Synthesis and Reactions of Alkynyl Oligosilanes

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Synthesis, properties, and reactions of various alkynyl oligosilanes, and their potassium derivatives are described. A series of tris(trimethylsilyl)silylalkynes have been prepared. Their reaction with potassium *tert*-butoxide leads to the corresponding potassium derivatives, which can be subjected to further derivatization. X-ray structures of three oligosilylalkynes are reported.

Introduction

Over the last five years we have developed an interest in the chemistry of silyl anions which permits the synthesis of both larger oligosilanes and metal silyl compounds.[1] Besides the advancements in this field it is still desirable to enhance the number of compatible functional groups which can be used. Hence, we decided to study alkynylsilanes. Alkynes can be further functionalized by employing addition and substitution reactions and in the case of metal silyl compounds the triple bond exhibits a charge-stabilizing effect.

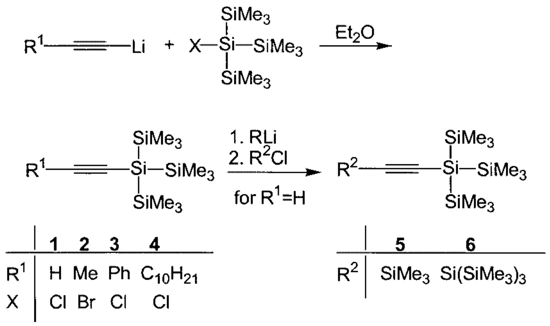
Alkynylsilanes are commonly prepared by the reaction of silyl halides or triflates with metal alkynyl compounds in organic solvents.[2–4] However, surprisingly few alkynyl-substituted oligosilanes are known[5] to date and the corresponding anions are almost completely unknown.[1b]

In connection with this we report on the selective synthesis of oligosilyl alkynes and their reactions with potassium *tert*-butoxide to form mono- or di-anions along with the further reactions that they are involved in.

Results and Discussion

Synthesis of Alkynylsilanes

The most convenient method for the synthesis of alkynylsilanes makes use of the reaction of silyl halides with metallated alkynes such as Grignard compounds.[6] Our preferred route was that of the lithiated alkynes. Although a two step synthesis was employed avoiding the use of dilithiated acetylene an excellent yield of over 80% was obtained for **6,** compared with the 5% reported.[7] The nature of the lithium alkyl used for the metallation of the alkyne was not important with the exception of the case of lithiation of phenylated alkynes where the use of methyllithium was found to be crucial. The reacting silanes were usually chlorosilanes, only for the 1-propinyl compound **2,** and also **10**, were the more reactive bromosilanes used (Scheme 1).



Scheme 1. General scheme for the synthesis of alkynylsilanes

Reaction of propargyl tosylate with potassium tris(trimethylsilyl)silane[1] affords propargylsilane **7** in a yield of 80%. Astonishingly deprotonation of the alkyne by the highly basic silyl anion was not a significant side reaction. Reaction towards the bissilylated compound **8** was easily achieved by lithiation of **7** and reaction with chlorotris(trimethylsilyl)silane (Scheme 2).

In order to obtain a compound bearing two alkynyl groups we treated 2,2-dibromohexamethyltrisilane with two equivalents of lithiated phenylacetylene (Scheme 3).

In an attempt to prepare a higher alkynyl oligosilane, bromopentakis(trimethylsilyl)disilane was treated with phenyl acetylide (Scheme 4).

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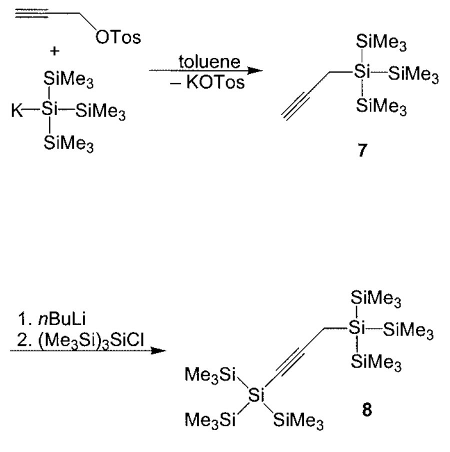
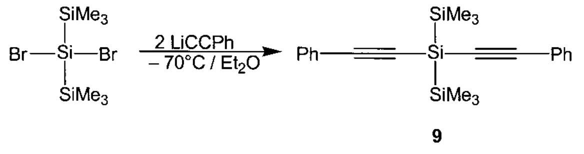
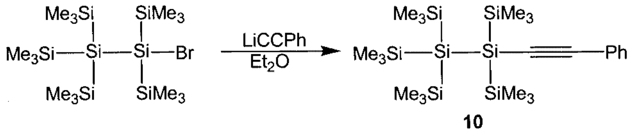


Scheme 2. Preparation of silylated propyne derivatives **7** and **8**



Scheme 3. Preparation of the dialkyne derivative **9**



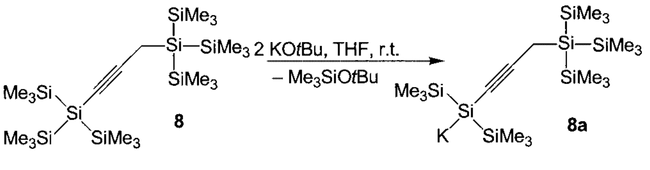
Scheme 4. Preparation of **10**

Preparation of Alkynyl Silyl Anions

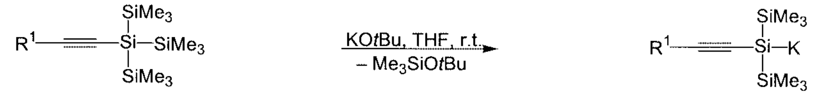
Recently, we described the reaction of oligosilanes with one or two molar equivalents of potassium *tert*-butoxide to give the respective mono-[1,16] or dianions[1b] and a silyl ether. Monoanions were formed in THF at ambient temperature, the formation of dianions, however, required a temperature of about 60 °C and reaction times of a few days. The use of benzene or toluene as a solvent and the addition of 18-crown-6 facilitated the formation of dianions so that complete conversion within a few hours at room temperature could be achieved. The alkynylsilanes discussed here proved to be considerably more reactive than the silanes studied so far. The conversion into the respective mono- or dianions proceeded smoothly at room temperature within minutes and even at −20 °C it proceeded within an hour. The alkynyl group seems to enhance reactivity towards the potassium alkoxide significantly. The effect is so pronounced that it is not possible to achieve clean mono metallation for the case of the alkynylidene-bridged compound **6**. Only a mixture of starting material, mono- and dianion could be detected upon reaction with one equivalent of potassium *tert*-butoxide. As already observed for the reactions with other oligosilanes, conversion only occurs in THF, DME or even more polar ethereal solvents. No conversion, even with the more reactive alkynylsilanes occurred in diethyl ether, benzene or toluene.

The metallations of compounds **2**, **3**, **4** and **5** proceeded as expected from our experience gained thus far. A trimethylsilyl group was formally replaced by a negative charge. All reactions were faster than the conversion with tetrakis(trimethylsilyl)silane,[1] with compound **3** being the most reactive. In THF the conversion of **3** at ambient temperature was completed within less than five minutes. Interestingly the reaction of tris(trimethylsilyl)silylacetylene (**1**) with potassium *tert*-butoxide did not yield the expected anion, instead the only product detected was the rearrangement product **5a** which can also be obtained from **5** (Scheme 5). The nature of the rearrangement is still unclear. It is, however, likely that a reaction of the initially formed compound **1a** with *tert*-butyltrimethylsilyl ether occurs.

Tris(trimethylsilyl)propargylsilane (**7**) underwent another unexpected rearrangement. The result of its reaction with potassium *tert*-butoxide was compound **2a**. A closer look at the reaction revealed an initial base catalyzed rearrangement of **7** to **2,** which then was followed by conversion into **2a**. In contrast to the rapid and exclusive reaction of **6** towards the dianion compound **6a**, **8** was showing very different behavior. Addition of one equivalent of potassium *tert*-butoxide did not effect the formation of the expected monoanion **8a**. A second equivalent of the alkoxide eventually resulted in the fast formation of **8a** but even after 72 h no dianion could be observed and complete decomposition had occurred (Scheme 6).



Scheme 6. Monometallation of **8**



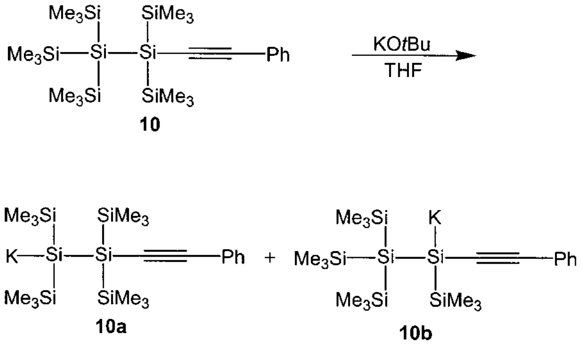
	1	2	3	4	5	6
R^1	H	Me	Ph	$C_{10}H_{21}$	$SiMe_3$	$Si(SiMe_3)_3$

	2a	3a	4a	5a	6a
R^1	Me	Ph	$C_{10}H_{21}$	$SiMe_3$	$Si(SiMe_3)_2K$

Scheme 5. Synthesis of potassium alkynylsilanes

The reaction of the dialkyne **9** with potassium *tert*-butoxide did not give a dialkynyl(trimethylsilyl)silyl anion. Although a vigorous and clearly exothermic reaction occurred no soluble silicon containing product was obtained. The brown insoluble material, which could be isolated, seemed to indicate a polymerization reaction. An early and isolated example by Gilman et al.[8] reported addition of two equivalents of triphenylsilyllithium across diphenylacetylene. Besides the addition product almost 90% of polymeric material was obtained. An anionic addition polymerization process may account for the course of reaction in both cases.

The behavior of starting material **10** in its reaction with potassium *tert*-butoxide was of special interest. In the analogous reaction with pentakis(trimethylsilyl)phenyldisilane we have observed a perfect regioselectivity for the cleavage of a trimethylsilyl group in the β-position to the phenyl group. However, for the case of **10** a mixture of the two possible anions **10a** to **10b** was found in a ratio of about 2 to 1 (Scheme 7).



Scheme 7. Reaction of **10** with potassium *tert*-butoxide

NMR Spectroscopy

^{29}Si NMR spectroscopy is most useful for the chemistry of oligosilanes. While the resonances for the tertiary silicon atom of alkylated tris(trimethylsilyl)silanes can be found at around −80 ppm, the alkynyl substituent causes a high-field shift to $\delta = -101$ ppm. Replacement of one trimethylsilyl group by potassium causes another shift to approximately $\delta = -155$ ppm. This behavior is in accordance with our previous observations on other silyl potassium compounds.[1]

Table 1. Increments for the calculation of ^{13}C NMR shifts of substituted alkynes[9,10,16]

Group	α	β
Me	+8.5	−3.6
*n*Bu	+11.1	−5.9
Ph	+12.7	−6.4
$SiMe_3$	+17.4	+21.8
$Si(SiMe_3)_3$	+11.5	+24.9
$CH_2Si(SiMe_3)_3$	+13.0	−4.3

In the case of alkynylsilanes ^{13}C NMR spectroscopy is also of some interest. As acetylenes have only two substituents it is easy to study their influence on the ^{13}C NMR shift. Using acetylene as a parent compound α- and β-shift effects can be observed upon replacement of a proton by another substituent.[9] While alkyl groups cause the α-carbon to resonate at a lower and the β-carbon at a higher field, phenyl groups effect both signals at a lower field with the β-shift being smaller. The trimethylsilyl group again gives rise to a shift to a lower field but the magnitude of the influence is reversed compared to the phenyl group.[10] The tris(trimethylsilyl)silyl group has a similar but even more pronounced influence (Table 1). This plain increment system can also be used advantageously for a rough estimate of disubstituted alkynes, as seen from Table 2, where the observed ^{13}C shift values for the tris(trimethylsilyl)silylated alkynes can be compared to those obtained by simple increment addition to the base value of $\delta = 71.9$ ppm for acetylene.

Table 2. ^{13}C NMR shifts of $(Me_3Si)_3Si-C(A)=C(B)-R$ in ppm; incremental values in brackets

Group R	δ C(A)	δ C(B)
Me	73.1 (79.8)	105.2 (105.3)
$C_{10}H_{19}$	76.5 (77.5)	113.9 (107.9)
Ph	76.5 (89.8)	111.3 (109.5)
$SiMe_3$	107.9 (105.2)	117.7 (114.2)
$Si(SiMe_3)_3$	109.6 (108.3)	109.6 (108.3)
$CH_2Si(SiMe_3)_3$	73.4 (79.1)	110.8 (109.8)

X-ray Crystallography

As has already been mentioned only a few oligosilylacetylenes have been synthesized to date. It is therefore not completely surprising that no crystal structures of tertiary silylacetylenes have been reported so far. Even for secondary silylacetylenes only two examples can be found.[2,11] One reason for this obvious lack of structural investigations may be difficulties in obtaining good quality crystals. Most compounds investigated by us were either oils or solids with melting points close to room temperature. Nevertheless, we were able to determine the first examples of crystal structures of isotetrasilanylacetylenes. Compounds **3**, **6**, and **9** could be subjected to structure analysis (Table 3, Figures 1−3). The structural features of all three compounds are within the ranges of what is expected. Examples of the acetylenic triple bond length of alkynylsilanes range from 1.16 Å to 1.22 Å.[12] **3** [1.185(5) Å], **6** [1.217(6) Å] and **9** [1.205(5), 1.204(5) Å] fit into this range with **6** exhibiting the longest bond, probably reflecting the two bulky silyl groups. The tetrahedral bond angles around the central silicon atoms are clearly a function of the spatial demand of the substituents. This can be observed best for the diacetylene compound **9**, where the two trimethylsilyl groups open up at an angle of 117.4°. Deviations from the expected 180° for the CCSi angle are comparatively small for **3** [176.5(4)°] and **6** [178.9(4)°] and only for **9** [178.7(4), 173.3(3)°] was a very slight bending observed. The two tris(trimethylsilyl)silyl groups of **6** exhibit an almost perfectly staggered conformation with respect to each other (Figure 2).

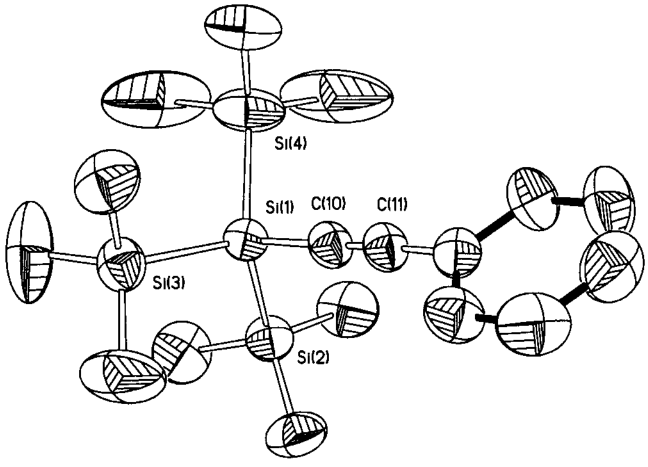


Figure 1. The molecular structure and numbering of **3** with 30% probability thermal ellipsoids; all hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Si(1)−Si(4) 2.317(2), Si(1)−Si(3) 2.3347(19), Si(1)−Si(2) 2.3454(18), Si(1)−C(10) 1.837(5), C(10)−C(11) 1.185(5), C(10)−Si(1)−Si(4) 106.00(15), C(10)−Si(1)−Si(3) 103.18(14), Si(4)−Si(1)−Si(3) 111.59(8), C(10)−Si(1)−Si(2) 107.97(15), Si(4)−Si(1)−Si(2) 114.81(7), Si(3)−Si(1)−Si(2) 112.33(7), Si(1)−C(10)−C(11) 176.5(4), C(10)−C(11)−C(12) 178.3(5)

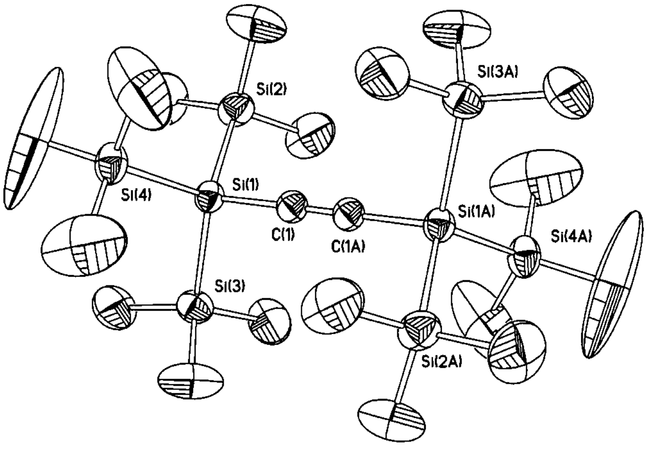


Figure 2. The molecular structure and numbering of **6** with 30% probability thermal ellipsoids; all hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Si(1)−C(1) 1.835(3), Si(1)−Si(2) 2.3430(15), Si(1)−Si(3) 2.3469(16), Si(1)−Si(4) 2.3466(13), C(1)−C(1A) 1.217(6), C(1)−Si(1)−Si(2) 105.73(11), C(1)−Si(1)−Si(3) 104.79(11), Si(2)−Si(1)−Si(3) 113.33(6), C(1)−Si(1)−Si(4) 104.76(10), Si(2)−Si(1)−Si(4) 112.98(6), Si(3)−Si(1)−Si(4) 114.11(6), C(1)−Si(1)−Si(2)−C(4) 178.7(4), Si(1)−C(1)−C(1A) 178.9(4)

Conclusion

A number of alkyne substituted oligosilanes have been prepared mainly by the reaction of lithiated alkynes with chloro- or bromooligosilanes. Reaction of these compounds with potassium *tert*-butoxide showed considerably enhanced reactivity compared to silyl or alkyl-substituted oligosilanes. Usually within minutes formation of a silyl potassium compound and *tert*-butyltrimethylsilyl ether was complete. Phenylacetylene derived compounds (**3, 10**) are the most reactive among all investigated materials. Reaction with a compound possessing two alkynyl substituents (**9**) led to a vigorous and strongly colored reaction which did not yield soluble silicon containing material. The reaction of a propargylsilane (**7**) with the potassium alkoxide gave an initial rearrangement to the propynylsilane (**2**) followed by the formation of a propynylsilyl potassium compound (**2a**). An alkynylidene-bridged bisoligosilyl compound (**6**) could be used to obtain an oligosilyl dianion (**6a**) by means of a smooth reaction. With a similar propargylidene bridged compound (**8**) only mono-metallation could be achieved.

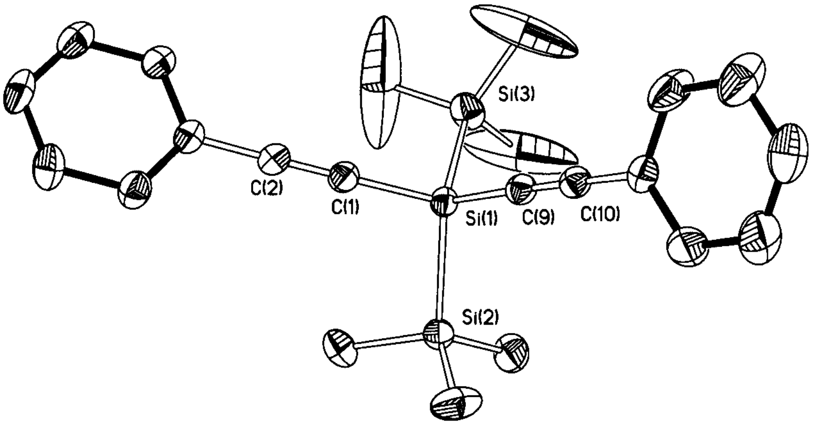


Figure 3. The molecular structure and numbering of **9** with 30% probability thermal ellipsoids; all hydrogen atoms have been omitted for clarity; selected bond lengths (Å) and bond angles (°) with estimated standard deviations: Si(1)−C(9) 1.843(4), Si(1)−C(1) 1.846(4), Si(1)−Si(3) 2.3501(16), Si(1)−Si(2) 2.3539(15), C(1)−C(2) 1.205(5), C(9)−C(10) 1.204(5), C(9)−Si(1)−C(1) 107.70(16), C(9)−Si(1)−Si(3) 109.34(13), C(1)−Si(1)−Si(3) 106.21(13), C(9)−Si(1)−Si(2) 109.38(12), C(1)−Si(1)−Si(2) 106.30(13), Si(3)−Si(1)−Si(2) 117.45(6), Si(1)−C(1)−C(2) 173.3(3), Si(1)−C(9)−C(10) 178.7(3)

In summary it can be concluded that alkynyl substituents substantially enhance the reactivity of oligosilanes towards potassium alkoxide attack. Given all the possible derivatization reactions of the alkynyl group, its introduction into oligosilyl anions considerably extends the scope of this chemistry.

Experimental Section

General Remarks: All reactions involving air-sensitive compounds were carried out under an atmosphere of nitrogen or argon using either Schlenk techniques or a glovebox. All solvents besides $CDCl_3$ were dried over sodium/potassium alloy under nitrogen and were freshly distilled prior to use. Potassium *tert*-butoxide was purchased from Merck. Other chemicals were obtained from different chemical suppliers and used as received.

Aqueous workup was performed by adding the reaction mixture to 2 M H_2SO_4 followed by separation of the layers. Subsequently, the aqueous layer was extracted twice with the indicated solvent. The combined organic layers were washed with a saturated aqueous sodium hydrogen carbonate solution and then dried over sodium sulfate.

^{1}H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. Samples for ^{29}Si NMR spectra were either dissolved in deuterated benzene or chloroform, or the reaction samples were measured in the presence of a D_2O capillary in order to provide an external lock frequency signal. To compensate for the low isotopic abundance of ^{29}Si the INEPT pulse sequence was used to amplify the signal.[13]

GC analyses were carried out on an HP 5890 series II equipped with capillary column HP-1ms (25 m × 0.251 mm; 0.33 μm) and an HP 5971 mass spectrometer.

GC/MS samples of derivatized silyl anions were obtained by adding a solution of the nucleophile to a mixture of 10% ethyl bromide in diethyl ether or to the organic layer of a mixture of diethyl ether/2 M H_2SO_4 to give the corresponding ethylated or protonated silane species in a very rapid, clean and quantitative reaction.

Elementary analyses were carried out using a Heraeus Vario Elementar. Tetrakis(trimethylsilyl)silane,[14] tris(trimethylsilyl)silane,[1a] chlorotris(trimethylsilyl)silane,[15] tris(trimethylsilyl)silylpotassium,[1,16] propargyltosylate,[17] tris(trimethylsilyl)silylethyne (**1**),[1b] bis[tris(trimethylsilyl)silyl]ethyne (**6**),[1b] and bis[potassiobis(trimethylsilyl)silyl]ethyne (**6a**)[1b] were prepared according to literature procedures.

Propynyltris(trimethylsilyl)silane (2)

Bromotris(trimethylsilyl)silane: Tris(trimethylsilyl)silane (24.0 g, 97.0 mmol) was dissolved at room temperature in bromoform (100 mL). After 16 h the solution was heated to 70 °C for 1 h. After complete conversion (reaction control by GC) bromoform and methylenebromide were distilled off leaving bromotris(trimethylsilyl)silane (28.9 g, 91%) as colorless, deliquescent crystals. ^{1}H NMR (C_6D_6): $\delta = 0.29$ (s, 27 H) ppm. ^{13}C NMR (C_6D_6): $\delta = 1.7$ ppm. ^{29}Si NMR (THF, D_2O): $\delta = -12.7, -24.0$ ppm. MS: *m/z* (%) = 326 (4), 328 (5) [M^+], 313 (6), 311 (5) [$M^+ - Me$], 174 (93) [Si_3Me_6], 159 (48) [Si_3Me_5], 73 (100) [$SiMe_3$].

Synthesis of 2: A 1-L round-bottomed flask was evacuated and then filled with propyne (approx. 41 mmol). The gas was condensed on diethyl ether (20 mL) at −70 °C in a flask equipped with a dropping funnel. At the same temperature *n*-butyllithium (21 mL, 42 mmol, 2 M in pentane) was added dropwise. The temperature was raised to −50 °C and bromotris(trimethylsilyl)silane (13.1 g, 40.0 mmol) in diethyl ether (20 mL) was added. The mixture was allowed to reach room temperature and was stirred for a further 16 h. Aqueous workup, evaporation of the solvent and distillation (100 °C, 0.05 mbar) yielded **2** (8.51 g, 75%) as a yellowish oil. ^{1}H NMR (C_6D_6): $\delta = 1.67$ (s, 3 H), 0.44 (s, 27 H) ppm. ^{13}C NMR (C_6D_6): $\delta = 105.2, 73.1, 5.2, 0.5$ ppm. ^{29}Si NMR (THF, D_2O): $\delta = -11.7, -100.5$ ppm. MS: *m/z* = 286 (9) [M^+], 271 (20) [$M^+ - Me$], 213 (18) [$M^+ - SiMe_3$], 174 (75) [$Si(SiMe_3)_2$], 73 (100) [$SiMe_3$].

Tris(trimethylsilyl)silylphenylacetylene (3): Synthesis according to literature.[18] ^{1}H NMR ($CDCl_3$): $\delta = 7.46$ (m, 2 H), 7.32 (m, 3 H), 0.23 (s, 27 H) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 132.0, 128.4, 127.9, 124.9, 108.6, 88.4, 0.7$ ppm. ^{29}Si NMR ($CDCl_3$): $\delta = -11.5, -100.5$ ppm. MS: *m/z* = 348 (13) [M^+], 275 (19) [$M^+ - SiMe_3$], 174 (70) [$Si(SiMe_3)_2$], 135 (25) [$PhSiMe_2$], 129 (26) [Si_3Me_3], 73 (100) [$SiMe_3$].

Dodecynyltris(trimethylsilyl)silane (4): In a 100-mL Schlenk flask equipped with a rubber septum and stirring bar, dodecyne (0.850 g, 5.11 mmol) was dissolved in diethyl ether (30 mL) and methyllithium (3.70 mL, 5.88 mmol, solution, 1.6 M in diethyl ether) was added dropwise via a syringe at −70 °C. After 20 min the temperature was raised to −20 °C followed by addition of chlorotris(trimethylsilyl)silane (1.70 g, 6.00 mmol) in diethyl ether (20 mL). The mixture was then stirred for 16 h at room temperature. Aqueous workup and evaporation of the solvent gave a brown oily solid, which was extracted with pentane (50 mL). Evaporation of the solvent and removal of the volatiles in vacuo (20 °C, 0.05 mbar) yielded **4** (1.84 g, 87%) as a yellow oil. ^{1}H NMR (C_6D_6): $\delta = 1.26$ (broad signal, 16 H), 0.98 (m, 5 H), 0.32 (s, 27 H) ppm. ^{13}C NMR (C_6D_6): $\delta = 111.3, 76.5, 32.7, 30.5, 30.4, 30.2, 29.9$ (2 ×), 29.4, 23.5, 21.1, 14.8, 1.0 ppm. ^{29}Si NMR (C_6D_6): $\delta = -11.7, -100.7$ ppm. MS: *m/z* = 412 (14) [M^+], 339 (10) [$M^+ - SiMe_3$], 174 (100) [$Si(SiMe_3)_2$], 159 (16) [$Si(SiMe_3)_2 - Me$], 73 (100) [$SiMe_3$].

1-Trimethysilyl-2-[tris(trimethylsily)silyl]ethyne (5): Similar procedure as for compound **4** using **1** (1.00 g, 3.67 mmol), methyllithium (2.6 mL, 4.2 mmol, 1.6 M in diethyl ether), and chlorotrimethylsilane (0.33 g, 4.07 mmol) to yield **5** (1.10 g, 87%) as a colorless oil.[19] ^{29}Si NMR (C_6D_6): $\delta = -12.2, -20.3, -101.2$ ppm. MS: *m/z* (%) = 344 (26) [M^+], 329 (16) [$M^+ - Me$], 271 (12) [$M^+ - SiMe_3$], 174 (54) [$Si(SiMe_3)_2$], 73 (100) [$SiMe_3$].

3-Propinyltris(trimethylsilyl)silane (7): Tris(trimethylsilyl)silylpotassium (4.24 mmol) in toluene (20 mL) was added to a solution of propargyltosylate (0.89 g, 4.24 mmol) in toluene (20 mL) at −50 °C. The solution was allowed to reach room temperature and was stirred for a further 16 h before the reaction was subjected to an extractive workup procedure. The residue was filtered through Celite yielding **7** (0.98 g, 81%) as a light yellow oil. ^{1}H NMR (C_6D_6): $\delta = 1.68$ (t, *J* = 3.0 Hz, 1 H), 1.55 (d, *J* = 3.0 Hz, 2 H), 0.22 (s, 27 H), ppm. ^{13}C NMR (C_6D_6): $\delta = 84.9, 67.6, 0.8, -3.9$ ppm. ^{29}Si NMR (C_6D_6): $\delta = -12.4, -78.0$ ppm. MS: *m/z* (%) = 286 (2) [M^+], 271 (19) [$M^+ - Me$], 213 (100) [$M^+ - SiMe_3$], 197 (26) [$(C_3H_2)Si_3Me_5$], 129 (27) [Si_3Me_3], 73 (100) [$SiMe_3$].

1,3-Bis[tris(trimethylsilyl)silyl]propyne (8): Similar procedure as for the synthesis of **4** employing **7** (3.49 g, 12.3 mmol), butyllithium (7.7 mL, 12.3 mmol, 1.6 M in hexane), and chlorotris(trimethylsilyl)silane (3.49 g, 12.3 mmol) to give a mixture of **8** and starting materials. Removal of the volatile products by Kugelrohr distillation leaves **8** (3.02 g, 46%) as a yellow oil. ^{1}H NMR (C_6D_6): $\delta = 1.80$

(s, 2 H), 0.35 (s, 27 H), 0.24 (s, 27 H) ppm. ^{13}C NMR (C_6D_6): δ = 110.8, 73.4, 0.9, 0.7, −1.3 ppm. ^{29}Si NMR (C_6D_6): δ = −12.3, −12.5, −80.2, −100.4 ppm. MS: *m/z* (%) = 532 (2) [M$^+$], 285 (100) [(C_3H_2)Si($SiMe_3$)$_3$], 197 (11) [(C_3H_2)Si_3Me_5], 73 (44) [$SiMe_3$].

Hexamethyl-2,2-bis(phenylethynyl)trisilane (9)

2,2-Dibromohexamethyltrisilane: On hexamethyl-2,2-diphenyltrisilane[20] (7.2 g, 21.9 mmol) hydrogen bromide (approx. 20 mL) was condensed at −80 °C. A reflux condenser cooled to −80 °C was put on the flask, the bath removed and the hydrogen bromide was refluxed for 2 h. Subsequently the remaining hydrogen bromide and all volatiles were condensed into a liquid nitrogen cooled trap. The whole procedure was repeated once to ensure complete conversion. The dibromide was obtained as deliquescent crystals at room temperature (7.15 g, 98%). ^{1}H NMR ($CDCl_3$): δ = 0.34 (s, 18 H) ppm. ^{13}C NMR (C_6D_6): δ = −3.0 ppm. ^{29}Si NMR ($CDCl_3$): δ = 23.7, −10.0 ppm. MS: *m/z* (%) = 332/334 (8) [M$^+$], 180/182 (25) [Me_3Si-SiBr], 73 (100) [$SiMe_3$].

Synthesis of 9: Similar procedure as for the synthesis of **4** using phenylacetylene (3.57 g, 35.0 mmol), *n*-butyllithium (22.0 mL, 35.2 mmol, 1.6 M in hexane), and 2,2-dibromohexamethyltrisilane (5.00 g, 15.0 mmol) to give **9** (2.76 g, 49%) as a colorless oil. B.p. 135−142 °C (0.1 bar). ^{1}H NMR (C_6D_6): δ = 7.41 (m, 4 H), 6.91 (m, 6 H), 0.39 (s, 18 H) ppm. ^{13}C NMR (C_6D_6): δ = 132.1, 128.5, 128.4, 123.8, 110.2, 86.9, −1.4 ppm. ^{29}Si NMR ($CDCl_3$): δ = −13.7, −80.8 ppm.

Pentakis(trimethylsilyl)(phenylethynyl)disilane (10)

Bromopentakis(trimethylsilyl)disilane: Pentakis(trimethylsilyl)phenylsilane[16,21] (3.40 g, 6.83 mmol) was treated as described above for the synthesis of 2,2-dibromohexamethyltrisilane. At room temperature colorless, deliquescent crystals (3.30 g, 97%) of the bromo compound were obtained. ^{1}H NMR (C_6D_6): δ = 0.34 (s, 27 H), 0.28 (s, 18 H) ppm. ^{13}C NMR (C_6D_6): δ = 3.9, 2.9 ppm. ^{29}Si NMR ($CDCl_3$): δ = −9.4, −12.5, −69.1, −128.2 ppm.

Synthesis of 10: Similar procedure as for the synthesis of compound **4** using phenylacetylene (1.5 g, 3.48 mmol), methyllithium (9.25 mL, 14.8 mmol, 1.6 M in diethyl ether), and bromopentakis(-trimethylsilyl)disilane (2.20 g, 4.21 mmol) to give **10** (1.11 g, 51%) as colorless crystals. M.p. 75−84 °C. ^{1}H NMR (C_6D_6): δ = 7.68 (m, 1 H), 7.43 (m, 2 H), 6.96 (m, 2 H), 0.41 (s, 18 H), 0.38 (s, 27 H) ppm. ^{13}C NMR (C_6D_6): δ = 137.7, 131.6, 128.4, 124.8, 110.1, 90.9, 3.6, 1.9 ppm. ^{29}Si NMR (C_6D_6): δ = −9.4, −10.4, −98.0, −129.3 ppm.

General Procedure for the Synthesis of Potassium Silyls: In a nitrogen filled glove box the respective silane and potassium *tert*-butoxide (1.05 equiv. for mono-, and 2.10 equiv. for the dipotassium compounds) were dissolved in THF. The solution immediately turned yellow and after some time dark brown. Complete conversion was controlled by ^{29}Si NMR spectroscopy of a small aliquot. Yields were not easily determined by removal of the solvent because different ratios of THF coordinate to the anions. Derivatization reactions with sulfuric acid or ethyl bromide, which were analyzed by GC/MS, showed that formation of the anions was almost quantitative within the limits of detection.

[Propynylbis(trimethylsilyl)silyl]potassium (2a): ^{1}H NMR (C_6D_6): δ = 1.75 (s, 3 H), 0.15 (s, 18 H) ppm. ^{13}C NMR (C_6D_6): δ = 99.6, 95.2, 36.9, 3.4 ppm. ^{29}Si NMR (C_6D_6): δ = −6.8, −155.3 ppm. MS (ethyl bromide quench): *m/z* (%) = 242 (31) [M$^+$], 213 (24) [M$^+$ − Et], 169 (11) [M$^+$ − $SiMe_3$], 130 (100) [Me_3SiSiEt], 102 (51) [HSiSi-Me_3], 73 (56) [$SiMe_3$].

[Bis(trimethylsilyl)silylphenylacetylene]potassium (3a): ^{1}H NMR (C_6D_6): δ = 7.00 (m, 2 H), 6.92 (m, 2 H), 6.77 (m, 1 H), 0.04 (s, 18 H) ppm. ^{13}C NMR (C_6D_6): δ = 129.8, 128.7, 127.5, 123.4, 115.2, 106.2, 3.3 ppm. ^{29}Si NMR (C_6D_6): δ = −7.0, −155.1 ppm.

[Dodecynylbis(trimethylsilyl)silyl]potassium (4a): ^{1}H NMR (C_6D_6): δ = 2.1 (m, 2 H), 1.35 (br. s, 4 H), 1.17 (br. s, 12 H), 0.77 (t, 3 H), 0.07 (s, 18 H) ppm. ^{13}C NMR (C_6D_6): δ = 103.7, 96.8, 32.0, 30.8, 29.9, 29.8, 29.6, 29.5, 29.0, 22.7, 21.5, 13.7, 3.4 ppm. ^{29}Si NMR (C_6D_6): δ = −7.3, −156.2 ppm. MS (ethyl bromide quench): *m/z* (%) = 368 (22) [M$^+$], 130 (90) [Si_2Me_3Et], 73 (100) [$SiMe_3$].

{1-Trimethysilyl-2-[bis(trimethylsily)silyl]acetylene}potassium (5a): ^{1}H NMR (C_6D_6): δ = −0.01 (s, 18 H), −0.04 (s, 9 H) ppm. ^{13}C NMR (C_6D_6): δ = 138.0, 109.9, 3.4, 1.1 ppm. ^{29}Si NMR (C_6D_6): δ = −7.6, −27.4, −159.6 ppm. MS (ethyl bromide quench): *m/z* (%) = 300 (20) [M$^+$], 227 (21) [M$^+$ − $SiMe_3$], 199 (40) [(Me_3Si)$_2$-Si(CC)H], 130 (37) [Me_3SiSiEt], 73 (100) [$SiMe_3$].

{1-Bis[bis(trimethylsilyl)silyl]-3-[tris(trimethylsily)silyl]propyne}-potassium (8a): ^{29}Si NMR (C_6D_6): δ = −8.1, −12.7, −82.0, −149.6 ppm.

[1,1,2,2-Tetrakis(trimethylsilyl)-1-(phenylethynyl)disilyl]potassium (10a): ^{29}Si NMR (C_6D_6): δ = −8.0, −13.2, −93.1, −188.9 ppm.

[1,1,1,2-Tetrakis(trimethylsilyl)-1-(phenylethynyl)disilyl]potassium (10b): ^{29}Si NMR (C_6D_6): δ = −6.0, −10.1, −128.4, −151.4 ppm.

Bis[bis(trimethylsilyl)methylsilyl]ethyne (6b): To the dipotassium compound **6a** (0.37 mmol) in diethyl ether (2 mL) dimethylsulfate (0.10 mL, 1.05 mmol) was added at 0 °C. The solution was stirred for 16 h at room temperature before it was subjected to an extractive workup. A colorless oil of **6b** (140 mg, 95%) was obtained. ^{1}H NMR (C_6D_6): δ = 0.26 (s, 6 H), 0.24 (s, 36 H) ppm. ^{13}C NMR (C_6D_6): δ = 114.2, −1.5, −7.8 ppm. ^{29}Si NMR (C_6D_6): δ = −15.6, −65.3 ppm. MS: *m/z* (%) = 402 (5) [M$^+$], 329 (29) [M$^+$ − $SiMe_3$], 232 (40) [Si − ($SiMe_3$)$_3$] − Me], 73 (100) [$SiMe_3$].

Bis[bis(trimethylsilyl)silyl]ethyne (6c): **6a** (0.39 mmol) was added to a vigorously stirred mixture of H_2SO_4 (2 M, 5 mL) and diethyl ether (5 mL). After 10 min the aqueous layer was removed, the organic residue diluted twice with toluene and the solvent removed under reduced pressure. A colorless oil of **6c** (123 mg, 85%) was obtained. ^{1}H NMR (C_6D_6): δ = 3.83 (s, 2 H), 0.26 (s, 36 H) ppm. ^{13}C NMR (C_6D_6): δ = 110.3, −0.6 ppm. ^{29}Si NMR (C_6D_6): δ = −14.3, −91.0 ppm. MS: *m/z* (%) = 374 (5) [M$^+$], 301 (18) [M$^+$ − $SiMe_3$], 285 (99) [M$^+$ − $SiMe_3$ − CH_4], 241 (31) [Me_3Si(Me)SiC=CSi-$SiMe_3$], 227 (36) [Me_3Si(H)SiC=CSiSiMe$_3$], 73 (100) [$SiMe_3$].

X-ray Crystallographic Studies: Measurements were carried out on a Bruker SMART Apex diffractometer with Mo-K_α radiation. The data were reduced to F_o^2 and corrected for absorption effects with SAINT[22] and SADABS,[23] respectively (Table 3). The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL-97).[24] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles.

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Table 3. Crystallographic data for compounds **3**, **6** and **9**

	3	**6**	**9**
Empirical formula	$C_{17}H_{32}Si_4$	$C_{20}H_{54}Si_8$	$C_{22}H_{28}Si_3$
M_w	348.79	519.35	376.71
Temperature [K]	293(2)	213(2)	150(2)
Size (mm)	0.44 × 0.30 × 0.28	0.66 × 0.49 × 0.10	0.72 × 0.55 × 0.10
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å)	13.829(5)	9.4732(19)	15.949(3)
b (Å)	9.335(3)	9.7130(19)	9.1430(18)
c (Å)	18.912(7)	12.774(3)	17.020(3)
α (°)	90	109.41(3)	90
β (°)	95.550(7)	92.80(3)	103.72(3)
γ (°)	90	119.03(3)	90
V [Å ^{3}]	2430.0(15)	937.3(3)	2411.0(8)
Z	4	1	4
$\rho_{calcd.}$ [gcm^{-3}]	0.953	0.920	1.038
Absorption coefficient [mm^{-1}]	0.240	0.293	0.199
F(000)	760	286	808
θ range	$1.48<\theta<20.81$	$1.75<\theta<23.26$	$2.00<\theta<26.35$
Reflections collected/unique	8327/2540	5750/2674	18232/4893
Completeness to θ [%]	99.7	99.2	99.5
Absorption correction	SADABS	SADABS	SADABS
Data/restraints/parameters	2540/0/199	2674/0/154	4893/0/232
Goodness of fit on F^2	0.980	1.044	1.080
Final R int [$I > 2\sigma(I)$]	$R1 = 0.0554$ $wR2 = 0.1459$	$R1 = 0.0548$ $wR2 = 0.1594$	$R1 = 0.0845$ $wR2 = 0.2173$
R int (all data)	$R1 = 0.0783$ $wR2 = 0.1585$	$R1 = 0.0600$ $wR2 = 0.1646$	$R1 = 0.1071$ $wR2 = 0.2335$
Largest diff. Peak/hole [e$^-$/ Å^3]	0.273/−0.205	0.482/−0.245	0.856/−0.606

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