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Geminal Bis(hypersilyl) Compounds: The Synthesis and Structure of Bis[tris(trimethylsilyl)silyl]methane

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Summary: The title compound ***6*** *was prepared by reductive coupling of [bromobis(trimethylsilyl)silyl]tris(trimethylsilyl)silylmethane (****5****) and chlorotrimethylsilane with lithium in THF. X-ray crystal structure analysis of* ***6*** *revealed the expected distortions of the molecular skeleton. Thus, the spatial demand of the two extended hemispherical $(Me_3Si)_3Si$ groups forces a widening of the Si−C−Si angle at the central sp^3 carbon atom to a value of 136°.*

The three trimethylsilyl substituents and the central silicon atom of the hypersilyl group form an extended hemispherical shield, providing the center, to which the $(Me_3Si)_3Si$ group is fixed, with an exceptional steric protection. The cone angles of $(Me_3Si)_3Si{-}E$ fragments of, for example, group 14 elements were calculated by Geanangel to be 168° for E = Sn, 175° for E = Ge, 182° for E = Si, and 199° for E = C, respectively,[1] indicating that for geminal bis(hypersilyl) derivatives, especially for those with a nonlinear arrangement of the two groups, an extreme steric congestion has to be expected. In this context we were particularly interested in geminal bis(hypersilyl) compounds with a central carbon atom. It proved to be unexpectedly facile to substitute two bulky $(Me_3Si)_3Si$ groups at one comparatively small sp^3 carbon atom. The synthesis of methoxybis[tris(trimethylsilyl)silyl]methane was accomplished by the reaction of tris(trimethylsilyl)silyllithium with dichloromethyl methyl ether.[2a] Bis(hypersilyl)methanol was prepared by reaction of tris(trimethylsilyl)silyllithium and *tert*-butyl formate,[2b] and tris(trimethylsilyl)silyllithium reacted with dialkyl(chloromethylene)ammonium chlorides to give dialkylaminobis[tris(trimethylsilyl)silyl]methanes.[2c] The structures of all these compounds are characterized by very large distortions of their molecular skeletons. In particular, the central Si−C−Si bond angles in these compounds are extremely widened, the individual values being dependent on the space demand of the other C-substituents. Therefore, the synthesis of the parent compound of the series, bis(hypersilyl)methane (**6**), was untertaken in order to study its structure and reactivity.

Attempts to prepare **6** by the reaction of tris(trimethylsilyl)silyllithium with methylene chloride or methylene bromide, respectively, in ether at −78 °C failed.

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[1] Aggarwal, M.; Ghuman, M. A.; Geanangel, R. A. *Main Group Met. Chem.* **1991**, *14*, 263.

[2] (a) Jeschke, E.; Gross, T.; Reinke, H.; Oehme, H. *Chem. Ber.* **1996**, *129*, 841. (b) Gross, T.; Kempe, R.; Oehme, H. *J. Organomet. Chem.* **1997**, *534*, 229. Gross, T.; Kempe, R.; Oehme, H. *Chem. Ber./Recl.* **1997**, *130*, 1709. (c) Gross, T.; Kempe, R.; Oehme, H. *Inorg. Chem. Commun.* **1998**, *1*, 128. Gross, T.; Kempe, R.; Oehme, H. *Eur. J. Inorg. Chem.* **1999**, 21.

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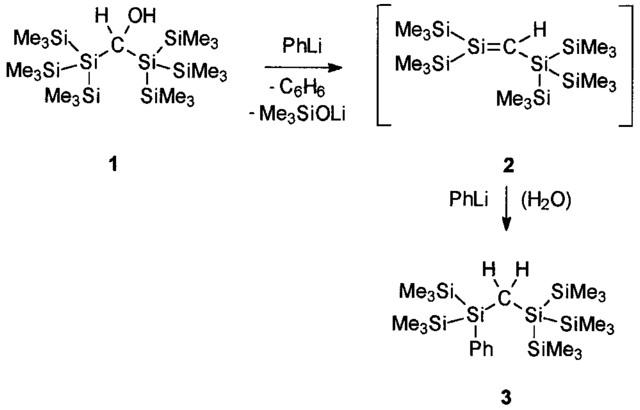
Scheme 1

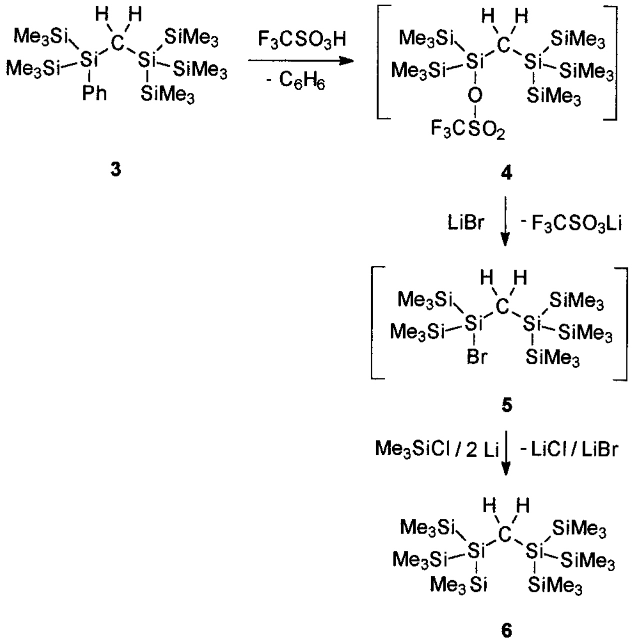


In all cases lithium/halogen exchange occurred and hexakis(trimethylsilyl)disilane[3] was obtained as final product. We succeeded in synthesizing **6** by a one-pot reaction starting with [phenylbis(trimethylsilyl)silyl]-tris(trimethylsilyl)silylmethane (**3**). Compound **3** was obtained by treatment of the alcohol **1** with excess phenyllithium (Scheme 1). After deprotonation of **1**, lithium trimethylsilanolate was eliminated according to a modified Peterson mechanism to form the transient silene **2**, which was trapped by the excess of PhLi present to give, after hydrolytic workup, the phenylsilane **3**.[2b] Replacement of phenyllithium in this reaction sequence by an excess of trimethylsilyllithium should lead directly to bis(hypersilyl)methane **6**, but in diethyl ether the deprotonation of **3** by $(Me_3Si)_3SiLi$ could not be achieved and the alcohol was recovered unchanged. In THF a clean reaction did not occur and a complex mixture of products was obtained, in which compound **6** could not be identified.

The title compound **6** was obtained by cleavage of the Si–Ph bond of **3** with trifluoromethanesulfonic acid,[4] giving the silyl triflate **4**. Without isolation of **4**, the triflate group was replaced by bromide, and subsequently, bromosilane **5** was coupled with Me_3SiCl in the presence of lithium in THF to give **6** in an overall yield of 17% (Scheme 2).[5]

The structure of **6** was elucidated on the basis of NMR and MS studies[5] and was confirmed by an X-ray crystal

Scheme 2



structure analysis.[6] As found for other bis(hypersilyl) derivatives,[2] the solution NMR spectra of **6** are very straightforward showing only one signal for the six $Si(CH_3)_3$ groups in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra. This indicates considerable mobility of the trimethylsilyl groups despite the extreme steric congestion of the molecule.

The results of the X-ray structural analysis, demonstrated in Figure 1, reveal the expected distortions of the molecular skeleton of **6**. Its structure is characterized by the two extended hemispherical hypersilyl shells, separated by the CH_2 group as a spacer, causing the angle in the molecular axis. The steric strain of the two bulky $(Me_3Si)_3Si$ substituents widens the Si1–C1–Si2 bond angle at the central sp^3 carbon atom to the extreme value of 136.2(2)°. The C1–Si1 and C1–Si2 bonds are only slightly elongated (1.896(4) and 1.918(4) Å, respectively). The usually tetrahedral configuration of the $CSiSi_3$ units is considerably distorted in a way that at positions where the two hemispheres touch each other the C1–Si–Si angles are widened, and at the opposite positions the C1–Si–Si angles are reduced. Thus, for the C1–Si1–Si5 angle a value of 120.38(14)° and for the C1–Si2–Si8 angle a value of 122.53(14)° were found. On the other hand, the angle at the central carbon atom and the low space demand of the two hydrogen atoms allow the trimethylsilyl groups in their neighborhood to evade the steric strain, leading to comparatively small angles (C1–Si1–Si3 101.06(14)°; C1–Si2–Si6 100.51(14)°). Obviously, the structure of the molecule is mainly determined by the

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(5) Experimental details of the preparation of **6**: To a solution of 0.60 g (1.2 mmol) of **3** in 20 mL of pentane 0.26 g (1.7 mmol) of trifluoromethanesulfonic acid were added at 0 °C. The reaction was monitored by TLC. After 3 h the volatile materials were separated in vacuo and the residue was dissolved in 20 mL of THF. To this solution 0.32 g (3.6 mmol) of LiBr was added, and after stirring for 0.5 h, 0.39 g (3.6 mmol) of Me_3SiCl was added at room temperature. The resulting suspension was added at −78 °C to a suspension of 0.08 g of lithium powder in THF. The stirred mixture was allowed to warm gradually to room temperature, and a further 0.2 g of Me_3SiCl was added. After 1 h the suspension was evaporated and the residue extracted with pentane. The extracts were filtered and evaporated. Sublimation of the residue (150 °C, 0.2 mbar) gave 0.105 g (17%, based on **3**) of **6**. Single crystals were obtained by recrystallization from ethyl acetate at − 25 °C. Mp: 140–145 °C. ^{1}H NMR (benzene-d_6): δ 0.22 (s, CH_2, 2H.; $^{1}J_{CH} = 112.2$ Hz), 0.29 (s, $SiCH_3$, 54H). ^{13}C NMR (benzene-d_6): δ −20.82 (CH_2), 1.73 ($SiCH_3$). ^{29}Si NMR (benzene-d_6): δ −78.51 [*Si*$(SiMe_3)_3$], −12.41 ($SiMe_3$). MS (*m*/*z* (%)): 508 (20) [M^+], 493 (1.7) [$M^+ - CH_3$], 435 (56) [$M^+ - SiMe_3$], 247 (9) [$Si(SiMe_3)_3{}^+$], 73 (100) [$SiMe_3{}^+$]. Anal. Calcd for $C_{19}H_{56}Si_8$ (509.34): C, 44.81; H, 11.08. Found: C, 44.71; H, 10.99.

(6) Crystal data for **6**: crystals from ethyl acetate (−25 °C), crystal size 0.8 × 0.4 × 0.2 mm; monoclinic, space group *P*2(1)/*c*; $Z = 4$; $a = 21.824(4)$ Å, $b = 9.841(2)$ Å, $c = 16.926(3)$ Å; $\beta = 98.73(3)°$; $V = 3593.1(13)$ Å^3; $d_{calcd} = 0.942$ g·cm^{-3}; diffr. STOE-IPDS; μ(Mo Kα) = 0.304 mm^{-1}; $T = 293(2)$ K; scan range (θ) = 1.89–24.31°; *hkl* range −25/0, −11/11, −17/17; measured reflns = 10 505; unique reflns 5458; observed reflns 2679; refined parameters 244; $R1$ [$I > 2\sigma(I)$] = 0.0516; $R1$ for all = 0.1130; GoF 0.805/1.062. The structure was solved by direct methods (SHELXS-86)[6] and refined by full matrix least-squares techniques against F^2 (SHELXL-93).[7] XP (Siemens Analytical X-ray Instruments) was used for the structure representations.

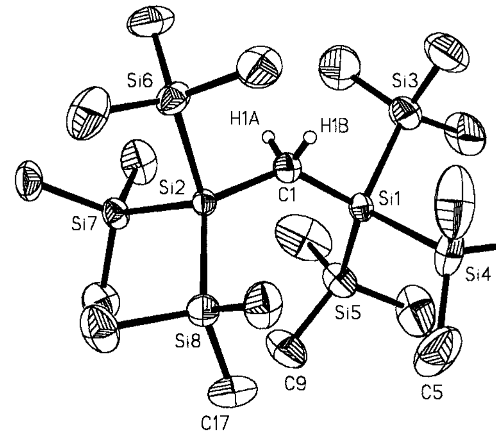

Figure 1. Molecular structure of **6** in the crystal (ORTEP, 30% probability, H atoms omitted except for C1 H). Selected bond lengths [Å] and angles [deg]: C1−Si1 1.896(4), C1−Si2 1.918(4), Si1−Si3 2.355(2), Si1−Si4 2.343(2), Si1−Si5 2.351(2), Si2−Si6 2.363(2), Si2−Si7 2.363(2), Si2−Si8 2.346(2); Si1−C1−Si2 136.2(2), C1−Si1−Si3 101.06(14), C1−Si1−Si4 110.86(15), C1−Si1−Si5 120.38(14), C1−Si2−Si6 100.51(14), C1−Si2−Si7 110.7(14), C1−Si2−Si8 122.53(14).

interaction of the trimethylsilyl groups of the two hypersilyl moieties, the bridging CH_2 group playing a secondary role. No Me_3Si substituent is in gauche conformation with the CH_2 group, since this would lead to an extreme disturbance of the trimethylsilyl groups in the anti positions. Instead, the six trimethylsilyl groups of **6** are arranged in a *pseudostaggered* conformation, almost neglecting the CH_2 bridge (Figure 2). But the resulting dihedral angles Si−Si1−Si2−Si not only deviate from the ideal values of 60° but also show considerable differences. This again is attributable to the steric congestion of **6**. Si5 and Si8, representing the two trimethylsilyl groups in the most crowded area of the molecule, evade the steric strain by rotating the hypersilyl shells, opening the dihedral angle Si5−Si1−Si2−Si8 to a value of 79.70(7)°. Due to the steric stress in the molecule, the methyl groups at Si5 and Si8 approach exceptionally short distances, e.g., the C5C17 distance (3.885(9) Å) and the C9C17 distance (3.819(7) Å) being significantly shorter than the sum of the van der Waals radii of two methyl groups, which amounts to about 4.00 Å.[7]

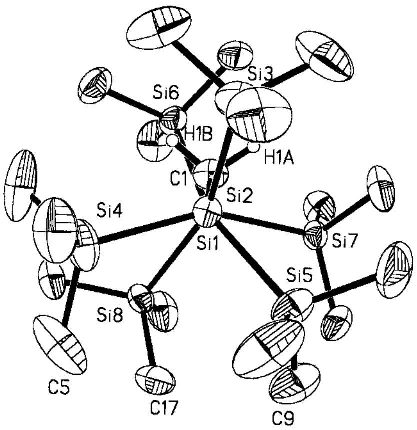

Figure 2. Projection of the molecular structure of **6** looking along the Si1−Si2 axis (ORTEP plot, 30% probability). Dihedral angles [deg]: Si3−Si1−Si2−Si7 86.23(8), Si7−Si2−Si1−Si5 35.82(8), Si5−Si1−Si2−Si8 79.70(7), Si8−Si2−S1−Si4 36.85(8), Si4−Si1−Si2−Si6 83.40(8), Si6−Si2−Si1−Si3 38.01(9).

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Supporting Information Available: Descriptions of the X-ray experimental details for **6**, including tables of crystal data, positional parameters, all bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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