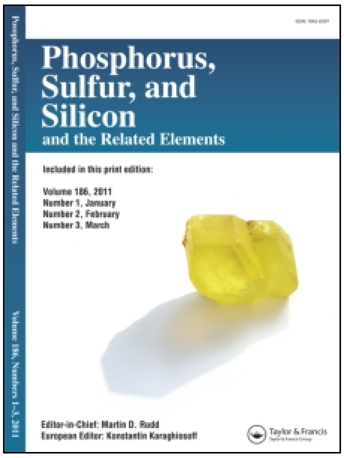

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# THE SYNTHESIS OF Si,Si'-BIS(TRISILYLMETHYL)DISILAZANE AND Si,Si'-BIS(TRISILYLMETHYL)DISILYLACETYLENE

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The synthesis of Si,Si'-bis(trisilylmethyl)disilazane and Si,Si'-bis(trisilylmethyl)disilylacetylene is presented. Both compounds have been fully characterized by standard spectroscopic methods.

*Key words:* Silanes, silyl triflates, silazanes, silylacetylenes.

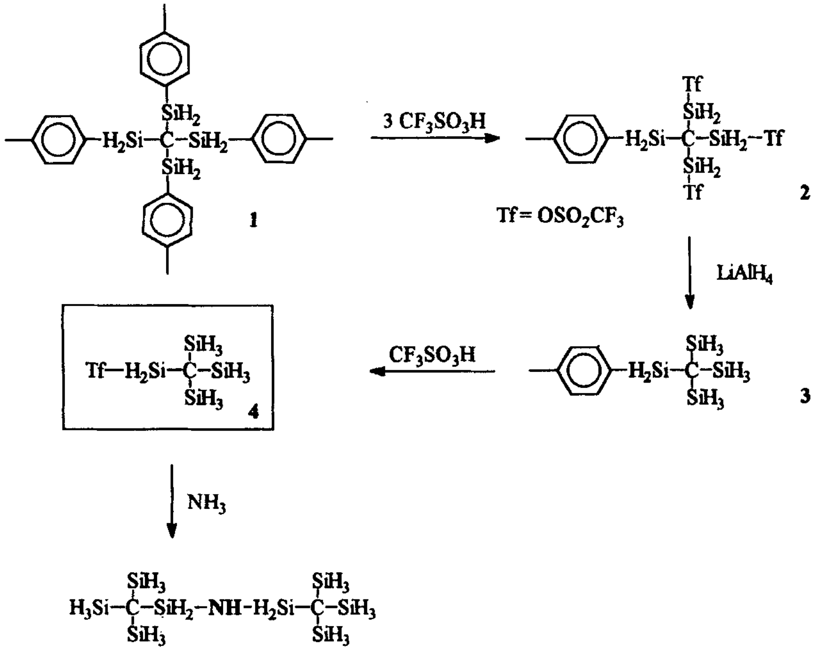
## INTRODUCTION

Si,Si'-bis(trisilylmethyl)disiloxane $[(H_3Si)_3CSiH_2]_2O^1$, a silicon- and hydrogen-rich molecule containing carbon and oxygen fully surrounded by silicon atoms is an interesting precursor for CV-deposition of carbon and oxygen containing silicon networks. In thin films generated from silane gas saturated with its vapour, the optoelectronical properties and the stability of the amorphous hydrogenated silicon (a-Si:H) produced are modified by the incorporation of both *carbon* or *oxygen.*[2] Following the same train of thoughts as in the synthesis of Si,Si'-bis(trisilylmethyl)-disil$\underline{ox}$ane $[(H_3Si)_3CSiH_2]_2\mathbf{O}$, its nitrogen analog Si,Si'-bis(trisilylmethyl)disil$\underline{az}$ane $[(H_3Si)_3CSiH_2]_2\mathbf{NH}$ has now also been prepared (Scheme 1). This molecule is expected to yield *carbide/nitride* type amorphous silicon films in thermal and plasma deposition processes.

The corresponding acetylide was included into the synthetic studies in order to provide an alternative precursor for prestructured silicon *carbon* alloys. Si,Si'-bis(trisilylmethyl)disilylacetylene $[(H_3Si)_3CSiH_2]_2C_2$, **6**, is a binary Si/C-system having Si—C bonds but no C—H bonds. Its stoichiometric Si/C ratio is 2:1. While tetrasilylmethane[4] (Si:C ratio 4:1), hexasilylbenzene[5] (1:1) and disilyacetylene[6] (1:1) have been successfully synthesized in this laboratory, tetrasilylethene, as an alternative with Si:C = 2:1, has only been identified in traces by standard spectroscopic methods, but not isolated.[5]

## RESULTS

Starting from tetrakis(p-tolylsilyl)methane[3] **1**, the key intermediate **4** is obtained after successive Si-aryl cleavage and reduction steps. Gaseous ammonia is the nitrogen source for Si,Si'-bis(trisilylmethyl)disilazane **5**, but also traps the triflic



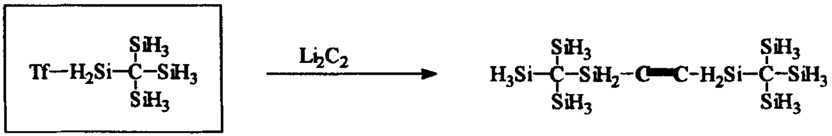
5

SCHEME I

TABLE I

NMR parameters of compounds 5 and 6

| | 5 | 6 |
|---|---|---|
| $^1$H NMR [δ, ppm; Hz] | 4.6 (d, SiH$_2$); $^1$J(HSi) = 217, $^3$J(HSiNH) = 5.7;<br>3.8 (s, SiH$_3$); $^1$J(SiH) = 205;<br>0.7 (br, NH) | 4.3 (s, SiH$_2$)<br>3.9 (s, SiH$_3$) |
| $^{29}$Si NMR [δ, ppm; Hz] | -21.0 (mtm, SiH$_2$); $^1$J(SiH) = 217;<br>-53.7 (qm, SiH$_3$); $^1$J(SiH) = 205 | -21.6 (tm, SiH$_2$); $^1$J(SiH) = 214;<br>-54.4 (q-Ψnon), SiH$_3$); $^1$J(SiH) = 207.2 |
| $^{15}$N NMR [δ, ppm; Hz] | -382.0 (dquin, NH); $^1$J(NH) = 70.3, $^2$J(NSiH) = 5.7 | |
| $^{13}$C NMR [δ, ppm; Hz] | -29.7 (s, CSi$_4$); $^1$J(CSi) = 31.2 | 109.4 (m, CC)<br>-29.3 (s, CSi$_4$) |



$Tf{-}H_2Si{-}C(SiH_3)_3 \xrightarrow{Li_2C_2} H_3Si{-}C(SiH_3)_2{-}SiH_2{-}C{\equiv}C{-}H_2Si{-}C(SiH_3)_3$

4

6

SCHEME II

acid released in the Tf/N-substitution. After separation of the ammonium triflate, distillation of the mother liquor yields the pure product **5**, which is easily identified by NMR spectroscopy (see Table I).

$^{15}N$-NMR-DEPT techniques are the appropriate means to obtain direct information about the bonding situation at the central nitrogen atom. As a result of $^1J(NH)$ coupling the $^{15}N$-NMR signal is split into a doublet. Through $^2J(NSiH)$-coupling, each signal is further split into a quintet. Analysis of the $^1H$, $^{13}C$, and $^{29}Si$ spectra is equally straightforward (Table I). It should be mentioned that not even traces of the trisilylamine $[(H_3Si)_3CSiH_2]_3N$ were detected in the reaction mixture. The third silylation step at nitrogen appears to be sterically hindered.

For the synthesis of **6**, (trisilylmethyl)silyltriflate **4** is also the key intermediate just as in the preparation of **5**. It is reacted with dilithiumacetylide in diethylether. $H/C_2$-substitution concurring with the $Tf/C_2$-substitution leads to a series of higher molecular weight compounds if the procedure is carried out at temperatures above −60°C. It is only under kinetically controlled reaction conditions (< −100°C) that the formation of **6** is prevailing. The thermolability of silylacetylenes requires isolation of the products by successive condensation steps under high vacuum conditions at temperatures only slightly higher than ambient temperature. At temperatures about 40°C decomposition occurs. Compound **6** has been fully characterized by NMR spectroscopy (see Table I). All data are within the expected ranges. As a part of an $A_2A'_2X$-spin system (A = $SiH_2$ protons), the $^{13}C$-resonance of the acetylene-bridge appears as the expected multiplet.

## EXPERIMENTAL

NMR spectra were recorded on a Jeol JMN-GX 400, mass spectra on a Varian MAT A317, and IR spectra on a Perkin Elmer FT-IR 577 spectrometer. Elemental analyses of the compounds gave consistently low C-values owing to silicon carbide formation upon combustion.

*Si,Si'-bis(trisilylmethyl)disilazane* (**5**): To a solution of 1.2 g (5.3 mmol) of (p-tolylsilyl)trisilylmethane **3**[1] in 25 ml of toluene, 0.5 ml (5.3 mmol) of triflic acid was added at a temperature of −78°C. After stirring for 1 h, the mixture was allowed to warm to room temperature. The crude product was treated with gaseous dry ammonia at −20°C for 20 min. Separation of the precipitated ammonium triflate from the mother liquor by filtration and distillation under high vacuum conditions yielded 0.23 g (30%) of **5** as a colourless liquid (b.p. 55°C/0.1 Torr).
NMR data see Table I. MS (EI, 70 eV): m/z = 282–285 ($C_2Si_8NH_x$), 253–255 ($C_2Si_7NH_x$), 220–223 ($C_2Si_6NH_x$), 180 ($CSi_5NH_{14}$), 148–150 ($CSi_4NH_x$), 116–119 ($CSi_3NH_x$), 101–104 ($CSi_3H_x$). IR (film) [$cm^{-1}$]: 3371.6 w $\nu$(NH), 2149.4 s $\nu$(SiH), 1182.2 m $\nu_{as}$(SiN), 862.4 s $\delta$(SiH).

*Si,Si'-bis(trisilylmethyl)disilylacetylene* (**6**): A freshly prepared solution of (trisilylmethyl)silyltriflate **4** [from 5.5 g (24 mmol) of (p-tolysilyl)trisilylmethane **3**[1] and 2.2 ml (25 mmol) of triflic acid] was added slowly to a suspension of dilithiumacetylide in diethyl ether [made from 4.21 g (12 mmol) 1,1,2,2-tetrabromoethane, dissolved in 40 ml of diethyl ether, and 31 ml of a 1.6 M solution of n-BuLi in diethyl ether] at −100°C. For completion of the reaction the mixture was stirred for 3 h at that temperature, then all volatile compounds were evaporated under high vacuum conditions. The oily residue was dissolved in toluene to achieve complete precipitation of the lithium salts. After separation of the mother liquor from the salts and evaporating the toluene, **6** was isolated by several condensation steps under high vacuum conditions in good purity [0.7 g yield (20%)].

NMR data see Table I. MS (EI, 70 eV): m/z = 290–294 ($C_4Si_8H_x$), 260–266 ($C_4Si_7H_x$), 231–235 ($C_4Si_6H_x$), 201–203 ($C_4Si_5H_x$), 183–189 ($C_2Si_5H_x$), 153–159 ($C_3Si_4H_x$), 126–128 ($C_3Si_3H_x$), 97–99 ($C_3Si_2H_x$).

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