Geminal Bis(hypersilyl) Compounds – The Reaction of Tris(trimethylsilyl)silyllithium with Dialkyl(chloromethylene)ammonium Chlorides

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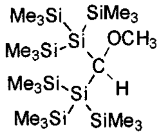
Tris(trimethylsilyl)silyllithium (**1**) reacts with dialkyl(chloromethylene)ammonium chlorides (molar ratio 2:1) to give the (dialkylamino)bis(hypersilyl)methanes $[(Me_3Si)_3Si]_2CHNR_2$ (**5a−c**; **a**: R = Me, **b**: R = Et, **c**: $R_2 = [CH_2]_5$). Due to the extreme bulkiness of the hemispherical $(Me_3Si)_3Si$ substituents, the structures of these geminal bis(hypersilyl) derivatives are characterized by tremendous distortions of their molecular skeletons. This was confirmed by X-ray structural analyses of **5a** and **5c**, which revealed considerable elongations of the central Si−C bonds (**5a**: 2.01 and 1.95 Å; **5c**: 1.99 and 1.97 Å) and an extreme widening of the Si−C−Si angles at the central sp^3-carbon atoms (**5a**: 132.6°; **5c**: 128.7°). By concentrated sulfuric acid, **5a** is converted to give, after hydrolysis, the silanol $(Me_3Si)_2Si(OH)CH_2Si(SiMe_3)_3$ (**13**). The formation of **13** is discussed as proceeding through the transient silene $(Me_3Si)_2Si{=}CHSi(SiMe_3)_3$ (**11**), generated by a formal (dimethylamino)trimethylsilane elimination from **5a** according to an acid-induced sila Peterson mechanism.

Contrary to our original expectations, the fixation of two spherically extended tris(trimethylsilyl)silyl (hypersilyl) groups at one comparatively small carbon atom proved to be surprisingly facile. Actually, geminal bis(hypersilyl) compounds are easily available by the reaction of tris(trimethylsilyl)silyllithium (**1**) with suitable C1 units. However, the experience gained from the synthesis of these compounds led to the conclusion that the approach of a second lithium silanide **1** to the α-carbon atom of a hypersilyl-substituted intermediate under conditions of a bimolecular process, i.e. with inversion of the reaction center, is hardly conceivable due to the extreme shielding of the $(Me_3Si)_3Si$ substituent in the substrate and the bulkiness of the Si nucleophile **1**. Thus, we succeeded in synthesizing methoxy−bis[tris(trimethylsilyl)silyl]methane (**2**) by consecutive replacement of the chlorine atoms of dichloromethyl methyl ether by **1**, the reaction very likely proceeding through a carbenium ion transition state.[1] Similarly, we obtained bis[tris(trimethylsilyl)silyl]methanol (**3**) from **1** and *tert*-butyl formate (2:1), as the result of the addition of **1** to the carbonyl group of the intermediate formyltris(trimethylsilyl)silane.[2] In both cases the final bis(hypersilyl) derivative is formed after attack of the lithium silanide **1** at an electrophilic planar sp^2-carbon center, thus making the steric problems, which are caused by the already fixed substituents, less significant.

A comparable stereochemical situation was expected for the reaction of **1** with dialkyl(chloromethylene)ammonium chlorides leading, as expected, to (dialkylamino)bis[tris(trimethylsilyl)silyl]methanes **5**. In this paper we describe the syntheses, the structures and the reactivity of these extremely congested functionalized geminal bis(hypersilyl) compounds. In addition, with the H_2SO_4-initiated degradation of (dimethylamino)bis[tris(trimethylsilyl)silyl]methane (**5a**) we present the first case of an acid-catalyzed sila Peterson reaction.



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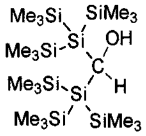

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The Synthesis and Structure of (Dialkylamino)bis[tris(trimethylsilyl)silyl]methanes $R_2N{-}CH[Si(SiMe_3)_2]$ (5a−c)

The reaction of **1** with (chloromethylene)dimethylammonium chloride, (chloromethylene)diethylammonium chloride or (chloromethylene)piperidinium chloride (molar ratio always 2:1) led to the corrersponding (dialkylamino)bis[tris(trimethylsilyl)silyl]methanes **5a−c** (Equation 1). We suppose the reaction to proceed through the intermediates **4a−c**, which are formed by nucleophilic substitution of one chlorine atom of the (chloromethylene)ammonium chlorides. Addition of a second equivalent of the silicon nucleophile **1** to the planar carbenium−immonium systems **4a−c** under elimination of lithium chloride affords the bis(hypersilyl) derivatives **5a−c**.

Actually, the gap formed by the two $(Me_3Si)_3Si$ hemispheres and the central carbon atom offers very limited space, obviously sufficient only for a small dialkylamino group. With increasing spatial demand of the amino sub-

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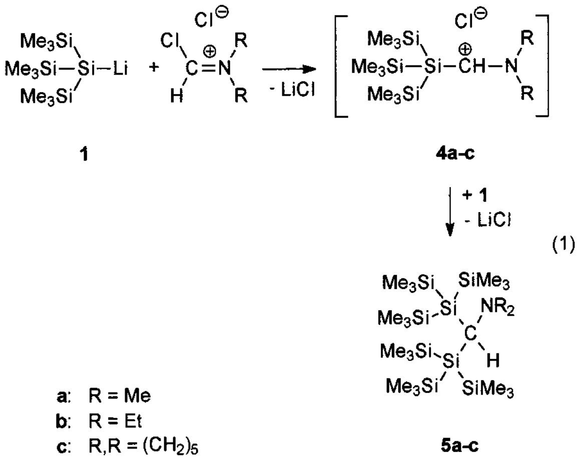


stituent the thermal stability of the compounds decreases. Thus, **5a** is moderately stable, but recrystallization from ethanol leads to partial decomposition, producing mainly hexakis(trimethylsilyl)disilane, small quantities of tris(trimethylsilyl)silane and some unidentified material. In the case of **5c** this tendency is increased, and the diethylamino derivative **5b** could not be obtained in a really pure form and was therefore characterized only by its ^{1}H-NMR spectrum where the signals of hexakis(trimethylsilyl)disilane and tris(trimethylsilyl)silane were always also identified. Single crystals of **5a** and **5c** were obtained by recrystallization from heptane at low temperature. The reaction of **1** with (chloromethylene)diisopropylammonium chloride, performed under the same conditions, failed. Besides large quantities of unidentified material only some tetrakis(trimethylsilyl)silane was isolated. Obviously, the considerable spatial demand of the diisopropylamino group prevents the fixation of two hypersilyl substituents at the central sp^{3}-carbon atom.

The sterically congested tertiary amines **5a**−**c** are colorless solids, and are stable at low temperature towards air and moisture. The structures of the compounds **5a** and **5c** were elucidated by ^{1}H-, ^{13}C-, and ^{29}Si-NMR and MS studies; for both compounds X-ray structural analyses were also performed. As found already for **2** and **3**, the solution-NMR spectra of **5a**, **c** are very straightforward. In the ^{1}H-NMR spectra, as well as in the ^{13}C-NMR spectra, only one signal was found for the $SiMe_3$ groups. The ^{29}Si-NMR spectra also show only one signal for the $SiMe_3$ silicon atoms, indicating considerable mobility of the trimethylsilyl substituents in the extremely congested molecules of **5a**, **c**. On the other hand, at room temperature separate signals were found for the two *N*-alkyl groups, which coalesce at elevated temperature. These results were interpreted as being due to a completely hindered rotation around the Si_2C-NR_2 bond (**5a**: T_c = 329 K, $\Delta\nu$ = 30.4 Hz, calcd. rotation barrier $\Delta G^{\neq}$ = 69 kJ/mol).

The results of the X-ray structural analyses of **5a** and **5c**, demonstrated in the Figures 1 and 2, confirm the expected steric congestion of the molecules. The $(Me_3Si)_3Si$ groups form two extended hemispherical shells, separated by one sp^{3}-carbon atom, thus opening a narrow slit, where the dialkylamino groups are placed. The amino group is hidden by the two hypersilyl groups and it is quite obvious that the rotation about the Si_2C-NR_2 bond is frozen. The steric strain leads to a considerable elongation of the central C−Si bonds and, additionally, the pyramidal structure of the amino groups causes significant differences in these bond lengths (**5a**: C1−Si1 2.01 Å, C1−Si2 1.95 Å; **5c**: C1−Si1 1.99 Å, C1−Si2 1.97 Å). The central Si−C−Si angles widen to values of 132.6° for **5a** and 128.7° for **5c**. These results are in good agreement with the structural data obtained for **2** and **3**.[1][2] The spatial demand of the OCH_3 group in **2** is slightly smaller than that of the dialkylamino groups in **5a** or **5c** (**2**: Si−C 1.94 Å both, Si−C−Si 132.7°). An OH group is considerably smaller. Thus, the relevant Si−C bonds in **3** are shorter (1.91 and 1.93 Å), and the bond angle at the central sp^{3}-carbon atom is even wider (135.5°). The dialkylamino groups push the hypersilyl hemi-

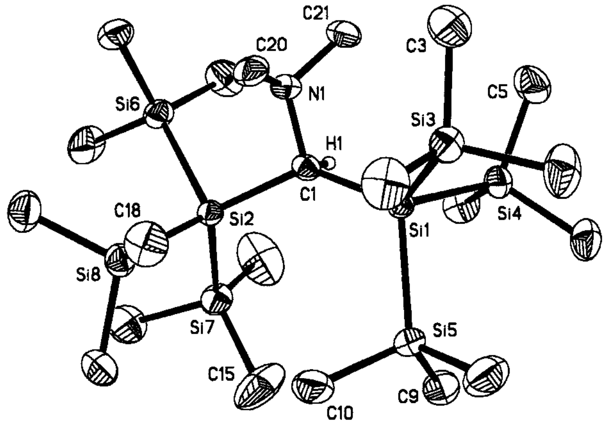


Figure 1. Molecular structure of **5a** in the crystal (ORTEP, 30% probability level, H atoms omitted except for C1H); selected bond lengths [Å] and angles [°]: C1−Si12.009(7), C1−Si2 1.947(6), C1−N1 1.493(7); Si1−C1−Si2 132.6(3), C1−Si1−Si3 120.1(2), C1−Si1−Si4 106.6(2), C1−Si1−Si5 116.9(2), C1−Si2−Si6 98.7(2), C1−Si2−Si7 114.8(2), C1−Si2−Si8 122.3(2), Si1−C1−N1 114.2(4), Si2−C1−N1 102.9(4), C1−N1−C21 115.0(5), C1−N1−C20 113.4(5), C20−N1−C21 112.5(6)

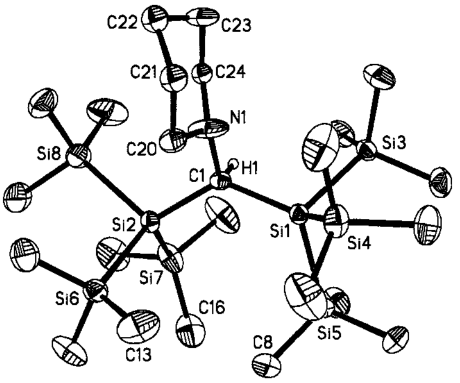
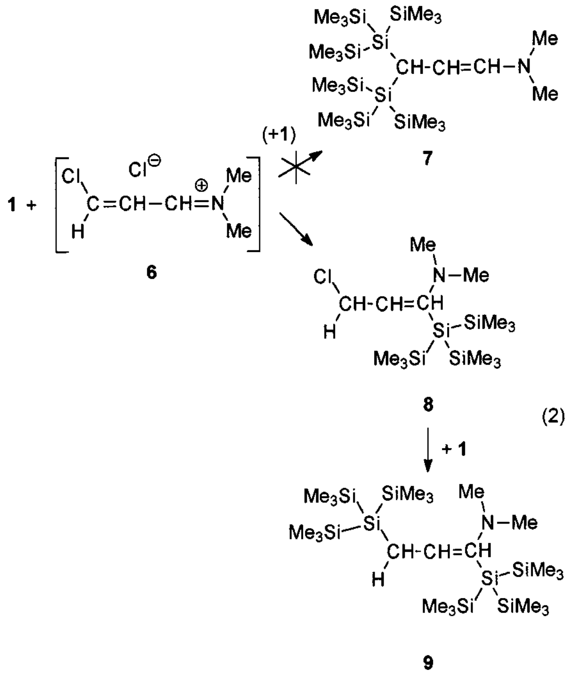


Figure 2. Molecular structure of **5c** in the crystal (ORTEP, 30% probability level, H atoms omitted except for C1 H, disordered atoms omitted for clarity); selected bond lengths [Å] and angles [°]: C1−Si1 1.992(3), C1−Si2 1.967(3), C1−N1 1.472(4); Si1−C1−Si2 128.7(2), C1−Si1−Si3 104.57(11), C1−Si1−Si4 120.96(11), C1−Si1−Si5 118.44(11), C1−Si2−Si6 120.76(12), C1−Si2−Si8 110.94(11), C1−Si2−Si7 109.29(11), N1−C1−Si1 107.1(2), N1−C1−Si2 114.0(2)

spheres aside causing a deformation of the $CSiSi_3$ tetrahedra in **5a** and **5c**. The average C1−Si−Si bond angles in **5a** are 111.8 and 114.5°, and for **5c** 114.7 and 113.7°, but the individual angles are markedly different. At positions where the two hemispheres touch each other, the angles are widened (**5a**: C1−Si1−Si5 116.9°, C1−Si2−Si8 122.3°; **5c**: C1−Si1−Si5 118.4°, C1−Si2−Si6 120.8°). On the other hand, the small hydrogen atoms at the central sp^3-carbon atoms of **5a** and **5c** allow the trimethylsilyl groups in their neighborhood to evade the steric strain leading to comparatively small C−Si−Si angles (**5a**: C1−Si1−Si4 106.6°, C1−Si2−Si6 98.7°; **5c**: C1−Si1−Si3 104.6°, C1−Si2−Si7 109.3°). Due to the steric stress in the molecule, the trimethylsilyl groups approach at exceptionally short distances (**5a**: C9−C15 3.64 Å, C10−C18 3.82 Å; **5c**: C8−C13 3.66, C8−C16 3.51 Å). Also the distances of the *N*-methyl groups in **5a** to the neighboring *Si*-methyl groups (C3−C20 3.62 Å, C3−C21 3.56 Å, C5−C21 3.57 Å) are significantly shorter than the sum of the van der Waals radii of two methyl groups which amounts to about 4.00 Å.[3]

Extensive variation of the reaction outlined in Equation 1 is limited by the spatial demand of the dialkylamino substituent. However, an attractive aim was the synthesis of [2-(dimethylamino)ethenyl]bis[tris(trimethylsilyl)silyl]methane (**7**), which was intended to be achieved by the reaction of two equivalents of **1** with the vinylogous (3-chloro-2-propenylidene)dimethylammonium salt **6**. We hoped that both tris(trimethylsilyl)silyl groups may be drawn to the γ-position of the dimethyliminium salt. Two products, identified as 3-chloro-1-(dimethylamino)-1-[tris(trimethylsilyl)silyl]-1-propene (**8**) (50%) and 1-(dimethylamino)-1,3-bis[tris(trimethylsilyl)silyl]-1-propene (**9**) (13%) were, however, obtained as the result of the reaction of these components (Equation 2).

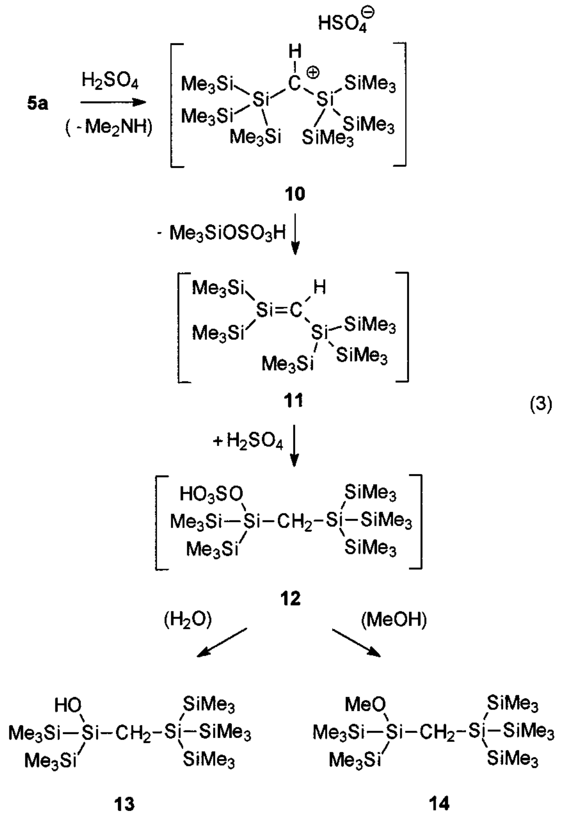


(2)

This result indicates that the first attack of the silicon nucleophile **1** occured at the α-carbon atom of the dimethyliminium chloride **6** affording **8**, and in a second reaction step the γ-chlorine atom of **8** was replaced by a further hypersilyl substituent giving **9**. A geminal bis(hypersilyl) compound could not be obtained this way.

The Conversion of 5a into the Transient 1,1-Bis(trimethylsilyl)-2-tris(trimethylsilyl)silylsilene (11) According to an Acid-Induced Sila Peterson Mechanism

Apart from their thermal instability due to the perfect shielding of the functional group, the geminal (dialkylamino)bis(hypersilyl)methanes **5a−c** were expected to be chemically rather inert. However, we noticed that **5a**, which was chosen for some studies on the reactivity of these compounds, undergoes a clean reaction with concentrated sulfuric acid. Actually, the conversion of **5a** by excess H_2SO_4 needed three days at room temperature to come to completeness, but aqueous workup afforded the silanol **13** in a yield of 60%. Workup of the same reaction mixture with methanol gave the methoxysilane **14** (30%) besides 40% of **13** (Equation 3).



(3)

The structures of **13** and **14** were proved by comprehensive spectroscopic analyses (see Experimental Section). For methoxybis(trimethylsilyl)[tris(trimethylsilyl)silylmethyl]silane (**14**) an X-ray crystal structure analysis was also performed (Figure 3), which again revealed considerable steric congestion of the molecule. The central Si−C bonds are elongated (C1−Si1 1.91 Å, C1−Si2 1.87 Å) and the angle at the methylene carbon atom is widened to a value of 123.9°.

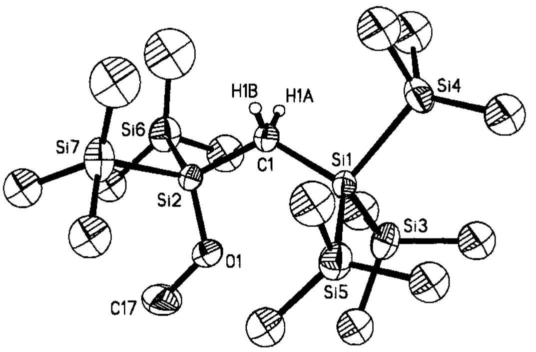


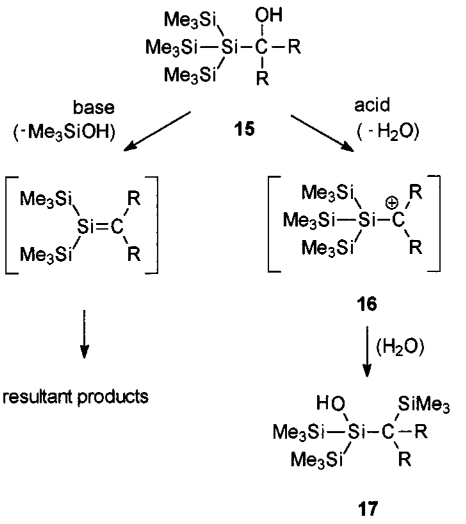
Figure 3. Molecular structure of **14** in the crystal (ORTEP, 30% probability, H atoms omitted except for C1 H$_2$, disordered atoms omitted for clarity); selected bond lengths [Å] and angles [°]: C1−Si1 1.914(5), C1−Si2 1.865(5), Si2−O1 1.644(4), O1−C171.432(7); Si1−C1−Si2 123.9(3), C1−Si1−Si3 113.2(2), C1−Si1−Si4 101.1(2), C1−Si1−Si5 115.1(2), C1−Si2−O1 106.2(2), C1−Si2−Si6 108.8(2), C1−Si2−Si7 111.5(2), Si2−O1−C17 124.1(4).

The formation of **13** and **14** is understood in terms of an acid-induced elimination of dimethylamine from **5a** under generation of the carbenium ion transition state **10**. Nucleophilic attack of the hydrogen sulfate ion at one trimethylsilyl group under cleavage of an Si−Si bond affords the silene **11**, which in the presence of excess sulfuric acid is trapped to give the silyl hydrogen sulfate **12**. Hydrolysis of **12** during the aqueous workup leads to the silanol **13**; methanolysis of **12** affords the methoxysilane **14**.

The conversion of **5a** into the silene **11** has to be interpreted as a direct Si analogue of the acid-catalyzed Peterson reaction. The original Peterson reaction, i.e. the elimination of trimethylsilanol from (2-hydroxyalkyl)trimethylsilanes with simultaneous formation of olefins, can be performed under basic as well as under acidic conditions.[4] The reaction priciple was modified in such a way, that the α-carbon atom in the (2-hydroxyalkyl)trimethylsilanes was replaced by a silicon atom. Thus, (1-hydroxyalkyl)tris(trimethylsilyl)silanes **15**, easily available by the reaction of tris(trimethylsilyl)silylmagnesium bromide with carbonyl compounds, were subjected to the conditions of the Peterson reaction and proved to be suitable starting materials for the generation of transient silaethenes according to the base-induced sila Peterson mechanism (Equation 4).[5]

On the other hand, treatment of **15** with strong acids gives no trimethylsilanol elimination and silene generation, but the (1-hydroxyalkyl)polysilanes **15** undergo a rapid isomerisation, involving a 1,2-OH/Me$_3$Si exchange, under formation of the silanols **17**.[6] Similar to the reaction **5a** → **13**, this rearrangement is also supposed to proceed through a polysilanylcarbenium ion transition state **16**, but here the 1,2-trimethylsilyl migration is favored over the Me$_3$SiX elimination (Equation 4).

The migration of one group from a tetracoordinated silicon atom to a nascent α-carbenium ion under generation of a thermodynamically more stable transient silylium ion appears to be a general process.[7] We suppose that this fast rearrangement generally prevents a trimethylsilanol elimination from polysilanylcarbenium ion transition states such as **16** and a silene formation along the acid-catalyzed modified Peterson mechanism. In case of the conversion **5a** → **13**, due to the extreme steric congestion of the carbenium ion **10** a shift of a trimethylsilyl group from the silicon atom to the central carbon atom is prevented or at least retarded for steric reasons, favoring in this particular case the nucleophilic attack of the hydrogen sulfate ion and the silene generation.



(4)

Experimental Section

General: All reactions involving organometallic reagents were carried out under purified argon. − NMR: Bruker AC 250 or Bruker ARX 300, tetramethylsilane as internal standard. − IR: Nicolet 205 FT-IR. − MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas. − The dialkyl(chloromethylene)ammonium chlorides were prepared using the procedure of Simchen et al.[8] applying bis(trichloromethyl) carbonate instead of phosgene as the chlorinating agent. (Me$_3$Si)$_3$SiLi · 3 THF was prepared as reported in the literature.[9] − All yields given refer to amounts obtained after chromatographic separation and purification. − The synthesis and structure of **5a** were described in a preliminary publication.[10]

(Diethylamino)bis[tris(trimethylsilyl)silyl]methane (5b): Under stirring, 0.82 g (1.7 mmol) of **1**, dissolved in 20 mL of ether, was added dropwise into a solution of 0.14 g (0.9 mmol) of (chloromethylene)diethylammonium chloride in 20 mL of ether at −78°C. Stirring was continued for another hour at the same temperature and for 2 h at room temperature. After addition of water, the ethereal phase was separated, dried, and concentrated. The residue was purified by chromatography (triethylamine-treated silica gel, heptane) to obtain 0.35 g of impure **5b** containing hexakis(trimethylsilyl)disilane and tris(trimethylsilyl)silane. − ^{1}H NMR ([D$_6$]benzene): δ = 0.38 (s, SiCH$_3$, 54 H), 1.04 and 1.09 (2 t, ^3J = 7.3 Hz, CCH$_3$, 2 × 3 H), 2.48 and 2.67 (2 q, ^3J = 7.3 Hz, CH$_2$, 2 × 2 H), 3.82 (s, CH, 1 H).

Bis[tris(trimethylsilyl)silyl]piperidylmethane (5c): Similarly, 1.3 g (2.8 mmol) of **1** and 0.23 g (1.4 mmol) (chloromethylene)piperidinium chloride gave, after chromatographic separation (silica gel, heptane), 0.35 g (43%) of **5c**, m.p. 112−113°C. − ^{1}H NMR

([D$_6$]benzene): δ = 0.39 (s, $SiCH_3$, 54 H), 1.41 (m, CH_2, 2H), 1.56 (m, CH_2, 4 H), 2.53 (t, ^3J = 5.2 Hz, NCH_2, 4 H), 3.43 (s, Si_2CHN, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = 4.7 ($SiCH_3$), 22.2, 25.6 and 32.2 (CH_2), 46.2 (CH). − ^{29}Si NMR ([D$_6$]benzene): δ = −74.6 (*Si*$SiMe_3$), −12.1 ($SiMe_3$). − MS; *m/z* (%): 590 (1) [M^+ − H], 344 (56) [M^+ − $Si(SiMe_3)_3$], 247 (100) [$Si(SiMe_3)_3{}^+$], 73 (64) [$SiMe_3{}^+$]. − $C_{24}H_{65}NSi_8$ (592.47): calcd. C 48.65, H 11.06, N 2.36; found C 46.54 (incomplete combustion), H 10.88, N 2.40.

Reaction of the Vinylogous (3-Chloro-2-propenylidene)dimethylammonium Salt 6 with 1. − Synthesis of (*E*)-3-Chloro-1-(dimethylamino)-1-[tris(trimethylsilyl)silyl]-1-propene (8) and (*E*)-1-(Dimethylamino)-1,3-bis[tris(trimethylsilyl)silyl]-1-propene (9): To a solution of 0.08 g (0.5 mmol) of **6** in 20 mL of ether, was added dropwise at −78°C, 0.49 g (1.0 mmol) of **1**, dissolved in 20 mL of ether. After warming up to room temperature, stirring was continued for 3 h. Water was added, the ethereal layer separated, dried, and concentrated. Chromatographic separation (silica gel, heptane/ethyl acetate, 20:1) gave 0.09 g (49%) of **8** (m.p. 124−126°C) and 0.04 g (13%) of **9** (m.p. 74−76°C).

8: ^{1}H NMR ([D$_6$]benzene): δ = 0.25 (s, $SiCH_3$, 27 H), 2.10 (s, NCH_3, 6 H), 3.14 (d, ^3J = 11.58 Hz, SiCHN, 1 H), 5.71 (d, ^3J = 13.13 Hz, CHCl, 1 H), 6.09 (dd, ^3J = 11.58 Hz, ^3J = 13.13, ClCCH, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = 1.9 ($SiCH_3$), 43.7 (NCH_3), 58.0 (CHN), 116.9 (ClC=*C*H), 131.8 (Cl*C*=CH). − ^{29}Si NMR ([D$_6$]benzene): δ = −73.8 (*Si*$SiMe_3$), −12.8 ($SiMe_3$). − MS; *m/z* (%): 366 (10) [M^+ − H], 350 (9) [M^+ − CH_3], 247 (8) [$Si(SiMe_3)_3{}^+$], 118 (100) [M^+ − $Si(SiMe_3)_3$], 73 (33) [$SiMe_3{}^+$]. − $C_{14}H_{36}ClNSi_4$ (366.24): calcd. C 45.91, H 9.91, Cl 9.68, N 3.82; found C 46.23, H 9.81, Cl 8.97, N 3.88.

9: ^{1}H NMR ([D$_6$]benzene): δ = 0.32 and 0.33 (2s, $SiCH_3$, 2 × 27 H), 2.30 (s, NCH_3, 6 H), 3.25 (d, ^3J = 10.38 Hz, SiCHN, 1 H), 5.67 (d, ^3J = 17.70 Hz, SiCH, 1 H), 6.27 (dd, ^3J = 10.38 Hz, ^3J = 17.90 Hz, NCCH, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = 1.4 and 2.2 ($SiCH_3$), 43.6 (NCH_3), 65.4 (CHN), 125.3 (SiC=*C*H), 145.4 (Si*C*=CH). − ^{29}Si NMR ([D$_6$]benzene): δ = −86.3 and −77.0 (*Si*$SiMe_3$), −13.1 and −12.8 ($SiMe_3$). − MS; *m/z* (%): 576 (2) [M^+ − H], 562 (8) [M^+ − CH_3], 533 (4) [M^+ − NMe_2], 330 (100) [M^+ − $Si(SiMe_3)_3$], 247 (9) [$Si(SiMe_3)_3{}^+$], 73 (14) [$SiMe_3{}^+$]. − $C_{23}H_{63}NSi_8$ (578.44): calcd. C 47.76, H 10.98, N 2.42; found C 47.91, H 10.86, N 2.66.

Bis(trimethylsilyl)[tris(trimethylsilyl)silylmethyl]silanol (13): To a solution of 0.1 g (0.18 mmol) of **5a** in 20 mL of THF, 2 mL of conc. H_2SO_4 was added gradually and the mixture was stirred for 3 d at room temperature. Then water was added, the mixture was extracted with ether and the combined extracts were neutralized with solid K_2CO_3 dried, and concentrated. Chromatographic separation (silica gel, heptane) of the residue gave 0.05 g (60%) of **13**, m.p. 65−67°C. − IR (nujol): $\tilde{\nu}$ = 3672 cm^{-1} (OH_{free}), 3360−3580 cm^{-1} ($OH_{ass.}$). − ^{1}H NMR ([D$_6$]benzene): δ = 0.18 (s, $SiCH_3$, 18 H), 0.31 (s, $SiCH_3$, 27 H), 0.46 (s, CH_2, 2 H). − ^{13}C NMR ([D$_6$]benzene): δ = −10.1 ($SiCH_2Si$), −0.93 {$Si[Si(CH_3)_3]_2$}, 1.46 {$Si[Si(CH_3)_3]_3$}. − ^{29}Si NMR ([D$_6$]benzene): δ = −83.1 [*Si*$(SiMe_3)_3$], −19.6 [Si(*Si*$Me_3)_2$], −12.6 [Si(*Si*$Me_3)_3$], 8.9 (SiOH). − MS; *m/z* (%): 451 (3) [M^+ − H], 437 (17) [M^+ − CH_3], 435 (10) [M^+ − OH], 379 (100) [M^+ − $SiMe_3$], 343 (51) [M^+ − $HOSiMe_3$], 247 (4) [$Si(SiMe_3)_3{}^+$]. − $C_{16}H_{48}OSi_7$ (453.16): calcd. C 42.41, H 10.68; found C 41.67 (incomplete combustion), H 10.40.

Methoxybis(trimethylsilyl)[tris(trimethylsilyl)silylmethyl]silane (14): A solution of 0.16 g (0.29 mmol) of **5a** and 2.0 mL of H_2SO_4 in 20 mL THF was stirred for 3 d at room temperature. After addition of 5 mL of dry methanol, stirring was continued for 1 h. Then water was added and the mixture was immediately extracted with ether. The ethereal extracts were dried and concentrated. Chromatographic separation of the residue (silica gel, heptane) gave 0.04 g (30%) of **14** besides 0.05 g (40%) of **13**.

14: ^{1}H NMR ([D$_6$]benzene): δ = 0.22 (s, $SiCH_3$, 18 H), 0.32 (s, $SiCH_3$, 27 H), 0.43 (s, CH_2, 2 H), 3.25 (s, $SiOCH_3$). − ^{13}C NMR ([D$_6$]benzene): δ = −11.7 (CH_2), −0.3 {$Si[Si(CH_3)_3]_2$}, 1.14 {$Si[Si(CH_3)_3]_3$}, 52.1 ($SiOCH_3$). − ^{29}Si NMR ([D$_6$]benzene): δ = −81.4 [*Si*$(SiMe_3)_3$], −19.9 [Si(*Si*$Me_3)_2$], −12.2 [Si(*Si*$Me_3)_3$], 13.9 (SiOMe). − MS; *m/z* (%): 465 (0.1) [M^+ − H], 451 (9) [M^+ − CH_3], 393 (100) [M^+ − $SiMe_3$], 247 (5) [$Si(SiMe_3)_3{}^+$], 73 (47) [$SiMe_3{}^+$]. − $C_{17}H_{50}OSi_7$ (466.22): calcd. C 43.76, H 10.81; found C 43.19, H 11.00.

Crystal-Structure Determination of 5c and 14: The crystal-structure determinations were performed with a STOE IPDS diffractometer using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS-86)[11] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[12] XP (Siemens Analytical X-ray Instruments) was used for structure representations. The X-ray analysis of **5c** revealed disorder for the piperidyl ring. For **14** complete disorder for all methyl groups of the trimethylsilyl substituents was found. Further details are compiled in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101350 (**5a**),[10] -102955 (**5c**), and -102956 (**14**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal structure data of **5c** and **14**

	5c	**14**
Formula	$C_{24}H_{65}NSi_8$	$C_{17}H_{50}OSi_7$
M [g mol^{-1}]	592.49	467.20
a [Å]	29.838(6)	9.101(2)
b [Å]	12.288(3)	11.745(2)
c [Å]	21.092(4)	16.690(3)
α [°]	90	98.05(3)
β [°]	90	101.17(3)
γ [°]	90	108.74(3)
V [Å^3]	7733.4(27)	1643.8(5)
ρ [g cm^{-3}]	1.018	0.944
Z	8	2
Crystal system	orthorhombic	triclinic
Space group	*Pccn*	*P*−1
μ (Mo-K_α) [mm^{-1}]	0.291	0.296
Crystal size [mm]	0.3 × 0.3 × 0.4	0.4 × 0.4 × 0.6
Temperature [°C]	293(2)	293(2)
Scan range (θ) [°]	1.79−21.03	1.88−24.17
hkl range	0/29, −12/12, −21/21	−10/10, −13/13, 0/19
Measured refl.	14676	4872
Unique refl.	4120	4872
Observed refl.	2880	2462
Refined param.	299	213
$R1$ [$I > 2\sigma(I)$]	0.0397	0.0665
$R1$ for all	0.0624	0.1227
GoF	0.962/1.108	0.887/1.138

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