Symmetric Tetraalkynyldisilanes

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Dedicated to Professor M. F. Hawthorne on the occasion of his 75th birthday

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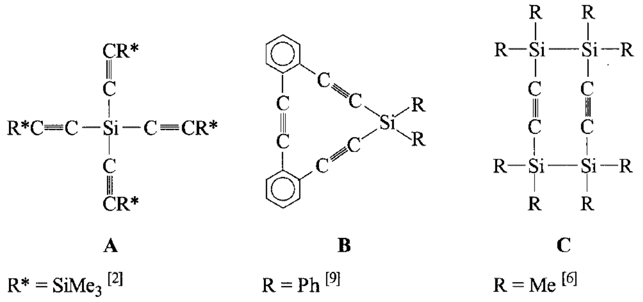
The reaction of the tetrachlorodisilane $R_2Si_2Cl_4$ (**1**) [R = $CH(SiMe_3)_2$] with the lithium salt $R^*C{\equiv}CLi$ of the parent alkyne results in the replacement of the chlorine atoms with alkynyl groups to yield the product $R_2Si_2(C{\equiv}CR^*)_4$ [R* = Ph (**2**), *t*Bu (**3**), $SiMe_3$ (**4**), *n*-C_3H_7 (**5**)]. Compounds **2** and **3** were characterized by X-ray structural analysis.

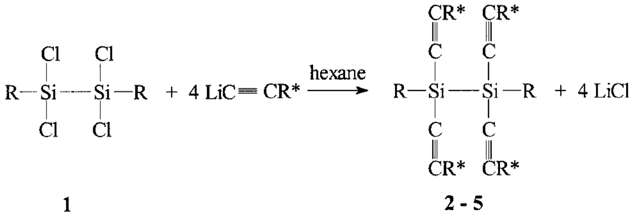
Introduction

In recent years many alkynylsilicon compounds have been synthesised[1] where the number of alkynyl groups attached to the central silicon atom varies from one to four (Scheme 1: **A**). Some of these products have been isolated.[2,3] Moreover, in a few compounds the alkynyl group acts as a linker between silicon and carbon atoms or two silicon atoms, respectively, forming chains[4,5] or heterocycles.[6,11] In Scheme 1 two examples of heterocycles containing alkynyl groups are shown. In compound **B** silicon and carbon atoms and in **C** two silicon atoms are linked together. However, to the best of our knowledge, a disilane carrying four alkynyl groups has not been reported previously.



Scheme 1

Recently we have reported the reaction of the tetraaminodisilane $R_2Si_2(NH_2)_4$ [R = $CH(SiMe_3)_2$] with HBr and HI, with elimination of ammonia and formation of the halodisilanes $R_2Si_2X_4$ (X = Br, I).[12] A similar reaction using alkynes did not succeed as their acidity is lower than both HBr and HI. As an alternative approach we used the lithium salts $R^*C{\equiv}CLi$ [R* = Ph (**2**), *t*Bu (**3**), $SiMe_3$ (**4**), *n*-C_3H_7 (**5**); Scheme 2] as a starting material for the reaction with the tetrachlorodisilane $R_2Si_2Cl_4$ (**1**) [R = $CH(SiMe_3)_2$] with elimination of LiCl.



R = $CH(SiMe_3)_2$

	2	3	4	5
R*	Ph	*t*Bu	$SiMe_3$	nC_3H_7

Scheme 2

Results and Discussion

Synthesis and Spectra

Lithiation of $R^*C{\equiv}CH$ was accomplished with a solution of butyllithium in hexane at −78 °C. The tetrachlorodisilane was then added at the same temperature. The reaction mixture was slowly warmed to room temperature, the LiCl separated by filtration and finally the solvent removed under vacuum to yield compounds **2−5**. The products **2−4** were obtained as colourless solids whereas **5** was isolated as a colourless oil. Single crystals of **2** and **3** suitable for X-ray crystallographic measurements were isolated from hexane solutions.

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In the mass spectra compounds **2**−**5** were identified by their molecular ion peaks [M^+] at *m*/*z* = 778 (**2**), 698 (**3**), 762 (**4**), and 642 (**5**); in the IR spectra the absorptions for the C≡C vibrations are in the range between 2100 and 2200 cm^{-1}.

The ^1H NMR spectra of **2**−**5** show resonances for the protons of the methyl groups of the bis(trimethylsilyl)methyl ligands in the range δ = 0.49 to 0.59 ppm, whereas the resonances of the corresponding CH groups are in the range between δ = 0.21 and 0.53 ppm. Additionally, the resonances of the substituents of the alkynyl groups are found in each spectrum. For compound **2** the aromatic protons are found as two multiplets, one at δ = 6.87 to 6.91 ppm (*m*-, *p*-Ph) and the other at δ = 7.47 to 7.52 ppm (*o*-Ph). The protons of the *t*Bu groups of **3** appear as a singlet at δ = 1.17 ppm and the trimethylsilyl protons resonate in the spectrum of **4** at δ = 0.13 ppm. The spectrum of **5** exhibits three multiplets for the aliphatic protons [δ = 0.83 ($CH_2{-}CH_3$), 1.38 ($CH_2{-}CH_3$), and 1.99 ppm ($C{\equiv}C{-}CH_2$)].

In the ^{13}C NMR spectra of **2**−**5** the resonances of the CH_3 groups of the ligands are in the range between δ = 3.3 and 3.5 ppm and those for the CH groups between δ = −0.3 and 0.4 ppm. The triple-bonded carbon atoms of the inner atoms with respect to the silicon atom exhibit resonances between δ = 110.6 and 120.2 ppm, while for the outer atoms they are observed between δ = 80.9 and 110.9 ppm. The resonances of the acetylenic substituents are found in the expected range.

The trimethylsilyl groups resonate in the ^{29}Si NMR spectra between δ = 0.8 and 1.2 ppm and the silicon atoms of the central disilane unit resonate between δ = −54.2 and −56.5 ppm.

X-ray Structural Analysis

The single-crystal structural analysis of compounds **2** (Figure 1) and **3** (Figure 2) shows that the central disilane unit is connected to four alkynyl groups in an anticlinic conformation. The coordination sphere of the silicon atoms is completed in each case by a bis(trimethylsilyl)methyl group.

The disilane **2** crystallises in the orthorhombic space group $Pna2_1$ and **3** in the monoclinic space group *C*2/*c*. The unit cell of **3** contains eight molecules of the disilane and an additional two molecules of cyclohexane and two more of *n*-hexane.

The Si−Si bond length in both compounds is essentially identical [2.378(1) Å (**2**) and 2.373(1) Å (**3**)] and is only slightly shorter than that in the chloro compound **1** [2.380(2) Å].[12]

The bond length between the central silicon atoms and the acetylenic carbon atoms averages to 1.833 Å for **2** and 1.832 Å for **3** and is similar to the corresponding bond length in $Si(C_2SiMe_3)_4$ (1.825 Å).[2] The C−Si−C angle at the silicon atom averages to 106.73° (**2**) and 107.75° (**3**). Selected bond lengths and angles for **2** and **3** are listed in Table 1.

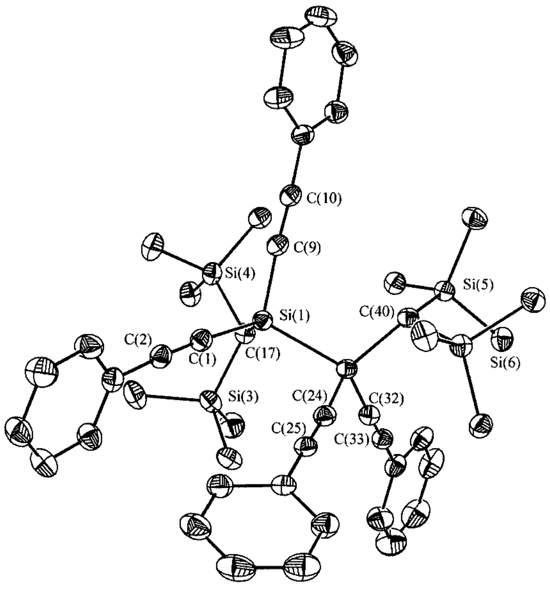

Figure 1. Molecular structure of **2** in the crystal (50% probability thermal ellipsoids)

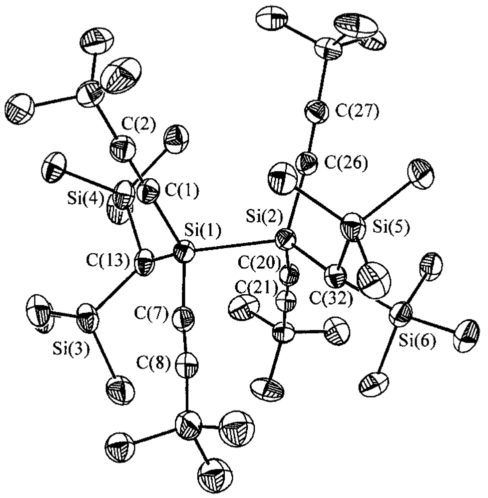

Figure 2. Molecular structure of **3** in the crystal (50% probability thermal ellipsoids)

Table 1. Selected bond lengths [Å] and angles [°] for **2** and **3**

Compound	**2**	**3**
Si(1)−Si(2)	2.378(1)	2.373(1)
Si(1)−C(1)	1.837(3)	1.827(3)
C(1)−C(2)	1.212(4)	1.200(4)
Si(1)−C(17/13)	1.863(2)	1.879(3)
C(1)−Si(1)−Si(2)	109.48(8)	114.80(9)
C(1)−Si(1)−C(9/7)	105.62(12)	106.24(13)
C(1)−Si(1)−C(17/13)	110.41(12)	109.18(13)

Conclusion

This work shows that alkynes are slim enough to allow fourfold substitution on a disilane sterically hindered by two bis(trimethylsilyl)methyl groups. The easiest way to synthesise this class of compounds is using the lithium salt of the corresponding alkyne and the tetrachlorodisilane. The products are useful precursors for heterocyclic and polymeric silicon-containing materials after manipulation of the alkyne groups.

Experimental Section

General Remarks: All reactions were performed under dry nitrogen using standard Schlenk and syringe techniques. The solvents were dried according to literature methods[13] and freshly distilled and saturated with nitrogen prior to use. Melting points were measured on a Büchi B-540 melting point apparatus. IR spectra were recorded using a BIO-RAD Digilab FTS 7 spectrophotometer. Mass spectra (MS) were obtained on a Finnigan MAT 95 or a Finnigan MAT 8200 spectrometer using the EI technique. NMR spectra were recorded on a Bruker AC 250 or a Bruker Avance 500 spectrometer; chemical shifts are quoted relative to external $SiMe_4$. Elemental analyses were performed by the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen.

General Procedure: A solution of butyllithium (40 mmol) in *n*-hexane (25 mL, 1.6 M) was added dropwise to a solution of the alkyne (40 mmol) in hexane (100 mL) at −78 °C. Subsequently **1** (5.2 g, 10 mmol) dissolved in *n*-hexane (50 mL) was added over a period of 30 min and the mixture was allowed to warm to room temperature overnight. The precipitate was removed from the solution by filtration and the volume of solvent was reduced to 20 mL under vacuum. Products **2−4** were obtained as colourless solids and **5** was obtained as a colourless oil after complete removal of the solvent.

1,2-Bis[bis(trimethylsilyl)methyl]tetra(phenylethynyl)disilane (2): Yield: 6.1 g (7.8 mmol, 78%). M.p. 110 °C. ^1H NMR (C_6D_6): δ = 0.53 [s, 2 H, $CH(SiMe_3)_2$], 0.59 [s, 36 H, $Si(CH_3)_3$], 6.87−6.91 (m, 12 H, *o*-, *p*-Ph-*H*), 7.47−7.52 (m, 8 H, *m*-Ph-*H*) ppm. ^{13}C NMR (C_6D_6): δ = 0.4 [$CH(SiMe_3)_2$], 3.4 [$Si(CH_3)_3$], 92.5 (Si-C≡C-Ph), 110.6 (Si-C≡C), 123.6, 128.5, 128.9, 132.0 (arom.-*C*) ppm. ^{29}Si NMR (C_6D_6): δ = −54.2 (*Si*-C≡C-Ph), 1.4 (*Si*Me_3) ppm. IR (KBr): $\tilde{\nu}$ = 2156, 1950, 1879, 1595, 1488, 1304, 1261, 1249, 1017, 916, 844, 755, 723, 689, 538 cm^{-1}. MS (EI): *m/z* (%) = 778 (28) [M^+], 736 (13) [M^+ − Me], 375 (100) [1/2M^+ − Me]. $C_{46}H_{58}Si_6$ (779.48): calcd. C 70.9, H 7.5, Si 21.6; found C 68.1, H 7.5, Si 20.6.[14]

1,2-Bis[bis(trimethylsilyl)methyl]tetra(*tert*-butylethynyl)disilane (3): Yield: 5.0 g (7.2 mmol, 72%). M.p. 265 °C. ^1H NMR (C_6D_6): δ = 0.41 [s, 2 H, $CH(SiMe_3)_2$], 0.52 [s, 36 H, $Si(CH_3)_3$], 1.17 [s, 36 H, $C(CH_3)_3$] ppm. ^{13}C NMR (C_6D_6): δ = 0.1 [$CH(SiMe_3)_2$], 3.4 [$Si(CH_3)_3$], 28.2 [$C(CH_3)_3$], 30.3 [$C(CH_3)_3$], 80.6 (Si-C≡C-*t*Bu), 119.2 (Si-C≡C-*t*Bu) ppm. ^{29}Si NMR (C_6D_6): δ = −57.4 (*Si*-C≡C), 0.8 (*Si*Me_3) ppm. IR (KBr): $\tilde{\nu}$ = 2196, 2154, 1301, 1253, 1202, 1096, 1018, 940, 842, 796, 773, 727, 679, 535, 418 cm^{-1}. MS (EI): *m/z* (%) = 698 (11) [M^+], 641 (21) [M^+ − *t*Bu], 349 (100) [1/2M^+]. $C_{38}H_{74}Si_6$ (699.52): calcd. C 65.2, H 10.7, Si 24.1; found C 63.2, H 10.6, Si 23.7.[14]

1,2-Bis[bis(trimethylsilyl)methyl]tetrakis(trimethylsilylethynyl)-disilane (4): Yield: 5.8 g (7.6 mmol, 76%). M.p. 245 °C. ^1H NMR (C_6D_6): δ = 0.13 [s, 36 H, C≡C$Si(CH_3)_3$], 0.47 [s, 2 H, $CH(SiMe_3)_2$], 0.52 [s, 36 H, $CH(SiMe_3)_2$] ppm. ^{13}C NMR (C_6D_6): δ = −0.5 [C≡C-$Si(CH_3)_3$] 0.2 [$CH(SiMe_3)_2$], 3.5 [$CH(SiMe_3)_2$],

Table 2. X-ray structure analysis data for **2** and **3**

Compound	**2**	**3**
Formula	$C_{46}H_{58}Si_6$	$C_{38}H_{74}Si_6 \cdot 1/4C_6H_{12} \cdot 1/4C_6H_{14}$
Molecular weight	779.46	720.80
Crystal system	orthorhombic	monoclinic
Space group	*Pna*2 (1)	*C* 2/*c*
Unit cell	a = 19.186(4) Å	a = 20.9598(12) Å
	b = 12.175(2) Å	b = 12.2564(8) Å
	c = 41.181(8) Å	c = 40.590(2) Å
	α = 90°	α = 90°
	β = 90°	β = 101.220(4)°
	γ = 90°	γ = 90°
Volume	9620(3) $Å^3$	10228.0(10) $Å^3$
Z	4	8
Density	0.538 g/cm^3	0.936 g/cm^3
Absorption coefficient	0.101 mm^{-1}	0.185 mm^{-1}
$F(000)$	1672	3186
Index range	$-21 \le h \le 21$	$-22 \le h \le 22$
	$-13 \le k \le 13$	$-13 \le k \le 13$
	$-47 \le l \le 46$	$-43 \le l \le 43$
Reflections collected	55676	80576
Independent reflections	15026 [R_{int} = 0.0556]	6680 [R_{int} = 0.0999]
Data/restr./param.	15026/1/932	6680/4/447
Data collection range	$1.74 \le \Theta \le 24.06°$.	$1.93 \le \Theta \le 22.50°$.
Final R indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0370	$R1$ = 0.0490
	$wR2$ = 0.1025	$wR2$ = 0.1566
Final R indices (all data)	$R1$ = 0.0386	$R1$ = 0.0566
	$wR2$ = 0.1033	$wR2$ = 0.1612
Goodness-of-fit on F^2[b]	1.088	1.092
Largest diff. peak and hole	0.258 and −0.243 $e \cdot Å^{-3}$	0.603 and −0.294 $e \cdot Å^{-3}$

[a] $R1 = \Sigma|F_o - F_c|/\Sigma|F_0|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. [b] Goodness of fit $S = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma$ (n-p)$]^{1/2}$).

110.9 (Si-C≡C-SiMe$_3$), 120.2 (Si-C≡C-SiMe$_3$) ppm ^{29}Si NMR (C_6D_6): δ = −58.3 (*Si*-*Si*-C≡C), −18.7 (C≡C-*Si*Me$_3$), 1.2 [CH(*Si*Me$_3$)$_2$] ppm. IR (KBr): $\tilde{\nu}$ = 2108, 1948, 1875, 1303, 1262, 1251, 1155, 1022, 845, 779, 760, 722, 679, 539, 429 cm^{-1}. MS (EI): *m*/*z* (%) = 762 (24) [M$^+$], 789 (19) [M$^+$ − SiMe$_3$], 381 (100) [1/2 M$^+$]. $C_{34}H_{74}Si_{10}$ (763.81): calcd. C 53.5, H 9.8, Si 36.8; found C 53.5, H 9.8, Si 35.1.

1,2-Bis[bis(trimethylsilyl)methyl]tetra(1-pentynyl)disilane (5): Yield: 4.0 g (6.2 mmol, 62%). ^{1}H NMR (C_6D_6): δ = 0.21 [s, 2 H, C*H*(SiMe$_3$)$_2$], 0.49 [s, 36 H, Si(C*H*$_3$)$_3$], 0.83 (m, C_4H_4-C*H*$_3$, 12 H), 1.38 (m, C*H*$_2$CH$_3$, 8 H), 1.99 (m, C≡C-C*H*$_2$, 8 H) ppm. ^{13}C NMR (C_6D_6): δ = −0.3 [*C*H(SiMe$_3$)$_2$], 3.3 [Si(*C*H$_3$)$_3$], 13.7, 22.0, 22.4, (*C*$_3$H$_7$), 83.2 (Si-C≡C-C$_3$H$_7$), 112.5 (Si-C≡C-C$_3$H$_7$) ppm. ^{29}Si NMR (C_6D_6): δ = −56.5 (*Si*-C≡C-C$_3$H$_7$), 1.0 (*Si*Me$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 2167, 2138, 1932, 1861, 1465, 1427, 1382, 1338, 1324, 1263, 1248, 1079, 1062, 1020, 980, 840, 797, 770, 726, 680, 646, 599, 579, 539, 501, 413 cm^{-1}. MS (EI): *m*/*z* (%) = 642 (5) [M$^+$], 627 (4) [M$^+$ − Me], 321 (100) [1/2 M$^+$]. $C_{34}H_{66}Si_6$ (643.41): calcd. C 63.5, H 10.3, Si 26.2; found C 62.1, H 10.1, Si 24.8.[14]

X-ray Crystallographic Study of 2 and 3

The crystals were mounted on glass fibre in rapidly cooled mineral oil. Diffraction data (see also Table 2) were collected on a Stoe IPDS II diffractometer at 133(2) K, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), using the ω-scan technique. The structures were solved by direct methods using SHELXS-97[15] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[16] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

CCDC-191736 (**2**) and CCDC-191737 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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