Synthesis and Structure of Methoxybis[tris(trimethylsilyl)silyl]methane – The First Geminal Di(hypersilyl) Compound with a Central Carbon Atom

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Methoxy-bis[tris(trimethylsilyl)silyl]methane (**4**), the first compound bearing two hypersilyl groups at a carbon atom, was synthesized by the reaction of tris(trimethylsilyl)silyllithium with dichloromethyl methyl ether. As a byproduct of the reaction, 1,2-dimethoxy-1,2-bis[tris(trimethylsilyl)silyl]ethane (**5**) could be identified. Possible pathways leading to **4** and **5** are discussed. The structure of **4**, elucidated by an X-ray crystal structure analysis, is characterized by tremendous distortions of the molecular skeleton due to the spatial demand of the two extended hemispherical $(Me_3Si)_3Si$ groups. For example, the central Si–C–Si angle is widened to 132.7°, the trimethylsilyl groups of the two hypersilyl substituents are pressed together to give an average Si–Si–Si angle of 105.6°, and the methoxy carbon atom and the nearest neighboring trimethylsilyl carbon atom approach to a distance of 3.25 Å, i.e. approx. 19% less than the sum of the van der Waals radii of two methyl groups.

The tris(trimethylsilyl)silyl group, the hypersilyl group[1], proved to be a function with unusual steric and electronic properties as well as a broad synthetic utility. The three trimethylsilyl substituents and the center silicon atom form an extended hemispherical shield providing the center, to which the $(Me_3Si)_3Si$ group is fixed, with an exceptional steric protection. This was discussed in terms of the cone angles of the substituent (which was calculated to be 199° for the $C-Si(SiMe_3)_3$ group)[2] and was also demonstrated by structure analyses of e.g. hexakis(trimethylsilyl)disilane $(Me_3Si)_3SiSi(SiMe_3)_3$[3a,3b,4] and 1,4-bis[tris(trimethylsilyl)silyl]benzene $(Me_3Si)_3Si-C_6H_4-Si(SiMe_3)_3$[3a,3c]. The ability of the $(Me_3Si)_3Si$ substituent to act as a π-acceptor was discovered by West et al. in the course of ESR studies of the phenyltris(trimethylsilyl)silane radical anion[5], and Bock et al. demonstrated that radical anions as well as radical cations of the aforementioned compounds are stabilized by delocalizing the negative or positive charge, resp., into the polysilanyl groups[3a,3c–d]. Concerning the synthetic use of tris(trimethylsilyl)silyl derivatives, only the pioneering work of Brook et al. leading to the generation of stable silenes by photolysis of acyltris(trimethylsilyl)silanes should be mentioned[6]. In our group 1-hydroxyalkyl-tris(trimethylsilyl)silanes were successfully converted into transient silenes according to a modified Peterson mechanism[7].

Of special interest – particularly from a structural point of view – are di(hypersilyl) compounds, in which two extremely bulky $(Me_3Si)_3Si$ substituents are fixed at the same central atom. The spatial demand of the two hemispherical groups is expected to cause tremendous steric distortions of the molecular skeleton. Some of those derivatives, mainly of transition metals and of heavier main group elements, were prepared and for a few compounds also X-ray crystal structure data are available. Thus, for $(Me_3Si)_3Si-Zn-Si(SiMe_3)_3$ a linear coordination at the zinc atom was found[8]. The Si–Fe–Si angle in the $[(Me_3Si)_3Si-Fe(Cl)-Si(SiMe_3)_3]^-$ anion is 136.9°[9]. The Si–Tl–Si angle in tetrakis(hypersilyl)dithallium was determined to be 125.1°[10]. Compared with an ideal tetrahedral structure, the Si–Sn–Si angle found to be 142.5° for $(Me_3Si)_3Si-SnCl_2-Si(SiMe_3)_3$ is considerably widened[11]. On the other hand, for $[(Me_3Si)_3Si]_2Sn \cdot LiBr \cdot 3\,THF$ an Si–Sn–Si angle of only 114.2° was reported[12]. $[(Me_3Si)_3Si]_2Ga(Cl)_2Li \cdot 2\,THF$ shows an Si–Ga–Si angle of 138.0°; the Si–In–Si angle of the analogous indium compound is 139.9°[13]. $(Me_3Si)_3Si-SiMe_2-Si(SiMe_3)_3$ was obtained by aluminium chloride-catalyzed rearrangement of permethylated polysilanes, but was not structurally characterized[14]. There are reports in the literature about unsuccessful attempts of the synthesis of bis[tris(trimethylsilyl)silyl] derivatives of germanium[11,15] and silicon[11,16]; on the other hand, Noeth et al. succeeded in synthesizing bis[tris(trimethylsilyl)silyl]boron derivatives[17]. Geminal bis[tris(trimethylsilyl)silyl] compounds with a central carbon atom were unknown so far.

Results and Discussion

In view of the extreme bulkiness of the hypersilyl substituent the fixation of two $(Me_3Si)_3Si$ groups at one comparatively small carbon atom appears to be a difficult undertaking. The more surprising was the result that tris(trimethylsilyl)silyllithium (**1**) reacts with dichloromethyl methyl ether under mild conditions to give a complex mix-

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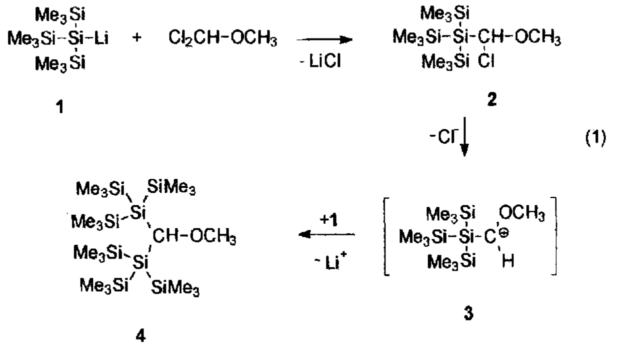
ture of products, from which methoxybis[tris(trimethylsilyl)silyl]methane (4) could be separated in a yield of 35%. The raw material, thus obtained, is contaminated with approx. 5% of a compound (5) behaving very similarly and which could not be separated chromatographically or by sublimation. But slow crystallization from ethanol gave pure 4 as colorless air-stable crystals.



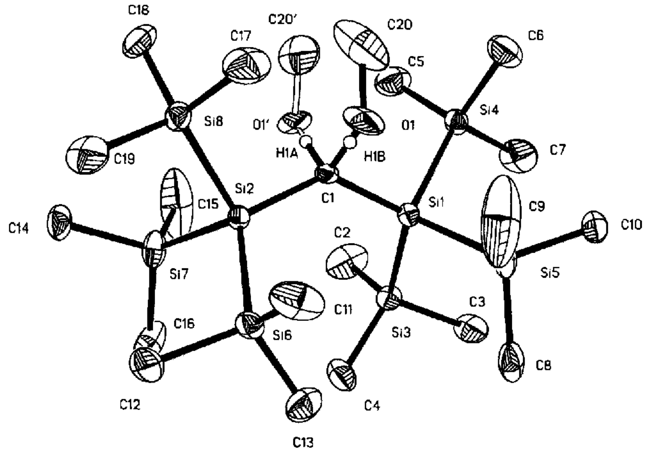
(1)

The formation of 4 is easily understood as a consecutive replacement of the two chlorine atoms of the dichloromethyl methyl ether by the silanide 1 (equation 1). Obviously, after replacement of the first chlorine atom of this ether by a hypersilyl group, the approach of the second lithium silanide 1 to the central sp^3 carbon atom of the intermediate 2 under conditions of a bimolecular nucleophilic substitution, i.e. with inversion of the configuration at the reaction center, is hardly conceivable due to the extreme steric shielding by the $(Me_3Si)_3Si$ group. Therefore, we suppose that the reaction proceeds via a carbenium ion transition state 3, which is easily formed because it is stabilized by the methoxy group as well as the polysilanyl substituent. Thus, the silicon nucleophile 1 can attack the electrophilic carbon atom from the "front side", and steric problems caused by already fixed substituents become less significant. Unfortunately, the complex composition of the reaction mixture did not allow a kinetic control of the formation of compound 4. Thus, the suggestions made are still unproven.

The structure of 4 was elucidated on the basis of NMR and MS data and is in full agreement with the results of an X-ray crystal structure analysis.

The crystals are considerably disordered. Thus, there are two possible configurations at C-1, that obviously occur approximately in a 1:1 ratio. The diffraction pattern is very similar to that of a structure with a twofold axis through C-1. Indeed, the automatic cell determination procedure of xscans (Siemens xscans V 2.10, 1994, Siemens Analytical X-ray Inst. Inc.) proposes a C-centered cell very soon and the Laue class *2/m*. After finishing the data collection, the automatic space group determination of SHELXTL would lead to the space group *C2*. A structure solution in *C2* is possible and consequently half the molecule is found in the asymmetric unit with C-1 in a special position (C_2 axis – pretended by the disorder problem). Consequently, in *C2* the number of reflections with poor fit is fairly high. In *P*1 the structure solution proceeds without any complication and the refinement reveals that all six trimethylsilyl groups possess a certain tendency for a rotation around the Si−Si bond.

Figure 1. Molecular structure of 4 in the crystal (H atoms omitted, ORTEP, 50% probability level)



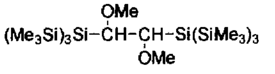
Selected bond lengths [Å] and angles [°]: C1−Si1 1.942(7), C1−Si2 1.954(7), C1−O1 1.471(18), O1−C20 1.371(10), Si1−Si4 2.381(3), Si1−Si5 2.374(3), Si1−Si3 2.355(3), Si2−Si6 2.358(3), Si2−Si7 2.370(3), Si2−Si8 2.372(3), C6−C20 3.25(3), C17−C20 3.30(3); Si1−C1−Si2 132.69(37), C1−Si1−Si3 120.31(25), C1−Si1−Si4 105.45(23), C1−Si1−Si5 111.98(25), C1−Si2−Si6 120.02(24), C1−Si2−Si7 111.64(26), C1−Si2−Si8 105.83(23), Si3−Si1−Si4 103.68(10), Si3−Si1−Si5 108.02(12), Si4−Si1−Si5 106.17(11), Si6−Si2−Si7 108.25(11), Si6−Si2−Si8 103.86(10), Si7−Si2−Si8 106.06(11), Si1−C1−O1 101.59(68), Si2−C1−O1 108.56(69), O1−C1−O1′ 98.86(113).

The results of the X-ray analysis give a good idea on the steric congestion in the molecule. As we see in Figure 1 the two hemispherical shells of the $(Me_3Si)_3Si$ groups, separated by one sp^3 carbon atom as a spacer, are squeezed together at one side and open a narrow slit, where the methoxy group and the hydrogen atom are placed. The spatial demand of the two $(Me_3Si)_3Si$ groups forces an extreme widening of the Si1−C1−Si2 angle to a value of 132.7° and additionally also the central carbon−silicon bonds are significantly elongated (C1−Si1 1.94 Å; C1−Si2 1.95 Å). Consequently, the Si−Si−Si angles in the $(Me_3Si)_3Si$ proups are pressed together, the average angle being 106.0°. Interestingly, in $[(Me_3Si)_3Si]_2SnCl_2$ due to the longer Si−Sn bond distances the average Si−Si−Si angle is 110.9°[11], which is only a little smaller than the average Si−Si−Si angle of 112.2° found for $[Si(SiMe_3)_3]_2Zn$, in which the linear Si−Zn−Si skeleton minimizes the steric strain of the two hypersilyl groups[8]. On the other hand, the average bond angles C1−Si1−Si and C1−Si2−Si of more than 112.5° are rather high, but the values of the individual angles differ remarkably. At the positions, where the two hemispheres contact each other, the angles are widened (C1−Si1−Si3 120.3°, C1−Si1−Si5 112.0°, C1−Si2−Si7 111.6°, C1−Si2−Si6 120.0°) and the whole shell is pushed aside with deformation of the originally tetrahedral configuration at the central silicon atom pressing the C1−Si1−Si4 angle (105.4°) and the C1−Si2−Si8 angle (105.8°) together. The methoxy group is fully enclosed by the $(Me_3Si)_3Si$ hemispheres, filling the gap between these two shells. Thus, the intramolecular distances between the methoxy carbon atom and the next neighboring Me_3Si carbon atoms are extremely short. The distances C6–C20 (3.25 Å) and C17–C20 (3.30 Å) are approx. 19% or 17.5%, resp., i.e. smaller than the sum of the van der Waals radii of two methyl groups amounting to about 4.00 Å[18].

Contrary to our expectations the solution NMR data of compound **4** are very straightforward. The ^{1}H-NMR spectrum shows only three signals with the correct intensities of 54:3:1. Also the ^{13}C-NMR spectrum consists of only three, the ^{29}Si-NMR spectrum of two signals. Dynamic NMR studies up to −80°C did not change the signal patterns. The magnetic equivalence of all six trimethylsilyl groups is really surprising and may suggest the picture of a cogwheel like gearing of the two $(Me_3Si)_3Si$ hemispheres. The data available till now do not allow us to give a description of the molecular dynamics of **4**, but a deeper insight into these processes is expected from solid-state NMR studies, the results of which will be communicated separately.

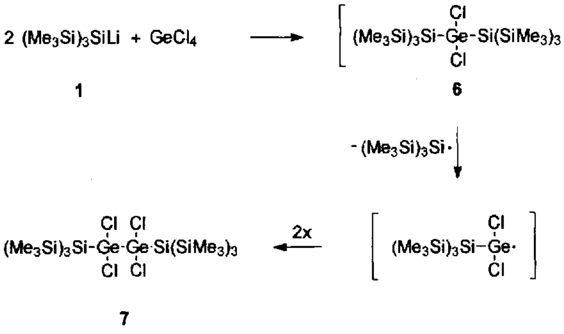
The extreme steric congestion gives rise to a remarkable chemical inertness of **4**. The two $(Me_3Si)_3Si$ groups are expected to stabilize anionic as well as cationic intermediates and the respective derivatives of **4** should be formed quite easily. But we did not succeed in realizing an acid-promoted elimination of the methoxy group by reaction with e.g. HCl. Whereas 1-hydroxyalkyl-tris(trimethylsilyl)silanes $(Me_3Si)_3Si-C(OH)RR'$ in the presence of an acid easily eliminate water to form carbenium ion transition states which undergo further rearrangements[19], the treatment of **4** under similar conditions let the compound unchanged. Obviously, the methoxy oxygen atom is perfectly shielded, so that its protonation and the elimination of methanol failed. Similarly, attempts of the deprotonation of **4** by strong bases, e.g. by organolithium reagents, to give a carbanion, stabilized by two neighboring $(Me_3Si)_3Si$ substituents, were unsuccessful. Unfortunately, also Si,Si-cleavage reactions by a prolonged interaction of **4** with methyllithium in THF – comparable with the extensively used preparation of $(Me_3Si)_3Si-Li$ by the reaction of tetrakis(trimethylsilyl)silane with MeLi[20] – affording the lithium silanide $(Me_3Si)_3SiCH(OMe)SiLi(SiMe_3)_2$ could not be performed. After all these experiments, **4** was recovered unchanged.

Compound **5**, obtained as a byproduct in the course of the synthesis of **4**, could not be isolated in a pure form. But NMR and MS studies of mixures of **5** containing approx. 70% of **4**, unambiguously revealed its structure as 1,2-dimethoxy-1,2-bis[tris(trimethylsilyl)silyl]ethane (**5**). This is interesting, since a similarly structured digermane **7** was described by Geanangel et al. as the result of an attempted synthesis of dichloro-di(hypersilyl)germane (**6**) by the reaction of germanium tetrachloride with **1** (eq. 2)[15]. They suppose the germane **6** to be unstable because of the steric strain caused by the two $(Me_3Si)_3Si$ substituents, and discuss a homolytic Ge–Si bond scission and a subsequent dimerization of the germyl radical to give **7**. In contrast, compound **4**, as described, proved to be stable. Also prolonged heating of **4** in boiling THF gave no **5**. So the formation of **5** along a pathway comparable to the suggested route to the digermane **7** is rather unlikely. Therefore, we suggest an alternative and plausible mechanism consisting in a partial metal-halogen exchange reaction between the lithium silanide **1** and the polysilanyl chloroether **2** to give the organolithium intermediate $(Me_3Si)_3Si-CHLi(OMe)$, which undergoes a coupling reaction with **2** to afford **5**.



$$(Me_3Si)_3Si-\overset{OMe}{C}H-\underset{OMe}{C}H-Si(SiMe_3)_3$$

5



(2)

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Experimental

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. – $(Me_3Si)_3SiLi \cdot 3$ THF was prepared as reported in the literature[21].

Reaction of **1** *with Dichloromethyl Methyl Ether:* To a solution of 1.9 g ($4 \cdot 10^{-3}$ mol) of $(Me_3Si)_3SiLi \cdot 3$ THF (**1**) in 70 ml of diethyl ether, an ethereal solution of 0.24 g ($2 \cdot 10^{-3}$ mol) of dichloromethyl methyl ether was added at room temperature and the mixture was stirred for 3 h. After addition of an aqueous NH_4Cl solution the organic material was extracted several times with ether, the combined extracts were dried and the solvent was evaporated. Chromatographic separation of the semisolid residue (silica gel, heptane) and recrystallization of the target product from ethanol gave 0.38 g (35%) of **4** contaminated with approx. 5% of **5**. Repeated recrystallization from ethanol furnished pure **4**: Colorless crystals, m.p. 190–192°C. – IR (nujol): $\tilde{\nu}$ = 1069 cm^{-1} (OCH_3). – ^{1}H-NMR ([D$_6$]benzene): δ = 0.36 (s, $SiCH_3$, 54H), 3.18 (s, OCH_3, 3H), 4.18 (s, CH, 1H). – ^{13}C NMR ([D$_6$]benzene): δ = 1.1 ($SiCH_3$), 59.3 (CH), 61.9 (OCH_3). – ^{29}Si NMR ([D$_6$]benzene): δ = −68.3 (*Si*SiMe$_3$), −12.8 ($SiMe_3$). – MS, *m/z* (%): 537 (13) [$M^+ - H$], 523 (85) [$M^+ - CH_3$], 507 (13) [$M^+ - OCH_3$], 465 (8) [$M^+ - SiMe_3$], 434 (27) [$M^+ - OCH_3 - SiMe_3$], 291 (100) [$M^+ - Si(SiMe_3)_3$]. – $C_{20}H_{58}OSi_8$ (539.4): calcd. C 44.54, H 10.84; found C 43.44, H 11.19.

After the separation of several fractions of **4**, by concentration of the ethanolic mother liquor a colorless solid was obtained consisting of **4** and **5** in a molar ratio of approx. 2.5:1. Abstracting the known signals for **4** we could assign the following spectral data to compound **5**: IR (nujol): $\tilde{\nu}$ = 1075 cm^{-1} (OCH_3). – ^1H NMR ([D_6]benzene): δ = 0.34 (s, $SiCH_3$, 54 H), 3.33 (s, OCH_3, 6 H), 4.12 (s, CH, 2 H). – ^{13}C NMR ([D_6]benzene): δ = 0.0 ($SiCH_3$), 56.7 (CH), 79.5 (OCH_3). – ^{29}Si NMR ([D_6]benzene): δ = −79.5 (*Si*-$SiMe_3$), −12.7 ($SiMe_3$). – MS, *m/z* (%): 582 (0.4) [M^+], 567 (10) [$M^+ - CH_3$], 551 (100) [$M^+ - OCH_3$], 509 (16) [$M^+ - SiMe_3$], 335 (52) [$M^+ - Si(SiMe_3)_3$].

Crystal Structure Determination: A crystal of **4** was transferred to perfluoropolyether RS 3000 (Riedel-de Haen) under cold nitrogen directly and fixed at 213 K. Crystal size 0.40 × 0.30 × 0.08 mm, $C_{20}H_{58}OSi_8$, formula weight 539.38, triclinic, $P1(1)$, a = 9.524(3), b = 9.735(2), c = 11.869(2) Å, α = 69.43(1), β = 89.95(2), γ = 60.73(2)°, V = 878.8(4) Å^3, Z = 1, $\rho_{calcd.}$ 1.019 g · cm^{-3}, Siemens P4 diffractometer, Mo-K_α λ = 0.71073 Å (graphite monochromator), $F(000)$ = 298, μ = 3.2 cm^{-1}, temperature −60 °C, ω-scan, scan range (2Θ) 3.74–45.0°, *hkl* range −10/10, −10/10, and −14/14; measured refl. 4539, unique refl. 4458, observed refl. 3410, $I > 2\sigma(I)$ refined param. 301, $R1$ for obs. 0.0616, $R1$ for all 0.09, $wR2$ for all 0.1574, GoF = 1.027, $\Delta\rho$0.299/−0.211 eÅ^{-3}. The structure was solved by direct methods (Siemens SHELXTL, 1990, Siemens Analytical X-ray Inst. Inc.) and refined by the full-matrix least-squares method of SHELXL-93[22]. All nonhydrogen atoms were first refined anisotropically. For some atom positions (C-8, C-9, C-15, C-16, C-20) the refinements point to possible split positions. However, taking this into consideration, no improvement of the calculation results was obtained. That is why the thermal ellipsoids of those atoms are fairly large in one direction. The Flack x parameter was found to be near 0.5, as it was expected due to the phenomena mentioned above. Another problem arose from the smaller electron density of the methoxy group atoms in the two possible positions. Since the position of C-20 was found first too near to O-1 a distance restraint was used to remove C-20 from O-1. The hydrogen atoms were put into their theoretical positions and refined according to the "riding model". The weighting scheme was calculated according to $w = 1/[\sigma^2(F_o^2) + (0.0548\,P)^2 + 0.2408\,P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informatiuon mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405206, the names of the authors, and the journal citation.

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[1] We follow the proposal made by N. Wiberg on the Xth International Symposium on Organosilicon Chemistry in Poznan (Poland) in August 1993 and denote the $(Me_3Si)_3Si$ substituent as the *hypersilyl group*; N. Wiberg in *Progress in Organosilicon Chemistry* (Eds.: B. Marciniec, J. Chojnowski), Gordon and Breach Publishers, Basel, **1995**, p. 20; see also ref.[10].
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