Tetra(alkynyl)silanes, a 3,6-Disila-triyn, a 3,6,9-Trisila-tetrayne, a 1,3,4,6-Tetrasiladiyne, and Bis(trimethylstannyl)ethyne.

Molecular Structures and Solid-state NMR Studies

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Z. Naturforsch. 2010, 65b, 119 – 127; received November 27, 2009

The molecular structures of three alkynylsilanes, tetrakis(ethynyl-p-tolyl)silane, 3,3,6,6-tetramethyl-3,6-disila-triyn, 3,3,6,6,9,9-hexamethyl-3,6,9-trisila-tetrayne, and of bis(trimethylstannyl)ethyne have been determined by X-ray diffraction. The same alkynylsilanes, and in addition 1,2-bis(trimethylsilyl)ethyne, were studied by solid-state 13C and 29Si MAS NMR spectroscopy. The results of these measurements were compared with crystallographic evidence and also with relevant solution-state NMR data.

Key words: Alkynes, Silanes, Organotin Compounds, NMR, X-Ray

Introduction

Alkynylsilanes are useful starting materials in organic and organometallic synthesis [1 – 3]. Some alkynylsilanes are commercially available, and many examples can be readily prepared by conventional methods, starting from the respective chlorosilanes. Similarly, alkynylstannanes also deserve attention, although they are somewhat more difficult to prepare and to handle owing to the greater reactivity of the Sn–C bonds, when compared with Si–C bonds. The molecular structures of several alkynylsilanes have already been reported [4 – 8], and in some cases solid-state 13C and 29Si NMR measurements have been carried out [9 – 11]. There are also studies on solid alkynylstannanes both by X-ray diffraction [12 – 14] and by solid-state 13C and 119Sn NMR [9, 10, 12]. In the present work, we report on three further examples of molecular structures of alkynylsilanes (1b, 2, 3) and combine this information with that from solid-state 13C and 29Si NMR spectroscopy for 1 – 4 (Scheme 1). In addition, the molecular structure of bis(trimethylstannyl)ethyne (5) has been determined which complements the thorough 13C and 119Sn NMR spectroscopic study of the same molecule [9, 10].

Results and Discussion

The tetraalkynylsilane 1b was prepared in the usual way [15] by the reaction of SiCl4 with four equivalents...
of the alkynyllithium reagent. The triyne 2 [16] and the
tetrayne 3 [17] were obtained via stepwise procedures as
reported. The disilane derivative 4 was obtained
from the reaction of 1,2-dichlorotetramethyldisilane
with two equivalents of trimethylsilylthiylithium.
Bis(trimethylstannyl)ethyne (5) was prepared from the
reaction of Li2C2 with two equivalents of Me3SnCl as
described [18]. Recently, we have reported that a mod-
ification of the work-up procedure also affords the use-
ful trimethylstannylethyne as a side product in moder-
ate yield [19].

X-Ray structural studies of the alkynylsilanes
1b, 2, 3, and of bis(trimethylstannyl)ethyne (5)
The molecular structures of the alkynylsilanes 1b, 2, 3,
and of bis(trimethylstannyl)ethyne (5) are shown in
the Figs. 1, 2, 3, and 4, respectively. Apparently inter-
molecular interactions appear to be weak or negligible
in all cases. All distances and angles are in the expected
range [4 – 8].

In all cases, the surroundings of the silicon and
tin atoms correspond to slightly distorted tetrahedra.
Expectedly, the distortion is small in 1b, mainly due
to the slight difference in the orientation of the aryl
groups (see, however, the solid-state 13C NMR spec-
tra in Fig. 6). There is a center of inversion in the
triyne 2 which is absent in the tetrayne 4, and this has
consequences for the solid-state 13C and 29Si NMR
spectra of the latter (vide infra). It should be noted
that the optimized geometries in the gas phase of 2
and 3, calculated [20] at the B3LYP/6-311+G(d,p)
level of theory (Fig. 5), show different conforma-
tions as far as the mutual orientation of the alkynyl
groups is concerned. Therefore, it can be assumed that
the packing in the crystal lattice is affected signifi-
cantly by the type of alkynyl moieties. In the case
of 2, the solid-state 13C NMR spectrum (vide infra)
indicates the presence of a second modification. Fi-
ally, the X-ray diffraction study of 5 shows that there
is a center of inversion which answers one question
left open in previous solid-state NMR studies of this
compound [9, 10].
Table 1. $^{13}$C and $^{29}$Si NMR data of alkynylsilanes 1–4 in solution and in the solid state.

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{13}$C ($\equiv$C)</th>
<th>$\delta^{13}$C (Si–C$\equiv$)</th>
<th>$\delta^{13}$C (R)</th>
<th>$\delta^{29}$Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>104.7, 78.6</td>
<td>4.5 (Me)</td>
<td>5.9, 5.5, 4.6, 4.4 (Me)</td>
<td>−95.1</td>
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<td>108.0, 106.2</td>
<td>78.5, 77.7</td>
<td>118.6(1), 130.2±1 (broad,2,3), 140.2(4), 21.8 (Me)</td>
<td>−97.6</td>
</tr>
<tr>
<td>1b</td>
<td>107.5, 86.5</td>
<td>120.2(1), 133.3(2), 130.1(3), 140.0(4), 118.6(1), 132 ± 1 (broad,2,3), 140.2(4), 22.7 (Me)</td>
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<tr>
<td>solid:</td>
<td>109.7, 85.7</td>
<td>120.2(1), 133.3(2), 130.1(3), 140.0(4), 118.6(1), 132 ± 1 (broad,2,3), 140.2(4), 22.7 (Me)</td>
<td>−92.7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>94.6(1)</td>
<td>−0.2 (SiMe$_2$)</td>
<td>0.7 (SiMe$_3$)</td>
<td>−40.0</td>
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<tr>
<td>solid:</td>
<td>98.4(1)</td>
<td>1.2, 0.4 (SiMe$_2$)</td>
<td>0.7 (SiMe$_3$)</td>
<td>−40.0</td>
</tr>
<tr>
<td>3</td>
<td>94.8(1)</td>
<td>0.0 (Si(3)Me$_2$), −0.1 (Si(6)Me$_2$)</td>
<td>−39.9(3)</td>
<td></td>
</tr>
<tr>
<td>solid:</td>
<td>98.5</td>
<td>1.3, 1.0, 0.5, 0.0, −0.5 (Si(3,6)Me$_2$)</td>
<td>−38.9, −39.3(3)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>111.9 (C–SiMe$_2$)</td>
<td>0.0 (SiMe$_3$), −2.9 (SiMe$_2$)</td>
<td>−18.9 (SiMe$_3$)</td>
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<tr>
<td>solid:</td>
<td>117.1 (C–SiMe$_3$)</td>
<td>3.3 (SiMe$_1$), 0.6, 0.2, −0.1, −0.4 (SiMe$_2$)</td>
<td>−38.0, −38.1 (SiMe$_2$)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>119.3, 119.4</td>
<td>112.79(14), C1–Sn–C4 112.00(12), C3–Sn1–C4 111.03(13), C2–C2A–Sn 179.6(4)</td>
<td>−18.9, −19.1 (SiMe$_1$)</td>
<td></td>
</tr>
</tbody>
</table>

* Measured in [D$_8$]THF; $^1J(29$Si,$^{13}$C) = 128.9 Hz, $^2J(29$Si,$^{13}$C) = 26.5 Hz; $^3$C NMR data given in ref. [1d] without assignment; measured here in C$_6$D$_6$, and the assignment is based on the coupling constants, as follows: $^1J(29$Si(Me$_2$),$^{13}$C$\equiv$) = 69.6 Hz, $^2J(29$Si(Me$_3$),$^{13}$C$\equiv$) = 12.5 Hz, $^1J(29$Si(Me$_3$),$^{13}$C$\equiv$) = 77.8 Hz, $^2J(29$Si(Me$_2$),$^{13}$C$\equiv$) = 10.5 Hz, $^1J(29$Si(Me$_2$),$^{15}$C(Me)) = 49.8 Hz, $^1J(29$Si(Me$_2$),$^{15}$C(Me)) = 56.3 Hz.

Solid-state $^{13}$C and $^{29}$Si NMR spectroscopic studies

The $^{13}$C and $^{29}$Si chemical shifts of the compounds 1–4 measured in solution differ very little from those measured in the solid state (Table 1), indicating weak or negligible intermolecular interactions. This fact is now clearly established by the results of the X-ray diffraction studies also for the bis(trimethylstannyl)ethyne (5). The differences in $^{13}$C and $^{29}$Si nuclear shielding between liquid and solid state are most pronounced (a few ppm) for $^{13}$C nuclei in peripheral positions, such as $\equiv$C–H or SiMe$_2$ groups, which is in support of different conformations preferred on average in solution when compared with the solid state.

and $^{29}$Si NMR spectroscopic studies

The solid-state $^{13}$C MAS NMR spectrum of 1b (Fig. 6) is only consistent with the result of the X-ray diffraction by considering a fast exchange regime on the NMR time scale, in which reorientation of the aryl groups takes place, leading on average to four identical surroundings for the alkynyl carbon atoms as well...
Fig. 6. Solid-state 75.1 MHz $^{13}$C($^1$H) MAS NMR spectra of 1b (recycle delay 20 s; upper trace 1536 transients; lower trace 512 transients). The exchange-broadened $^{13}$C$_{2,3}$ NMR signals could only be observed at high spinning rates (lower trace). Rotational side bands (lower trace) are indicated by asterisks. At lower spinning rate (upper trace), only the fairly sharp $^{13}$C NMR signals for alkynyl carbons, aryl carbons C$^1$, C$^4$ and CH$_3$ were readily observed together with the rotational side bands. The solid-state 59.6 MHz $^{29}$Si($^1$H) NMR spectrum of 1b (insert; single pulse, recycle delay 20 s) is a fairly sharp line, even without MAS.

as the C$^1$, C$^4$ and CH$_3$ carbon atoms. The proposed rotation of the aryl groups is evident by inspection of the exchange-broadened $^{13}$C$_{2,3}$ NMR signals. In the case of 1a which was studied previously, motional averaging was slow on the NMR time scale, and the four different propynyl groups, found by X-ray diffraction [8], were clearly distinguished in the solid-state $^{13}$C NMR spectrum [11] (see also Table 1).

According to the molecular structure of 2 in the crystal, the solid-state $^{29}$Si and $^{13}$C MAS NMR spectra (Fig. 7) should be simple, showing one and five signals, respectively. However, in addition to the expected signals, there are three $^{13}$C NMR signals of minor intensity in the alkynyl range as marked. Therefore, in the bulk material of 2, a small amount of a second modification is most likely present, of which the $^{29}$Si and $^{13}$C(SiMe$_2$) NMR signals are not resolved.

Solid-state $^{13}$C and $^{29}$Si MAS NMR spectra of the tetrayne 3 (Fig. 8) are in perfect agreement with the results from X-ray diffraction. Except of the methyl groups linked to the central silicon atom, and the alkynyl carbon atoms C$^2$-10, all other $^{13}$C NMR signals are clearly resolved. The absence of a mirror plane or a center of inversion in solid 3 is also illustrated by two different $^{29}$Si NMR signals for Si$^{3,9}$ in addition to the signal for Si$^6$.

In the case of the disilane derivative 4, attempts failed to obtain suitable single crystals for X-ray diffraction. However, the solid-state $^{13}$C (Fig. 9) and $^{29}$Si (Fig. 10) MAS NMR spectra of the microcrystalline material could be measured. The different $^{13}$C NMR signals for the alkynyl carbons and for all methyl groups at the disilane unit clearly indicate the absence of a mirror plane or a center of inversion in the solid-state molecular structure of 4. Different $^{13}$C(SiMe$_3$) signals were not resolved. In addition to expectedly small differences in the chemical shifts of the SiMe$_3$ groups (see the $^{29}$Si NMR spectrum in Fig. 10), these $^{13}$C NMR signals may be slightly exchange-broadened by $2\pi/3$ propeller jumps [9,10]. The assignment of the alkynyl $^{13}$C NMR signals was based on the solution-state $^{13}$C NMR spectra. The solid-state $^{29}$Si MAS NMR spectrum measured at high spinning rate shows two resolved pairs of signals for the SiMe$_3$ and SiMe$_2$ groups, consistent with the $^{13}$C NMR spectra. At low spinning rate, the
Fig. 7. Solid-state 100.6 MHz $^{13}$C$^{1}$H and 79.5 MHz $^{29}$Si$^{1}$H MAS NMR spectra of the triyne 2 (recycle delay 8 s; 64 transients for $^{13}$C and 26 transients for $^{29}$Si).

Fig. 8. Solid-state 100.6 MHz $^{13}$C$^{1}$H and 79.5 MHz $^{29}$Si$^{1}$H NMR MAS spectra of the tetrayne 3 (recycle delay 8 s; 32 transients for $^{13}$C and $^{29}$Si). Rotational side bands (rotation 6 kHz) are indicated.
Fig. 9. Solid-state 100.5 MHz $^{13}$C-$^1$H NMR spectrum of the disilane derivative 4 (recycle delay 10 s; 492 transients; rotation 9 kHz).

Fig. 10. Solid-state 79.5 MHz $^{29}$Si-$^1$H NMR spectrum of the disilane derivative 4 measured at different spinning rates (recycle delay 8 s; 32 transients). At a spinning rate of 970 Hz the rotational side bands become visible, and their pattern is consistent with non-axially symmetric (SiMe$_2$) and close to axially symmetric (SiMe$_3$) $^{29}$Si shielding tensors.
rotational side bands expectedly indicate $^{29}$Si shielding tensor patterns typical of a non-axial symmetry of the SiMe$_2$ groups and close to axial symmetry for the SiMe$_3$ groups.

**Conclusions**

Crystallographic evidence and solid-state $^{13}$C and $^{29}$Si MAS NMR results are in good agreement for alkylnylsilanes. Dynamic processes such as reorientation of aryl groups are mirrored by exchange-broadened $^{13}$C NMR signals. Furthermore, the solid-state NMR spectra indicate the presence of modifications so far not readily apparent from single crystal X-ray diffraction studies, as shown in the case of the triyne 2. The crystal structure study of bis(trimethylstannyl)ethyne (5) has answered the question left open after temperature-dependent solid-state $^{13}$C and $^{119}$Sn MAS NMR investigations [9, 10], the results of which are in perfect agreement with the particular inversion symmetry of this molecule.

**Experimental Section**

**Starting materials and measurements**

The preparations and all handling of samples were carried out under an inert atmosphere (Ar), and carefully oven-dried glassware, and dry solvents were used throughout. $^4$BuLi in hexane (1.6 M), 1-ethynyl-4-methylbenzene, ethynyltrihexylsilane, SiCl$_4$, and Me$_2$SiCl$_2$ were commercial products. The 3,3,6,6,-tetramethyl-3,6-disila-triyne (2) [16], 3,3,6,6,9,9-hexamethyl-3,6,9-trisila-tetrayne (3) [17], and bis(trimethylstannyl)ethyne (5) [18] were prepared adopting the literature procedures. Single crystals of 2 and 3 were collected after slow sublimation at ambient temperature. Single crystals of 5 were grown from concentrated hexane solutions at ambient temperature. Solution-state NMR measurements were carried out in [D$_8$]THF (1b) and C$_2$DCl$_2$ (4) in 5 mm o.d. tubes at 296 ± 1 K: Varian Inova 300 or 400 MHz and Bruker ARX 250 spectrometer for $^1$H, $^{13}$C, and $^{29}$Si NMR; chemical shifts are given with respect to Me$_2$Si (0 ppm). Solid-state $^{13}$C and $^{29}$Si NMR spectra were measured at ambient temperature with Bruker Avance II 300 and Bruker Avance 400 spectrometers, using 4 mm zirconia rotors in double-bearing probe heads. All MAS spectra were measured with variable amplitude cross polarization (VACP) [21], and the SPINAL pulse sequence [22] was used to achieve efficient $^1$H decoupling. 1H-MS spectra: Finnigan MAT 8500 spectrometer (ionisation energy 70 eV) with direct inlet. The $m/z$ data refer to the isotopes $^1$H, $^{12}$C, and $^{29}$Si. The melting points (uncorrected) were determined using a Büchi 510 melting point apparatus.

### Table 2. Crystallographic data of the alkylnylsilanes 1b, 2, 3 and of bis(trimethylstannyl)ethyne (5).

<table>
<thead>
<tr>
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<th>1b</th>
<th>2a</th>
<th>3</th>
<th>5b</th>
</tr>
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<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C$<em>{56}$H$</em>{28}$Si</td>
<td>C$<em>{54}$H$</em>{26}$Si$_2$</td>
<td>C$<em>{54}$H$</em>{28}$Si$_3$</td>
<td>C$<em>{56}$H$</em>{30}$Si$_2$</td>
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<td><strong>Crystal</strong></td>
<td>needle</td>
<td>prism</td>
<td>prism</td>
<td>prism</td>
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<tr>
<td><strong>Dimensions, mm$^3$</strong></td>
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<td>0.60 × 0.50 × 0.50</td>
<td>0.66 × 0.28 × 0.09</td>
<td>0.36 × 0.23 × 0.11</td>
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<tr>
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<td>193(2)</td>
<td>193(2)</td>
<td>133(2)</td>
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<tr>
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<td>$R3$</td>
<td>$P2_1/n$</td>
<td>$P2_1/c$</td>
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<tr>
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<td>90</td>
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<td>$\gamma$, deg</td>
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<tr>
<td>Refined parameters</td>
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<td>83</td>
<td>234</td>
<td>49</td>
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<tr>
<td>$wR_2/R_1 (I \geq 2\sigma(I))$</td>
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<td>0.076 / 0.075</td>
<td>0.099 / 0.030</td>
<td>0.041 / 0.017</td>
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<tr>
<td>Max. / min. resid. electron density, e pm$^{-3}$ × 10$^{-6}$</td>
<td>0.19 / –0.27</td>
<td>0.23 / –0.15</td>
<td>0.14 / –0.31</td>
<td>0.55 / –0.39</td>
</tr>
</tbody>
</table>

a Absorption corrections did not improve the parameter set.
Synthesis of tetraalkyn-1-ylsilane 1b

Tetrachlorosilane (3 mL; 10 mmol) was added slowly at low temperature (−78 °C) to a suspension of Li–C≡C–C₆H₄–4-Me (39.4 mmol) in 75 mL of hexane. The reaction mixture was allowed to warm to r.t., heated to reflux for 2 h and stirred for further 10 h at r.t. The solid materials were separated and washed with an excess of toluene. The toluene fractions were collected, and all volatiles were removed in a vacuum. The solid residue left was mainly the product 1b (3.8 g, 77 %). It was washed with hexane and dissolved in THF. Needle-like crystals (m.p. > 263 °C, decom.) suitable for X-ray structural analysis were grown from concentrated THF solutions at r.t. – 1H NMR (400 MHz) data: δ = 2.4, 7.3, 7.6 (s, m, m, 28H, 4-Me-C₆H₄).

Synthesis of 1,3,4,6-tetrasiladiyne 4

A solution of 1,2-dichloro-tetramethyldisilane (4.14 g, 35.3 mmol) in hexane (20 mL) was added at room temperature to a suspension of Li–C≡C–C₆H₄–4-Me (39.4 mmol) in 75 mL of hexane. The reaction mixture was heated at reflux for 12 h, insoluble materials were filtered off, and the solvent was removed in a vacuum to give a suspension of Li–C≡C–C₆H₄–4-Me (3.8 g, 62 %). – 1H NMR (250 MHz in C₆D₆): δ = 0.24 (s, 12H, SiMe₂), 0.02 (s, 18H, SiMe₃). – EI-MS (70 eV); m/z = 310 (10) [M]+, 295 (28) [M–15]+, 73 (100) [SiMe₃]+.

X-ray crystal structure analyses of compounds 1b, 2, 3, and 5

The X-ray crystal structural analyses of 1b, 2, 3, and 5 were carried out at 133(2) K (1b), 193(2) K (2, 3) on single crystals selected in perfluorinated oil [23] at r.t., using a Stoe IPDS II (MoKα radiation, λ = 71.069 pm) system equipped with an Oxford Cryostream low-temperature unit. Structure solutions and refinement were accomplished using SIR97 [24], SHELXL-97 [25], and WINGX [26]. Pertinent data are given in Table 2. Since the solid-state NMR spectra of 1b were measured at r.t. and showed dynamic processes, the X-ray diffraction of 1b was repeated at r.t. (Stoe IPDS I) with a single crystal sealed in a Lindemann capillary. The results were essentially identical with those obtained at 133 K.

CCDC 753787 (1b), 753788 (2), 753789 (3), and 753790 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. E. K. and A. B. thank the DAAD and HEC (Pakistan), and E. M. the Alexander-von-Humboldt Stiftung for fellowships.


