(3)
Bond angles:		
O(1)−Si(1)−O(3)	106.6(1)	106.2(1)
O(1)−Si(1)−O(4)	111.4(1)	111.2(1)
O(3)−Si(1)−O(4)	110.1(1)	110.0(1)
O(1)−Si(1)−C(11)	108.7(1)	109.8(1)
O(3)−Si(1)−C(11)	109.1(1)	108.7(1)
O(4)−Si(1)−C(11)	110.8(1)	110.9(1)
O(1)−Si(2)−O(2)	105.5(1)	111.4(1)
O(1)−Si(2)−O(5)	109.2(1)	112.5(1)
O(2)−Si(2)−O(5)	112.9(1)	105.5(1)
O(1)−Si(2)−C(21)	108.5(1)	107.3(1)
O(2)−Si(2)−C(21)	108.7(1)	109.7(1)
O(5)−Si(2)−C(21)	111.7(1)	110.3(1)
O(2)−Si(3)−O(3)	106.9(1)	106.5(1)
O(2)−Si(3)−O(6)	112.4(1)	111.3(1)
O(3)−Si(3)−O(6)	110.4(1)	112.0(1)
O(2)−Si(3)−C(31)	108.0(1)	106.4(1)
O(3)−Si(3)−C(31)	105.5(1)	106.4(1)
O(6)−Si(3)−C(31)	113.3(1)	113.8(1)
Si(1)−O(1)−Si(2)	134.4(1)	132.3(1)
Si(2)−O(2)−Si(3)	133.3(1)	132.4(1)
Si(1)−O(3)−Si(3)	132.5(1)	131.9(1)

rounding siloxanolate oxygen atoms, water and alcohol molecules (ethanol in **3**, and methanol in **4**, respectively). In spite of the differences in the number of solvate molecules in sodium salts **2** and **3**, both are characterized by some common features: only two of the cations are directly connected to the siloxanolate ring's oxygen atoms, while the coordination sphere of the third cation contains only the solvate molecules, and thus can consequently be described as a "bridging cation". An equivalent "bridging sodium" was previously detected in the corresponding salt **1**[4] and therefore is probably a general feature of such sodium salts. In contrast to compounds **1−3**, in salt **4** all potassium atoms are linked to the siloxanolate ring's oxygen atoms; this is probably due to the larger van der Waals radius of potassium cations. The number of oxygen atoms coordinated to the potassium or to the sodium cations in **2−4** varies between five and six and is dependent mainly on the type of coordinated oxygen atoms (in water or in alcohol molecules). The Na−O and K−O distances are 2.287(3)−2.599(2) Å, and 2.625(3)−3.053(3) Å, respectively, with the shortest contacts to the water molecules. The coordination polyhedra of the alkali metal atoms are distorted trigonal-bipyramidal or octahedral, depending on the coordination number.

The presence of a significant amount of solvate molecules (water and alcohol) leads to the formation of a complicated hydrogen-bonding network, with O···O distances varying from 2.568(1) to 3.037(2) Å. Analysis of the crystal structures of **2−4** revealed that, depending on the solvate contents and the nature of the cations, the hydrogen bonds are formed solely between the solvate and Si−O$^-$ (**3**) and/or only between the solvate molecules (**2**, **4**). In general, the hydrogen bonds between solvate and $^-$O−Si are characterized by slightly shorter O···O distances than those between solvate molecules. The maximum number of hydrogen bonds formed by the siloxanolate oxygen atoms is three, with a pseudo-tetrahedral arrangement around the oxygen atom. The number and strength of these hydrogen bonds is mainly dominated by the coordination of the corresponding Si−O$^-$ bond to the alkali metal atom, resulting in a systematic shortening of the hydrogen bond lengths of the centers weakly coordinated or uncoordinated by alkali.

In **2−4** the hydrogen-bonding pattern leads to an overall supramolecular architecture: the molecules are assembled into double layers (Figure 5), which have a hydrophilic "filling" (alkali, water and alcohol molecules) and a hydrophobic "coating" (Ph groups).

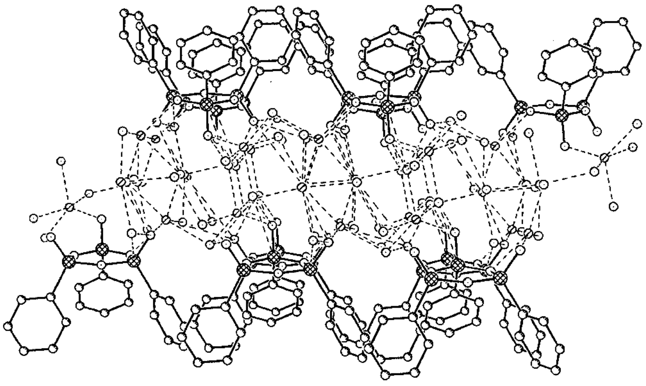


Figure 5. Double-layer structure in **2**−**4**

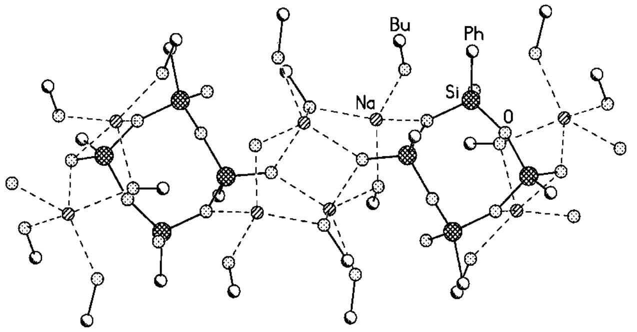
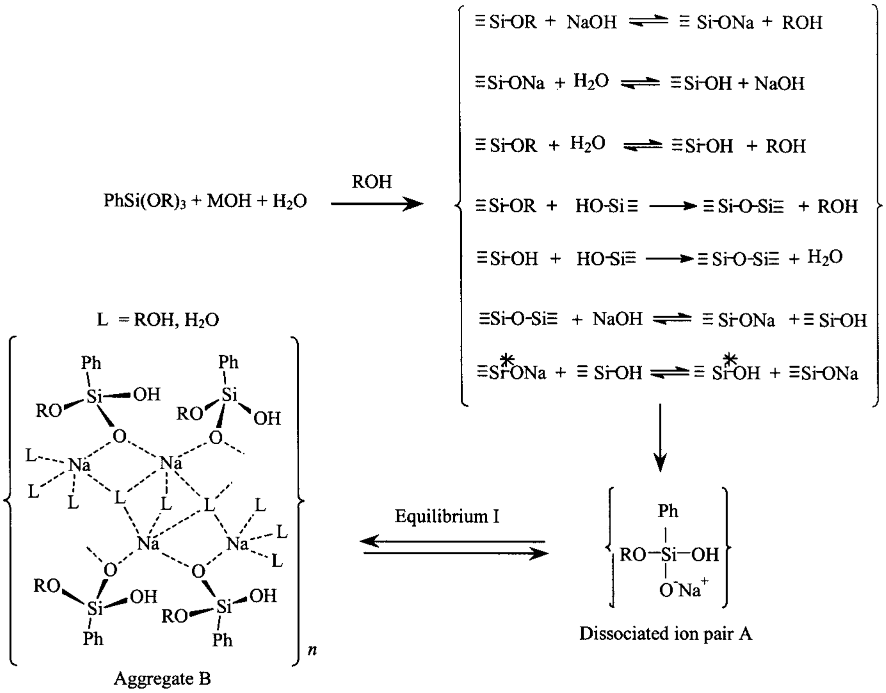


Figure 6. Cyclotetrasiloxanolate tetraanion/tetracation arrangement to form chains in **1**;[4] phenyl groups are omitted for clarity

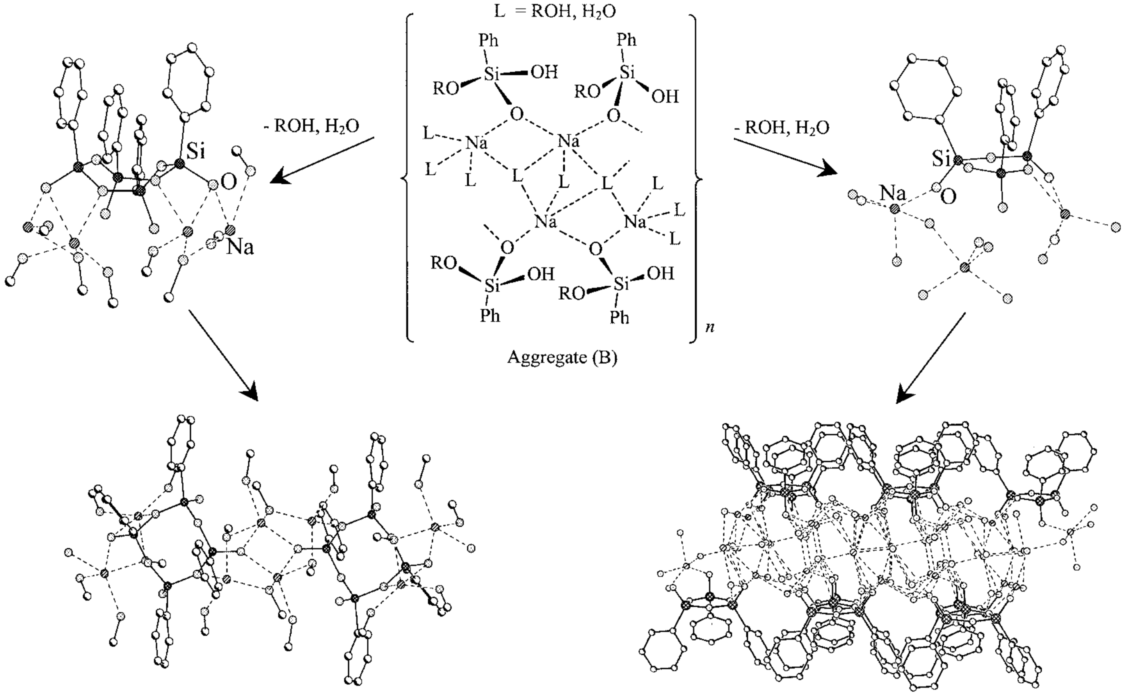
The packing of the sodium phenylsiloxanolates **2** and **3**, based on trisiloxanolate cycles, is different from that of the sodium phenylsiloxanolate based on a tetrasiloxanolate cycle:[4] the molecules of the latter are assembled into a chain-like structure by coordination bonds. Each chain is surrounded by phenyl substituents and solvated alcohol molecules without bridging ions connecting neighboring chains (Figure 6).

Discussion

Several coupled equilibrium reactions must take place when the hydrolysis of trialkoxysilane is performed in an alcoholic medium in the presence of an equimolar amount of the base (e.g. NaOH; Scheme 3. As a result of these reactions, and a rapid proton-cation exchange,[7] the generation of a labile alkaline intermediate, suggested[4] to be [PhSi(OH)(OR)(O^-Na^+)] (A) (Scheme 3), is quite possible. Presumably, these alkaline intermediates, containing solvent-separated ion pairs,[8] tend to associate (equilibrium I),[9] forming complex aggregates (B) in which an ionic part (alkali metal ion, alcohol and water molecules) is surrounded by silicon species containing functional OH and OR groups. These groups can undergo a condensation process with both water and alcohol elimination resulting in the formation of either a mixture of oligomers or cyclic products, depending on the reaction parameters (Scheme 4). The equilibrium I is a function[10] of the charge density of M^+, the solvating ability of the solvent, the nucleophilicity of the anion, and the solvent/salt ratio. Such a complicated and multi-argument process leads to results that are relatively difficult to predict. In the course of our study we found an appropriate set of conditions whereby the condensation process can be selectively directed to the generation of cyclotri- or cyclotetrasiloxanolate anions as-



Scheme 3



Scheme 4

sembled into supramolecular architectures (double layers or chains) through coordination with metal cations and hydrogen bonding.

The high-yield crystallization of sodium phenylsiloxanolate of different structural types in a wide range of conditions can be explained by the possible shift of equilibrium I to the formation of the complex aggregates (B).

In contrast, crystallization of potassium phenylsiloxanolate from an alcohol solution is quite rare. Moreover, an excess of water ($H_2O/Si > 1.5:1$) prevents crystallization. This could be caused by the tendency of potassium phenylsiloxanolate to exist as a solvent-separated ion pair (A). A decrease in the dielectric constant of the reaction medium should shift the equilibrium I to the opposite side and force the crystallization. This is in line with the experimental data — a high-yield crystallization of potassium phenylsiloxanolate was achieved only upon addition of non-polar aromatic solvents.

The *cis* configuration of sodium and potassium phenylsiloxanolates of both structural forms should be governed by the existence of aggregates B as micelles in the reaction solutions. The presence of these micelles was detected in our preliminary investigations of the reaction solutions by a light-scattering method. These results are now under further investigation and will be published elsewhere.

The removal of metal ions by treatment of the crystals obtained with Me_3SiCl gave the corresponding cyclosiloxanes without a change of their size or configuration. It has to be noted that the *cis*-tetraphenyl(trimethylsiloxy)cyclotetrasiloxane obtained exhibits properties of a plastically crystalline (3D) mesophase.[11] The analogous removal of metal ions from Na-PhS-4 by reaction with dilute HCl solution gives *cis*-$[PhSi(O)OH]_4$ in high yield.[3b]

Experimental Section

General: ^1H and ^{29}Si NMR spectra were recorded with a Bruker DRX-500 spectrometer (500 MHz for ^1H and 99 MHz for ^{29}Si) at 20 °C in C_6D_6 or $CDCl_3$ as solvents and with TMS as internal reference standard. GPC was performed with a Waters instrument with an M-600 pump and an M-484 UV detector (wavelength 254 nm) on U-Styragel 500, 1000 Å columns, using a Maxima information processing computer system. Structure-determined[12] crystals of $[PhSi(OSiMe_3)O]_{12}$ (retention time = 16.12 min), $[PhSi(OSiMe_3)O]_6$ (retention time = 16.95 min), $[PhSi(OSiMe_3)O]_4$ (retention time = 17.43 min) and $[PhSi(O)OSiMe_3]_3$ [13] (retention time = 17.79 min) were used as the standards. THF was used as an eluent. Calculations on KOH were made based on the content of KOH (85%, Aldrich). The H_2O/Si ratio in the synthesis with KOH was calculated taking into account the water content in KOH (15% according to Aldrich).

General Synthesis of Na-PhS: A mixture of phenyltrialkoxysilane, sodium hydroxide, water and solvents was stirred vigorously either at room temperature or under reflux conditions until the solution became completely transparent; for completion, the solution was stirred for an additional hour. Within a few hours or days (depending on the alkoxysilane and amount of water) crystals formed and precipitated from the solution. The crystalline bulk was separated by filtration through a Schott filter, washed with hexane and dried in vacuo (10 Torr/40 °C/1 h).

General Synthesis of K-PhS: A mixture of phenyltrialkoxysilane, potassium hydroxide, water and solvents was vigorously stirred at room temperature until a clear solution had formed. For completion, stirring was continued for an additional hour. Most of the solvents (ca. 75%) were removed in a rotary evaporator, and an equal amount of an aromatic solvent was added to the residue. White, tiny needle-like crystals precipitated within 20 h (usually after cooling of the reaction mixture to ca. 10 °C). The crystalline solid was filtered, washed with hexane and dried in vacuo (10 Torr/40 °C/1 h).

General Procedure for the Trimethylsilylation of Alkali Metal Phenylsiloxanolates: Na-PhS or K-PhS was added as a solid to a vigorously stirred mixture of dry hexane, Me_3SiCl and pyridine at room temperature. The mixture was refluxed for 1 h, then cooled to room temperature, filtered and washed with water until it was chloride-free. After drying with Na_2SO_4, the solvent was removed and the residue was dried under vacuum (10 Torr/40 °C/1.5 h). The remaining product was characterized by NMR spectroscopy and GPC.

Na-PhS Obtained from $PhSi(O\textit{n}Bu)_3$ and Trimethylsilylation:[4] $PhSi(O\textit{n}Bu)_3$ (5 g, 15.4 mmol), NaOH (0.62 g, 15.4 mmol), and H_2O (0.28 g, 15.4 mmol) in *n*-butanol (15 mL). Yield of Na-PhS-4: 2.35 g (78%). $[C_6H_5Si(O)ONa]_4{\cdot}3\textit{n}BuOH = C_{36}H_{50}Na_4O_{11}Si_4$ (863): calcd. C 50.10, H 5.84, Na 10.66, Si 13.02; found C 50.43, H 6.14, Na 10.95, Si 12.98. The Na-PhS-4 obtained above (2.35 g, 2.7 mmol), Me_3SiCl (1.17 g, 10.8 mmol) and pyridine (0.64 g, 8.1 mmol) in benzene (40 mL) were allowed to react to give 2.3 g (96%) of a white solid product. GPC (THF): one peak corresponding to $[PhSi(OSiMe_3)O]_4$ (retention time: 17.43 min).

Na-PhS Obtained from $PhSi(OEt)_3$ in Ethanol and Trimethylsilylation: $H_2O/Si = 1:1$ (Table 1, Entry 1). $PhSi(OEt)_3$ (4.98 g, 20.7 mmol), NaOH (0.83 g, 20.7 mmol), and H_2O (0.37 g, 20.7 mmol) were allowed to react in ethanol (10.5 mL). Yield of Na-PhS-4: 3.18 g (83%). $[C_6H_5Si(O)ONa]_4{\cdot}2EtOH = C_{28}H_{32}Na_4O_{10}Si_4$ (733): calcd. C 45.89, H 4.40, Na 12.55, Si 15.33; found C 45.51, H 4.27, Na 12.62, Si 15.13. Na-PhS-4 (3.18 g, 4.3 mmol), Me_3SiCl (5.65 g, 52.0 mmol), and pyridine (3.48 g, 44.0 mmol) were allowed to react in hexane (50 mL) according to the General Procedure. Yield of the white solid product: 2.49 g (74%). GPC (THF): one peak corresponding to $[PhSi(OSiMe_3)O]_4$ (retention time: 17.43 min).

Na-PhS Obtained from $PhSi(OEt)_3$ in Ethanol and Trimethylsilylation: $H_2O/Si = 4:1$ (Table 1, Entry 2). $PhSi(OEt)_3$ (4.98 g, 20.7 mmol), NaOH (0.83 g, 20.7 mmol), and H_2O (1.49 g, 82.8 mmol) were allowed to react in ethanol (35 mL). Yield of crystalline Na-PhS-3: 1.59 g (42%). $[C_6H_5Si(O)ONa]_3{\cdot}3H_2O = C_{18}H_{21}Na_3O_9Si_3$ (535): calcd. C 40.44, H 3.96, Na 12.91, Si 15.76; found C 40.50, H 3.73, Na 12.80, Si 15.63. Na-PhS-3 (1.59 g, 3.0 mmol), Me_3SiCl (3.83 g, 35.2 mmol), and pyridine (1.85 g, 23.4 mmol) were allowed to react in benzene (40 mL). A colorless, transparent liquid was formed: 1.6 g (85%). GPC (THF): one peak corresponding to $[PhSi(OSiMe_3)O]_3$ (retention time 17.79 min).

Na-PhS Obtained from $PhSi(OEt)_3$ in Ethanol and Trimethylsilylation: $H_2O/Si = 12:1$ (Table 1, Entry 3). $PhSi(OEt)_3$ (4.98 g, 20.7 mmol), NaOH (0.83 g, 20.7 mmol) and H_2O (4.48 g, 248.4 mmol) were allowed to react in ethanol (15 mL). Yield of crystalline Na-PhS-3: 2.33 g (60%). A suitable single crystal was analyzed by X-ray crystallography to give the molecular composition $[(Na^+)_3\{PhSi(O)O^-\}_3]{\cdot}8H_2O$ (**3**). $[C_6H_5Si(O)ONa]_3{\cdot}4H_2O = C_{18}H_{23}Na_3O_{10}Si_3$ (553): calcd. C 40.54, H 5.04, Na 11.66, Si 16.17; found C 40.12, H 5.20, Na 11.49, Si 16.25. Na-PhS-3 (2.33 g, 4.2 mmol), Me_3SiCl (5.00 g, 46.0 mmol), and pyridine (2.64 g, 33.4 mmol) were allowed to react in benzene (80 mL). A colorless, transparent liquid product was formed: 1.58 g (63%). GPC (THF): one peak corresponding to $[PhSi(OSiMe_3)O]_3$ (retention time. 17.79 min).

Na-PhS Obtained from $PhSi(OEt)_3$ in Ethanol/Hexane and Trimethylsilylation: $H_2O/Si = 1:1$ (Table 1, Entry 4). $PhSi(OEt)_3$ (4.98 g, 20.7 mmol), NaOH (0.83 g, 20.7 mmol), and H_2O (0.38 g, 20.7 mmol) were allowed to react in a mixture of ethanol (7 mL) and hexane (10 mL) to give two fractions of crystals. Yield of the first fraction: 1.64 g (45%). $[C_6H_5Si(O)ONa]_4{\cdot}EtOH = C_{26}H_{26}Na_4O_9Si_4$ (687): calcd. C 45.47, H 3.82, Na 13.39, Si 16.36; found C 45.52, H 3.63, Na 12.98, Si 16.19. Yield of the second fraction: 1.82 g (50%). $[C_6H_5Si(O)ONa]_3{\cdot}2H_2O = C_{18}H_{19}Na_3O_8Si_3$ (517): calcd. C 41.85, H 3.71, Na 13.36, Si 16.31; found C 41.70, H 4.05, Na 13.17, Si 17.08. A suitable single crystal from the second fraction was analyzed by single-crystal X-ray crystallography, giving the molecular composition $[(Na^+)_3\{PhSi(O)O^-\}_3]{\cdot}4H_2O{\cdot}EtOH$ (**2**). The first fraction of the Na-PhS crystalline compound (1.64 g, 2.4 mmol), Me_3SiCl (2.78 g, 25.6 mmol), and pyridine (1.21 g, 15.3 mmol) were allowed to react in hexane (30 mL) to give 1.28 g (76%) of a white solid product. GPC (THF): one peak corresponding to $[PhSi(OSiMe_3)O]_4$ (retention time: 17.43 min). The second fraction of the Na-PhS crystalline product (1.82 g, 3.5 mmol), Me_3SiCl (2.66 g, 24.5 mmol), and pyridine (1.11 g, 14.0 mmol) were allowed to react in hexane (20 mL). A colorless liquid product was formed: 1.72 g (78%). GPC (THF): one peak corresponding to $[PhSi(OSiMe_3)O]_3$ (retention time: 17.79 min).

Na-PhS Obtained from $PhSi(OEt)_3$ in Ethanol/Hexane and Trimethylsilylation: $H_2O/Si = 2:1$ (Table 1, Entry 5). $PhSi(OEt)_3$ (4.98 g, 20.7 mmol), NaOH (0.83 g, 20.7 mmol), and H_2O (0.75 g, 41.4 mmol) were allowed to react in a mixture of ethanol (21 mL) and hexane (21 mL). Yield: 3.56 g (95%) of a crystalline solid. $[C_6H_5Si(O)ONa]_3{\cdot}3H_2O = C_{18}H_{21}Na_3O_9Si_3$ (535): calcd. C 40.44, H 3.96, Na 12.91, Si 15.76; found C 40.71, H 4.28, Na 13.32, Si 16.01. Na-PhS (3.56 g, 6.6 mmol), Me_3SiCl (6.45 g, 59.3 mmol), and pyridine (3.13 g, 39.6 mmol) were allowed to react in hexane (35 mL). A colorless liquid product was formed: 2.92 g (70%). GPC (THF): one peak corresponding to $[PhSi(OSiMe_3)O]_3$ (retention time: 17.79 min).

K-PhS Obtained from $PhSi(O\textit{n}Bu)_3$ in *n*BuOH ($H_2O/Si = 1:1$) and Trimethylsilylation: $PhSi(O\textit{n}Bu)_3$ (4.73 g, 14.6 mmol), KOH (0.96 g, 14.6 mmol), and H_2O (0.12 g, 6.6 mmol) in *n*BuOH (5 mL) were allowed to react. Yield: 0.85 g (28.6%) of needle-like crystals. $[C_6H_5Si(O)OK]_4{\cdot}\textit{n}BuOH{\cdot}2H_2O = C_{28}H_{34}K_4O_{11}Si_4$ (815): calcd. C 41.25, H 4.20, K 19.18, Si 13.78; found C 41.19, H 4.03, K 19.28, Si 13.53. K-PhS-4 (0.85 g, 1 mmol), Me_3SiCl (1.57 g, 14.4 mmol), and pyridine (0.76 g, 9.6 mmol) in hexane (10 mL) were allowed to react to give a white crystalline product: 0.69 g (82%). GPC (THF): one peak corresponding to $[PhSi(O)OSiMe_3]_4$ (retention time: 17.43 min).

K-PhS Obtained from $PhSi(OEt)_3$ in EtOH ($H_2O/Si = 1:1$) and Trimethylsilylation: $PhSi(OEt)_3$ (4.98 g, 20.7 mmol), KOH (1.37 g, 20.7 mmol), and H_2O (0.17 g, 9.3 mmol) in EtOH (5 mL) were allowed to react to give 0.4 g (10%) of small needle-like crystalline material. $[C_6H_5Si(O)OK]_4{\cdot}EtOH = C_{26}H_{26}K_4O_9Si_4$ (751): calcd. C 41.57, H 3.49, K 20.82, Si 14.95; found C 41.75, H 3.38, K 20.95, Si 15.07. K-PhS-4 (0.4 g, 0.5 mmol), Me_3SiCl (0.62 g, 5.7 mmol), and pyridine (0.27 g, 3.4 mmol) in hexane (10 mL) were allowed to react to yield a white crystalline product: 0.3 g (67%). GPC (THF): one peak corresponding to $[PhSi(O)OSiMe_3]_4$ (retention time: 17.43 min).

K-PhS Obtained from $PhSi(O\textit{n}Bu)_3$ in *n*BuOH/*o*-Xylene ($H_2O/Si = 1.5:1$) and Trimethylsilylation: $PhSi(O\textit{n}Bu)_3$ (4.73 g, 14.6 mmol), KOH (0.96 g, 14.6 mmol), and H_2O (0.26 g, 14.6 mmol) were allowed to react in a mixture of butanol (7 mL) and *o*-xylene (28 mL). A crystalline solid product was formed: 2.43 g (72%). $[C_6H_5Si(O)OK]_3{\cdot}3H_2O{\cdot}n\text{BuOH} = C_{22}H_{31}K_3O_{10}Si_3$ (657): calcd. C 39.14, H 4.93, K 17.38, Si 12.48; found C 38.77, H 4.62, K 17.21, Si 12.83. K-PhS-3 (2.43 g, 3.7 mmol), Me_3SiCl (3.04 g, 28.0 mmol), and pyridine (1.33 g, 16.8 mmol) were allowed to react in hexane (30 mL). A colorless liquid product was formed. Yield 1.53 g (67%). GPC (THF): one peak corresponding to $[PhSi(OSiMe_3)O]_3$ (retention time: 17.79 min).

K-PhS Obtained from $PhSi(OEt)_3$ in EtOH/Toluene (H_2O/Si = 1.5:1) and Trimethylsilylation: $PhSi(OEt)_3$ (4.98 g, 20.7 mmol), KOH (1.37 g, 20.7 mmol), and H_2O (0.37 g, 20.7 mmol) were allowed to react in a mixture of ethanol (7 mL) and toluene (28 mL). Yield of solid K-PhS-3: 3.97 g (92%). $[C_6H_5Si(O)OK]_3{\cdot}5H_2O = C_{18}H_{25}K_3O_{11}Si_3$ (619): calcd. C 35.68, H 4.46, K 17.64, Si 14.02; found C 35.93, H 4.07, K 17.52, Si 13.61. K-PhS-3 (3.97 g, 6.4 mmol), Me_3SiCl (6.12 g, 56.3 mmol), and pyridine (2.67 g, 33.8 mmol) were allowed to react in hexane (100 mL). A colorless liquid product was formed. Yield 3.29 g (81%). GPC (THF): one peak corresponding to $[PhSi(OSiMe_3)O]_3$ (retention time: 17.79 min).

K-PhS Obtained from $PhSi(OMe)_3$ in MeOH/Benzene (H_2O/Si = 1.5:1) and Trimethylsilylation: $PhSi(OMe)_3$ (5.31 g, 26.8 mmol), KOH (1.77 g, 26.8 mmol), and H_2O (0.48 g, 26.8 mmol) were allowed to react in a mixture of methanol (7 mL) and benzene (28 mL). Crystalline K-PhS-3 formed: 5.09 g (95%). $[C_6H_5Si(O)OK]_3{\cdot}MeOH{\cdot}2H_2O = C_{19}H_{23}K_3O_9Si_3$ (597): calcd. C 38.23, H 3.88, K 19.65, Si 14.12; found C 38.01, H 3.69, K 19.61, Si 13.86. A single crystal was analyzed by X-ray crystallography. The molecular composition is $[(K^+)_3\{PhSi(O)O^-\}_3]_2{\cdot}7H_2O{\cdot}3MeOH$ (**4**). K-PhS-3 (5.06 g, 8.5 mmol), Me_3SiCl (7.85 g, 72.2 mmol), and pyridine (3.43 g, 43.4 mmol) were allowed to react in hexane (80 mL). A liquid, colorless product formed. Yield 4.47 g (83%). GPC (THF): one a peak corresponding to $[PhSi(OSiMe_3)O]_3$ (retention time: 17.79 min).

NMR Data for $[PhSi(OSiMe_3)O]_4$: ^{1}H NMR (500 MHz, C_6D_6, 20 °C): $\delta = 0.21$ (s, 9 H, $SiMe_3$), 7.11 (t, $^3J = 7.4$ Hz, 2 H, *m*-C_6H_5Si), 7.28 (t, $^3J = 7.4$ Hz, 1 H, *p*-C_6H_5Si), 7.33 (d, $^3J = 7.4$ Hz, 2 H, *o*-C_6H_5Si) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 20 °C): $\delta = 10.99$ ($OSiMe_3$), −78.49 (O_3SiPh) ppm.

NMR Data for $[PhSi(OSiMe_3)O]_3$: ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = 0.24$ (s, 9 H, $SiMe_3$), 7.25 (t, $^3J = 7.4$ Hz, 2 H, *m*-C_6H_5Si), 7.36 (t, $^3J = 7.4$ Hz, 1 H, *p*-C_6H_5Si), 7.50 (d, $^3J = 7.4$ Hz, 2 H, *o*-C_6H_5Si) ppm. $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 20 °C): $\delta = 11.58$ ($OSiMe_3$), −69.56 (O_3SiPh) ppm.

X-ray Crystal Structure Determination: Colorless single crystals of compounds **2**, **3**, and **4** were grown from solutions (see above). Details of crystal data, data collection and structure refinement parameters for siloxanolate salts **2**−**4** are given in Table 2. The structures were solved by direct methods and refined by a full-matrix least-squares technique against F^2, with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms in **2**−**4** were located from the Fourier synthesis of electron density and refined in the isotropic approximation. Data reduction and further calculations were performed using SAINT[14] and SHELXTL PLUS 5[15] on an IBM PC AT. CCDC-217730 to -217732 for crystal structures **2**−**4** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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