Geminal Di(hypersilyl) Compounds – The Synthesis and Structure of Bis[tris(trimethylsilyl)silyl]methanol

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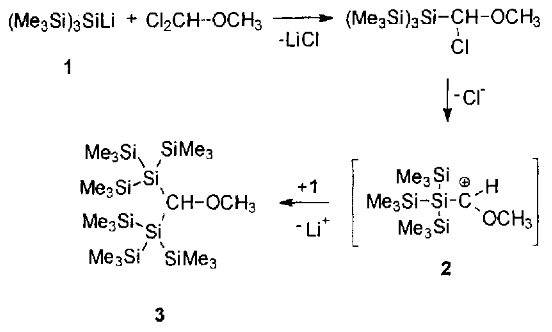
Tris(trimethylsilyl)silyllithium (**1**) reacts with methyl formate in diethyl ether (molar ratio 2:1) to give 1,2-di(hypersilyl)-ethylene **13**. The formation of **13** proceeds through the intermediates formyl tris(trimethylsilyl)silane (**4**) and lithium bis-[tris(trimethylsilyl)silyl]methoxide (**5**). In diethyl ether, the alkoxide **5** spontaneously eliminates lithium trimethylsilanolate thereby generating 1,1-bis(trimethylsilyl)-2-[tris(trimethylsilyl)silyl]silene (**9**), which undergoes a formal [2+2] cycloaddition with the carbonyl compound **4** to afford **13**. This was verified by crossover experiments. In pentane, the alkoxide **5** is moderately stable. Thus, the intermediate **5**, prepared by reaction of **1** with *tert*-butyl formate in pentane, was protonated with water to give the di(hypersilyl)methanol **6** in good yield. The structure of **6** was elucidated by an X-ray crystal structure analysis, which expectedly revealed tremendous 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 135.5°.

Recently, we succeeded in synthesizing methoxybis[tris-(trimethylsilyl)silyl]methane (**3**), the first compound bearing two hypersilyl groups at one carbon atom. As expected, due to the extreme spatial demand of the two extended hemispherical $(Me_3Si)_3Si$ groups, structural analysis of **3** revealed tremendous distortions of the molecular skeleton[1]. The compound is stable, but chemically completely inert, so that all attempts at further derivatizations failed.

The synthesis of **3** was achieved by the reaction of tris(trimethylsilyl)silyllithium (**1**) with dichloromethyl methyl ether. The ease of the formation of **3** was really surprising, since we had expected serious difficulties in the fixation of these two bulky groups at one comparatively small sp^3 carbon atom and, furthermore, there are reports in the literature about unsuccessful attempts of the synthesis of di(hypersilyl) derivatives of silicon[2][3] and germanium[2][4], and severe steric interactions have been discussed as a reason to account for the instability of di(hypersilyl) derivatives of the smaller group-14 elements[2][3][5]. On the other hand, $[(Me_3Si)_3Si]_2SiMe_2$ has been described as the product of an $AlCl_3$-catalyzed rearrangement of linear permethylnonasilane[6a], and recently a number of di(hypersilyl)silanes have been prepared by substitution reactions at the central silicon atom starting from $[(Me_3Si)_2Si]_2SiHCl$[6b]. Thus, we believe the availability of these compounds to be mainly a question of the reaction route.

Obviously, as illustrated in Eq. 1 for the synthesis of **3**, the reaction proceeds through a carbenium ion **2**, the planar structure of which facilitates the approach of the silicon nucleophile **1** to the sterically extremely congested reaction centre.



(1)

A stereochemical situation similar to the approach of **1** to the carbenium ion **2** is expected for the addition of **1** to the carbonyl group of acyltris(trimethylsilyl)silanes. Therefore, as a target molecule we chose bis[tris(trimethylsilyl)silyl]methanol (**6**), which we intended to prepare by the reaction of **1** with formyltris(trimethylsilyl)silane (**4**). Di(hypersilyl)methanol **6** is of interest from a structural viewpoint and promises to be a suitable starting material for the synthesis of the sterically extremely congested 1,1-bis(trimethylsilyl)-2-[tris(trimethylsilyl)silyl]silene (**9**). However, as we reported in a preliminary communication[7], attempts to prepare **6** by the reaction of **1** with methyl formate (molar ratio 2:1), which should afford in a first step the formylsilane **4** and, after addition of a second equivalent of the silicon nucleophile **1** at the formyl group of **4**, the di(hypersilyl)-methoxide **5**, gave only traces of the alcohol **6**. Unexpec-

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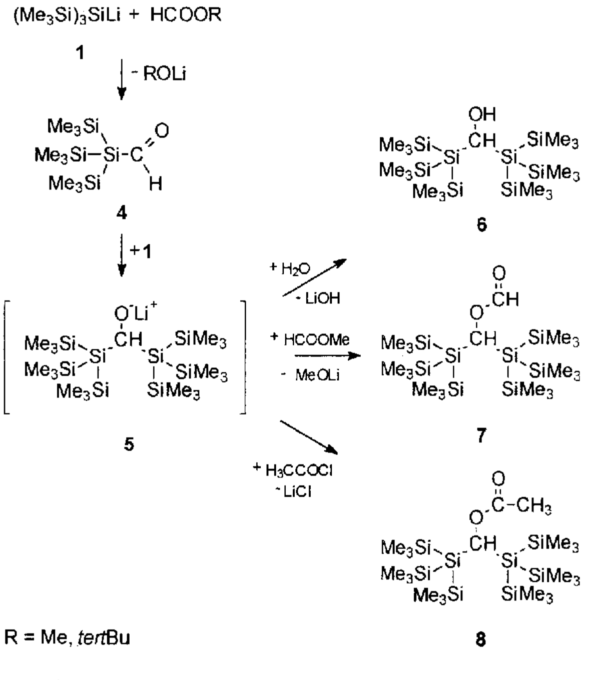
tedly, the main product of the reaction of **1** with methyl formate was 1,2-bis[tris(trimethylsilyl)silyl]ethylene (**13**)[7].

Continued studies in this field led to the development of an improved method for the synthesis of **6** and succeeded in revealing the mechanism of the formation of the 1,2-di(hypersilyl)ethylene **13**, in which, as we have since learned, the silene **9** acts as an intermediate.

The Reaction of Tris(trimethylsilyl)silyllithium (1) with Formic Acid Esters

The reaction of tris(trimethylsilyl)silyllithium (**1**) with methyl formate in a molar ratio of 2:1 in diethyl ether affords 1,2-bis[tris(trimethylsilyl)silyl]ethylene (**13**) in a yield of 61%[7]. The mechanism of its formation will be discussed below. At this point, it is sufficient to note that formyltris(trimethylsilyl)silane (**4**), generated in the first step of the reaction of **1** with methyl formate, is an important intermediate (Scheme 1). This could be unequivocally proven by a 1:1 reaction of the components leading to an oily substance, which gave NMR data identical to those described for **4**[8]. The formylsilane **4** would be expected to react in situ with another equivalent of **1** to give the di(hypersilyl)methoxide **5** and, indeed, when the reaction is carried out at −78°C in pentane and quenched in the cold after 30 min by the addition of water, di(hypersilyl)methanol **6** is obtained in a yield of 12% . Attempts to enhance the yield of **6** by employing longer reaction times or by increasing the temperature failed, but led to a new product identified as formyloxybis[tris(trimethylsilyl)silyl]methane (**7**, 30%, Scheme 1).

Scheme 1. The reaction of tris(trimethylsilyl)silyllithium (**1**) with methyl formate or *tert*-butyl formate, respectively, in pentane



The di(hypersilyl)methyl formate **7** derives from the interaction of the alkoxide **5** with the apparent excess of methyl formate, thus diminishing the yield of the target product **6**. This, despite the extensive shielding, indicates a considerable nucleophilic activity of the alkoxide oxygen atom of **5**. In line with expectation, this side reaction could be suppressed by the use of a bulky formic acid ester instead of methyl formate in the reaction with the lithium silanide **1**. Whereas the formation of the formylsilane **4** should not be significantly affected by the nature of the ester group, the approach of a seriously congested formic acid ester to the nucleophilic alkoxide oxygen atom of **5**, located in a narrow slit formed by the two extended hemispherical $(Me_3Si)_3Si$ groups, would most probably be ruled out. Indeed, reaction of **1** with *tert*-butyl formate in pentane affords **6** almost quantitatively.

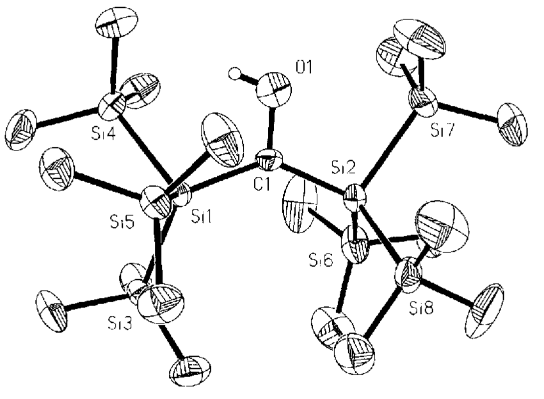
The reactivity of the alkoxide **5** was also demonstrated by its reaction with acetyl chloride, affording the di(hypersilyl)methyl acetate **8**. Acylations with chlorides of higher aliphatic or aromatic carboxylic acids failed, most probably for steric reasons.

Compounds **6**−**8** are colorless solids. Their NMR spectra are very straightforward, showing only one signal for the trimethylsilyl groups in the ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra. IR and MS data are also supportive of the proposed structures (see Experimental Section).

X-ray analysis of **6** revealed a disordered solid-state structure. Obviously, similar to the situation in the di(hypersilyl)methyl methyl ether **3**[7], the OH group at the central carbon atom is completely hidden and the structure of **6** is determined predominantly by the two bulky $(Me_3Si)_3Si$ groups. Thus, the OH group and the C1−H are 1:1 disordered since no preferred orientation is adopted in the crystal. The bond parameters obtained confirm the expected distortions of the molecular skeleton (Figure 1). The spatial demand of the two extended hemispherical hypersilyl groups leads to a significant elongation of the two central carbon−silicon bonds (C1−Si1 1.93 Å; C1−Si2 1.91 Å) and an extreme widening of the Si1−C1−Si2 angle to a value of 135.5°. Of course, the spatial demand of the OH group in **6** is smaller than that of the OCH_3 group in **3**. Thus, the relevant C−Si bonds in **3** are longer (1.94 Å and 1.95 Å, respectively), and the bond angle at the central carbon atom is smaller (132.7°). Consequently, the deformation of the $CSiSi_3$ tetrahedra in **6** is smaller than in **3**. The average C1−Si−Si angles in **6** are 111.6° and 110.9°, respectively (in **3** both are 112.5°), but the values of the individual angles differ markedly. At the positions where the two hemispheres contact each other, the angles are widened (C1−Si1−Si3 122.0°, C1−Si1−Si5 110.7°, C1−Si2−Si6 110.4°, C1−Si2−Si8 120.3°) and the two shells are pushed aside under deformation of the originally tetrahedral configuration at the central silicon atom, compressing the C1−Si1−Si4 (102.0°) and the C1−Si1−Si7 angles (101.9°).

Attempts to use the procedure leading to the di(hypersilyl)methanol **6** for a general synthesis of 1,1-di(hypersilyl) alcohols were unsuccessful. Under the conditions applied, the 2:1 reaction of **1** with carboxylic acid esters is restricted to the use of formic acid esters only. In all other cases, the reaction is terminated after the addition of one equivalent

Figure 1. Molecular structure of the di(hypersilyl)methanol **6** in the crystal (H atoms omitted except for that of the OH group, ORTEP, 30% probability level)[a]



[a]Selected bond lengths [Å] and angles [°]: C1−Si1 1.926(4), C1−Si2 1.905(4), C1−O1 1.441(8), Si1−Si3 2.353(2), Si1−Si4 2.364(2), Si1−Si5 2.3738(15), Si2−Si6 2.364(2), Si2−Si7 2.371(2), Si2−Si8 2.349(2); Si1−C1−Si2 135.5(2), O1−C1−Si1 107.5(4), O1−C1−Si2 111.4(4), C1−Si1−Si3 122.01(14), C1−Si1−Si4 102.01(13), C1−Si1−Si5 110.66(15), C1−Si2−Si6 110.4(2), C1−Si2−Si7 101.94(14), C1−Si2−Si8 120.28(14).

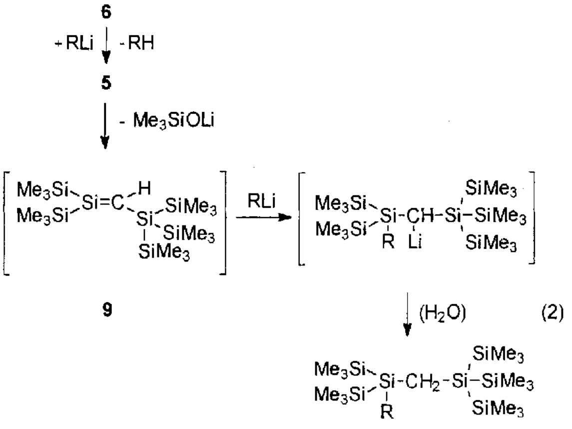
of the silanide **1** at the ester group. Side reactions, such as Si−Si bond cleavage reactions of the resulting acyltris(trimethylsilyl)silanes leading to formation of lithium silenolates, as described by Ishikawa et al.[9], were not observed under the conditions employed. However, it should be mentioned that the reaction of **1** with carboxylic acid esters can be used generally as an easy route to acyltris(trimethylsilyl)silanes. Thus, the acylsilanes $R-C(O)-Si(SiMe_3)_3$ (R = Me, 38%; R = *t*Bu, 58%; R = Ph, 72%; R = 3,5-$Me_2C_6H_3$, 51%), prepared by Brook et al. from **1** and acyl chlorides[10], were prepared from **1** and the respective methyl carboxylates in diethyl ether.

Base-Induced Conversion of Di(hypersilyl)methanol 6 into the Transient 1,1-Bis(trimethylsilyl)-2-[tris(trimethylsilyl)silyl]silene (9)

1-Hydroxyalkyltris(trimethylsilyl)silanes proved to be suitable precursors for the synthesis of transient silenes. After deprotonation of the polysilanyl alcohol with organolithium reagents in diethyl ether, trimethylsilanolate was eliminated according to a sila-Peterson-type mechanism with the formation of silaethenes, which were characterized by various addition and dimerization reactions[11]. An in situ modification of this method is the generation of silenes by the reaction of tris(trimethylsilyl)silyllithium with carbonyl compounds[12], and, very recently, Apeloig et al. successfully applied this concept to the preparation of novel stable silenes[13].

Deprotonation of the di(hypersilyl)alcohol **6** with an organolithium base and subsequent elimination of lithium trimethylsiloxide according to the mechanism described above should afford 1,1-bis(trimethylsilyl)-2-tris(trimethylsilyl)silylsilene **9** (Eq. 2). Due to the extensive steric protection of the Si=C function by the hypersilyl group and the two trimethylsilyl groups, **9** may be expected to be a moderately stable silene.

The reaction of **6** with excess methyllithium or phenyllithium gives the polysilanes **10** and **11**, respectively (Eq. 2). The formation of **10** and **11** results from the addition of the organolithium reagents to the polar Si=C group of **9**, leading to organolithium intermediates, which are hydrolyzed in the course of the aqueous work-up. At the same time, the formation of polysilanes of this type is considered as providing unambiguous proof of the intermediate existence of reactive silenes[14]. Thus, the high yields of **10** and **11** indicate a clean elimination of trimethylsilanolate from **5** and a straightforward formation of the silene **9**. The intermediate organolithium derivative (Eq. 2), formed by addition of excess MeLi to the silene double bond of **9**, is stable under the applied reaction conditions. Work-up of the mixture with D_2O gave $(Me_3Si)_2MeSi-CHD-Si(SiMe_3)_3$ (**D-10**).



10: R = Me
11: R = Ph

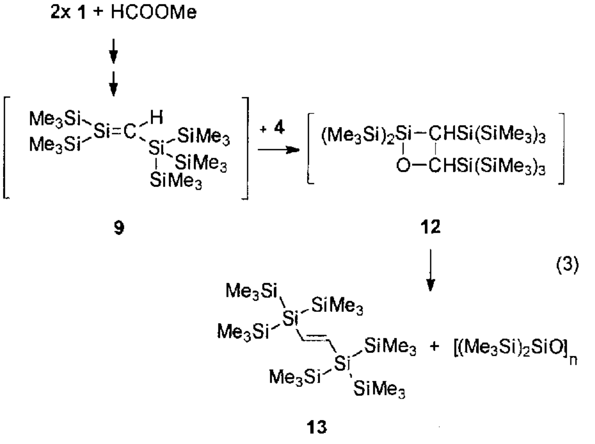
Unfortunately, the reaction of **6** with equimolar quantities of methyllithium again led to the MeLi/silene addition product **10**, besides considerable quantities of the unreacted alcohol **6**. Neither the silene **9** nor its dimerization products could be detected. This result proved to be independent of the reaction temperature or the solvent. Clearly as the consequence of the extreme steric congestion of the alcohol, the deprotonation of **6** proceeds very slowly. Fast elimination of lithium trimethylsilanolate affords the silene **9**, which invariably comes into contact with the effective excess of the organolithium reagent. Thus, **9** is immediatedly trapped by methyllithium to give **10**.

Synthesis of 1,2-Di(hypersilyl)ethylene 13

As mentioned above, the reaction of tris(trimethylsilyl)silyllithium (**1**) with *tert*-butyl formate in pentane (molar ratio 2:1) affords the di(hypersilyl)methanol **6**. When methyl formate was used in the reaction with **1** in pentane instead of the *tert*-butyl ester, **6** was obtained in very low yields, but after prolonged reaction times **7** was isolated in a yield of about 30% . When the reaction of **1** with methyl formate was carried out in diethyl ether, another new colorless crystalline product was isolated in approximately 60% yield and identified as 1,2-bis[tris(trimethylsilyl)silyl]ethylene (**13**).

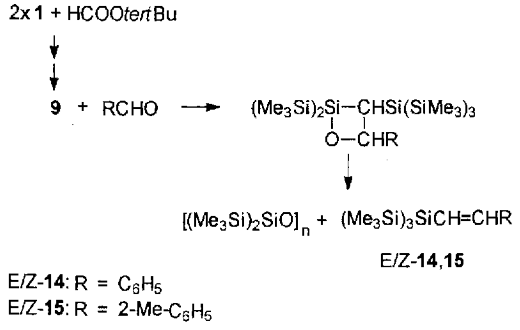
The structure of **13** was elucidated on the basis of NMR as well as MS and Raman studies. The NMR spectra of **13** are very straightforward, showing only one signal for the trimethylsilyl groups in the ^1H, ^{13}C and ^{29}Si spectra. A strong Raman absorption band at 1529 cm^{-1} is considered as being indicative of a symmetrically substituted C=C function. X-ray analysis of **13** revealed a complete disorder of all the trimethylsilyl groups and, therefore, a full accurate structure determination could not be performed. Nevertheless, the data obtained confirm the proposed constitution and an *E* configuration was unambiguously found for the two hypersilyl groups.

In view of the clean elimination of lithium trimethylsilanolate from **5** with simultaneous generation of **9**, the mechanism of the formation of the di(hypersilyl)ethylene **13** involving the transient silene **9** appears to be obvious and our proposal conforms to the known reaction pattern of reactive silenes with non-enolizable carbonyl compounds (Eq. 3). The reaction of two equivalents of the lithium silanide **1** with methyl formate first results in the formation of the alkoxide **5**. In pentane, **5** is moderately stable and allows further reactions with methyl formate or acetyl chloride to give **7** and **8**, respectively, or, after protonation, the alcohol **6**. In diethyl ether, **5** is labile and undergoes rapid elimination of lithium trimethylsilanolate with formation of the silene **9**. The solvent dependent differences in the behavior of **5** are easily understood in terms of an increasing nucleophilic activity of the alkoxide oxygen atom with increasing donor properties of the solvent. Expectedly, because of the congestion of both the carbonyl compound and the silicon nucleophile, the addition reaction of **1** with the formyl silane **4** is a slow process relative to the elimination reaction **5** → **9**. Thus, when **9** is generated, there will always be an effective excess of **4** in the solution, and the silene is trapped by the formylsilane to give the 1,2-oxasiletane **12**. Cycloreversion of the oxasiletane ring results in the formation of **13** and bis(trimethylsilyl)silanone, which undergoes further oligomerization reactions.



(3)

[2+2] Cycloadditions of Si=C systems with non-enolizable carbonyl compounds are considered to be standard reactions of reactive silenes[15]. The 1,2-oxasiletanes thus formed could be isolated only in a few cases[16]. Generally, they are unstable and decompose with formation of an olefin and a silanone, which oligomerizes to give cyclosiloxanes[15].



(4)

The discussed reaction pathway was proven by crossover experiments. Half an hour after mixing **1** and *tert*-butyl formate in pentane, excess benzaldehyde or 2-methylbenzaldehyde, respectively, were added to the still cold reaction mixture. The aldehydes were expected to add to the silene double bond of the transient silene **9** to give after [2+2] cycloaddition and cycloreversion, the corresponding styryltris(trimethylsilyl)silanes. In fact, workup gave approximately 10% of an *E*/*Z* mixture of 1-phenyl-2-tris(trimethylsilyl)silylethylene (**14**) and 15% of (*E*/*Z*)-1-(*o*-tolyl)-2-tris(trimethylsilyl)silylethylene (**15**), respectively, besides unidentified material (Eq. 4). The spectral data obtained for **14** were identical to those described in the literature[17]. **15** was separated into its geometrical isomers and *E*-**15** and *Z*-**15** were characterized by a full spectral analysis.

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Experimental Section

All reactions involving organometallic reagents were carried out under purified argon. – NMR: Bruker AC 250, Bruker ARX 300 and (for ^{29}Si) Bruker ARX 400, 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[18]. – All yields quoted refer to amounts obtained after chromatographic separation and purification. – The synthesis and the spectral data characterizing the structure of **13** have been described previously[7].

Bis[tris(trimethylsilyl)silyl]methanol (**6**): As an improvement of the procedure described previously[7], *tert*-butyl formate was used for the reaction with **1** instead of methyl formate. Thus, 3.70 g (7.9 mmol) of $(Me_3Si)_3SiLi \cdot 3$ THF (**1**) in 150 ml of pentane and 0.47 g (3.9 mmol) of *tert*-butyl formate gave 1.7 g (82%) of **6**.

Bis[tris(trimethylsilyl)silyl]methyl Formate (**7**): In the dark at −78°C, 0.18 g (1.7 mmol) of *tert*-butyl formate was added to a solution of 1.60 g (3.4 mmol) of **1** in 30 ml of pentane. After stirring for 25 min, 0.20 g (3.4 mmol) of methyl formate was added to the cold solution. After 30 min, the mixture was allowed to warm up, water was added, the hydrocarbon phase was separated and the aqueous phase was extracted with diethyl ether. The pooled extracts were dried, the solvents were evaporated and **7** was separated from the residue by column chromatography (silica gel; heptane) and recrystallized from ethanol. Colorless crystals, m.p. 173−175°C, yield 0.63 g (67%). − IR (Nujol): $\tilde{\nu}$ = 1712 cm^{-1} (CO). − ^{1}H NMR ([D$_6$]benzene): δ = 0.15 (s, SiCH$_3$, 54 H), 6.31 (d, ^4J = 0.9 Hz, CH, 1 H), 7.69 (d, ^4J = 0.9 Hz, CHO, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = 3.23 (SiCH$_3$), 55.5 (CH), 161.2 (CHO). − ^{29}Si NMR ([D$_6$]benzene): δ = −12.8 (SiMe$_3$), −64.8 (*Si*SiMe$_3$). − MS; *m/z* (%): 551 (1) [M$^+$ − H], 537 (20) [M$^+$ − CH$_3$], 507 (100) [M$^+$ − OCHO], 479 (42) [M$^+$ − SiMe$_3$], 435 (19) [M$^+$ − SiMe$_3$ − CO$_2$]. − $C_{20}H_{56}O_2Si_8$ (553.35): calcd. C 43.41, H 10.20; found C 43.32, H 10.16.

Bis[tris(trimethylsilyl)silyl]methyl Acetate (**8**): To a stirred solution of 2.50 g (5.3 mmol) of **1** in 30 ml of pentane, 0.27 g (2.7 mmol) of *tert*-butyl formate was added at −78°C. After 25 min, 0.63 g (8.0 mmol) of freshly distilled acetyl chloride was added and stirring was continued for a further 30 min. Aqueous workup as described above gave 0.39 g (26%) of **8**; m.p. 170−175°C. − IR (Nujol): $\tilde{\nu}$ = 1726 cm^{-1} (CO). − ^{1}H NMR ([D$_6$]benzene): δ = 0.35 (s, SiCH$_3$, 54 H), 1.83 (s, CCH$_3$, 3 H), 6.27 (s, CH, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = 3.37 (SiCH$_3$), 23.38 (CCH$_3$), 55.67 (CH), 169.62 (CO). − ^{13}C NMR ([D$_6$]benzene): δ = −12.81 (SiMe$_3$), −66.17 (*Si*SiMe$_3$). − MS *m/z* (%): 566 (0.5) [M$^+$], 551 (6) [M$^+$ − CH$_3$], 493 (100) [M$^+$ − SiMe$_3$], 73 [SiMe$_3^+$]. − $C_{21}H_{58}O_2Si_8$ (567.37): calcd. C 44.46, H 10.30; found C 44.52, H 10.24.

[Methylbis(trimethylsilyl)silyl]tris(trimethylsilyl)silylmethane (**10**): At room temperature, 0.30 g (0.6 mmol) of **6**, dissolved in 30 ml of diethyl ether, was added gradually to a tenfold molar excess of methyllithium in ether. After stirring for 3 h, dilute aq. HCl was added and the organic layer was separated. The aqueous phase was extracted with diethyl ether and the combined ethereal solutions were dried and concentrated. Chromatographic purification (silica gel; heptane) of the residue gave 0.21 g (82%) of **10**; m.p. 43−45°C. − ^{1}H NMR ([D$_6$]benzene): δ = 0.18 (s, CH$_2$, 2 H), 0.19 [s, Si(SiMe$_3$)$_2$, 18 H], 0.28 [s, Si(SiMe$_3$)$_3$, 27 H], 0.33 (s, CH$_3$, 3 H). − ^{13}C NMR ([D$_6$]benzene): δ = −17.53 (CH$_2$), −5.07 (CH$_3$), −0.48 [Si(SiMe$_3$)$_2$], 1.51 [Si(SiMe$_3$)$_3$]. − ^{29}Si NMR ([D$_6$]benzene): δ = −13.0 [Si(*Si*Me$_3$)$_3$], −15.8 [Si(*Si*Me$_3$)$_2$], −44.8 [*Si*(SiMe$_3$)$_2$], −81.75 [*Si*(SiMe$_3$)$_3$]. − MS; *m/z* (%): 450 (17) [M$^+$], 435 (100) [M$^+$ − CH$_3$], 377 (32) [M$^+$ − SiMe$_3$], 247 (8) [Si(SiMe$_3$)$_3^+$], 73 (21) [SiMe$_3^+$]. − $C_{17}H_{50}Si_7$ (451.18): calcd. C 45.26, H 11.17; found C 45.16, H 11.21.

[Phenylbis(trimethylsilyl)silyl]tris(trimethylsilyl)silylmethane (**11**): According to the procedure described for **10**, 0.16 g (0.3 mmol) of **6** gave, after the reaction with excess phenyllithium, 0.09 g (52%) of **11**; m.p. 155−160°C. − ^{1}H NMR ([D$_6$]benzene): δ = 0.23 [s, Si(SiMe$_3$)$_3$, 27 H], 0.26 [s, Si(SiMe$_3$)$_2$, 18 H], 0.48 (s, CH$_2$, 2 H), 7.2−7.5 (m, Ph, 5 H). − ^{13}C NMR ([D$_6$]benzene): δ = −17.5 (CH$_2$), 0.01 [Si(SiMe$_3$)$_2$], 1.55 [Si(SiMe$_3$)$_3$], 128.27, 128.68, 135.65 (arom. CH), 138.04 (arom. quat. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −12.4 [Si(*Si*Me$_3$)$_3$], −15.9 [Si(*Si*Me$_3$)$_2$], −38.7 [*Si*(SiMe$_3$)$_2$], −81.75 [*Si*(SiMe$_3$)$_3$]. − MS; *m/z* (%): 512 (59) [M$^+$], 497 (35) [M$^+$ − CH$_3$], 439 (60) [M$^+$ − SiMe$_3$], 362 (100) [M$^+$ − SiMe$_3$ − Ph], 73 (43) [SiMe$_3^+$]. − $C_{22}H_{52}Si_7$ (513.25): calcd. C 51.48, H 10.21; found C 51.53, H 10.05.

Reaction of **1** *with tert-Butyl Formate and Benzaldehyde or o-Tolylaldehyde. − Generation of* **14** *and* **15**: To a solution of 1.15 g (2.45 mmol) of (Me$_3$Si)$_3$SiLi · 3 THF (**1**) in 30 ml of pentane, 0.13 g (1.2 mmol) of *tert*-butyl formate was added at −78°C in the dark. After 25 min, 0.64 g (6.0 mmol) benzaldehyde was added to the still cold solution and after stirring for 30 min the mixture was allowed to warm up to ambient temperature. Aqueous workup as described above and chromatographic separation (silica gel; heptane) gave 0.02 g (5%) of *Z*-**14** and 0.03 g (6%) of *E*-**14**[17].

Similarly, 1.56 g (3.3 mmol) of **1**, 0.17 g (1.65 mmol) of *tert*-butyl formate and 0.60 g (5.0 mmol) of *o*-tolylaldehyde gave 0.04 g (7%) of *Z*-**15** and 0.05 g (8%) of *E*-**15**. − *(Z)-1-(o-Tolyl)-2-tris(trimethylsilyl)silylethylene* (*Z*-**15**): − ^{1}H NMR ([D$_6$]benzene): δ = 0.19 (s, SiCH$_3$, 27 H), 2.12 (s, CH$_3$, 3 H), 5.99 (d, ^3J = 14.6 Hz, =CH, 1 H), 7.24 (m, arom. CH, 4 H), 7.42 (d, ^3J = 14.1 Hz, =CH, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = 1.32 (SiCH$_3$), 19.79 (CH$_3$), 124.71, 146.56 (olef. C), 126.41, 128.29, 128.54, 130.04 (arom. CH), 136.07, 140.92 (arom. quat. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −12.4 (SiMe$_3$), −89.2 (*Si*SiMe$_3$). − *(E)-1-(o-Tolyl)-2-tris(trimethylsilyl)silylethylene* (*E*-**15**): ^{1}H NMR ([D$_6$]benzene): δ = 0.29 (s, SiCH$_3$, 27 H), 2.25 (s, CH$_3$, 3 H), 6.49 (d, ^3J = 18.6 Hz, =CH, 1 H), 7.01 (m, arom. CH, 3 H), 7.35 (d, ^3J = 18.9 Hz, =CH, 1 H), 7.53 (m, arom. CH, 1 H). − ^{13}C NMR ([D$_6$]benzene): δ = 1.04 (SiCH$_3$), 19.86 (CH$_3$), 123.87, 144.75 (olef. C), 125.64, 126.58, 128.29, 130.55 (arom. CH), 134.78, 138.89 (arom. quat. C). − ^{29}Si NMR ([D$_6$]benzene): δ = −12.99 (SiMe$_3$), −83.2 (*Si*SiMe$_3$). − *E/Z*-**15**: MS; *m/z* (%): 364 (15) [M$^+$], 349 (4) [M$^+$ − CH$_3$], 247 (3) [Si(SiMe$_3$)$_3^+$], 174 (100) [Si(SiMe$_3$)$_2^+$], 73 (70) [SiMe$_3^+$]; exact mass calcd. for $C_{18}H_{36}Si_4$ 364.18941; found 364.18799.

Crystal-Structure Determination of **6**: X-ray diffraction data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo-K_α radiation. Crystal size 0.7 × 0.5 × 0.3 mm, formula $C_{19}H_{56}OSi_8$, formula weight 525.34, monoclinic, $P2_1/c$, a = 16.852(4), b = 9.819(2), c = 21.794(3) Å, β = 98.66(3)°, Z = 4, temperature 293 K, μ = 0.31 mm^{-1}, Θ range 2.28−24.38°, peak/hole 0.65/−0.43 eÅ^{-3}, measured refl. 10360, independent refl. 5604, observed refl. 3692, R (int) 0.04, no. parameters 252, $R1$ [$I > 2\sigma(I)$] 0.059, $\omega R2$ (all data) 0.184. The structure was solved by direct methods (SHELXS-86[19]) and refined by full-matrix least-square techniques against F^2 (SHELXL-93[20]). XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. Further details of the crystal structure determination are available upon request from The Director, Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ (UK), on quoting the deposition number CSD-100437, the names of the authors, and the journal citation.

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[1] E. Jeschke, T. Gross, H. Reinke, H. Oehme, *Chem. Ber.* **1996**, *129*, 841−844.

[2] S. P. Mallela, R. A. Geanangel, *Inorg. Chem.* **1990**, *29*, 3525−3528.

[3] Y. Derouiche, P. D. Lickiss, *J. Organomet. Chem.* **1991**, *407*, 41−49.

[4] S. P. Mallela, R. A. Geanangel, *Inorg. Chem.* **1991**, *30*, 1480−1482 and **1994**, *33*, 1115−1120.

[5] S. M. Whittacker, M.-C. Brun, F. Cervantes-Lee, K. H. Pannell, *J. Organomet. Chem.* **1995**, *499*, 247−252.

[6] [6a] M. Ishikawa, J. Iyoda, H. Ikeda, K. Kotake, T. Hashimoto, M. Kumada, *J. Am. Chem. Soc.* **1981**, *103*, 4845−4850. − [6b] Y. Apeloig, M. Yuzefovich, M. Bendikov, D. Bravo-Zhivotovskii, *Organometallics* **1997**, *16*, 1265−1269.

[7] T. Gross, R. Kempe, H. Oehme, *J. Organomet. Chem.***1997**, *534*, 229−231.

[8] F. H. Elsner, H.-G. Woo, T. D. Tilley, *J. Am. Chem. Soc.* **1988**, 110, 313−314.

[9] J. Ohshita, S. Masaoka, J. Morimoto, M. Sano, M. Ishikawa, *Organometallics* **1997**, *16*, 1132−1129; J. Ohshita, S. Masaoka, M. Ishikawa, *Organometallics* **1996**, *15*, 2198−2200; J. Ohshita, Y. Masaoka, S. Masaoka, M. Ishikawa, A. Tachibana, T. Yano, T. Yamabe, *J. Organomet. Chem.* **1994**, *473*, 15−17.

[10] A. G. Brook, J. W. Harris, J. Lennon, M. El-Sheikh, *J. Am. Chem. Soc.* **1979**, *101*, 83−95; A. G. Brook, S. C. Nyburg, W. F. Reynolds, Y. C. Poon, Y.-M. Chang, J.-S. Lee, *J. Am. Chem. Soc.* **1979**, *101*, 6750−6752.

[11] C. Krempner, D. Hoffmann, R. Kempe, H. Oehme, *Organometallics* **1997**, *16*, 1828−1832 and literature cited therein.

[12] D. Bravo-Zhivotovskii, V. Brande, A. Stanger, M. Kapon, Y.

Apeloig, *Organometallics* **1992**, *11*, 2326–2328; J. Ohshita, Y. Masaoka, M. Ishikawa, *Organometallics* **1991**, *10*, 3775–3776; J. Ohshita, Y. Masaoka, M. Ishikawa, T. Takeuchi, *Organometallics* **1993**, *12*, 876–879; H. Oehme, R. Wustrack, A. Heine, G. M. Sheldrick, D. Stalke, *J. Organomet. Chem.* **1993**, 452, 33–39.

[13] Y. Apeloig, M. Bendikov, M. Yuzefovich, M. Nakash, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, *J. Am. Chem. Soc.* **1996**, *118*, 12228–12229.

[14] C. Krempner, H. Reinke, H. Oehme, *Chem. Ber.* **1995**, *128*, 143–149.

[15] G. Raabe, J. Michl in *The Chemistry of Organic Silicon Compounds* (Ed.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, part 2, chapter 17, p. 1090.

[16] A. G. Brook, W. J. Chatterton, J. F. Sawyer, D. W. Hughes, K. Vorspohl, *Organometallics* **1987**, *6*, 1246–1256; N. Wiberg, G. Preiner, K. Schurz, G. Fischer, *Z. Naturforsch., B* **1988**, *43*, 1468–1474; A. G. Brook, S. S. Hu, W. J. Chatterton, A. J. Lough, *Organometallics* **1991**, *10*, 2752–2757.

[17] H.-M. Chen, J. P. Oliver, *J. Organomet. Chem.* **1986**, *316*, 255–260; B. Kopping, C. Chatgilialoglu, M. Zehnder, B. Giese, *J. Org. Chem.* **1992**, *57*, 3994–4000.

[18] G. Gutekunst, A. G. Brook, *J. Organomet. Chem.* **1982**, *225*, 1–3.

[19] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[20] G. M. Sheldrick, University of Göttingen, Germany, **1993**.

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