ELSEVIER

Preliminary communication

1,2-Di(hypersilyl)-ethylene — the unexpected result of the reaction of tris(trimethylsilyl)silyllithium with formic acid methyl ester

Thoralf Gross [a], Rhett Kempe [b], Hartmut Oehme [a],*

[a] *Fachbereich Chemie der Universität Rostock, Rostock D-18051, Germany*
[b] *Max-Planck-Gesellschaft, AG "Komplexkatalyse" an der Universität Rostock, Buchbinderstr. 5–6, D-18055 Rostock, Germany*

Abstract

Tris(trimethylsilyl)silyllithium reacts with methyl formate in a molar ratio of 2:1 under formation of 1,2-bis[tris(trimethyl-silyl)silyl]ethene (9). As reaction intermediates formyl-tris(trimethylsilyl)silane (5) and lithium bis[tris(trimethylsilyl)silyl]methoxide (6) were identified. 6 is quenched with water to give bis[tris(trimethylsilyl)silyl]methanol (7).

1. Results and discussion

Recently we succeeded in synthesizing the first geminal di(hypersilyl) compound with a central carbon atom [1]. The reaction of tris(trimethylsilyl)silyllithium (1) with dichloromethyl-methylether (2) after a straightforward replacement of the two chlorine atoms of 2 affords the bis[tris(trimethylsilyl)silyl]methyl-methylether (4). Obviously, the extreme steric shielding of the hypersilyl substituent, which is illustrated by a cone angle of 199° for the $(Me_3Si)_3Si-C$ group [2], should not allow the approach of a hypersilyl nucleophile at an already hypersilyl substituted sp^3 carbon atom to form a di(hypersilyl) derivative by a bimolecular nucleophilic substitution process, i.e. with inversion of the configuration at the reaction centre. Therefore we suppose the reaction of 1 with the dichloromethylether 2 to proceed through a carbenium ion intermediate 3. 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 (Eq. (1)).

(1)

A stereochemical situation similar to the approach of 1 at the carbenium ion 3 is expected for the addition of 1 at the carbonyl group of acyl-tris(trimethyl-silyl)silanes. That is why we started studying the reaction of tris(trimethylsilyl)silyllithium (1) with carboxylic acid esters following the intention to get in a first step acyl-tris(trimethylsilyl)silanes, which after ad-

---

* Corresponding author.

dition of a second equivalent of **1** and subsequent protonation should result in the formation of 1,1-di(hypersilyl)alcohols. The reaction of **1** with methyl formate in a 2:1 molar ratio should give the formylhypersilane **5**, which is expected to be converted in situ by addition of the second equivalent of the silicon nucleophile **1** at the carbonyl group of the formmylsilane to afford the lithium di(hypersilyl)methoxide **6**, which should be protonated during the aqueous work-up to give the di(hypersilyl)methanol **7**. But actually, the result of the experiments is not the formation of **7**, but we obtained in a yield of more than 60% 1,2-di(hypersilyl)ethylene **9** (Scheme 1).

The structure elucidation of **9** is based on NMR as well as on MS and Raman studies (see Section 2). The NMR spectra of **9** are very straightforward showing only one signal for the trimethylsilyl groups in both the ^{1}H-, ^{13}C- and ^{29}Si-spectra. An intensive Raman absorption band at $1529\,\mathrm{cm}^{-1}$ is considered as being indicative for the symmetrically substituted C=C-function. The X-ray analysis of **9** revealed a complete disorder of all trimethylsilyl groups and therefore a full accurate structure determination could not be performed. Nevertheless the data obtained confirm the proposed constitution and for the two hypersilyl groups unambiguously an *E*-configuration was found.

The mechanism of the formation of **9** is not really clear. One may assume that the lithium alkoxide **6** because of the extreme steric strain caused by the extended hemispherical $(Me_3Si)_3Si$ groups undergoes a Brook rearrangement leading to an intermediate **8**, which decomposes under formation of lithium-tris(trimethyl-

silyl)silanolate and tris(trimethylsilyl)silylcarbene which finally dimerizes under formation of **9**. A similar rearrangement and C,O-bond cleavage was proposed for the formation of substituted stilbenes found as by-products in the synthesis of transient silenes by deprotonation of 2,4-di-*tert*-butylphenyl tris(trimethylsilyl)silylmethanol or 2,4,6-triisopropylphenyl-tris(trimethylsilyl)silylmethanol, respectively, by a modified Peterson reaction [3] and appears to be typical for highly strained 1-hypersilylalkoxides. Of course, also alternative pathways to **9**, involving for instance elimination reactions of **6** and an intermediate silene, may be discussed. The exploration of these problems is the subject of current studies.

The intermediate existence of the formylsilane **5** and the di(hypersilyl)methoxide **6** in the course of the synthesis of the di(hypersilyl)ethylene **9** could actually be proved. Acyl-tris(trimethylsilyl)silanes, as we learned meanwhile, are best prepared by the interaction of **1** with carboxylic acid esters [4], and consequently the 1:1 reaction of **1** with methyl formate in ether results in the formation of **5**. The oily substance obtained after removal of the solvent, extraction of the residue with pentane and evaporation of the solution gave NMR data identical with those described [5]. When the 2:1 reaction of **1** with methyl formate in ether is interrupted after a short reaction time by addition of water, small quantities of di(hypersilyl)methanol **7** could be isolated. Optimization experiments, including the change of the solvent, gave maximum yields of 12% of **7**, when the reaction was carried out at $-78\,^\circ$C in pentane and the water was added to the cold solution after 30 min.
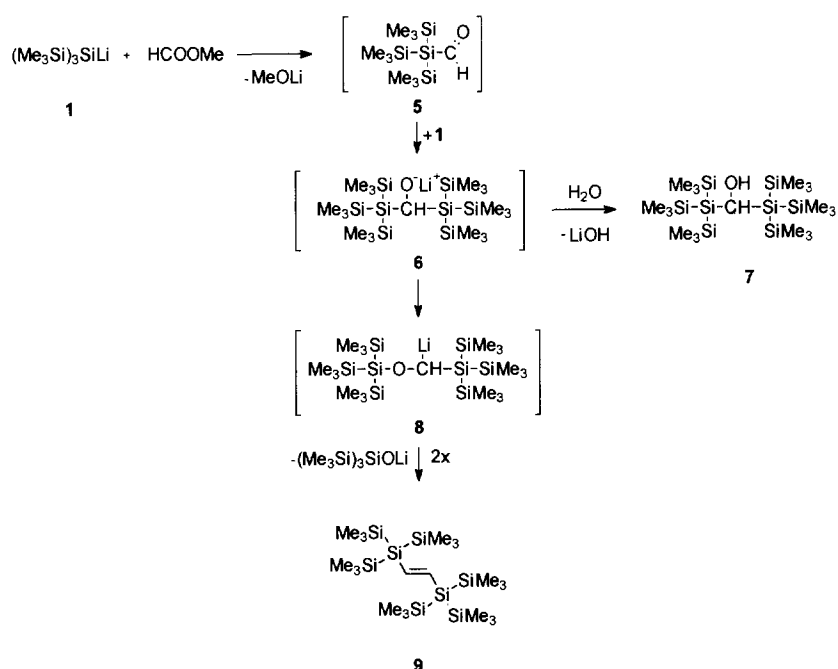
Scheme 1. The reaction of tris(trimethylsilyl)silyllithium (**1**) with methylformate.

7 is a colorless solid. Again, solution NMR studies indicate all six trimethylsilyl groups to be magnetically equivalent. Also IR and MS data agree with the proposed structure (see Section 2).

2. Experimental details

7. At $-78\,^{\circ}$C 0.05 g (0.8 mmol) methyl formate are added at once to an intensively stirred suspension of 0.8 g (1.6 mmol) of $(Me_3Si)_3SiLi \cdot 3THF$ [6] in 50 ml pentane. After 30 min water is added to the cold solution; the organic layer is separated, dried and evaporated. **7** is isolated by column chromatography (silica gel, heptane) and recrystallized from ethanol. Yield 0.05 g (12%), m.p. 164–167 °C (under partial sublimation). IR (Nujol): $\nu = 3611$ and 3583 cm^{-1} (OH$_{free}$), 3380 cm^{-1} (OH$_{ass}$). ^{1}H NMR (benzene-d_6): $\delta = 0.34$ (s, SiCH$_3$, 54H), 0.83 (d, $^3J = 7.53$ Hz, CHOH, 1H), 4.59 (d, $^3J = 7.63$ Hz, CHOH, 1 H). ^{13}C NMR (benzene-d_6): $\delta = 2.8$ (SiCH$_3$), 53.1 (COH). ^{29}Si NMR (benzene-d_6): $\delta = -13.1$ (SiMe$_3$), -65.8 (SiSiMe$_3$). MS (CI, isobutane) m/z (%): 523 (2) [M$^+$ $-$ H], 507 (100) [M$^+$ $-$ OH], 434 (17)[M$^+$ $-$ OH $-$ SiMe$_3$], 247 (14) [Si(SiMe$_3$)$_3^+$]. C$_{19}$H$_{56}$OSi$_8$ (525.25): calcd. C, 43.44; H, 10.74; found C, 42.37; H, 10.49.

9. At room temperature 1.7 g (3.6 mmol) of $(Me_3Si)_3SiLi \cdot 3THF$, dissolved in 50 ml of ether, are added gradually to an ethereal solution of 0.11 g (1.8 mmol) methyl formate. After 3 h stirring water is added, the organic layer is separated, evaporated and the residue is purified by column chromatography (silica gel, heptane), vacuum sublimation and recrystallization from ethanol. Yield 0.29 g (61%), m.p. 175–180 °C.

Raman: $\nu = 1529$ cm^{-1} (C=C). ^{1}H NMR (benzene-d_6): $\delta = 0.29$ (s, SiCH$_3$, 54H), 6.79 (s, C=CH, 2H). ^{13}C NMR (benzene-d_6): $\delta = 0.0$ (SiCH$_3$), 145.5 (C=C). ^{29}Si NMR (benzene-d_6): $\delta = -13.0$ (SiMe$_3$), -80.9 (SiSiMe$_3$). MS (CI, isobutane) m/z (%): 520 (30)[M$^+$], 505 (5)[M$^+$ $-$ CH$_3$], 447 (22)[M$^+$ $-$ SiMe$_3$], 273 (33) [M$^+$ $-$ Si(SiMe$_3$)$_3$], 73 (100) [SiMe$_3^+$]. C$_{20}$H$_{56}$Si$_8$ (521.35): calcd. C, 46.08; H, 10.83; found C, 44.83; H, 10.65.

References

[1] E. Jeschke, T. Gross, H. Reinke and H. Oehme, *Chem. Ber., 129* (1996) 841.

[2] M. Aggarwal, M.A. Ghuman and R.A. Geanangel, *Main Group Met. Chem., 14* (1991) 26.

[3] F. Luderer, H. Reinke and H. Oehme, *J. Organomet. Chem., 510* (1996) 181. F. Luderer, H. Reinke and H. Oehme, *Chem. Ber., 129* (1996) 15.

[4] T. Gross, D. Hoffmann and H. Oehme, unpublished results, 1996.

[5] F.H. Elsner, H.-G. Woo and T.D. Tilley, *J. Am. Chem. Soc., 110* (1988) 313.

[6] G. Gutekunst and A.G. Brook, *J. Organomet. Chem., 225* (1982) 1.