Hypercoordinated Oligosilanes Based on Aminotrisphenols
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ABSTRACT: The hypercoordinated silicon chlorides ClSi-[\(\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2\text{N}\)] (3) and ClSi[(\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2\text{N})] \(\text{N}\) (5) were used for the synthesis of catenated derivatives (MeSi)\(\text{SiSi}-\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2\text{N}\) (9), (MeSi)\(\text{SiSiMeSiMe-Si} (\text{SiMe}_3)\text{Si}[\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2\text{N}] (11), and (MeSi)\(\text{SiSi} [\text{OC}_6\text{H}_2\text{Me}_2\text{CH}_2\text{N}] (13) in reactions with (MeSi)\(\text{SiSiTHF} (7) or \text{MeSiSi[OC}_6\text{H}_2\text{Me}_2\text{CH}_2\text{N}] (8). It was found that the nature of the (MeSi)\(\text{SiSi solvate determines the product of interaction, resulting in the formation of (MeSi)\(\text{SiSi[OC}_6\text{H}_2\text{Me}_2\text{CH}_2\text{N}] (12 or 13. Compounds obtained were characterized using multinuclear NMR and UV−vis spectroscopy and mass spectrometry. The molecular structures of 3, 9, and 11−13 were investigated by single-crystal X-ray analysis, featuring hypercoordinated Si atoms in a trigonal-bipyramidal coordination environment with O atoms in the equatorial plane. The structure of the side product \[\text{N(CH}_2\text{C}_6\text{H}_2\text{Me}_2\text{O}]\text{Si[OC}_6\text{H}_2\text{Me}_2\text{CH}_2\text{N}] (6) was also studied, indicating highly tetrahedrally distorted trigonal-bipyramidal environment at the Si atoms, which was confirmed by crystal density functional theory calculations indicating the very weak Si−N interaction. The Si−N interatomic distances span a broad range (2.23−2.78 Å). The dependence of structural and NMR parameters for hypercoordinated catenated compounds from the type of the ligand was established.

INTRODUCTION

Currently, the organometallic chemistry of group 14 elements (E = Si, Ge, Sn, Pb; E(IV)) comprises two main directions of development, including catenated (containing E−E bonds)1 and hypercoordinated (with coordination number of E being higher than 4)2 compounds. This is due to academic interest and also due to broad practical applications in chemistry. Work with silicon compounds serves as a model of other group 14 derivatives but is also advantageous with respect to its special characteristic features (like magnetic activity of Si), high abundance, and low cost for possible practical application.

In general, hypercoordination of chemical compounds is usually achieved by applying special ligands, like triethanolamine, N(CH_2CH_2OH)_3, resulting in this case in the formation of atrane molecules.4 Compounds of this type are very valuable in various fields such as organic synthesis,5 medicine,6 sol−gel techniques,7 and material chemistry.8 The increased stability of such derivatives based on tetradentate O,N-type ligands is a characteristic feature. Nevertheless, application of other ON-polydentate ligands for hypercoordinated Si compounds (like tridentate iminophenols,9 tridentate alkanolaminophenols,10 tetradeinate salens,11 and others) is also known. Furthermore, there are several cases of application of other types of O,N ligands, like aminotrisphenols,12 homotrialkanolamines,13 and aminotris(alkylphenol),14 or alkanolaminobis(phenol)15 for Si derivatives.

Influence of hypercoordination on the structure and UV−vis absorption properties of oligosilane properties was studied previously by El-Sayed et al. who utilized amide side chains.16 Extending the types of ligands in the synthesis of catenated derivatives increases the range of substances and their possible application, and it opens new possibilities to study structure−property relationships. Due to σ-conjugation along the E−E bonds, catenated compounds exhibit useful properties, such as luminescence,17 conductivity,18 and so on. Therefore, the synthesis of a wide range of catenated hypercoordinated compounds may be regarded as an actual scientific area of interest.

Although some hypercoordinated oligosilanes based on polydentate ligands are known and even have found application (e.g., in cross-coupling reactions19), in general their range is really very narrow,20−22 (Scheme 1).

The aim of the present work is the synthesis of molecular hypercoordinated oligosilanes, based on polydentate amino-
phenols, and the establishment of their structures and properties. In continuation of our works on hypercoordinated group 14 catenated derivatives, the synthesis of molecular oligosilanes 9–11 and 13 is reported in this work.

**RESULTS AND DISCUSSION**

**Synthesis.** In the current study, two types of ligands, aminotrisphenols 1 and 2, were used (Scheme 2). These ligands are phenols and therefore significantly different in structure from previously investigated trialkanolamine derivatives; furthermore, they are also different with respect to the nature of the donating nitrogen atom, which is either bound directly to the aromatic ring (as in 1) or not (in 2). Ligand 1 forms rigid five-membered chelates with a Si atom, while ligand 2 forms more flexible six-membered chelates. This structural difference may result in divergent properties in silatranes based on 1 and 2.

Both compounds are known, but for 1,12a an improved synthetic protocol and analytical data are provided (for details, see the Experimental Section).

According to previous experiments, the best way for the attachment of the silatrane unit to a polysilane chain is to react a silatranyl electrophile containing a suitable leaving group with a silanide.19a Therefore, silatranyl-like chlorides 3 and 5 were obtained at the first stage. Chloride 3 was prepared following the procedure reported by Frye et al. (Scheme 3).12a Removal of the formed HCl in this case is possible due to low basicity of the anilinic N of 1. Compound 3 was isolated as a beige powder, stable in dry atmosphere and sparingly soluble in polar common organic solvents (chloroform, dichloromethane).

Despite the successful synthesis of 3, similar synthetic ways to 5 did not work out. Neither reaction of silyl ether N(CH₂C₆H₄Me₂OSiMe₃)₃ with SiCl₄ under prolonged heating in toluene, as was used for the synthesis of ClSi[(OC₆H₂Me₂CH₂)₃N] (Scheme 3).

**Scheme 1. Known Hypercoordinated Oligosilanes Based on Polydentate Ligands**

**Scheme 2. Ligands 1 and 2, Used for the Synthesis of Hypercoordinated Oligosilanes**

**Scheme 3. Synthesis of Hypercoordinated Chlorosilanes 3 and 5**
For the synthesis of the targeted hypercoordinated oligosilanes, in a second step chlorides 3 and 5 were reacted with potassium silanide reagents. Thus, oligosilanylsilatrane 9 was prepared by reaction of oligosilanylpotassium 7 with ClSi(OCH2CH2)3N (Scheme 5). NMR spectroscopy of the reaction mixture showed exclusive formation of 9 without any observable side products, like hydrosilane (Me3Si)3SiH. In contrast, the reaction of oligosilanylpotassium 7 with 1-chlorosilatrane ClSi(OCH2CH2)3N did not proceed cleanly due to its lower reactivity, explained by the unusual geometry.

Compound 9 was successfully metallated by t-BuOK/18-crown-6 giving 10, which is sufficiently stable and was characterized by multinuclear NMR spectroscopy (for details, see the Experimental Section); compounds related to 10 may be used for the synthesis of other derivatives. Thus, metallation of 9 with in situ formation of the related potassium reagent followed by reaction with (Me5Si)3SiMeMe2SiMe2Cl gave compound 11 (Scheme 5).

In contrast to the synthesis of 9, reaction of oligosilanylpotassium reagent 7 with [N(CH2C6H4Me2O)3]SiCl (5) unexpectedly gave oligosilanylsilatrane 12 (Scheme 6). According to crystal structure analysis of 12 (Figure 4), tetrahydrofuran (THF) ring opening occurred, with the oxygen atom of the THF attached to the hypercoordinated silicon atom and the α-carbon atom of THF bound to the oligosilanyl unit.

The formation of oligosilanylsilatrane 12 is a typical case of THF opening in the presence of strong Lewis acids. We have observed related chemistry previously for instance in the reaction of silanide 7 and related substances with HfCl4 and YbI2. In this occasion, compound 5 may be regarded as Lewis acid also (compare with the results of Holmes and co-workers, who have reported a new class of silatrane-like molecules [N(CH2C6H4Me2O)3]SiX (X = Me, OMe, Ph, CCl3) with acidic Si atoms). Coordination of THF to 5 activates the α-position of THF toward the nucleophilic attack of silanide 7, which then is the actual ring-opening event.

Oligosilanylsilatrane 13 was eventually prepared by reaction of tris(trimethylsilyl)silyl potassium-18-crown-6 (8) with [N(CH2C6H4Me2O)3]SiCl (5) (Scheme 6). To avoid THF ring opening such as in the previous reaction, oligosilylanylpotassium 8 was prepared in toluene in the presence of 18-crown-6. Therefore, the course of the reaction with silyl potassium reagents strongly depends on the nature of this reagent.

The difference in reactivities of 3 and 5 toward oligosilanes deserves additional explanation. Explanation including “spillover
effect (increase of acidity of hypercoordinated group 14 center) may be regarded as implausible. Apparently, the increase of this bond length of Si is explained by the more flexible ligand framework and also is based on the dissociation of N → Si interaction (compare with dynamic NMR behavior and in related derivatives based on X-ray diffraction (XRD); see below) with significant geometry distortion at Si (from five- to four-coordinated) and thereby increase of acidity (‘strain release Lewis acidity’).  

Compounds 9, 11, 12, and 13 were isolated as colorless crystalline materials, stable under ambient conditions and soluble in common organic solvents. The identities of crystalline materials, stable under ambient conditions and soluble in common organic solvents. The identities of compounds were established by elemental analysis and mass spectrometry (MS), and structures were studied by multinuclear NMR spectroscopy (1H, 13C, 29Si) in solution; X-ray single-crystal diffraction analysis (XRD) was used for investigation of structures 2-HCl (Figure S1, Supporting Information), 3, 6, 9, and 11–13 in solid state. The degree of conjugation along the Si–N bond was studied by UV–vis spectroscopy.

**Crystal Structures.** The molecular structures of compounds 3, 6, 9, and 11–13 (Figures 1–6) in the solid state were investigated by single-crystal XRD analysis. A main question in the investigation of these structures is the study of the level of N → SiO→X interaction, its influence on the trans-Si–X bond, and the establishment of coordination geometry around the central Si atom (tetrahedral vs trigonal bipyramidal (TBP)). It should be noted that for the case of catenated compounds, the rules, found earlier for silatranes (more electron- withdrawing groups X in N → Si–X fragment result in shortening of the Si–N bond), are not so evident due to the equal nature of silicon atoms (X = SiR3). According to the Cambridge Structural Database (CSD, February 2018), the Si–N bond varies within 1.965°–2.33° in silatranes, within 2.025°–2.839° in benzyl silatrane-like molecules based on 2 and related ligands, and within 2.256–2.344° for phenylene silatrane-like molecules based on 1 and related ligands, wherein for the last case the variation range is the smallest one due to the rigid structure of the ligand. XRD investigations indicate that substitution of the ethylene bridge in silatranes by phenylene and benzylene groups results in increased Si–N distances.

Chlorosilatrane-like molecule 3 (Figure 2) was found to crystallize in the monoclinic space group P21/n. The geometry

**Figure 1.** Molecular structure of ClSi[(o-OC6H4)3N] (3) in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)–N(1) 2.2125(17), Si(1)–O(1) 1.6526(17), Si(1)–O(2) 1.6544(17), Si(1)–O(3) 1.6514(16), Si(1)–Cl(1) 2.0707(8), Cl(1)–Si(1)–N(1) 179.23(5), O(3)–Si(1)–O(1) 119.18(9), O(3)–Si(1)–O(2) 117.74(9), O(1)–Si(1)–O(2) 119.23(9), O(3)–Si(1)–Cl(1) 95.92(6), O(1)–Si(1)–Cl(1) 97.13(6), O(3)–Si(1)–N(1) 83.44(7), C(12)–N(1)–C(22) 114.49(17), and C(12)–N(1)–Si(1) 103.46(13).

**Figure 2.** Molecular structure of [N(CH2C6H2Me2O)3Si]2O (6) in the crystal (top: view perpendicular to the Si–O–Si axis; bottom: view along the Si–O–Si axis). There are two molecules in the asymmetric unit. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Si(1)–O(1) 1.6094(6), Si(1)–O(2) 1.6274(9), Si(1)–N(1) 1.7730(9); O(1)–Si(1)–O(2) 104.11(4), O(2)–Si(1)–O(2A) 114.26(3), Si(1)–O(1)–Si(1) 180.00(4), N(1)–Si(1)–O(1) 179.97(3), and N(1)–Si(1)–O(2) 75.90(4).
(OCH2CH3)3N, the Si–N bond length in 3 (2.2125 Å) is significantly longer than the Si–N bond in ClSi(OCH2CH3)2N (2.023 Å)37 or in ClSi(OH2Me(t-Bu)CH2)2N (2.045 Å).14c This in fact shows to some extent the mobility of the Si–N bond even in the presence of three phenyl groups in the structure of 3. Another difference among the structures of ClSi(o-OH2CH3)2N (3), ClSi(OCH2CH3)2N, and ClSi(OH2Me(t-Bu)CH2)2N is the difference of Si–Cl bond lengths (2.0707, 2.153, and 2.180 Å, respectively), whereas Si–O bonds (alkoxide and phenoxide) are almost identical (1.6528, 1.649, and 1.629 Å). Comparison of these three related structures indicates the dependence of the structural parameters from the ligand used, where the flexibility of the chelate rings is the most important.

Compound 6 (Figure 2) crystallizes in the trigonal space group R3; the molecule occupies a threefold axis. According to the Cambridge Crystallographic Database (CSD), structures with SiV–O–SiV coordination motif are very rare,26,55 and there are no structures with SiNO4 coordination of such type. The main features of 6 consist of an almost linear N–Si–O–Si–N fragment and a staggered conformation of two NSiO3 frameworks along the Si–O–Si bond, which may be explained by steric reasons. The introduction of two voluminous Si(OC6H2Me2CH2)3N units to O not only contributes to its linearity, but also led to sufficient increase of the Si–N distance (2.77730 in 6 vs 2.633 Å in related MeO Si(OCH2H2Me2CH2)3N14a and Si–Oeq bonds (1.6274 vs 1.616 Å), whereas the Si–Oax distances are almost identical (1.6094 vs 1.609 Å). At the same time, C–N–Si–O are almost in eclipsed conformation in deference of other cases. Apparently, there is very weak N–Si interaction in 6 (2.77730 vs 1.965–2.838 Å, typical for silatranes and related compounds; see above),32 and the Si atom has a highly tetrahedrally distorted trigonal-bipyramidal geometry, which was additionally confirmed by crystal density functional theory (DFT) calculations (see below). Six-membered chelate OSiNC3 cycles are in almost ideal boat conformations, where the O and CH3 units are the ones that moved out of the plane formed by the other atoms.

According to the crystallographic data of oligosilanylsilatrane 9 (Figure 3), two molecules of 9 with noticeably different structural parameters are in the asymmetric unit in the monoclinic space group C2/c. The Si–N bond length increases from 2.2125 Å in ClSi(o-OH2CH3)2N (3) or 2.292 Å in (Me3Si)2SiCl(OCH2CH3)2N42 to 2.455 and 2.509 Å in oligosilanylsilatrane 9, which shows the flexibility of the silatrane cage and the mobility of nitrogen atom even in the presence of three rigid phenylene groups. In reverse Si–SiO3 bond lengths decrease from 2.3509 Å in (Me3Si)2SiCl(OCH2CH3)2N to 2.3096 and 2.3245 Å in oligosilanylsilatrane 9. This fact can be explained by the electron-withdrawing character of the phenylene groups in the ligand framework. Unequal values of three O(x)–Si(1)–O(x’), angles (for details, see the Supporting Information) in spite of approximate C3 symmetry in the structure along the Si–SiO3 bond is due to torsion in the silatranyl group, which is created by three rigid phenylene groups. In 9, the hypercoordinated silicon atoms Si(1)/Si(6) have a distorted TBP-S geometry with N and Si(2) atoms in apical positions.

For 9, the whole molecule has a staggered conformation along Si(1)–Si(2) bond (torsion Si–Si(2)–Si(1)–O is 65.21(8)/54.78(8)°). The nitrogen atom is highly flattened (sum of the angles is 351.22/353.70°). The five-membered chelate cycles are in distorted envelope conformation with Si atom as a flap.

Figure 3. Molecular structure of 1,1-aminotris(phenyl-2'-oxy)-2,2-bis(trimethylsilyl)trimethylsilane (9) in the crystal. There are two molecules in the asymmetric unit; only one molecule is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): molecule 1: Si(1)–N(1) 2.5090(17), Si(1)–O(1) 1.6500(17), Si(1)–O(2) 1.6583(17), Si(1)–O(3) 1.6487(16), Si(1)–Si(2) 2.3096(9), Si(2)–Si(3) 2.3380(10), Si(2)–Si(1)–N(1) 178.31(10), Si(2)–Si(1)–O(1) 103.30(6), O(1)–Si(1)–O(2) 114.48(10), N(1)–Si(1)–O(1) 76.05(10), C(6)–N(1)–C(14) 118.21(17), C(8)–N(1)–C(14) 98.05(17); molecule 2: Si(2)–N(6) 2.4550(16), Si(6)–O(4) 1.6564(15), Si(6)–O(5) 1.6555(16), Si(6)–O(6) 1.6575(16), Si(6)–Si(7) 2.3245(9), Si(7)–Si(9) 2.3426(9), Si(7)–Si(6)–N(2) 178.80(9), Si(7)–Si(6)–O(4) 102.96(6), O(5)–Si(6)–O(6) 115.61(9), N(2)–Si(2)–O(5) 77.68(9), C(26)–N(2)–C(24) 117.95(16), and C(24)–N(2)–Si(6) 99.78(16).

For 11 (monoclinic space group P21/c; Figure 4), the Si–SiO3 bond is shortened (2.319 vs 2.347–2.377 Å) in comparison with the other ones. The nitrogen atom is again highly flattened (sum of the angles is 350.31°). The geometry of hypercoordinated Si(2) may be described as distorted TBP-S
with the oxygen atoms in the equatorial plane; five-membered chelate rings are in envelope conformations with Si as a valve. Conformation along Si–Si–Si–O is staggered (torsions are 42.53/77.47°); σ-conjugation along the Si–Si bonds is possible (angle Si–Si–Si varies in the 111–118° range; 120° for the ideal conjugation), but the terminal silicon atoms deviate from the planarity with the central ones. Comparison of the structural parameters of 9 and 11 indicates that the elongation of the silicon chain as substituent at hypercoordinated Si atom resulted in significant changes in the Si–N bond, which may be explained by steric and packing reasons.

According to the crystallographic data, there are two molecules of oligosilanylsilatrane 12 in the asymmetric unit; the structural parameters are significantly different possibly due to packing effects (Figure 5). Compound 12 crystallizes in the triclinic space group $\text{P}1\overline{1}$, where the coordination geometry of Si(5) may be described as TBP-5 with N and O(1) in apical positions. Si–N bonds of 2.527 and 2.717 Å and O–SiO3 bonds of 1.644 and 1.619 Å, respectively, were observed, which means that the structure with a shorter Si–N bond has a longer O–SiO3 bond, and in contrast, the structure with a longer Si–N bond has a shorter O–SiO3 bond. This in fact is in accordance with Gordon’s rule.34 Unequal values of three O(x)–Si(5)–O(x′) angles (for details, see the Supporting Information) with close to 10° difference are mainly caused by the alkylene chain of THF, which is located between the silatranyl and (Me3Si)3Si groups. In contrast to three unequal O(x)–Si(5)–O(x′) three C(x)–N(1)–C(x′) angles are very close to each other. Although the O(x)–Si(5)–O(x′) units are under steric tension, the torsion does not transfer to the three C(x)–N(1)–C(x′) angles due to the flexibility of the silatranyl ligand. The six-membered chelate rings are in boat conformation with O and CH₃ as valves. Comparing the structural parameters of 12 (both molecules) to those of 6 indicates significant changes in Si–N bond length (2.527, 2.717 vs 2.773 Å) but only insignificantly influences the equatorial Si–O bonds (1.630, 1.628 vs 1.6274 Å), whereas the changes in axial Si–O bonds are more significant (1.644, 1.619 vs 1.6094 Å, respectively), indicating the strong effect of hypercoordination in the X–Si ← N fragment.

The molecule of oligosilanylsilatrane 13 (Figure 6) crystallizes in the trigonal space group $\text{P}3_1\overline{1}$. Due to the presence of a symmetry axis along the N–Si–Si bond, three O(x)–Si(1)–O(x′) angles as well as three C(x)–N(1)–C(x′) angles are equal to each other (for details, see the Supporting Information). However, the related oligosilanylsilatrane (Me₅Si)₂Si(Si(OCH₂CH₂)₃N)² with the trialkylamine ligand or oligosilanylsilatrane 9 with the triphenylenamine ligand are symmetric molecules, but a symmetric crystal structure was not observed in their case.

The hypercoordinated atom Si(1) in 13 features trigonal bipyramidal (TBP-5) geometry with oxygen atoms in equatorial positions. The torsional angles along Si–Si–Si–O (torsions are 56.71/63.36°) indicate a staggered conformation; six-membered chelate cycles are in half-chair conformation with N and CH₃ in vertices.

It is interesting to compare structural data for the related catenated derivatives 13, (Me₅Si)₂Si(Si(OCH₂CH₂)₃N)² and 9 with the hypercoordinated Si atom in a similar Si₅O₂N coordination environment. Elongation of Si ← N bonds apparently is caused by the rigid ligand structure (geometric reason) (2.237 in 13, 2.292 in (Me₅Si)₂Si(Si(OCH₂CH₂)₃N)² and 2.455/2.509 Å in 9) and accompanied by shortening of the Si–Si (2.3770 vs 2.3509 vs 2.3245/2.3096 Å) bond. At the same time, Si–O bonds (1.6669 vs 1.650 vs 1.6565/1.6523 Å) are changed not so evidently, possibly due to packing effects, although the same tendency is visible. Anyway, the similarity of
Table 1. Comparison of the Main Structural Parameters for Several Hypercoordinated Oligosilanes

| compound | Si−N, Å | Δ, Å | average O−Si−N−C torsion, deg | reference |
|----------|---------|------|-----------------------------|-----------|
| [Me3O(Si(OCH2CH2)2)N][BF4] | 1.965 | −0.017 | 16.44 | 32 |
| ClSi(OCH2CH2)2N | 2.023 | −0.095 | 9.16 | 27 |
| (Me3Si)2Si(OCH2CH2)2N | 2.292 | −0.267 | 9.70 | 22a |
| cycle-(Si(Me2Si3N)2Si(OCH2CH2)2N) | 2.333 | −0.291 | 8.34 | 22b |
| Cl3Si(OCH2Me2CH2)2N | 2.025 | 0.033 | 39.0 | 14a |
| ClSi[(OCH2Me2CH2)2N] | 2.045 | 0.013 | 38.07 | 14c |
| (Me3Si)2Si(H)Si(OCH2CH2)2N | 2.153 | −0.202 | 3.75 | 22c |
| MeO(Si(OCH2Me2CH2)2N) | 2.633 | −0.315 | 17.2 | 14a |
| (2-Py)CH2Si[(OCH2Me2CH2)2N] | 2.838 | −0.439 | 6.92 | 14b |
| PhSi(o-OC6H4)2N | 2.344 | −0.287 | 0 | 12b |
| ClSi(o-OC6H4)2N (3) | 2.2125 | −0.189 | 2.63 | this work |
| O(Si[(OCH2Me2CH2)2N])2 (6) | 2.773 | −0.397 | 5.47 | this work |
| (Me3Si)2Si(o-OC6H4)2N (9) | 2.455 | −0.352 | 9.56 | this work |
| (Me3Si)2Si(o-OC6H4)2N | 2.509 | −0.391 | 15.39 | this work |
| (Me3Si)2SiMe2SiMe2SiMe2Si(o-OC6H4)2N (11) | 2.417 | −0.349 | 15.18 | this work |
| (Me3Si)2Si(CH2)4O(Si(OCH2Me2CH2)2N) (12) | 2.527 | −0.258 | 21.87 | this work |
| (Me3Si)2SiSi[(OCH2Me2CH2)2N] (13) | 2.717 | −0.361 | 11.50 | this work |
| (Me3Si)2SiSi[(OCH2Me2CH2)2N] (14) | 2.236 | −0.150 | 46.29 | this work |

Table 2. 29Si NMR Data of SiO3 Group for 3−5, 9−13, and Related Compounds

| compound | chemical shift of SiO3δ, ppm | solvent | reference |
|----------|-------------------------------|---------|-----------|
| (MeO)2Si | −79.91 | CDCl3 | 38 |
| (EtO)2Si | −82.24 | CDCl3 | 38 |
| (PhO)2Si | −101.89 | CDCl3 | 38 |
| ClSi(OMe)2 | −66.6 | CDCl3 | 11 |
| ClSi(o-OC6H4Ph)2 | −84.79 | CDCl3 | 39 |
| MeO(Si(OCH2CH2)2N) | −95.4 | CDCl3 | 32 |
| ClSi(OCH2CH2)2N | −85.2 | CP/MAS | 40 |
| ClSi(o-OC6H4)2N (3) | −97.8 | DMSO-d6 | this work |
| MeO(Si(OCH2Me2CH2)2N) (4) | −119.0 | CDCl3 | 14a |
| ClSi[(OCH2Me2CH2)2N] (5) | −124.5 | CDCl3 | this work |
| (Me3Si)2Si[(K)Si(OCH2CH2)2N]·18-crown-6 | −11.8 | C6D6 | 22a |
| (Me3Si)2Si[(K)Si(o-OC6H4)2N]·18-crown-6 (10) | −9.5 | C6D6 | this work |
| (Me3Si)2SiSi(OH)2 | −3.22 | CDCl3 | 22c |
| (Me3Si)2SiSi(OCH2CH2)2N | −5.26 | CDCl3 | 22a |
| (Me3Si)2Si(o-OC6H4)2N (9) | −45.9 | CDCl3 | 22a |
| (Me3Si)2SiMe2SiMe2SiMe2Si(o-OC6H4)2N (11) | −46.3 | CDCl3 | this work |
| (Me3Si)2SiMe2SiMe2SiMe2Si(OCH2CH2)2N | −53.8 | CDCl3 | 22a |
| (Me3Si)2Si[(CH2)4O][O(Si(OCH2Me2CH2)2N) (12) | −117.1 | CDCl3 | this work |
| (Me3Si)2SiSi[(OCH2Me2CH2)2N] (13) | −107.7 | CDCl3 | this work |

Si−O bond for alkoxides and phenoxides of such types should be mentioned.

Using data for 3 and 6, it is evident that the XSi ← N bond length depends on the electron properties of X (electron-withdrawing groups result in shortening) 34,35 but also on the steric size of X (increasing size of X results in elongation of X−Si and Si ← N). The Bader analysis of the theoretical electron density showed the presence of the bond critical point between the Si and N atoms. The electron density equals to 0.056 au for 3 and 0.021 au for 6. The energies of the Si ← N interaction are 43.5 and 14.2 kJ/mol for 3 and 6, respectively. It should be noted that in related tritans, N(CH2CH2O)3SiSi(SiMe3)2R (R = H, Me, Et, Ph, SiMe3, Si2Me5Sil, Si(OCH2CH2)2N), the Si−N bond distances are in the 2.15−2.42 Å range. 22 For oligosilanylsilatrane-like molecules 9 and 11 based on ligand 1, this bond is significantly elongated (up to 2.41−2.51 Å), whereas for 13, based on ligand 2, the Si−N distance is in accord with typical hypercoordinated interaction. Anyway, in all compounds, the interaction is present, even in 6, despite a long Si−N distance. These data clearly indicate the dependence of structural parameters on the ligand electronic and geometric properties. The insertion of N atom into the conjugation with O by phenylene as in 1 results in decreased electron-withdrawing properties of alkoxides at the Si atom. The Si−Si bond length in 9, 11, and 13 vary between 2.30 and 2.39 Å, which correlates with data for single Si−Si bond length. The Si−O bonds in 9, 11, and 13 based on aminotrisphenols are in the range of 1.65−1.68 Å, typical for oligosilanylsilatrane 22a (0.361 11.50), indicating a weak effect of conjugation of O with aryl group in phenols on Si geometry. The similarity in the Si−N bond length for 13 and classical silatrane N(CH2CH2O)3SiSi(SiMe3)2 reflects the role of fluxional
behavior of five- and six-membered chelate rings, which is not restricted by ring constraints.

Generalized structural data for 3, 6, 9, and 11–13 and several related derivatives are presented in Table 1, where \( \Delta \) is the displacement of the silatrane Si atom with respect to the plane formed by the equatorial O atoms (positive values indicate an out-of-plane displacement toward N).

It should be noted that the main dependence is evident from these data. Attachment of the bulky X group to the central Si atom results not only in Si–X elongation in \( \bar{X} = \bar{N} \) but also in increased Si ← N distances. The flexibility of the ligand framework, arising from the nonrigidity and increased size of the chelate cycles, is able to compensate steric interaction (appearing in increasing \( \Delta \), Si ← N distance, and O ← Si ← N C torsion). It results in elongation of \( \Delta \) with lengthening of Si ← N. As was observed earlier, elongation of the Si ← N distance is connected to shifting the Si atom from the O3 plane and not to movement of the N atom away from this plane. At the same time, all these relationships are discussible especially due to the high impact of crystal packing effects on the structural parameters (e.g., see two different molecules for 12).

**Structure in Solution.** In general, the NMR spectra of hypercoordinated compounds 3–5 and 9–13 indicate that in solution, the structure corresponds to that found in a crystal. It should be noted that for 13, dynamic behavior is observed in solution. Thus, at room temperature (rt), the signals for the NCH(H) group in \(^1\)H NMR appear as singlet (\( \delta = 3.67 \text{ ppm, } 6\text{H}; \) fast H–H exchange on the NMR time scale). On cooling to \(-40^\circ\text{C}, \) these protons become diastereotopic (\( \delta = 4.44 \) and 2.94 ppm, both \( d, J \) 14.5 Hz, each \( 3\text{H} \)). Apparently, this is explained by fast conformation transitions of the chelate six-membered cycles (pseudorotation with exchange of axial-equatorial protons).\(^{14c,26c,37}\) Crude estimation of rate constants can be obtained from these spectral data using approximate formula\(-s,^{14a}\) giving at \(-40^\circ\text{C}\) \( \Delta G^\circ = 9.2 \text{ kcal/mol with } t_{1/2} = 0.3 \text{ ms.} \) In contrast to this, for 9 and 11, based on aminotrisphenol 1, a rigid structure is observed.

Comparing \(^{29}\)Si NMR chemical shift values (Table 2) for 3–5, 9–13, and several known related compounds indicates the dependence of the experimental data on the structure of the ligand used. Interaction between Si and N atoms results in upfield shifts of \(^{29}\)Si NMR signals of the SiO\(_3\) fragment,\(^{22a}\) as is evident from a comparison of chemical shifts for

### Table 3. UV–Vis Absorption Data for Several Si Compounds

| compound | \( \lambda, \text{ nm} \) | absorptivity, \( \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \) | solvent | reference |
|----------|------------------------|---------------------------------|---------|-----------|
| Me\(_3\)SiMe\(_2\)SiMe\(_3\) | 215 | 0.90 | cyclohexane | 47 |
| (Me\(_3\)Si)\(_2\)SiMe\(_2\)Si(SiMe\(_3\))\(_3\) | 258 | 2.4 | hexane | 46 |
| Me\(_3\)SiMe\(_2\)Si(SiMe\(_3\))\(_3\)Si(OCH\(_2\)CH\(_2\))\(_2\)N | 223 | 1.85 | n-pentane | 22a |
| (Me\(_3\)Si)\(_2\)SiMe\(_2\)Si(SiMe\(_3\))\(_3\)Si(OCH\(_2\)CH\(_2\))\(_2\)N | 254 | 5.45 | n-pentane | 22a |
| [N(CH\(_3\)CH\(_2\))\(_2\)]\(_2\)Si(SiMe\(_3\))\(_3\)SiMe\(_2\)Si(SiMe\(_3\))\(_3\) | 252 | 7.48 | Et\(_2\)O | 22a |
| (Me\(_3\)Si)\(_2\)Si(Si(OCH\(_2\)CH\(_2\))\(_3\))\(_2\)N | 276 | 1.14 | Et\(_2\)O | this work |
| (Me\(_3\)Si)\(_2\)SiMe\(_2\)Si(SiMe\(_3\))\(_3\)Si(OCH\(_2\)CH\(_2\))\(_3\)N (9) | 282 | 1.36 | Et\(_2\)O | this work |
| (Me\(_3\)Si)\(_2\)SiMe\(_2\)Si(SiMe\(_3\))\(_3\)Si(OCH\(_2\)CH\(_2\))\(_3\)N (11) | 254 | 6.50 | Et\(_2\)O | this work |
| (Me\(_3\)Si)\(_2\)Si(OCH\(_2\)CH\(_2\))\(_3\)N (12) | 278 | 0.96 | | |
| (Me\(_3\)Si)\(_2\)Si(OCH\(_2\)CH\(_2\))\(_3\)N (13) | 285 | 1.11 | | |
| (Me\(_3\)Si)\(_2\)Si(Si(OCH\(_2\)CH\(_2\))\(_3\)N (14) | 225 | 2.62 | Et\(_2\)O | this work |
| (Me\(_3\)Si)\(_2\)Si(Si(OCH\(_2\)CH\(_2\))\(_3\)N (15) | 273 | 0.41 | | |
| (Me\(_3\)Si)\(_2\)Si(Si(OCH\(_2\)CH\(_2\))\(_3\)N (16) | 281 | 0.38 | | |
| (Me\(_3\)Si)\(_2\)Si(Si(OCH\(_2\)CH\(_2\))\(_3\)N (17) | 235 | 3.66 | Et\(_2\)O | this work |
| (Me\(_3\)Si)\(_2\)Si(Si(OCH\(_2\)CH\(_2\))\(_3\)N (18) | 278 | 0.62 | | |
| (Me\(_3\)Si)\(_2\)Si(Si(OCH\(_2\)CH\(_2\))\(_3\)N (19) | 287 | 0.39 | | |
absorption and, therefore, the changing of highest occupied molecular orbital/lowest unoccupied molecular orbital levels. The effect of weakly hypercoordinated groups is insignificant, whereas the trifluorophenyls like (HOC₆H₄Me₂CH₂)N may bathochromically shift absorption bands. The band at 225 nm for 12 is caused by hypercoordinated Si atom, which is red shifted to 235 nm in 13 due to conjugation.

It is evident that the bands at 270–290 nm with lower absorptivity (0.40–1.40 × 10⁻³) for 9 and 11–13 are referred to the absorption of the aromatic groups of the ligand frameworks (291 nm for 14 and 286 nm for 2). The highly intensive band at 254 nm for 12 corresponds to the Si6 framework, and in this case, a weak hypercoordination results in weak hypsochromic shift compared to the all-methylated reference compound. Furthermore, the effect of hypercoordination based on aminotrisphenols with terminal modification 18 is very weak.

## CONCLUSIONS

In this work, the synthesis of a novel class of hypercoordinated silicon derivatives, oligosilyllasilatrane-like molecules, based on aminotrisphenols is presented. In contrast to previously investigated cases, high reactivity and clean reaction of silatrane-like molecules containing aromatic ligands and chloride as a leaving group were observed with silanilyl anions; that is why the precise choice of the starting materials is very important. Single-crystal XRD analysis showed that Si–N distances in catenated silatrane-like molecules with aromatic ring vary within a wide range (2.23–2.72 Å), as the nature of the ligand strongly affects the structural parameters. Apparently, the introduction of oligosilyl substituents to the central Si atom in silatrane results in Si–N bond elongation irrespective of the ligand type, which is in part explained by steric reasons, mostly due to repulsions between voluminous Si(SiMe₃)₂R fragments and rigid silatranyl- or silatranyl-like groups; the flexibility of the ligands’ "arms" (which increases in the range of o-C₆H₄ < CH₂CH₂ < CH₂<CH₂-C₆H₄Me₂) results in diminished steric impact, and, therefore, the electronic nature of the substituents gains more influence on the central Si geometry. NMR spectroscopy of hypercoordinated derivatives also indicates that the 29Si chemical shift of SiO₃ changes in wide limits (~45 to ~117.1 ppm) depending on the ligand type. Furthermore, the analysis of obtained and literature data for all groups of atranes and related derivatives indicates that the axial substituent X at the central X–SiO₃ atom strongly affects the Si–N distance. Thus, there are three main factors influencing the structure and properties of silatranes and related compounds: nature of the ligand (formation of chelate cycles and their flexibility), geometric volumes of the substituents, and its electronic properties.

## 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. Solvents were dried using a column solvent purification system. Potassium tert-butoxide was purchased exclusively from Merck, thionyl chloride 99.5% from Acros, and silicon tetrachloride 99% from Riedel-de Haën.

Chemical substances used as starting materials like tris(2-methoxyphenyl)amine, tris(2-hydroxy-4,6-dimethylbenzyl)-amine, (Me₃Si)₂SiSiMe₃SiMe₃Cl, aminotris(3’,5’-dimethylbenzyl-2’-oxy)silyl methoxide (4), tetrakis(triethylsilyl)silane, and (Me₃Si)₃SiSiMe₃SiMe₃Cl, aminotris(3’,5’-dimethylbenzyl-2’-oxy)silyl methoxide (4), tris(triethylsilyl)silyl potassium-THF (7), and tris(trimethylsilyl)silyl potassium-18-crown-6 (8) were prepared according to literature procedures.

### 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 BRUKER-AXS SMART APEX and SMART APEX II CCD diffractometers using graphite-monochromated Mo Kα radiation (0.71073 Å). The data were reduced to F₀ and corrected for absorption effects using SAINT and SADABS separately. Structures were solved by direct methods and refined by the full-matrix least-squares method (SHELXL97 and SHELX2013). All nonhydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions to correspond to standard bond lengths and angles and refined using a riding model. Crystal 3 represented a pseudomorphed twin with domain ratio 0.678(2)/0.322(2). All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity.

Crystallographic data for the structures of compounds 2-HCl, 3, 6, 9, 11, 12, and 13 (Tables S1 and S2, Supporting Information) reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1836096 (2-HCl), 1836095 (3), 1836094 (6), 1836092 (9), 1836093 (11), 1836090 (12), and 1836091 (13). Copies of 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 and rendered using POV-Ray 3.6.

Attention! Special caution (anhydrous conditions, hood, or drybox) should be exercised when working with chemical hazards (KOH, SiCl₄, and SOCl₂).

### Synthesis of Compounds. Tris(2-methoxyphenyl)amine

Modified procedure was used. To a three-necked flask equipped with a reflux condenser, Dean-Stark trap, and stir bar were added o-anisidine (4.96 g, 40.27 mmol), o-iodoanisole (18.30 g, 78.19 mmol), powder of K₂CO₃ (23.50 g, 170.30 mmol), spongy copper powder (5.0 g), and nitrobenzene (15 mL). The flask was then heated for 3 h at reflux with flashes of nitrogen to remove the water from the reaction mixture and...
collected in Dean-Stark trap. The reaction mixture was then cooled, and the product was extracted with hot chloroform and filtered over filter paper. Chloroform was removed by vacuum. Nitrobenzene was distilled of at 55 °C, 1 mbar. The residue was dissolved in ethylacetate and mixed with 100 mg of activated carbon and passed through a silica gel column. The used ethylacetate was removed by vacuum. The residue was dissolved in 10 mL of hot chloroform, and then, 5 mL of n-hexane was added and left for crystallization. Colorless crystals of tris(2-methoxyphenyl)amine (8.53 g, 65%) were obtained by filtering the solution mixture with a filter. mp: 152–153 °C. NMR (δ in ppm): 1H: 7.05–7.01 (m, 3H, aryl), 6.87–6.78 (m, 9H, aryl), 3.57 (s, 9H, OCH3). 13C: 153.1 (aryl), 137.7 (aryl), 124.4 (aryl), 123.7 (aryl), 120.6 (aryl), 112.5 (aryl), and 55.7 (OMe). Tris(2-hydroxyphenyl)amine (1).12a A mixture of tris(2-methoxyphenyl)amine (1.00 g, 2.98 mmol, 1.0 equiv) and AlCl3 (0.91 g, 6.82 mmol, 2.3 equiv) in toluene (5 mL) was refluxed for 90 min. After cooling the mixture to rt, 10% HCl (20 mL) was added, stirred for 2 h, then extracted with EtOAc, and dried over Na2SO4. After the solvent was removed, 1.04 g of crude 1 was obtained. It was dissolved in a mixture of diethyl ether and pentane (1:2) and filtered. Colorless crystals of 1 (480 mg, 55%) were obtained after recrystallization from dichloromethane. mp: 174–175 °C. NMR (δ in ppm): 1H: 7.08 (m, 3H, aryl), 6.94–6.85 (m, 9H, aryl), 5.70 (s, 3H, OH). 13C: 149.8 (aryl), 133.4 (aryl), 126.7 (aryl), 125.4 (aryl), 121.5 (aryl), and 117.3 (aryl). Aminotris(phenyl-2’-oxy)silylchloride (3). A mixture of 1 (348 mg, 1.18 mmol, 1.0 equiv) and SiCl4 (222 mg, 1.30 mmol, 1.1 equiv) in dibutylether (5 mL) was refluxed, stirred for 20 h, then added dropwise over 1 h to a slurry of 110 mg, 0.312 mmol, 1.00 equiv) in toluene (1 mL) under stirring. After 12 h, the volatile was removed by vacuum and the residue was dissolved in benzene and filtered with filter paper. Colorless crystals of 3 (105 mg, 60%) were obtained after recrystallization from diethyl ether. mp: 253–257 °C. NMR (δ in ppm): 1H: 7.72 (m, 3H, aryl), 7.13 (m, 3H, aryl), 6.91 (m, 6H, aryl), 0.35 (s, 27H, (CH3)3Si). 13C: 154.4 (aryl), 136.5 (aryl), 128.6 (aryl), 127.9 (aryl), 121.9 (aryl), 118.1 (aryl), 2.2 (SiMe3). 29Si: −9.8 (Me,Si), −46.1 (SiO3), −135.7 (Si), [6] [EIMS (70 eV) m/z (%): 565 (21) [M+], 550 (8) [M−Me], 492 (6) [M−SiMe3], 434 (2) [Si2C6H3NO3]+, 407 (8) [Si2C6H5NO3]+, 392 (31) [Si2C6H4NO3]+, 376 (14) [Si4C16H14NO4]+, 335 (5) [Si3C6H3NO3]+, 318 (100) [Si3C6H5NO3]+, 305 (7) [Si3C6H4NO3]+, 300 (6) [Si3C6H4NO2]+, 267 (4) [Si2C6H4NO3]+, 232 (73) [SiC6H4]+, 217 (2) [SiC6H3]+, 174 (31) [SiC6H18]+, 159 (26) [SiC6H15]+, 131 (15) [C6H14NO]+, 115 (11) [C6H13N]+, 91 (8) [C6H12N]+, 73 (100) [SiMe5]. UV−vis absorption (EtOH): λ 276 nm (ε 1.14 × 104 M−1 cm−1), 282 nm (ε 1.10 × 104 M−1 cm−1). Elemental analysis: calc for: C24H28NO5Si6: C 57.92, H 6.94, N 2.47. Found: C 56.95, H 6.79, N 2.50. Bis(trimethylsilyl)silyl Potassium 18-Crown-6 [2,2′,2′′-Nitrilotriphenoxy)siloxane (10). A mixture of 9 (53 mg, 0.093 mmol, 1.0 equiv), KOBu (11 mg, 0.098 mmol, 1.05 equiv) and 18-crown-6 (26 mg, 0.098 mmol, 1.05 equiv) was dissolved in Cd6 (1 mL) and left for 14 h. After NMR spectroscopic analysis confirmed formation of oligosilylpyrrolotitanium, the solution mixture was left for crystallization. Compound 10 (74 mg, >99%) was isolated as a red greasy substance. NMR (δ in ppm): 1H (Cd6): 7.43 (m, 3H, aryl), 7.11 (m, 3H, aryl), 6.92 (m, 3H, aryl), 6.74 (3H, aryl), 0.72 (s, 18H, (CH3)3Si). 13C (Cd6): 156.5 (aryl), 138.8 (aryl), 131.4 (aryl), 129.3 (aryl), 126.8 (aryl), 121.2 (aryl), 7.0 (SiMe3). 29Si (Cd6): −3.6 (Me,Si), −9.5 (SiO3), −213.2 (Si2O). Ethylbromide derivatization: EIMS (70 eV) m/z (%): 521 (21) [M]+, 506 (6) [M−Me], 502 (3) [C6H12NO5Si]+, 497 (2) [C6H12NO4Si]+, 492 (2) [M−Et]+, 477 (2) [C2H52H2NO3Si]+, 448 (14) [C2H52H2NO3Si]+, 443 (1) [C2H52H2NO3Si]+, 420 (4) [C2H52H2NO3Si]+, 407 (6) [C2H52H2NO3Si]+, 404 (5) [C2H52H2NO3Si]+, 392 (23) [C2H52H2NO3Si]+, 376 (12) [C2H52H2NO3Si]+, 362 (2) [C2H52H2NO3Si]+, 346 (2) [C2H52H2NO3Si]+, 335 (3) [C2H52H2NO3Si]+, 318 (100) [C2H52H2NO3Si]+, 300 (7) [C10H14O2Si]+, 264 (5) [C10H14O2Si]+, 219 (20) [C10H14O2Si]+, 188 (23) [C10H14O2Si]+, 182 (2) [C6H12NO3]+, 166 (4) [C6H12N]+, 160 (5) [C6H12N]+, 154 (1) [C6H12N]+, 131 (10) [C6H12N]+, 119 (2) [C6H12N]+, 100 (3) [C6H12Si]+, 91 (4) [C6H12N]+, 73 (18) [SiMe5]+, 69 (23) [C6H12NO3]+, [N(C6H5)3SiSi(SiMe3)3SiMe3Si(SiMe3)3Si]+ (11). A mixture of 9 (119 mg, 0.210 mmol, 1.00 equiv) and KOtBu (24 mg, 0.220 mmol, 1.05 equiv) was dissolved in THF (1 mL). The solution color turned orange immediately. After NMR spec-
troscopy confirmed formation of oligosilylamine potassium reagent, the solvent was removed. Afterward, the oligosilylamine potassium reagent obtained was dissolved in toluene (2 mL) and added very fast to a solution of 1-chloro-3,3,3-bis(trimethylsilyl)heptamethyldisiloxane (84 mg, 0.210 mmol, 1.00 equiv) in toluene (2 mL). After 4 h, the solvent was removed and the residue was dissolved in n-pentane and filtered with filter paper. Colorless crystals of 1 (125 mg, 71%) were obtained by crystallization from n-pentane at −55 °C mp: 112−118 °C. NMR (δ in ppm): 1H (CD3OD): 7.40−7.37 (m, 3H, aryl), 7.03−7.00 (m, 3H, aryl), 6.84−6.79 (m, 3H, aryl), 6.67−6.61 (m, 3H, aryl), 0.77 (s, 6H, Si(CH3)2), 0.65 (s, 6H, Si(CH3)2), 0.54 (s, 18H, [(CH3)3Si]Si), 0.33 (s, 27H, [(CH3)3Si]Si). 13C (CD3OD): 154.5 (aryl), 137.0 (aryl), 128.9 (aryl), 128.1 (aryl), 122.4 (aryl), 118.4 (aryl), 3.7 ([(Me3Si)3Si]N), 3.3 ([(Me3Si)2Si]N, 1.2 (SiMe3), 1.18 (SiMe3). 29Si(CD3OD): −9.1 [(Me3Si)3Si], −9.8 ([(Me3Si)2Si]N), −29.7 and −31.1 [(Me3Si)3Si], −463 (SiO2), −129.3 and −130.6 (Si). El/MS (70 eV) m/z (%): 840 (1) [M′−Me], 608 (10) [C6H42NO2Si3], 550 (57) [C26H26NO2Si5], 502 (10) [C26H32NOSi5], 492 (2) [C24H30NO3Si4], 450 (2) [C21H26NO3Si4], 414 (7) [C17H22NO3Si4], 392 (6) [C17H20NO3Si5], 376 (3) [C17H18NO3Si5], 318 (14) [C16H22NO3Si5], 264 (15) [C16H20NO3Si6], 232 (3) [C16H20Si4], 219 (53) [C14H2NO3Si5], 173 (3) [C13H7NO3Si5], 157 (3) [C13H6NO3Si5], 131 (34) [C13H4NO3Si5], 119 (6) [C6H4(NO)Si], 100 (8) [(CH3)3Si], 91 (100) [(CH3)3Si]N, 73 (14) [SiMe3], 69 (66) [C14H2NO3Si5], UV−vis absorption (EtO): λ 254 nm (ε 6.50 × 104 M−1 cm−1), 278 nm (ε 0.96 × 104 M−1 cm−1), 285 nm (ε 1.10 × 104 M−1 cm−1). Elemental analysis: calc'd for: C69H42NO2Si5: C 62.87, H 8.57, N 1.83. Found: C 62.84, H 8.38, N 1.92.

1,1,1-Aminotris(3′,5′-dimethylbenzyl-2′-oxy)-(4′-tris(trimethylsilyl)silyl)butanol-oxysilane (12). A mixture of tetrakis(trimethylsilyl)silane (280 mg, 0.873 mmol, 1.00 equiv) and KOtBu (101 mg, 0.899 mmol, 1.03 equiv) was dissolved in THF (3 mL). The solution color turned orange immediately. After NMR spectroscopy confirmed formation of 7, THF was removed. Afterward, 7 was dissolved in toluene (5 mL) and added dropwise over 10 min to a slurry of compound 5 (419 mg, 0.873 mmol, 1.00 equiv) in toluene (3 mL) under stirring. After 12 h, the volatile was removed and the residue was dissolved in benzene and filtered with filter paper. Colorless crystals of 12 (425 mg, 64%) were obtained after recrystallization from a mixture of acetone and diethyl ether (1:2): mp: 144−153 °C. NMR (δ in ppm): 1H: 6.87 (s, 3H, aryl), 6.66 (s, 3H, aryl), 4.14 (t, J = 6.5 Hz, 2H, OCH2), 3.45 (s, 6H, NCH3), 2.28 (s, 9H, aryl-CH2), 2.19 (s, 9H, aryl-CH2), 1.79 (m, 2H, CH2), 1.57 (m, 2H, CH2), 0.88 (m, 2H, SiCH2), 0.17 (s, 27H, (CH3)3Si). 13C (benzene, D2O-capillary): 149.0 (aryl), 131.1 (aryl), 130.7 (aryl), 129.2 (aryl), 129.0 (aryl), 127.2 (aryl), 63.0 (CH3), 56.4 (NCH3), 37.7 (CH2), 25.9, 20.2 (aryl-Me), 17.0 (aryl-Me), 7.9 (CH3), 1.1 (Me3-Si-Si). 29Si: −12.8 (Me3Si), −82.1 [(Me3Si)3Si], −117.1 (SiO2). El/MS (70 eV) m/z (%): 763 (2) [M′], 690 (1) [M′−SiMe3], 628 (37) [Si3C13H28NO3], 556 (3) [Si2C25H56NO3], 500 (20) [Si2C25H56NO3], 444 (100) [Si2C25H56NO3], 417 (4) [Si2C25H56NO3], 382 (15) [Si2C25H56NO3], 326 (5) [SiC11H26NO3], 263 (4) [SiC11H26NO3], 247 (13) [SiC11H26NO3], 231 (34) [SiC11H26NO3], 191 (6) [SiC11H26NO3], 175 (59) [SiC11H26NO3], 147 (7) [SiC11H26NO3], 131 (22) [SiC11H26NO3], 119 (18) [(CH3)O], 91 (9) [(CH3)O], 73 (93) [SiMe3]. UV−vis absorption (EtO): λ 225 (sh) nm (ε 2.62 × 104 M−1 cm−1), 273 nm (ε 0.41 × 104 M−1 cm−1), 281 nm (ε 0.38 × 104 M−1 cm−1). Elemental analysis: calc'd for: C64H42NO4Si4: C 62.85, H 8.57, N 1.83. Found: C 62.84, H 8.38, N 1.92.

Solid-State DFT. Solid-state DFT computations were performed in the CRYSTAL09 software package using the B3LYP functional with all-electron Gaussian-type orbital basis set 6-31G**. 88-31G* basis set was used for Si.59 London dispersion interactions were taken into account by using the semiempirical D2 scheme.60 The periodic structures with the experimental atomic positions were used.61 The Bader analysis of the periodic electron density28 obtained from the crystalline wave function was performed with TOPOND.62 The energy of the particular noncovalent interaction Eint was estimated as Eint = 0.429-G0 (in atomic units). G0 is the positively defined local electronic kinetic energy density at the bond critical point.

ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01402.

Crystallographic information, NMR spectra (1H, 13C, 29Si) of the compounds obtained (PDF).

Crystallographic data for compounds 2-HCl, 3, 6, 9, and 11−13 (CIF).

Calculated structures (XYZ)
Research to IGIC RAS.

Equipment within the State Assignment on Fundamental Coord. Chem. Rev. 489. (c) Verkade, J. G. Main group atranes: chemical and structural examples with unexpected properties.

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