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Oligosilanylsilatranes

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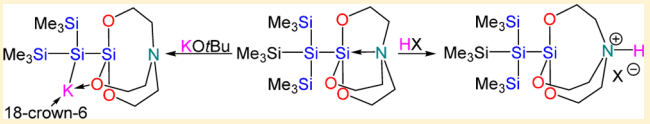
Supporting Information

ABSTRACT: Oligosilanes with attached silatranyl units were obtained by reactions of potassium oligosilanides with a silatranyl triflate. Interaction between Si and N atoms was observed in the ^{29}Si NMR spectra (upfield-shifted SiO_3 resonances) and in the solid-state structures (Si–N distances between 2.29 and 2.16 Å). The Si–N interaction can be "switched off" either by protonation of the nitrogen lone pair or by potassium silanide formation caused by trimethylsilyl group cleavage in the presence of potassium *tert*-butoxide.



INTRODUCTION

Due to the four valence electrons that group 14 elements possess, they exhibit a strong prevalence for tetravalent compounds. However, even for carbon, compounds with both diminished (lower) and higher coordination sphere are known. As carbon is a rather small atom, hypervalent coordination states usually lead to steric interactions between substituents. Therefore, such situations are typically not stable but only represent intermediates or transition states, such as in S_N2 reactions.[1−3]

For the heavier elements silicon, germanium, and tin the situation is somewhat different. While they share the electronic situation of carbon, their atomic radii are larger and therefore they can more easily accommodate additional substituents. Today, numerous stable penta- and hexacoordinate compounds are known for silicon,[4−8] germanium,[7−9] and tin.[10−12] In particular, the so-called atrane molecules (silatranes, germatranes, and stannatranes), substances which feature the heavy group 14 element with a trialkanolamine ligand N-$[(CR^1R^2)_nO]_3ER$ (E = Si, Ge), have been studied to quite some extent. In many cases it was found that hypercoordination has a profound influence on the bond located trans to the nitrogen atom.

Interestingly, a survey of known sila- and germatranes with different triethanolamine substituents reveals that, despite the large variety of attached groups R which have been studied, almost no compounds of atranes with bonds to other heavy group 14 elements exist.[13,14] Only very recently Zaitsev et al. published a first study addressing compounds where an atrane unit is attached to a heavy group 14 oligomer unit.[15] In the current account we want to present our activities concerning the synthesis and chemistry of silatranyl-substituted oligosilanes.

RESULTS AND DISCUSSION

In recent years we have put some effort into the investigation of conformational properties of oligosilanes.[16−20] In particular, compounds with bulky end groups such as the tris(trimethylsilyl)silyl unit were found to exhibit a strong preference for transoid arrangements of chains. This conformation is of some importance, as it is known to facilitate the delocalization of σ-bonding electrons.[21] In addition to conformational properties, also electronic factors such as substituent electronegativity[22−26] and hypercoordination[27,28] can influence the optical absorption properties. We therefore were interested in introducing silyl substituents into oligosilanes, which have a weakened Si–Si bond.

Synthesis. One issue that has to be dealt with when hypercoordinate entities are incorporated into oligosilanes is the choice of which group should be used. We decided that the plain silatrane consisting of a silicon atom with a triethanolamine ligand would serve best as a starting point.

In principle there are two ways to prepare a silatranyl-substituted oligosilane. Either the silatrane silicon atom is introduced first and then the triethanolamine unit is attached or the silatranyl unit is prepared first and is then attached as a whole to the oligosilane. After some experiments we found both strategies possible but concentrated on the second one, which proved to be more general and gave better yields in our hands.

For the attachment of the silatrane unit the obvious way to proceed seemed to be reaction of a silatrane with a suitable leaving group with a silanyl anion. While we found that reactions with silatranyl chloride **1** are a possible option, it turned out that the use of the respective triflate **2** gave better yields. Synthesis of silatranyl triflate **2** was accomplished by reaction of silatranyl chloride[29] **1** with trimethylsilyl triflate (Scheme 1).[30]

Reaction of silatranyl triflate **2** with tris(trimethylsilyl)silyl potassium[31] gave the expected neopentasilane **3** in an acceptable yield of 51% (Scheme 2). In an analogous way also the related compounds **4** and **5** were obtained.

With the reaction of isotetrasilanides and **2** being established, the question arose whether 2-trisilanides would also react the same way. During the course of our studies on oligosilanyl

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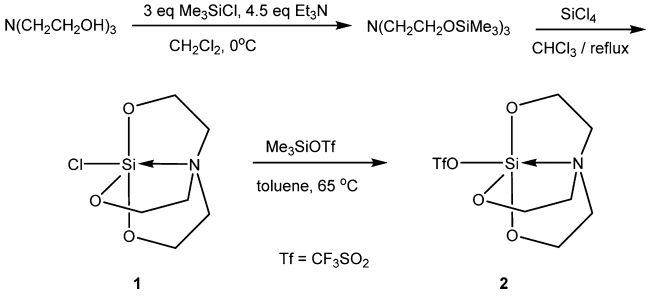
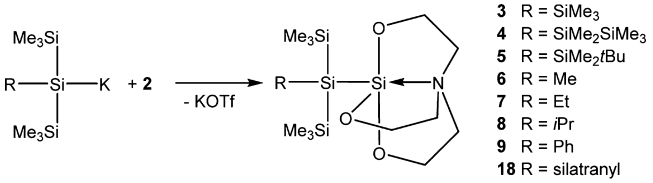
Scheme 1. Synthetic Access to Silatranyl Triflate 2



Scheme 2. Formation of Oligosilanylsilatranes using Salt Elimination Reactions



anions, on several occasions the reactivity of 2-trisilanides differed substantially from that of isotetrasilanides.[32] However, for the case of the reactions with **2**, the use of a series of 2-trisilanides occurred smoothly. Reaction of **2** with methylbis(trimethylsilyl)silyl potassium gave **6** in a respectable yield of 75%, reflecting the better steric accessibility of the silanide (Scheme 2). With sterically more demanding silanides carrying ethyl, isopropyl, and phenyl the reactions also proceeded to **7**–**9**; however, these reactions gave less satisfying yields (Scheme 2).

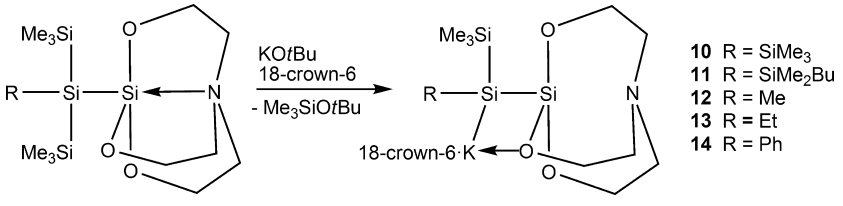
Given the access to this series of oligosilanylsilatranes, we wanted to find out whether these compounds could be used as building blocks. Therefore, compound **3** was reacted with potassium *tert*-butoxide to cleanly obtain compound **10**, which is the product of trimethylsilyl abstraction (Scheme 3). An analogous reaction was carried out with compound **5** to give **11**. In every case attack of the butoxide was selective for a trimethylsilyl group. When the same reaction was attempted with the alkylated oligosilanylsilatranes **6** and **7**, again the expected silatranylsilanides **12** and **13** were formed. However, in these cases the reactions were not as clean and also attack at the silatranyl unit was observed, yielding the bis(trimethylsilyl)-alkylsilyl potassium species and the silatranyl *tert*-butyl ether as side products. For the methylated substrate **6** the ratio between the silanide **12** and the silatranyl ether was about 2:1, whereas for the sterically somewhat better shielded ethylated compound **7** the ratio of **13** to the silatranyl ether was about 8:1. The phenylated compound **9**, however, displayed a clean reaction with potassium *tert*-butoxide to selectively afford silanide **14**.

For a proper comparison of the UV-absorption properties of oligosilanes with and without silatranyl units it was desirable to obtain derivatives of 2,2,5,5-tetrakis(trimethylsilyl)-decamethylhexasilane.[20] Reaction of the respective silanide $(Me_3Si)_3Si(Me_2Si)_2Si(K)(SiMe_3)_2$[33,34] with **2** did not proceed to **16** with a satisfactory yield due to the increased steric bulk of the anion. However, reaction of the anion **10**, which was already substituted with silatranyl, with 1-chloro-3,3-bis(trimethylsilyl)heptamethyltetrasilane **15**[19] allowed the isolation of compound **16** (Scheme 4). Following the same strategy, the 2,5-disilatranylhexasilane compound **17** was obtained by reaction of 2 equiv of **10** with 1,2-dichlorotetramethyldisilane (Scheme 4). Although silanide **10** is sterically more demanding than tris(trimethylsilyl)silyl potassium it can react with another equivalent of **2** to give neopentasilane **18** containing two silatranyl units (Scheme 2).

The fact that the silatrane nitrogen atom donates electron density to the silicon diminishes its basicity. For a number of silatranes, in particular ones with electronegative substituents, it has been shown that protonation occurs preferentially at one of the oxygen atoms, which also exhibit a stronger kinetic basicity.[35,36] Theoretical calculations predict, however, that for a silylated silatrane protonation should occur preferentially at the nitrogen atom.[35] To estimate the degree of the nitrogen donation on the Si–Si bond of **3**, it was treated with trifluoromethanesulfonic acid to protonate the nitrogen lone pair and thus switch off the Si–N interaction. The obtained ammonium salt **19·OTf** forms cleanly and the shut-off Si–N interaction is visible in the NMR spectra and the solid-state structure (Scheme 5). While protonation with the extremely strong trifluoromethanesulfonic acid ($pK_a = -14$)[37] could be expected, an attempt to achieve protonation with excess acetic acid ($pK_a = 4.76$)[37] failed completely. Reaction of **3** with trichloroacetic acid ($pK_a = 0.65$)[37] was not complete with a stoichiometric amount of Cl_3CCO_2H, but a 5-fold excess gave **19·TCA**. Other than an osmium complex with a silatranyl ligand,[38,39] **19·OTf** seems to be the only structurally characterized example of a silatrane protonated at the nitrogen atom.

NMR Spectroscopy. The compounds of this study were characterized by multinuclear NMR spectroscopy (Table 1). The proton spectra of the neutral compounds (**3**–**9**, **16**–**18**) in $CDCl_3$ exhibit the typical pattern of two triplets ($^3J_{H-H}$ =5.6 Hz) for the two methylene groups of the silatrane unit with chemical shifts of ca. 3.65 ppm for the O-CH_2 units and 2.72 ppm for the neighboring N-CH_2 moieties. It is interesting to note that a relatively strong solvent effect is observed for the proton spectra, which shall be exemplified for compound **3**, for which the methylene resonances OCH_2/CH_2N were found at 3.65/2.72 ppm in $CDCl_3$ and 3.30/1.83 ppm in C_6D_6. The respective ^{13}C resonances of the neutral compounds, which are also all very similar, were found around 58.5 ppm for the O-CH_2 and 51.9 ppm for the N-CH_2 units (in both $CDCl_3$ and

Scheme 3. Formation of Silatranyl Oligosilanides by Trimethylsilyl Abstraction



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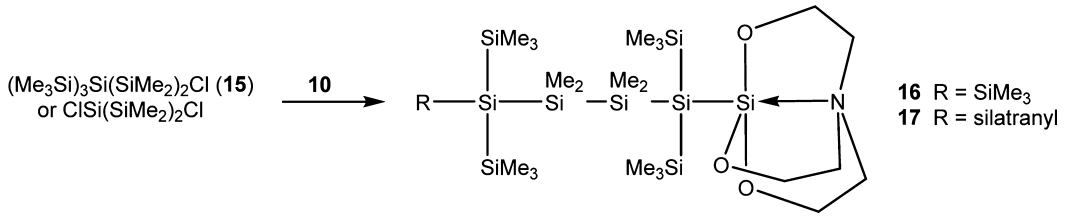
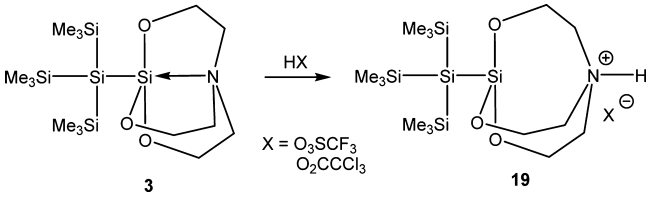
Scheme 4. Synthesis of Larger Silatranylated Oligosilanes 16 and 17



Scheme 5. Protonation of Silatrane 3 with Trifluoromethanesulfonic Acid or Trichloroacetic Acid



C_6D_6). For the silyl anions **10**–**14** (in C_6D_6) the proton resonances shift considerably to lower field to values around 3.80 ppm for the methylene groups attached to oxygen atoms and 2.84 ppm for the amino-substituted atoms. The anionic compounds exhibit also slightly diminished coupling constants between the methylene groups. As can be expected, ^{29}Si NMR spectroscopy provides the most direct insight into the electronic situation of the compounds involved in this study (Table 1).

To understand the influence exerted by the nitrogen atom on the silicon atom in the silatranyl unit, comparison with the chemical shift of a related trialkoxysilylated oligosilane is required. The chemical shift of the MeO_3Si group of $(MeO_3Si)_4Si$[40] is −35 ppm, and thus the more shielded chemical shift of ca. −53 ppm found for **3**–**5**, **16**, and **17** should reflect the degree of hypercoordination (interaction between Si and N). The respective chemical shifts of compounds **6**–**9**, with more electronegative alkylsilyl substituents, are further shifted to values close to −57 ppm, thus reflecting a stronger degree of hypercoordination, which is consistent with what is observed in the solid-state structures (vide infra). Silatranes, where the attached silyl group bears only methyl and phenyl groups such as Me_3Si, Me_2PhSi, and $MePh_2Si$,[13] which are less electron donating than the $(Me_3Si)_2SiR$ groups reported here, allow an even higher degree of hypercoordination and therefore shift even further upfield to values of −64.0, −67.0, and −69.0 ppm, respectively.[13] Interestingly, the chemical shift for the geminal disilatranylsilane **18** of −46.8 ppm indicates a substantially diminished degree of hypercoordination. The chemical shift of the respective resonance of **19** at −22.8 ppm shows the effect of a silatranyl unit with Si−N interaction turned off by protonation of the nitrogen lone pair. For the silyl anions **10**–**14** a downfield shift of the silatranyl resonance can be expected. Indeed, a shift from −52.6 ppm for **3** to −11.8 ppm for the respective anion **10** is observed, which reflects not only the expected downfield shift of a silyl group in a position α to a negatively charged atom but also the fact that the Si−N interaction is turned off in these compounds, as is also clearly visible in the solid-state structures (vide infra). Another point worth mentioning is that the ^{29}Si NMR resonances of the negatively charged silicon atoms in compounds **10** (−210.5 ppm) and **11** (−215.7 ppm) appear at considerably higher field in comparison to $(Me_3Si)_3SiK$ (−191.1 ppm).[41] Compounds **11** and **14** are chiral silanides, and **11** is particularly interesting, as the *tert*-butyldimethysilyl group has two diastereotopic methyl groups which allow determination of the configurational stability of the chiral silanide. Given the additional coordination

Table 1. NMR Spectroscopic Data of Oligosilanyl Silatranes

	^{29}Si					
compd	$SiMe_3$	SiO_3	Si_q	other	^{13}C OCH_2/CH_2N	^{1}H OCH_2/CH_2N
3	−9.9	−52.6	−133.9		58.6/52.2[a]	3.65/2.72[a]
					58.6/51.5[b]	3.30/1.83[b]
4	−9.3	−54.0	−132.2	−15.0, −40.0	58.4/51.9[a]	3.66/2.73[a]
5	−9.7	−51.5	−136.8	4.0 ($tBuMe_2Si$)	58.7/52.1[a]	3.65/2.72[a]
6	−12.9	−57.8	−88.0		58.3/51.8[a]	3.69/2.74[a]
7	−13.2	−56.6	−78.4		58.3/51.9[a]	3.66/2.71[a]
8	−13.5	−56.6	−69.6		58.5/52.0[a]	3.67/2.73[a]
9	−13.1	−56.6	−76.2		58.1/51.6[a]	3.75/2.76[a]
10	−3.2	−11.8	−210.5		61.0./54.3[b]	3.86/2.84[b]
11	−3.0	−11.0	−215.7	11.3	61.0/54.2[b]	3.81/2.82[b]
12	−5.1	−14.9	−144.0		60.9./54.2[b]	3.76/2.80[b]
13	−6.2	−15.0	−125.1		61.0./54.3[b]	3.88/2.88[b]
14	−7.7	−19.4	−113.0		61.1/54.2[b]	3.84/2.81[b]
16	−9.2/−9.6	−53.8	−128.6/−129.3	−30.6/−30.8 (Me_2Si),	58.5/51.8[a]	3.66/2.73[a]
17	−9.2	−53.2	−129.5	−31.2	58.8/51.5[b]	3.36/1.90[b]
18	−9.5	−46.8	−135.5		59.4/52.7[b]	3.68/2.71[b]
19	−9.7	−22.8	−141.1		56.4/53.1[b]	3.34/2.64[b]

[a]Measured in $CDCl_3$. [b]Measured in C_6D_6.

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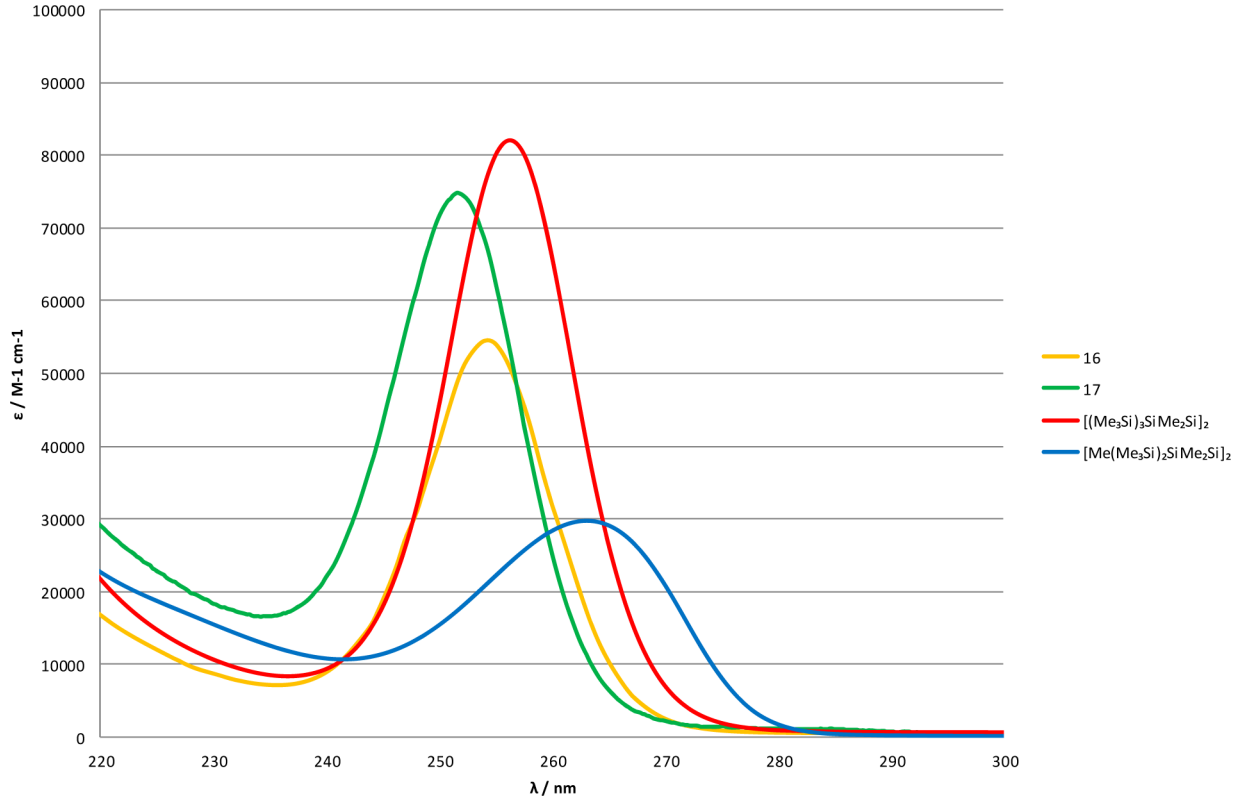

Figure 1. UV spectra of compounds **16** and **17** and of $[(Me_3Si)_3SiMe_2Si]_2$ and $[Me(Me_3Si)_2SiMe_2Si]_2$ in pentane.

to the silatranyl oxygen, an increased configurational stability might be possible. However, at ambient temperature two different methyl resonances could not be observed either in the ^1H or in the ^{13}C NMR spectrum. Therefore, it has to be concluded that at room temperature pyramidal inversion of silanide **11** is fast on the NMR time scale.

UV Spectroscopy. The UV absorption spectra of the silatranes **3**, **5**−**9**, and **18** exhibit the expected absorption bands associated with the trisilane segment around 210 nm only as badly recognizable shoulders. Compound **4**, containing a tetrasilane unit, showed an absorption maximum at 223 nm. For a meaningful comparison to other oligosilanes it is essential to have compounds with well-resolved absorption bands and a number of compounds with similar structures. Compounds **16** and **17**, with one and two silatranyl units, meet these requirements and are therefore best suited to estimate the influence of the siltranyl units on the property of σ-bond electron delocalization. In order to compare these to structurally related compounds UV spectra of 2,2,5,5-tetrakis(trimethylsilyl)decamethylhexasilane[42] and 2,5-bis(trimethylsilyl)dodecamethylhexasilane[33] are also shown in Figure 1.

In the branched oligosilanes with hexasilane units as the longest chain segments the effect of the silatranyl units in comparison to that of trimethylsilyl groups is not very pronounced. For compound **16**, containing one silatranyl group, the longest wavelength absorption band (254 nm) shows a 2 nm hypsochromic shift. The same band is shifted further toward blue by another 2 nm for compound **17**. While the molecular structure of **17** in the solid state indicates the silatranyl units as part of the all-transoid hexasilane conformer, it needs to be pointed out that for **16** and **17** in solution rotation of the bulky tris(silyl)silyl group is likely to be facile and therefore all-transoid hexasilane conformers with trimethylsilyl end groups are presumably contributing to the hexasilane absorption band.

Conversely, for 2,5-bis(trimethylsilyl)-dodecamethylhexasilane, where two trimethylsilyl groups are exchanged for methyl groups, the hexasilane band shows a bathochromic shift of 7 nm to an absorption maximum of 263 nm. This behavior is consistent with the typically observed trend of electron-withdrawing substituents causing a bathochromic shift of the absorption maxima and electron-donating groups being responsible for contrasting behavior.[43]

Crystal Structure Analysis. Compounds **3**, **5**−**7**, **9**−**11**, **14**, and **17**−**19** of this study were subjected to single-crystal XRD analysis. For compound **3** (Figure 2) it was found to be impossible to conduct the measurement at 100 K, as the crystals at this temperature lost structural integrity. At 200 K the structure was solved in the triclinic space group $P\bar{1}$.

Crystals of the more asymmetric compound **5** (Figure 3) were not sensitive to low temperature and crystallize in the trigonal space group $R\bar{3}$. Both trimethylsilyl groups and also the *tert*-butyldimethylsilyl group showed some disorder. The methylated and ethylated isotetrasilanes **6** (Figure 4) and **7** (Figure 5) both crystallize in the orthorhombic space group *Pcca*, with the latter compound exhibiting somewhat elongated axes. For **7** some disorder of the ethyl CH_3 group can be found. The phenylated compound **9** (Figure 6) crystallizes in the orthorhombic space group $Pca2_1$ with two crystallographically independent molecules in the asymmetric unit. The silanides **10** (Figure 7) and **11** (Figure 8) both crystallize in the monoclinic space group $P2_1/n$. For compound **10** some disorder in the silatranyl unit was found. For the phenylated silanide **14** (Figure 9), crystallizing in the triclinic space group $P\bar{1}$, an additional benzene molecule was found in the

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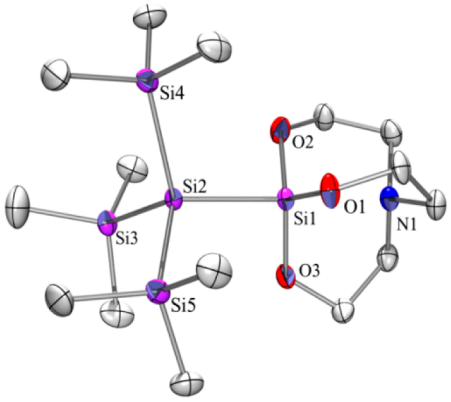

Figure 2. Molecular structure of **3** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(1)−O(1) 1.650(3), Si(1)−N(1) 2.292(4), Si(1)−Si(2) 2.3509(18), Si(2)−Si(3) 2.3351(18), Si(3)−C(13) 1.863(5), N(1)−C(1) 1.462(6), N(1)−C(5) 1.461(5), O(1)−C(2) 1.420(5), C(1)−C(2) 1.522(6); C(1)−N(1)−C(5) 114.4(4), C(2)−O(1)−Si(1) 123.4(3), C(4)−O(2)−Si(1) 123.9(3), C(6)−O(3)−Si(1) 123.6(3).

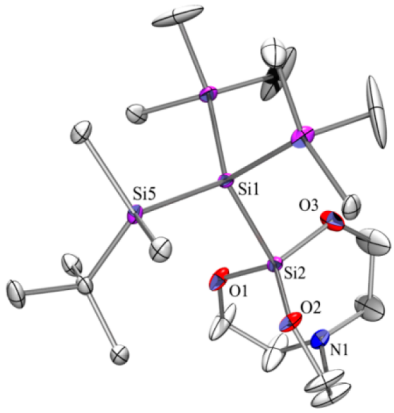

Figure 3. Molecular structure of **5** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(5)−C(13) 1.883(7), Si(5)−Si(1) 2.3510(18), Si(6)−C(23) 1.885(7), Si(1)−Si(4) 2.3456(12), Si(1)−Si(2) 2.346(1), Si(2)−O(1) 1.661(2), Si(2)−N(1) 2.283(3), O(1)−C(2) 1.376(4), N(1)−C(1) 1.446(5), C(1)−C(2) 1.393(5); O(3)−Si(2)−O(2) 117.55(15), O(3)−Si(2)−O(1) 116.97(15), O(2)−Si(2)−O(1) 117.83(12), C(5)−N(1)−C(1) 114.4(4).

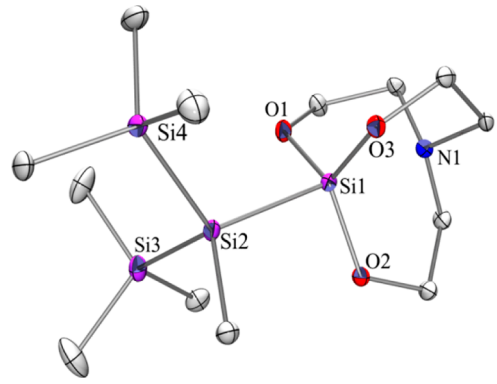

Figure 4. Molecular structure of **6** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(1)−O(3) 1.670(2), Si(1)−O(1) 1.673(2), Si(1)−O(2) 1.682(2), Si(1)−N(1) 2.167(3), Si(1)−Si(2) 2.3523(13), Si(2)−C(7) 1.908(3), Si(3)−C(8) 1.871(4), N(1)−C(1) 1.474(4); O(3)−Si(1)−O(1) 117.43(12), O(1)−Si(1)−O(2) 120.09(12), C(1)−N(1)−C(4) 113.7(2).

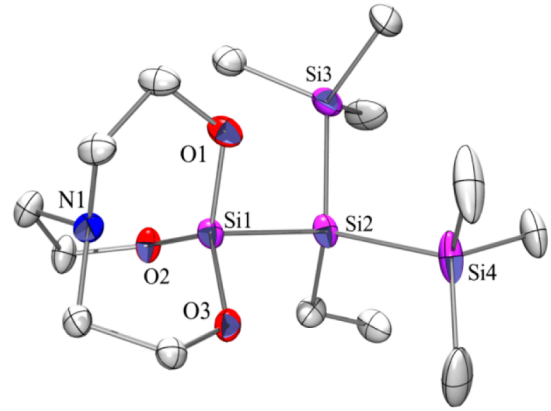

Figure 5. Molecular structure of **7** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(1)−O(1) 1.671(3), Si(1)−N(1) 2.182(3), Si(1)−Si(2) 2.3443(15), Si(2)−C(7) 1.907(4), Si(2)−Si(4) 2.3341(17), N(1)−C(2) 1.473(5), O(1)−C(1) 1.409(5); O(1)−Si(1)−O(3) 117.49(14), O(1)−Si(1)−O(2) 120.03(15), O(1)−Si(1)−N(1) 82.58(13), Si(4)−Si(2)−Si(1) 113.38(6), C(6)−N(1)−C(4) 114.1(3).

asymmetric unit. Compound **17** (Figure 10) crystallizes in the monoclinic space group $P2_1/c$ with two crystallographically independent half-molecules in the asymmetric unit, for which the second halves are generated by a center of inversion. Also for **17** a disordered silatranyl unit was found. The disilatrane **18** (Figure 11) crystallizes in the monoclinic space group $C2/c$. The silatranylium triflate **19** (Figure 12), which crystallizes in the monoclinic space group $P2_1/c$, shows three crystallographically independent ion pairs in addition to half a molecule of benzene on a special position in the asymmetric unit. The hydrogen attached to the nitrogen atom of **19** was detected in the experimental electron density map.

The number of structures determined in the course of this study allows a fair assessment of the influence of the silatranyl unit on the oligosilane structure. The most important structural values with respect to this are the Si−N distance and the bond between the silatranyl unit and the oligosilane (Table 2).

For the chlorosilatrane **1** the Si−N distance has been determined to be 2.023 Å.[5] For the isotetrasilanyl-substituted compounds **3** (Figure 2) and **5** (Figure 3) elongated distances of 2.293(3) and 2.283(2) Å consistent with the more electron donating and sterically much more demanding character of the attached silyl substituents were found. For compounds **6** (Figure 4), **7** (Figure 5), and **9** (Figure 6) the smaller size of the attached group but also its more electronegative character of the alkyl and aryl substituents cause a shortening of the Si−N distances to values of 2.167(3), 2.182(4), and 2.162(5) Å. The respective value for a $PhMe_2Si$-substituted silatrane was found to be even shorter: 2.153(2) Å.[13]

The Si−SiO_3 distances of **3**, **5**−**7**, and **9** are 2.351(2), 2.346(1), 2.352(1), 2.344(2), and 2.383(2) Å, respectively, which are rather typical Si−Si bond lengths observed in oligosilanes. Along with the silanide formation, which causes a localization of negative charge on the silicon atom trans to the

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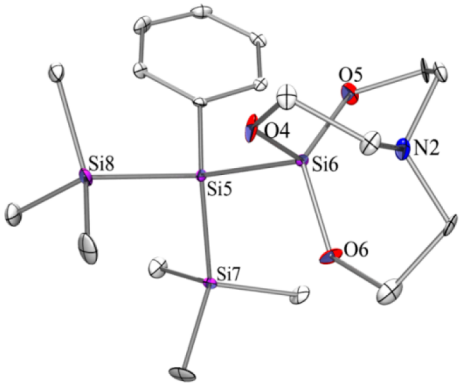

Figure 6. Molecular structure of **9** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(1)−C(3) 1.910(6), Si(1)−Si(4) 2.342(2), Si(5)−Si(6) 2.383(2), Si(5)−C(9) 1.904(6), Si(6)−O(4) 1.662(5), Si(6)−O(6) 1.674(5), Si(6)−O(5) 1.682(5), Si(6)−N(2) 2.176(6), N(1)−C(26) 1.496(8), N(2)−C(32) 1.486(8), O(1)−C(25) 1.430(8); O(4)−Si(6)−O(6) 119.7(3), O(4)−Si(6)−O(5) 118.4(3), O(6)−Si(6)−O(5) 117.3(3), C(36)−N(2)−C(32) 114.2(5).

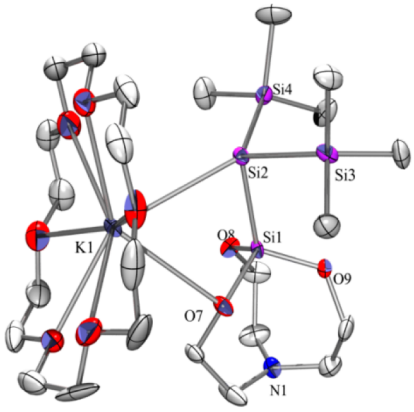

Figure 7. Molecular structure of **10** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): O(7)−Si(1) 1.659(4), O(7)−K(1) 3.197(5), O(8)−C(15) 1.407(7), O(8)−Si(1) 1.684(4), Si(1)−Si(2) 2.3080(18), Si(2)−K(1) 3.3634(16), N(1)−C(16) 1.430(7); Si(1)−O(7)−K(1) 97.9(2), C(14)−N(1)−C(16) 119.9(6), C(14)−N(1)−C(17) 122.1(6), C(16)−N(1)−C(17) 117.4(5).

nitrogen, an interaction between silicon and nitrogen is no longer observable in compounds **10**, **11**, and **14**. The Si−N distances are between 3.10 and 3.18 Å. Along with this shut-off Si−N interaction Si−SiO_3 bond distances of 2.308(2), 2.295(1), and 2.3088(8) Å for **10**, **11**, and **14** are substantially shorter than those in the neutral compounds **3**, **5**, and **9**, indicating nondisturbed Si−Si bonds. The structural motif of the silanides **10**, **11**, and **14** is different from the usual potassium silanide crown ether complexes. Typically the position of the potassium atom in the solid-state structure is that of a tetrahedral substituent. Complexes **10**, **11**, and **14** show a distortion of the potassium position in order to coordinate to one of the silatrane oxygen atoms. A similar coordination situation was observed for the case of $(Me_3Si)_2Si$-(K)OMe.[44] This coordination behavior is taken to an extreme by Krempner's silanides $(MeOMe_2Si)_3SiK$[45] and $(MeOCH_2CH_2OMe_2Si)_3SiK$,[46] where the potassium ion only

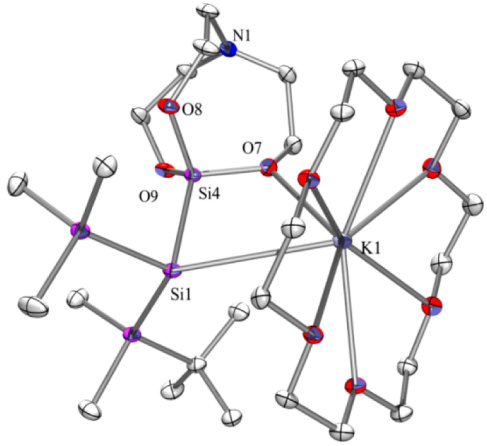

Figure 8. Molecular structure of **11** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(1)−Si(4) 2.2947(12), Si(1)−Si(2) 2.3276(13), Si(1)−Si(3) 2.3391(14), Si(1)−K(1) 3.6321(13), Si(2)−C(19) 1.878(4), Si(4)−O(8) 1.656(2), Si(4)−K(1) 3.8618(15), O(5)−C(8) 1.430(3), N(1)−C(18) 1.430(4); O(8)−Si(4)−O(9) 105.61(12), O(8)−Si(4)−O(7) 106.14(12), Si(1)−K(1)−Si(4) 35.49(2), C(18)−N(1)−C(14) 119.8(3).

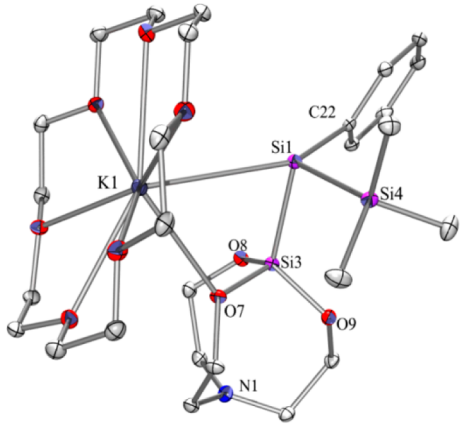

Figure 9. Molecular structure of **14** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(1)−C(22) 1.9141(17), Si(1)−Si(3) 2.3087(7), Si(1)−K(1) 3.5722(9), Si(3)−O(9) 1.6642(12), Si(4)−C(19) 1.8841(19), K(1)−O(7) 2.9983(12), N(1)−C(16) 1.441(2), O(1)−C(1) 1.421(2); O(9)−Si(3)−K(1) 145.02(5), C(16)−N(1)−C(18) 120.35(14), C(16)−N(1)−C(13) 119.81(14), C(18)−N(1)−C(13) 119.59(14), Si(3)−O(7)−K(1) 111.86(5).

coordinates to the alkoxy groups. However, the Si−K distances of **10**, **11**, and **14** are comparable to what was observed for $(Me_3Si)_3SiK$·18-crown-6[41] and also the distances between potassium and the silatranyl oxygen are only slightly elongated in comparison to K−O distances of the crown ether. The structural properties of compound **17** were expected to be close to those of **3** and **5**. However, the Si−N distances of the two crystallographically independent molecules of **17** are 2.223(4) and 2.209(4) Å and thus are significantly shorter, while the Si−SiO_3 bond distances are comparable to those of **3** and **5**. The two independent molecules exhibit all-transoid hexasilane conformations, with the silatranyl silicon atoms being starting and ending points of this particular conformational subunit.

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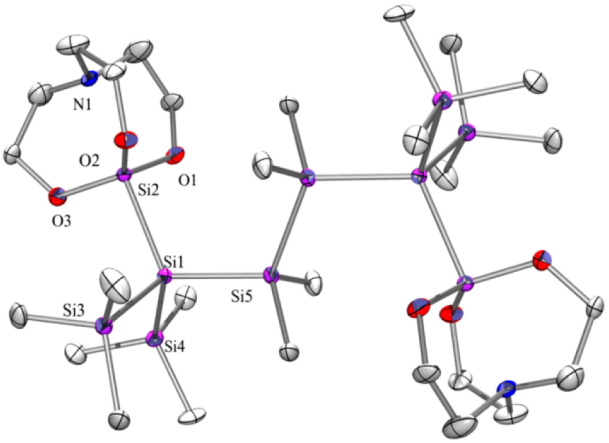

Figure 10. Molecular structure of **17** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(1)−Si(2) 2.3504(18), Si(2)−O(1) 1.657(4), Si(2)−N(1) 2.223(4), Si(3)−C(9) 1.872(7); O(2)−Si(2)−O(3) 117.5(2), N(1)−Si(2)−Si(1) 177.79(14), C(4)−N(1)−C(2) 115.2(6).

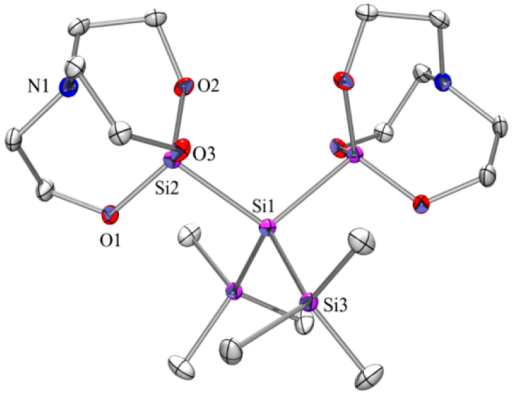

Figure 11. Molecular structure of **18** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(1)−Si(3) 2.3343(5), Si(1)−Si(2) 2.3416(5), Si(2)−O(2) 1.6512(10), Si(3)−C(9) 1.8728(15), N(1)−C(6) 1.4574(17), O(1)−C(1) 1.4232(17); Si(3)−Si(1)−Si(2) 108.594(17), O(2)−Si(2)−O(3) 116.47(5), C(6)−N(1)−C(2) 115.79(12), C(6)−N(1)−C(4) 115.73(11), C(2)−N(1)−C(4) 116.37(11).

Then again, in accordance with what was found by NMR spectroscopy for the geminal disilatrane **18**, the respective Si−N distance for **18** is 2.421(1) Å, being the longest of the neutral silatranyloligosilanes, but still the Si−SiO_3 bond distance is in the same range as for all the other neutral compounds. For the protonated silatrane **19** no interaction between silicon and nitrogen can be detected; the Si−N distances for the three crystallographically independent molecules are around 3.39 Å (Table 2), which is even longer than those for the silanide cases of **10**, **11**, and **14**. Accordingly, the Si−SiO_3 bond distances are shortened (2.301(1)/2.304(1)/2.307(1) Å) to about the same extent that was detected for **10**, **11**, and **14**. The triflate counterions are situated above the silatrane close to the protonated nitrogen with H−O distances between 1.73(2) and 1.76(2) Å.

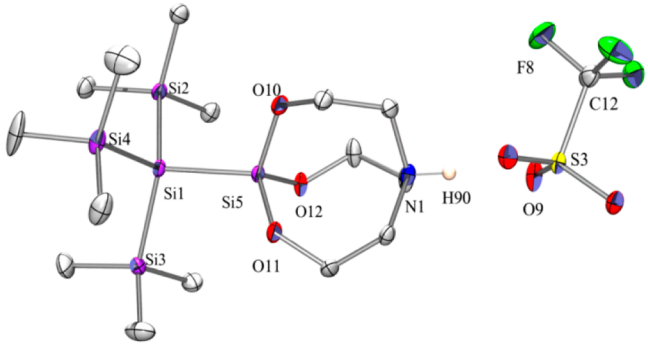

Figure 12. Molecular structure of **19** (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity. Selected bond lengths (in Å) and angles (in deg): Si(1)−Si(5) 2.3072(12), Si(1)−Si(3) 2.3439(13), Si(2)−C(26) 1.868(4), Si(5)−O(11) 1.637(2), N(1)−C(18) 1.503(4), O(9)−S(3) 1.447(2), O(10)−C(13) 1.414(4), S(3)−C(12) 1.824(4), F(8)−C(12) 1.338(4); Si(5)−Si(1)−Si(3) 105.74(5), Si(5)−Si(1)−Si(4) 107.83(5), O(11)−Si(5)−O(10) 106.94(12), C(18)−N(1)−C(16) 116.8(3).

CONCLUSION

Although silatranes are a substance class that has been known for some time, almost no examples exist with silyl substituents. Our interest in the chemistry and properties of oligosilanes led us to investigate possibilities to attach silatranyl units to oligosilanes. While reactions of potassium oligosilanides with chlorosilatrane did not give the expected compounds in satisfactory yields, it was found that analogous reactions with a silatranyl triflate give the oligosilanylated silatranes in acceptable yields.

^{29}Si NMR spectroscopy clearly suggests a Si−N interaction, as indicated by upfield-shifted SiO_3 resonances. In addition, the solid-state structures with Si−N distances between 2.29 and 2.16 Å are supportive of this. Weakening of the Si−Si bond trans to the Si−N interaction, however, becomes only obvious upon comparing the Si−Si distances of structurally related compounds with the Si−N interaction either active or "turned off" by protonation of the nitrogen lone pair. Accordingly, the weakening of the $(Me_3Si)_3Si$−Si bond by the silatrane effect accounts to an elongation of about 0.05 Å.

Attempts to submit the obtained oligosilanlysilatranes to further silanide formation by reaction with potassium *tert*-butoxide were successful. By single-crystal XRD analysis and multinuclear NMR spectroscopy it was found that upon silanide formation again the silatrane Si−N interaction is turned off. The obtained silanides can be used as building blocks for the construction of more extended oligosilane systems or for the preparation of a geminal disilatranylsilane.

EXPERIMENTAL SECTION

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen or argon using either Schlenk techniques or a glovebox. Reagent grade $CHCl_3$ was used for the synthesis of chlorosilatrane **1**. All other solvents were dried using a column-based solvent purification system.[47] Ethyltris(trimethylsilyl)silane,[31] isopropyltris(trimethylsilyl)silane,[48] phenyltris(trimethylsilyl)silane,[48] 2,2-bis(trimethylsilyl)octamethyltetrasilane,[42] (*tert*-butyldimethylsilyl)tris(trimethylsilyl)silane,[31] 1-chloro-3,3-bis(trimethylsilyl)heptamethyltetrasilane,[19] and 1,2-dichlorotetramethyldisilane[49,50] were prepared according to previously published procedures. Methyltris(trimethylsilyl)silane[51] was prepared similarly to ethyltris(trimethylsilyl)silane[31] by reaction of tris(trimethylsilyl)silyl

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Table 2. Compilation of Structural Data Derived by Single-Crystal XRD Analysis of 3, 5−7, 9−11, 14, and 17−19

compd	$d_{Si\cdot\cdot N}$ (Å)	d_{Si-SiO_3} (Å)	$d_{Si-SiMe_3}$ (Å)	d_{Si-R} (Å)	$\angle_{Me_3SiSiR}$ (deg)
3	2.292(3)	2.351(2)	2.335(2)−2.341(2)		
5	2.283(2)	2.346(1)	2.341(1)−2.346(1)	2.351(3)	
6	2.167(3)	2.352(1)	2.339(1)/2.346(1)	1.908(3)	
7	2.182(4)	2.344(2)	2.334(2)/2.356(2)	1.907(5)	
9	2.162(5)	2.383(2)	2.342(2)−2.358(2)	1.904(6)/1.911(7)	
10	3.134(4)	2.308(2)	2.312(2)/2.318(2)	3.363(2)	103.42(7)
11	3.184(3)	2.295(1)	2.328(1)	2.339(1)/3.632(1)	104.65(5)
14	3.103(2)	2.3088(8)	2.3431(8)	1.914(2)/3.5722(8)	100.25(5)
17	2.223(4)/2.209(4)	2.350(2)/2.342(2)	2.343(2)−2.346(2)	2.358(2)-2.369(2)	
18	2.421(1)	2.3415(5)	2.3343(5)		
19	3.394(3)/3.389(3)/3.397(3)	2.301(1)/2.304(1)/2.307(1)	2.339(1)−2.351(1)		

potassium with dimethyl sulfate. All other chemicals were obtained from different suppliers and used without further purification.

^{1}H (300 MHz), ^{13}C (75.4 MHz), ^{19}F (282.2 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer and are referenced to tetramethylsilane (TMS) for ^{1}H, ^{13}C, and ^{29}Si and to $CFCl_3$ for ^{19}F. In the case of reaction samples a D_2O capillary was used to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si, the INEPT pulse sequence[52,53] was used for the amplification of the signal. Elemental analysis was carried out using a Heraeus VARIO ELEMENTAR instrument. GC/MS analyses were carried out on a Agilent 7890A (capillary column HP-5MS; 30 m × 0.250 mm; film 0.25 μm) with an Agilent 5975C mass spectrometer.

X-ray Structure Determination. For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F_o^2 and corrected for absorption effects with SAINT[54] and SADABS,[55] respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).[56] If not noted otherwise, all non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. Crystallographic data (excluding structure factors) for the structures of compounds **3**, **5**−**7**, **9**−**11**, **14**, and **17**−**19** reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 1062942 (**3**), 1062948 (**5**), 1062943 (**6**), 1062944 (**7**), 1062946 (**9**), 1062945 (**10**), 1062951 (**11**), 1062947 (**14**), 1062941(**17**), 1062949 (**18**), and 1062950 (**19**). Data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/request/.

Figures of solid-state molecular structures were generated using Ortep-3 as implemented in WINGX[57] and rendered using POV-Ray 3.6.[58]

N(CH$_2$CH$_2$OSiMe$_3$)$_3$. To a solution of triethanolamine (10.0 g, 0.067 mol) in dichloromethane (100 mL) in a 500 mL two-neck flask was added triethylamine (30.0 g, 0.301 mol), and the mixture was cooled to 0 °C in an ice bath. Within 1 h trimethylchlorosilane (25.5 g, 0.234 mol) was added dropwise to the flask. After the ice bath was removed, the reaction mixture was warmed to room temperature with stirring over 2 h. The reaction mixture was then added slowly to water (100 mL), and the organic phase was separated from the aqueous layer, which was washed twice with small portions of dichloromethane. The combined organic phases were dried over Na_2SO_4. The organic solvent was removed under vacuum, and a pale yellow oil (18.0 g, 0.049 mol, 73%) was obtained as the product with spectroscopic properties in accordance with reported data.[59] NMR (δ ppm, $CDCl_3$): ^{1}H, 3.51 (t, J = 6.8 Hz, 6H, OCH_2), 2.59 (t, J = 6.8 Hz, 6H, NCH_2), 0.00 (s, 27H, $SiMe_3$); ^{13}C, 61.05 (OCH_2), 57.59 (NCH_2), −0.69 (Me_3Si); ^{29}Si, 17.6.

Silatranyl Chloride (1). A mixture of N(CH$_2$CH$_2$OSiMe$_3$)$_3$ (14.0 g, 0.0383 mol) and $SiCl_4$ (7.00 g, 0.0412 mol) was dissolved in chloroform (40 mL) in a 250 mL three-neck flask with condenser. The reaction mixture was stirred and heated for 6 h to reflux. After all volatiles were removed under vacuum, the residue was washed with chloroform and 1-chlorosilatrane (7.10 g, 0.0339 mol, 82%) was obtained as a white powder with spectroscopic properties in accordance with reported data.[60] NMR (δ ppm, $CDCl_3$): ^{1}H, 3.97 (t, J = 5.9 Hz, 6H, OCH_2), 3.01 (t, J = 5.9 Hz, 6H, NCH_2); ^{29}Si, −85.9.

Silatranyl Triflate (2). A slurry of 1-chlorosilatrane (2.00 g, 9.54 mmol, 1.00 equiv) and trimethylsilyl triflate (4.24 g, 19.07 mmol, 2.00 equiv) in toluene (1 mL) was strongly stirred and heated for 72 h to 65 °C. The progress of the reaction was monitored by ^{1}H NMR spectroscopic analysis of the peaks of trimethylsilyl triflate and the formed trimethylchlorosilane. Compound **2** was obtained as an air-sensitive white powder (2.92 g, 9.50 mmol, 99%) after removing volatiles under vacuum. NMR (δ ppm, DMSO-d_6): ^{1}H, 3.84 (t, J = 5.9 Hz, 6H, OCH_2), 3.13 (t, J = 5.9 Hz, 6H, NCH_2); ^{13}C, 118.33 (q, J = 318 Hz, CF_3), 57.52 (OCH_2), 50.69 (NCH_2); ^{29}Si, −97.1; ^{19}F, −77.45. Anal. Calcd for $C_7H_{12}F_3NO_6SSi$ (323.31): C, 26.00; H, 3.74; N, 4.33; S, 9.92. Found: C, 25.73; H, 3.54; N, 4.20; S, 9.69.

Tris(trimethylsilyl)silatranylsilane (3). Tetrakis(trimethylsilyl)-silane (2.00 g, 6.23 mmol) and KO^{t}Bu (734 mg, 6.54 mmol) in THF (5 mL) were stirred for 14 h. After the formation of the organosilyl anion was confirmed by means of NMR spectroscopy, the solvent was removed and toluene was added (5 mL). To a solution of this compound was added a suspension of **2** (2.22 g, 6.85 mmol) in toluene (2 mL) dropwise within 2 h. After 12 h the precipitate was removed by filtration and washed with pentane (3 mL) and then the solvent was removed. After sublimation (40 °C, 1 mbar) and recrystallization with hexane colorless crystalline **3** (1.35 g, 51%) was obtained. Mp: 144−146 °C. NMR (δ ppm, $CDCl_3$): ^{1}H, 3.65 (t, J = 5.6 Hz, 6H, OCH_2), 2.72 (t, J = 5.6 Hz, 6H, NCH_2), 0.15 (s, 27H, Me_3Si); ^{13}C, 58.56 (OCH_2), 52.15 (NCH_2), 2.20 (Me_3Si); ^{29}Si, −9.9 (Me_3Si), −52.6 (SiO_3), −133.9 (Si_q). NMR (δ ppm, C_6D_6): ^{1}H, 3.30 (t, J = 5.6 Hz, 6H, OCH_2), 1.83 (t, J = 5.6 Hz, 6H, NCH_2), 0.53 (s, 27H, Me_3Si); ^{13}C, 58.55 (OCH_2), 51.53 (NCH_2), 2.77 (Me_3Si). Anal. Calcd for $C_{15}H_{39}NO_3Si_5$ (421.91): C, 42.70; H, 9.32; N, 3.32. Found: C, 43.29; H, 8.62; N, 3.25. MS (70 eV) m/z (%): 423(3) [M^- + H], 406(4) [M^+ − Me], 278(3) [$(SiMe_3)_3SiSiH_3^+$], 249(1) [$(SiMe_3)_3SiH$], 232(2) [$Si_4Me_8^+$], 174(100) [$N(CH_2CH_2O)_3Si^+$], 147(1) [$N(CH_2CH_2O)_3^+$], 73(13) [$SiMe_3^+$].

1,1-Bis(trimethylsilyl)-1-silatranylpentamethyltrisilane (4). The same procedure as for **9** was used, with 2,2-bis(trimethylsilyl)-octamethyltetrasilane (435 mg, 1.15 mmol), KO^{t}Bu (135 mg, 1.21 mmol), and **2** (408 mg, 1.26 mmol). After recrystallization from diethyl ether/acetonitrile 1/1 colorless crystalline **4** (320 mg, 58%) was obtained. Mp: 78−79 °C. NMR (δ ppm, $CDCl_3$): ^{1}H, 3.66 (t, J = 5.6 Hz, 6H, OCH_2), 2.73 (t, J = 5.6 Hz, 6H, NCH_2), 0.19 (s, 6H, Me_2Si), 0.17 (s, 18H, $(Me_3Si)_2Si$), 0.09 (s, 9H, Me_3Si); ^{13}C, 58.41 (OCH_2), 51.85 (NCH_2), 2.60 ($(Me_3Si)_2$-Si), −1.24 (Me_3Si), −2.01 (Me_2Si); ^{29}Si, −9.3 ($(Me_3Si)_2Si$), −15.0 (Me_3Si-$SiMe_2$), −40.0 (Me_3Si-$SiMe_2$), −54.0 (SiO_3), −132.2 (Si_q). Anal. Calcd for $C_{17}H_{45}NO_3Si_6$ (480.06): C, 42.53; H, 9.45; N, 2.92. Found: C,

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42.43; H, 8.94; N, 2.70. MS (70 eV) *m/z* (%): 464(10) [M^+ − Me], 406(100) [M^+ − $SiMe_3$], 290(3) [$Si_5C_{10}H_{30}^+$], 174(50) [N-$(CH_2CH_2O)_3Si^+$], 131(3) [$NC_6H_{13}O_2^+$], 73(10) [$SiMe_3^+$]. UV: λ 223 nm ($\varepsilon = 1.85 \times 10^4$ M^{-1} cm^{-1}).

(*tert*-Butyldimethylsilyl)bis(trimethylsilyl)silatranylsilane (5). The same procedure as for **3** was used, with (*tert*-butyldimethylsilyl)-tris(trimethylsilyl)silane (500 mg, 1.38 mmol), KO^{t}Bu (162 mg, 1.45 mmol), and **2** (490 mg, 1.51 mmol). After recrystallization from hexane colorless crystalline **5** (268 mg, 42%) was obtained. Mp: 124−126 °C. NMR (δ ppm, $CDCl_3$): ^{1}H, 3.65 (t, J = 5.4 Hz, 6H, OCH_2), 2.72 (t, J = 5.4 Hz, 6H, NCH_2), 0.93 (s, 9H, (Me_3C), 0.18 (s, 18H, 2 Me_3Si), 0.12 (s, 6H, Me_2Si); ^{13}C, 58.68 (OCH_2), 52.09 (NCH_2), 27.98 (Me_3C), 18.43 (Me_3C), 2.77 (Me_3Si), −1.61 (Me_2Si); ^{29}Si, 4.0 (^{t}BuMe$_2$Si), −9.7 (Me_3Si), −51.5 (SiO_3), −136.8 (Si_q). Anal. Calcd for $C_{18}H_{45}NO_3Si_5$ (463.99): C, 46.60; H, 9.78; N, 3.02. Found: C, 46.78; H, 8.99; N, 3.05. MS (70 eV) *m/z* (%): 463(3) [M^+], 448(8) [M^+ − Me], 406(15) [M^+ − tBu], 290(2) [$tBuSi_4Me_8H$], 174(100) [$N(CH_2CH_2O)_3Si^+$], 73(10) [$SiMe_3^+$].

Bis(trimethylsilyl)methylsilatranylsilane (6). The same procedure as for **3** was used, with methyltris(trimethylsilyl)silane (1.50 g, 5.70 mmol), KO^{t}Bu (672 mg, 5.98 mmol), and **2** (2.03 g, 6.27 mmol) After sublimation (34 °C, 1 mbar) and recrystallization from hexane colorless crystalline **6** (1.16 g, 75%) was obtained. Mp: 109−111 °C. NMR (δ ppm, $CDCl_3$): ^{1}H, 3.69 (t, J = 5.6 Hz, 6H, OCH_2), 2.74 (t, J = 5.6 Hz, 6H, NCH_2), 0.09 (s, 18H, 2 Me_3Si), 0.03 (s, 3H, MeSi); ^{13}C, 58.33 (OCH_2), 51.79 (NCH_2), −0.03 (2 Me_3Si), −12.66 (MeSi); ^{29}Si, −12.9 (Me_3Si), −57.8 (SiO_3), −88.0 (SiMe). Anal. Calcd for $C_{13}H_{33}NO_3Si_4$ (363.75): C, 42.93; H, 9.14; N, 3.85. Found: C, 43.20; H, 8.56; N, 3.72. MS (70 eV) *m/z* (%): 364(4) [M^+], 348(5) [M^+ − Me], 309(39) [$Me(SiMe_3)_2SiSiO_3C_3H_8^+$], 294(13) [Me-$(SiMe_3)_2SiSiO_3C_2H_5^+$], 279(10) [$Me(SiMe_3)_2SiSiO_3CH_2^+$], 260(3) [$N(CH_2CH_2O)_3SiSi_2Me_2^+$], 193(5) [$Me_4Si_3O_3H^+$], 174(100) [N-$(CH_2CH_2O)_3Si^+$], 132(3) [$Si_3O_3^+$], 73(9) [$SiMe_3^+$].

Bis(trimethylsilyl)ethylsilatranylsilane (7). The same procedure as for **3** was used, with ethyltris(trimethylsilyl)silane (600 mg, 2.17 mmol), KO^{t}Bu (255 mg, 2.27 mmol), and **2** (772 mg, 2.39 mmol). After sublimation (38 °C, 1 mbar) and recrystallization from hexane colorless crystalline **7** (205 mg, 25%) was obtained. Mp: 109−111 °C. NMR (δ ppm, $CDCl_3$): ^{1}H, 3.66 (t, J = 5.6 Hz, 6H, OCH_2), 2.71 (t, J = 5.6 Hz, 6H, NCH_2), 1.05 (t, J = 7.9 Hz, 3H, CH_2CH_3), 0.72 (q, J = 7.3 Hz, 2H, CH_2CH_3), 0.10 (s, 18H, 2 Me_3Si); ^{13}C, 58.34 (OCH_2), 51.86 (NCH_2), 12.79 (CH_2CH_3), 0.73 (2 Me_3Si), −0.02 (CH_2CH_3); ^{29}Si, −13.2 (Me_3Si), −56.6 (SiO_3), −78.4 (SiEt). Anal. Calcd for $C_{14}H_{35}NO_3Si_4$ 377.78: C, 44.51; H, 9.34; N, 3.71. Found: C, 44.96; H, 9.08; N, 3.57. MS (70 eV) *m/z* (%): 377(5) [M^+], 362(7) [M^+ − Me], 309(13) [$Et(SiMe_3)_2SiSiO_3C_2H_6^+$], 294(4) [$Et(SiMe_3)_2SiSiO_3CH_3^+$], 279(3) [$Et(SiMe_3)_2SiSiO_3^+$], 193(3) [$Me_4Si_3O_3H^+$], 174(100) [N-$(CH_2CH_2O)_3Si^+$], 130(3) [$NC_6H_{12}O_2^+$], 73(7) [$SiMe_3^+$].

Bis(trimethylsilyl)isopropylsilatranylsilane (8). The same procedure as for **3** was used, with isopropyltris(trimethylsilyl)silane (500 mg, 1.28 mmol), KO^{t}Bu (147 mg, 1.31 mmol), and **2** (453 mg, 1.40 mmol). After recrystallization from hexane colorless crystalline **8** (283 mg, 56%) was obtained. Mp: 118−120 °C. NMR (δ ppm, $CDCl_3$): ^{1}H, 3.67 (t, J = 5.6 Hz, 6H, OCH_2), 2.73 (t, J = 5.6 Hz, 6H, NCH_2), 1.34 to 1.18 (m, 1H, CH), 1.12 (d, J = 6.4 Hz, 6H, Me_2CH), 0.14 (s, 18H, 2 Me_3Si); ^{13}C, 58.48 (OCH_2), 52.03 (NCH_2), 23.30 (Me_2CH), 11.05 (Me_2CH), 1.40 (Me_3Si); ^{29}Si, −13.5 (Me_3Si), −56.6 (SiO_3), −69.6 (Si^iPr). Anal. Calcd for $C_{15}H_{37}NO_3Si_4$ 391.19: C, 45.98; H, 9.52; N, 3.57. Found: C, 45.22; H, 8.98; N, 3.52. MS (70 eV) *m/z* (%): 391(5) [M^+], 376(7) [M^+ − Me], 202(2) [$^iPrSi_3Me_5^+$], 174(100) [$N(CH_2CH_2O)_3Si^+$], 130(2) [$NC_6H_{12}O_2^+$], 73(8) [$SiMe_3^+$].

Bis(trimethylsilyl)phenylsilatranylsilane (9). The same procedure as for **3** was used, with tris(trimethylsilyl)phenylsilane (2.00 g, 6.16 mmol), KO^{t}Bu (712 mg, 6.34 mmol), and **2** (2.19 g, 6.77 mmol). After recrystallization using hexane colorless crystalline **9** (700 mg, 27%) was obtained. Mp: 161−163 °C. NMR (δ ppm, $CDCl_3$): ^{1}H, 7.65 (m, 2H, Ph), 7.23 (m, 3H, Ph), 3.75 (t, J = 5.6 Hz, 6H, OCH_2), 2.76 (t, J = 5.6 Hz, 6H, NCH_2), 0.17 (s, 18H, 2 Me_3Si); ^{13}C, 136.91 (Ph), 129.07 (Ph), 127.03 (Ph), 126.40 (Ph), 58.14 (OCH_2), 51.62 (NCH_2), 0.54 (Me_3Si); ^{29}Si, −13.1 (Me_3Si), −56.6 (SiO_3), −76.2 (Si_q). Anal. Calcd for $C_{18}H_{35}NO_3Si_4$ 425.82: C, 50.77; H, 8.28; N, 3.29. Found: C, 49.84; H, 7.86; N, 3.19. MS (70 eV) *m/z* (%): 425(4) [M^+], 410(4) [M^+ − Me], 352(2) [M^+ − $SiMe_3$], 309(11) [$(SiMe_3)_2SiSiO_3C_4H_{11}^+$], 279(3) [$(SiMe_3)_2SiSiO_3C_2H_5^+$], 253(4) [$(SiMe_3)_2SiSiO_3H_3^+$], 193(2) [$Me_4Si_3O_3H^+$], 174(100) [N-$(CH_2CH_2O)_3Si^+$], 135(6) [$Si_3O_3H_3^+$], 73(3) [$SiMe_3^+$].

Bis(trimethylsilyl)silatranylsilyl Potassium 18-Crown-6 (10). A solution of **3** (50 mg, 0.12 mmol), KO^{t}Bu (14 mg, 0.12 mmol), and 18-crown-6 (33 mg, 0.12 mmol) in benzene (1 mL) was stirred. After 14 h NMR spectroscopic analysis showed full conversion to **10**. By addition of benzene (1 mL) pale orange crystals (77 mg, >99%) suitable for X-ray analysis could be obtained. NMR (δ ppm, C_6D_6): ^{1}H, 3.86 (t, J = 5.1 Hz, 6H, OCH_2), 3.30 (s, 24H, 18-cr-6), 2.84 (t, J = 5.1 Hz, 6H, NCH_2), 0.78 (s, 18H, 2 Me_3Si); ^{13}C, 70.23 (18-cr-6), 60.96 (OCH_2), 54.26 (NCH_2), 7.18 (Me_3Si); ^{29}Si, −3.2 (Me_3Si), −11.8 (SiO_3), −210.5 (Si_q). MS (70 eV) *m/z* (%) (after treatment with ethyl bromide): 377(6) [M^+], 362(8) [M^+ − Me], 304(3) [M^+ − $SiMe_3$], 174(100) [$N(CH_2CH_2O)_3Si^+$], 130(3) [$NC_6H_{12}O_2^+$], 73(6) [$SiMe_3^+$].

(*tert*-Butyldimethylsilyl)trimethylsilylsilatranylsilyl Potassium 18-Crown-6 (11). The same procedure as for **10** was used, with **5** (50 mg, 0.107 mmol), KO^{t}Bu (13 mg, 0.133 mmol), and 18-crown-6 (30 mg, 0.113 mmol). After crystallization using heptane pale yellow crystalline **11** (74 mg, >99%) was obtained. NMR (δ ppm, C_6D_6): ^{1}H, 3.81 (t, J = 5.0 Hz, 6H, OCH_2), 3.28 (s, 24H, CH_2O), 2.82 (t, J = 5.0 Hz, 6H, NCH_2), 1.19 (s, 9H, $(CH_3)_3C$), 0.71 (s, 9H, $(CH_3)_3Si$), 0.70 (s, 6H, $(CH_3)_2Si$); ^{13}C, 70.06 (18-cr-6), 60.97 (OCH_2), 54.23 (NCH_2), 29.22 (Me_3C), 19.22 (Me_3C), 7.37 ((Me_3Si)Si), 1.95 ((Me_2Si)Si); ^{29}Si, 11.3 (tBuMe$_2$Si), −3.0 (Me_3Si), −11.0 (SiO_3), −215.7 ((Me_3Si)*Si*). MS (70 eV) *m/z* (%) (after treatment with ethyl bromide): 419(3) [M^+], 404(6) [M^+ − Me], 362(22) [M^+ − tBu], 246(3) [$Si_3C_{11}H_{30}^+$], 174(100) [N-$(CH_2CH_2O)_3Si^+$], 130(3) [$NC_6H_{12}O_2^+$], 73(8) [$SiMe_3^+$].

Trimethylsilylmethylsilatranylsilyl Potassium 18-Crown-6 (12). A solution of **6** (200 mg, 0.55 mmol), KO^{t}Bu (63 mg, 0.56 mmol), and 18-crown-6 (150 mg, 0.56 mmol) in C_6D_6 (2 mL) was stirred. After 14 h observation by NMR spectroscopy showed a mixture of the three products **12**, bis(trimethylsilyl)methylsilyl potassium.18-crown-6, and $N(CH_2CH_2O)_3SiO^tBu$. **12**: NMR (δ ppm, C_6D_6): ^{1}H, 3.76 (t, J = 4.4 Hz, 6H, OCH_2), 3.26 (s, 24H, 18-cr-6), 2.80 (t, J = 4.4 Hz, 6H, NCH_2), 0.52 (s, 9H, Me_3Si), 0.45 (s, 3H, MeSi); ^{13}C, 70.03 (CH_2O), 60.91 (OCH_2), 54.17 (NCH_2), 4.06 (Me_3SiSi), −9.24 (CH_3Si); ^{29}Si, −5.1 (Me_3Si), −14.9 (SiO_3), −144.0 (Si_q). MS (70 eV) *m/z* (%) (after treatment with ethyl bromide): 318(1) [M^+ − H], 304(10) [M^+ − Me], 290(3) [M^+ − Et], 276(3) [$N(CH_2CH_2O)_3SiSi_2C_3H_{10}^+$], 246(10) [$M^+$ − $SiMe_3$], 218(41) [$N(CH_2CH_2O)_3SiSiCH_4^+$], 193(8) [$Me_4Si_3O_3H^+$], 174(100) [N-$(CH_2CH_2O)_3Si^+$], 149(4) [$NC_6H_{15}O_3^+$], 130(4) [$NC_6H_{12}O_2^+$], 73(7) [$SiMe_3^+$].

Trimethylsilylethylsilatranylsilyl Potassium 18-Crown-6 (13). A solution of **7** (50 mg, 0.13 mmol), KO^{t}Bu (15 mg, 0.14 mmol), and 18-crown-6 (36 mg, 0.14 mmol) in benzene (1 mL) was stirred. After 14 h observation by NMR spectroscopy showed conversion to the three products **13**, bis(trimethylsilyl)ethylsilyl potassium 18-crown-6, and $N(CH_2CH_2O)_3SiO^tBu$. **13**: NMR (δ ppm, C_6D_6): ^{1}H, 3.88 (t, J = 5.2 Hz, 6H, OCH_2), 3.27 (s, 24H, 18-cr-6), 2.88 (t, J = 5.2 Hz, 6H, NCH_2), 1.68 (t, J = 7.5 Hz, 3H), 1.41 (q, J = 7.8 Hz, 2H), 0.74 (s, 9H, Me_3Si); ^{13}C, 70.08 (CH_2O), 60.95 (OCH_2), 54.29 (NCH_2), 19.42 (CH_3CH_2), 4.85 (Me_3SiSi), 2.68 (CH_3CH_2); ^{29}Si, −6.2 (Me_3Si), −15.0 (SiO_3), −125.1 (Si_q). MS (70 eV) *m/z* (%) (after treatment with ethyl bromide): 333(1) [M^+], 318(8) [M^+ − Me], 304(4) [M^+ − Et], 290(3) [$N(CH_2CH_2O)_3SiSi_2Me_4^+$], 276(3) [N-$(CH_2CH_2O)_3SiSi_2C_3H_{10}^+$], 260(11) [$M^+$ − $SiMe_3$], 246(3) [N-$(CH_2CH_2O)_3SiSiC_3H_8^+$], 232(42) [$N(CH_2CH_2O)_3SiSiC_2H_6^+$], 218(2) [$N(CH_2CH_2O)_3SiSiCH_4^+$], 204(3) [$N(CH_2CH_2O)_3SiSiH_2^+$], 174(100) [$N(CH_2CH_2O)_3Si^+$], 130(4) [$NC_6H_{12}O_2^+$], 73(5) [$SiMe_3^+$].

Trimethylsilylphenylsilatranylsilyl Potassium 18-Crown-6 (14). A solution of **9** (50 mg, 0.12 mmol), KO^{t}Bu (14 mg, 0.12 mmol), and 18-crown-6 (32 mg, 0.12 mmol) in benzene (1 mL) was

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stirred. After 14 h observation by NMR spectroscopy showed quantitative conversion to **14**. By addition of benzene (1 mL) yellow crystals (77 mg, >99%) suitable for X-ray analysis were obtained. NMR (δ ppm, C_6D_6): ^{1}H, 8.13 (d, 2H, Ph), 7.02 (m, 3H), 3.84 (t, J = 5.0 Hz, 6H, OCH_2), 3.20 (s, 24H, CH_2O), 2.81 (t, J = 5.0 Hz, 6H, NCH_2), 0.69 (s, 9H, Me_3Si); ^{13}C, 157.75 (Ph), 137.61 (Ph), 126.19 (Ph), 121.69 (Ph), 70.15 (18-cr-6), 61.14 (OCH_2), 54.17 (NCH_2), 4.58 (Me_3Si); ^{29}Si, −7.7 (Me_3Si), −19.4 (SiO_3), −113.0 (Si_q). MS (70 eV) m/z (%) (after treatment with ethyl bromide): 366(5) [M^+ − Me], 308(10) [M^+ − $SiMe_3$], 280(31) [$N(CH_2CH_2O)_3SiSiPhH^+$], 253(4) [$PhSi_3O_3C_3H_8^+$], 174(100) [$N(CH_2CH_2O)_3Si^+$], 135(7) [$Si_3O_3H_3^+$], 73(3) [$SiMe_3^+$].

2,5,5-Tris(trimethylsilyl)-2-silatranyldecamethylhexasilane (16). **3** (350 mg, 0.75 mmol) and KO^{t}Bu (87 mg, 0.77 mmol) were dissolved in THF (2 mL). After 14 h the formation of the silyl anion **10** was confirmed by means of NMR spectroscopy; the solvent was removed, and benzene was added (3 mL). This solution was added dropwise to 1-chloro-3,3-bis(trimethylsilyl)heptamethyltetrasilane (300 mg, 0.75 mmol) in toluene (3 mL) at 0 °C within 1 h. After 12 h the solvent was removed, the residue treated with pentane, and the insoluble parts were filtered off. The solvent was again removed, and recrystallization with diethyl ether/acetonitrile (1/1) afforded colorless crystalline **16** (354 mg, 66%). Mp: 130−136 °C. NMR (δ ppm, $CDCl_3$): ^{1}H, 3.66 (t, J = 5.56 Hz, 6H, OCH_2), 2.73 (t, J = 5.61 Hz, 6H, NCH_2), 0.39 (s, 6H, Me_2Si), 0.35 (s, 6H, Me_2Si), 0.24 (s, 27H, 3 Me_3Si), 0.20 (s, 18H, 2 Me_3Si); ^{13}C, 58.50 (OCH_2), 51.84 (NCH_2), 3.52 (Me_3Si), 2.97 (Me_3Si), 0.53 (Me_2Si), 0.40 (Me_2Si); ^{29}Si, −9.2 (Me_3Si), −9.6 (Me_3Si), −30.6 (Me_2Si), −30.8 (Me_2Si), −53.8 (SiO_3), −128.6 (Si_q), −129.3 (S_q). Anal. Calcd for $C_{25}H_{69}NO_3Si_{10}$ (712.68): C, 42.13; H, 9.76; N, 1.97. Found: C, 41.66; H, 9.65; N, 1.73. UV: λ 254 nm (ε = 5.45 × 10^4 M^{-1} cm^{-1}).

2,5-Bis(trimethylsilyl)-2,5-disilatranyldecamethylhexasilane (17). The same procedure as for **3** was used, with **3** (500 mg, 1.19 mmol), KO^{t}Bu (137 mg, 1.22 mmol), and dichlorotetramethyldisilane (116 mg, 0.62 mmol). Recrystallization with diethyl ether/acetonitrile (1/1) afforded colorless crystalline **17** (200 mg, 41%). Mp: 244−248 °C. NMR (δ ppm, C_6D_6): ^{1}H, 3.36 (t, J = 5.6 Hz, 12H, OCH_2), 1.90 (t, J = 5.6 Hz, 12H, NCH_2), 0.84 (s, 12H, $(CH_3)_2Si$), 0.61 (s, 36H, $(CH_3)_3SiSi$); ^{13}C, 58.75 (OCH_2), 51.49 (NCH_2), 3.54 ($(Me_3Si)_2Si$), 0.56 (Me_2Si); ^{29}Si, −9.2 ($(Me_3Si)_3Si$), −31.2 (Me_2Si), −53.2 (SiO_3), −129.5 ($(Me_3Si)_3Si$). MS (70 eV) m/z (%): 799(1) [M^+ − Me], 640(1) [$N(CH_2CH_2O)_3SiSi_8O_3C_{13}H_{38}^+$], 464(11) [$N(CH_2CH_2O)_3SiSi_5C_{10}H_{30}^+$], 406(100) [$N(CH_2CH_2O)_3SiSi_4C_8H_{24}^+$], 362(3) [$N(CH_2CH_2O)_3SiSi_4C_5H_{16}^+$], 278(3) [$(SiMe_3)_2SiSiO_3C_2H_4^+$], 246(2) [$Si_4O_3C_6H_{14}^+$], 207(7) [$Si_4O_3C_3H_{11}^+$], 174(32) [$N(CH_2CH_2O)_3Si^+$], 117(3) [$NC_5H_{11}O_2^+$], 73(10) [$SiMe_3^+$]. Anal. Calcd for $C_{28}H_{72}N_2O_6Si_{10}$ (813.74): C, 41.33; H, 8.92; N, 3.44. Found: C, 41.27; H, 8.22; N, 3.28. UV: λ 252 nm (ε = 7.48 × 10^4 M^{-1} cm^{-1}).

Bis(trimethylsilyl)disilatranylsilane (18). The same procedure as for **6** was used, with **3** (310 mg, 0.73 mmol), KO^{t}Bu (85 mg, 1.03 mmol), and **2** (261 mg, 0.81 mmol). After recrystallization with pentane colorless crystalline **6** (90 mg, 23%) was obtained. Mp: 138−140 °C. NMR (δ ppm, $CDCl_3$): ^{1}H, 3.68 (t, J = 5.4 Hz, 12H, OCH_2), 2.71 (t, J = 5.4 Hz, 12H, NCH_2), 0.17 (s, 18H, 2 Me_3Si); ^{13}C, 59.38 (OCH_2), 52.71 (NCH_2), 1.72 (Me_3Si); ^{29}Si, −9.5 (Me_3Si), −46.8 (SiO_3), −135.5 (Si_q). Anal. Calcd for $C_{18}H_{42}N_2O_6Si_5$ (522.97): C, 41.34; H, 8.10; N, 5.36. Found: C, 42.56; H, 7.38; N, 5.28. MS (70 eV) m/z (%): 522(3) [M^+], 507(6) [M^+ − Me], 449(6) [M^+ − $SiMe_3$], 393(1) [$N(CH_2CH_2O)_3SiSi_3O_3C_6H_{15}^+$], 347(17) [$N(CH_2CH_2O)_3SiSi_3C_6H_{17}^+$], 309(13) [$(SiMe_3)_2SiSiO_3C_4H_{11}^+$], 279(3) [$(SiMe_3)_2SiSiO_3C_2H_5^+$], 248(3) [$Si_4O_3C_6H_{16}^+$], 218(11) [$Si_4O_3C_4H_{10}^+$], 174(100) [$N(CH_2CH_2O)_3Si^+$], 130(6) [$NC_6H_{12}O_2^+$], 73(5) [$SiMe_3^+$].

Tris(trimethylsilyl)silatranyliumsilane Triflate (19·OTf). To an ice-cold solution of **3** (93 mg, 0.22 mmol) in toluene (1 mL) was added triflic acid (31 mg, 0.21 mmol in 1 mL of toluene) dropwise. After 3 h the solvent was removed and crystallization from benzene afforded colorless crystalline **19·OTf** (84 mg, 0.15 mmol, 67%). Mp: 156−160 °C. NMR (δ ppm, C_6D_6): ^{1}H, 10.68 (s, 1H, NH), 3.34 (s, 6H, OCH_2), 2.64 (s, 6H, NCH_2), 0.25 (s, 27H, $(Me_3)_3Si$); ^{13}C, 121.52 (q, J = 319 Hz, CF_3), 56.44 (OCH_2), 53.13 (NCH_2), 2.11 (Me_3SiSi); ^{29}Si, −9.7 (Me_3Si), −22.8 (SiO_3), −141.1 ($(Me_3Si)_2Si$); ^{19}F, −77.85.

Tris(trimethylsilyl)silatranyliumsilane Trichloroacetate (19·TCA). To a solution of **3** (30 mg, 0.07 mmol) in C_6D_6 (0.5 mL) was added trichloroactic acid (60 mg, 0.37 mmol). ^{1}H NMR spectroscopic monitoring showed quantitative conversion to **19·TCA**. NMR (δ ppm, C_6D_6): ^{1}H, 10.73 (bs, 5H, NH and Cl_3CCO_2H), 3.49 (s, 6H, OCH_2), 2.72 (s, 6H, NCH_2), 0.26 (s, 27H, $(Me_3)_3Si$); ^{29}Si, −9.7 (Me_3Si), −23.2 (SiO_3), −141.1 ($(Me_3Si)_2Si$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables, figures, and CIF files containing crystallographic information for compounds **3**, **5**−**7**, **9**−**11**, **14**, and **17**−**19** and NMR spectra for **9**−**14**, **18**, and **19**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00404.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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