

# Formation and characterization of cyclic and polycyclic silthianes containing Si–Si bonds

U. Herzog <sup>a,\*</sup>, U. Böhme <sup>a</sup>, G. Roewer <sup>a</sup>, G. Rheinwald <sup>b</sup>, H. Lang <sup>b</sup>

<sup>a</sup> Institut für Anorganische Chemie der TU Bergakademie Freiberg, Leipziger Straße 29, D-09596 Freiberg, Germany

<sup>b</sup> Institut für Chemie der TU Chemnitz, Straße der Nationen 62, D-09111 Chemnitz, Germany

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## Abstract

The reactions of several organochlorosilanes and -oligosilanes with H<sub>2</sub>S and NEt<sub>3</sub> have been investigated. Different bicyclic silthianes with bis-cyclopentyl, bicyclo-[3,3,0]-octane, bicyclo-[2,2,1]-heptane (norbornane), bicyclo-[3,2,1]-octane, bicyclo-[2,2,2]-octane and bicyclo-[3,2,1]-nonane skeletons were formed and have been characterized by MS and <sup>1</sup>H-, <sup>13</sup>C- and <sup>29</sup>Si-NMR. The reaction of 1,1,2,2-tetrachlorodimethyldisilane with H<sub>2</sub>S and NEt<sub>3</sub> yields 1,3,5,7,9,11-hexamethyl-1,3,5,7,9,11-hexasila-2,4,6,8,10,12-hexathiatetracyclo-[5,5,0<sup>3,11</sup>,0<sup>5,9</sup>]-dodecane (**4c**) containing three disilane units. Density functional theory calculations proved the general observation that compounds with Si<sub>3</sub>S<sub>2</sub> five-membered rings are preferred. The crystal structures of **4c**, 1,3,3,5,7,7-hexamethyl-1,3,5,7-tetrasilane-2,4,6,8-tetrathiabicyclo-[3,3,0]-octane (**6**) and 1,2,2,4,4,5,6,6,8,8-decamethyl-1,2,4,5,6,8-hexasila-3,7-dithiabicyclo-[3,3,0]-octane (**9**) have been determined. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Silane; Oligosilane; Silthiane; <sup>29</sup>Si-NMR; X-ray structure

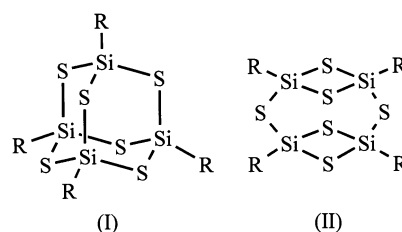
## 1. Introduction

Cyclic and polycyclic silthianes have been investigated for some time but most research has been concentrated on silthianes derived from monosilanes R<sub>4-n</sub>SiCl<sub>n</sub>. Starting from dichlorosilanes the four- and six-membered ring compounds (R<sub>2</sub>SiS)<sub>2,3</sub> can be synthesized, and trichlorosilanes yield silsesquithianes (RSiS<sub>3/2</sub>)<sub>4</sub> which usually possess an adamantane-like structure (I) [1], but in cases of sterically more demanding substituents (R = 1,1,2-trimethylpropyl) a double-decker-like structure (II) has also been observed [2] (Scheme 1).

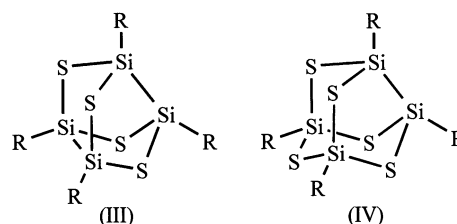
Attempts to build a bis-noradamantane-like structure (III) by reacting <sup>t</sup>BuSiCl<sub>2</sub>–<sup>t</sup>BuSiCl<sub>2</sub> with Li<sub>2</sub>S in THF resulted in extensive insertion of sulfur into Si–Si bonds and formation of (<sup>t</sup>BuSi)<sub>4</sub>S<sub>5</sub> with a noradamantane structure (IV) in 20% yield [3] (Scheme 2).

Only a few reports deal with cyclic silthianes containing Si–Si bonds. Cyclo-(SiMe<sub>2</sub>)<sub>x</sub>S (*x* = 4, 5, 6) have been prepared by reaction of α,ω-dichlorooligosilanes

Cl(SiMe<sub>2</sub>)<sub>x</sub>Cl with Li<sub>2</sub>S in THF [4]. 1,2-Dichlorotetramethyldisilane reacts with H<sub>2</sub>S in the presence of pyridine to form the six-membered ring compound S(Si<sub>2</sub>Me<sub>4</sub>)<sub>2</sub>S (**1**) [5]. If **1** is heated with (Me<sub>2</sub>SiS)<sub>3</sub> (**2a**)



Scheme 1.



Scheme 2.

\* Corresponding author. Tel.: +49-3731-394343; fax: +49-3731-394058.

E-mail address: herzog@merkur.hrz.tu-freiberg.de (U. Herzog)

Table 1

NMR chemical shifts (ppm) and  $^1J_{\text{SiC}}$  (Hz) data of silthianes **3a–c**, **4c** and **5a**

| compound  | $\delta_{\text{Si}}$                           | $^1J_{\text{SiC}}$             | $\delta_{\text{C}}$ (SiMe)               | $\delta_{\text{H}}$ (SiMe)               |
|-----------|------------------------------------------------|--------------------------------|------------------------------------------|------------------------------------------|
| <b>3a</b> |                                                |                                |                                          |                                          |
|           | A: 11.0<br>B: 34.1                             | 46.5<br>58.3                   | 1.09<br>8.46                             | 0.48<br>0.62                             |
| <b>3b</b> |                                                |                                |                                          |                                          |
|           | A: 11.4<br>B: 25.5                             | 46.7<br>60.3 (Me)<br>76.8 (Ph) | 0.84 / 1.05<br>1.91 <sup>a</sup>         | 0.35 / 0.51<br>0.84 <sup>a</sup>         |
| <b>3c</b> |                                                |                                |                                          |                                          |
|           | A: 11.1<br>B: 17.8                             | 46.7                           | 0.88 <sup>b</sup>                        | 0.40 <sup>b</sup>                        |
| <b>4c</b> |                                                |                                |                                          |                                          |
|           | A: 28.5 <sup>c)</sup><br>B: 14.1 <sup>c)</sup> |                                | 4.14 <sup>c)</sup><br>4.88 <sup>c)</sup> | 0.71 <sup>c)</sup><br>0.78 <sup>c)</sup> |
| <b>5a</b> |                                                |                                |                                          |                                          |
|           | A: 20.25<br>B: 12.55                           | 48.6<br>46.2                   | 7.17<br>1.41 / 0.90                      | 0.73<br>0.49 / 0.50                      |

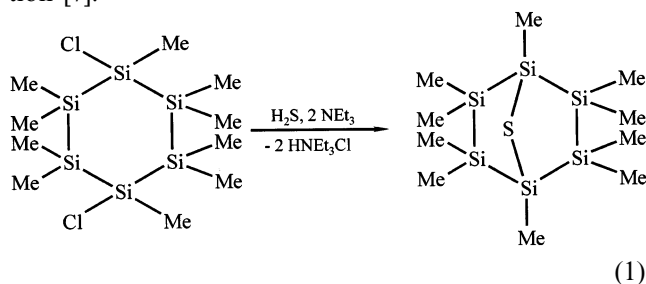
<sup>a</sup>) Ph:  $^{13}\text{C}$ : i: 138.5, o: 133.6, m: 127.7, p: 129.9,  $^1\text{H}$ : 7.36 (3 H), 7.73 (2 H)

<sup>b</sup>) Ph:  $^{13}\text{C}$ : i: 136.6, o: 134.7, m: 127.7, p: 130.1,  $^1\text{H}$ : 7.35 (3 H), 7.72 (2 H)

<sup>c</sup>): in  $\text{C}_6\text{D}_6$

for 3 days (70°C) in the presence of pyridine, the five-membered ring compound  $\text{Si}_2\text{Me}_4(\text{S})_2\text{SiMe}_2$  (**3a**) is formed in 75% yield [6], which suggests that a five-membered  $\text{Si}_3\text{S}_2$  ring is the most stable ring size in this system.

1,4-Dichlorodecamethylcyclohexasilane forms on treatment with  $\text{H}_2\text{S}$  in the presence of  $\text{NEt}_3$  decamethylhexasila-7-thianorbornane in a surprisingly clean reaction [7]:



The crystal structure of the norbornane has an SiS bond length of 2.169(3) Å and a relatively small SiSSI

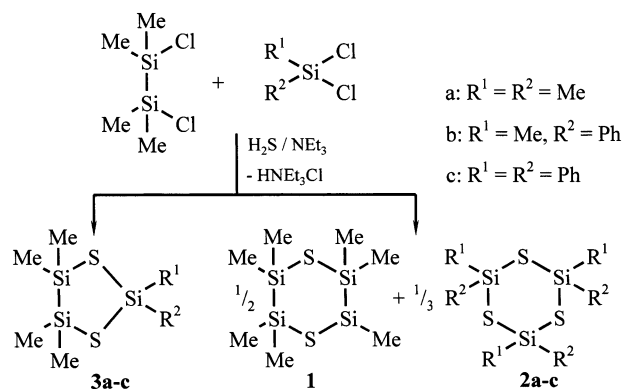
angle of 94.9° as a result of the topology of this bicyclic skeleton.

## 2. Results and discussion

In this work we report on the formation of cyclic, bicyclic and tetracyclic silthianes from methylchlorooligosilanes by treatment with hydrogen sulfide and triethylamine.

### 2.1. 1,2,4-Trisila-3,5-dithiacyclopentanes

Based on the observation made in Ref. [6] that five-membered rings  $\text{Si}_3\text{S}_2$  appear to be the most stable ring size, we tried to synthesize such compounds directly by mixing a dichloromonosilane with 1,2-dichlorotetramethyldisilane in a 1:1 molar ratio and subsequently treating this mixture with  $\text{H}_2\text{S}$  and  $\text{NEt}_3$  in hexane solution. NMR investigations showed that indeed the five-membered ring compounds **3a–c** are



Scheme 3.

formed in a 55 mol% amount, but the six-membered ring compounds **1** and **2a–c** are also present. The NMR data of **3a–c** are summarized in Table 1 (Scheme 3).

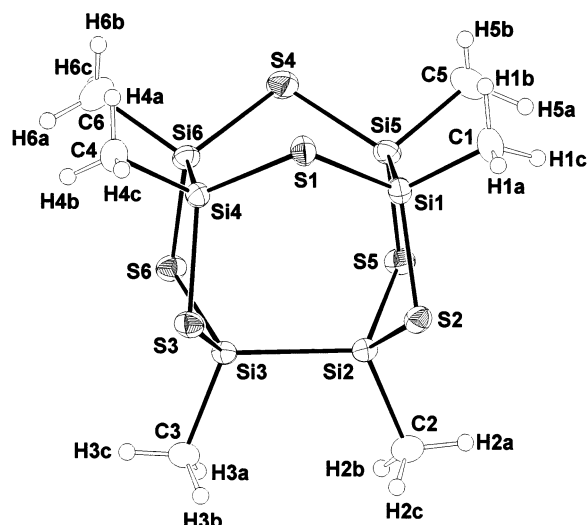
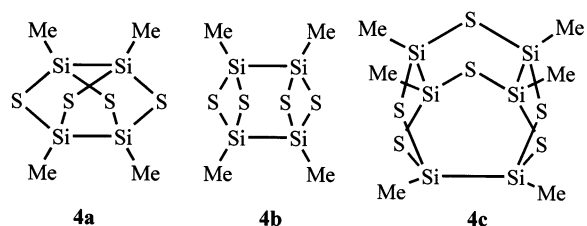
Compared with the acyclic thiobutyl substituted compounds  $\text{Me}_2\text{Si}(\text{SBu})_2$  and  $\text{BuS}(\text{SiMe}_2)_2\text{SBu}$  [8] containing the same silyl units, the six-membered rings **1** and **2a** show a  $^{29}\text{Si}$ -NMR shift to higher field (**1**:  $-3.2$  ppm relative to  $\text{BuS}(\text{SiMe}_2)_2\text{SBu}$  and **2a**:  $-3.7$  ppm relative to  $\text{Me}_2\text{Si}(\text{SBu})_2$ ), whereas the resonances of the same silyl groups in the five-membered ring **3a** are shifted significantly to lower field, the  $\text{S}_2\text{SiMe}_2$  unit by 9.3 ppm and the  $\text{Si}_2\text{Me}_4$  unit by 12.6 ppm. The five-membered ring compounds **3b** and **3c** behave similarly in comparison with the acyclic silanes  $\text{PhMeSi}(\text{SBu})_2$  and  $\text{Ph}_2\text{Si}(\text{SBu})_2$  [8] and the six-membered rings  $(\text{PhMeSiSi})_3$  and  $(\text{Ph}_2\text{SiSi})_3$  [9].

Density functional theory (DFT) calculations on compounds **1**, **2a** and **3a** (see Table 2) indicate that six molecules of **3a** are  $36.0 \text{ kJ mol}^{-1}$  lower in energy than three molecules of **1** and two molecules of **2a** according to the redistribution (Eq. (2)):



## 2.2. 1,3,5,7,9,11-Hexamethyl-1,3,5,7,9,11-hexasila-2,4,6,8,10,12-hexathiatetracyclo-[5,5,0,0<sup>3,11</sup>,0<sup>5,9</sup>]-dodecane (**4c**)

The treatment of 1,1,2,2-tetrachlorodimethyldisilane with  $\text{H}_2\text{S}$  and  $\text{NEt}_3$  yielded no hexane soluble products,

Fig. 1. The molecular structure of **4c**.

Scheme 4.

and therefore the reaction was carried out in toluene. Colorless crystals were obtained after filtration from precipitated  $\text{HNEt}_3\text{Cl}$  and evaporation of the solvent. Initially we expected the formation of a bis-noradaman-tan structure (**4a**) or a bis-nordoubledecker structure (**4b**), but  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{29}\text{Si}$ -NMR spectroscopy revealed two signals in a 2:1 ratio, which can only be explained by a structure with at least three disilane units. A crystal structure analysis of the product confirmed that three disilane units are indeed present, forming a tetracyclo-[5,5,0,0<sup>3,11</sup>,0<sup>5,9</sup>]-dodecane cage, **4c** (Fig. 1, Scheme 4).

The observed SiS as well as SiSi bond lengths in **4c** (Table 3) are in the usual range of  $2.11$ – $2.18 \text{ \AA}$  [10] for SiS single bonds and  $2.33$ – $2.38 \text{ \AA}$  [11] for Si–Si single bonds. The SiSSi bond angles at S(1) and S(4), which

Table 2  
Calculated geometry parameters and total energies (B3LYP/6-31G\*) of the compounds **1**, **2a** and **3a**

| Compound  | $d(\text{SiSi})$ (Å) | $d(\text{SiS})$ (Å)                     | $\angle \text{SiSSi}$ (°) | $\angle \text{SiSiS}$ (°) | $\angle \text{SSiS}$ (°) | Total energy (H) | Total energy with zero point corr. (H) |
|-----------|----------------------|-----------------------------------------|---------------------------|---------------------------|--------------------------|------------------|----------------------------------------|
| <b>1</b>  | 2.365                | 2.187                                   | 109.2                     | 110.5                     | –                        | –2273.89799      | –2273.59077                            |
| <b>2a</b> | –                    | 2.172                                   | 109.0                     | –                         | 113.4                    | –2302.80119      | –2302.56720                            |
| <b>3a</b> | 2.358                | 2.179 <sup>a</sup> / 2.185 <sup>b</sup> | 103.8                     | 102.2                     | 111.6                    | –1904.55117      | –1904.32007                            |

<sup>a</sup>  $\text{S}-\text{Me}_2\text{Si}-\text{S}$ .

<sup>b</sup>  $\text{Si}-\text{Me}_2\text{Si}-\text{S}$ .

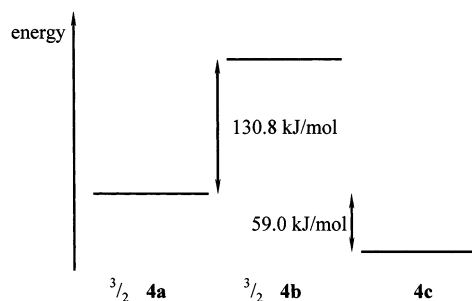
Table 3

Selected bond lengths and angles of **4c**

| Atoms       | Bond lengths (Å) | Atoms             | Bond angles (°) |
|-------------|------------------|-------------------|-----------------|
| Si(1)–Si(1) | 2.1404(10)       | Si(1)–Si(1)–Si(4) | 105.06(4)       |
| Si(1)–Si(4) | 2.1499(10)       | Si(1)–Si(2)–Si(2) | 100.14(4)       |
| Si(2)–Si(1) | 2.1469(10)       | Si(3)–Si(3)–Si(4) | 100.27(4)       |
| Si(2)–Si(2) | 2.1515(10)       | Si(5)–Si(4)–Si(6) | 104.95(4)       |
| Si(3)–Si(3) | 2.1438(10)       | Si(5)–Si(5)–Si(2) | 100.59(4)       |
| Si(3)–Si(4) | 2.1444(10)       | Si(6)–Si(6)–Si(3) | 100.47(4)       |
| Si(4)–Si(5) | 2.1286(10)       | Si(1)–Si(1)–Si(2) | 114.49(4)       |
| Si(4)–Si(6) | 2.1340(11)       | Si(1)–Si(1)–Si(5) | 113.58(4)       |
| Si(5)–Si(5) | 2.1386(10)       | Si(2)–Si(1)–Si(5) | 105.96(4)       |
| Si(5)–Si(2) | 2.1498(10)       | Si(5)–Si(2)–Si(2) | 109.31(4)       |
| Si(6)–Si(6) | 2.1387(10)       | Si(5)–Si(2)–Si(3) | 110.32(4)       |
| Si(6)–Si(3) | 2.1448(9)        | Si(2)–Si(2)–Si(3) | 110.20(4)       |
| Si(1)–Si(5) | 2.3481(11)       | S(3)–Si(3)–Si(6)  | 110.33(4)       |
| Si(2)–Si(3) | 2.3642(11)       | S(3)–Si(3)–Si(2)  | 110.40(4)       |
| Si(4)–Si(6) | 2.3578(10)       | S(6)–Si(3)–Si(2)  | 110.12(4)       |
| Si(1)–C(1)  | 1.863(3)         | S(3)–Si(4)–Si(1)  | 112.95(4)       |
| Si(2)–C(2)  | 1.857(3)         | S(3)–Si(4)–Si(6)  | 105.87(4)       |
| Si(3)–C(3)  | 1.859(3)         | Si(1)–Si(4)–Si(6) | 114.13(4)       |
| Si(4)–C(4)  | 1.850(3)         | S(4)–Si(5)–Si(5)  | 114.27(5)       |
| Si(5)–C(5)  | 1.862(3)         | S(4)–Si(5)–Si(1)  | 114.86(4)       |
| Si(6)–C(6)  | 1.862(3)         | S(5)–Si(5)–Si(1)  | 105.46(4)       |
|             |                  | S(4)–Si(6)–Si(6)  | 114.14(5)       |
|             |                  | S(4)–Si(6)–Si(4)  | 113.84(4)       |
|             |                  | S(6)–Si(6)–Si(4)  | 105.61(4)       |

are part of six-membered rings, are 4–5° larger than the SiSSi bond angles at the other four sulfur atoms, which are part of five-membered rings. Ab initio calculations of **4a–c** (Table 4) reveal that **4a** is lower in energy than **4b** and that the structure of **4c** is energetically even more preferred (Scheme 5).

The lower energy of **4a** with respect to **4b** correlates with the fact that **4a** contains four of the preferred five-membered rings Si<sub>3</sub>S<sub>2</sub>, whereas in **4b** only the less favorable four-membered rings Si<sub>2</sub>S<sub>2</sub> and six-membered rings Si<sub>4</sub>S<sub>2</sub> can be found. The high overall ring strain of such small tricyclic systems (calculated SiSSi bond angles in **4a** and **4b** are smaller than 90°) forces the system to form the larger tetracyclic cage **4c**. The optimized geometry of **4c** calculated by ab-initio methods is in complete agreement with the X-ray structure analysis, however the calculated Si–Si as well as SiS bond lengths



Scheme 5.

are 0.02–0.03 Å larger and the SiSSi bond angles at S(1) and S(4) are 2–3° larger than the observed data.

Compared with the acyclic compound (BuS)<sub>2</sub>SiMe–SiMe(SBu)<sub>2</sub>, which exhibits a <sup>29</sup>Si-NMR shift of 9.1 ppm [8], the <sup>29</sup>Si-NMR chemical shifts in **4c** are shifted to lower field. The four equivalent silicon atoms, which take part in both a Si<sub>3</sub>S<sub>2</sub> five-membered ring and in a Si<sub>4</sub>S<sub>2</sub> six-membered ring are shifted by 5.0 ppm, while the two other silicon atoms (part of five-membered rings) are shifted to a lower field by 19.4 ppm. These effects parallel the trends in monocyclic silthianes, where the formation of a five-membered ring is accompanied by a low-field shift of 10–14 ppm, and a six-membered ring results in a high-field shift of 3–5 ppm in comparison with acyclic thiobutyl substituted compounds containing the same silyl unit.

### 2.3. Bis-(1,3,3,4,4-pentamethyl-1,3,4-trisila-2,5-dithiacyclopent-1-yl) (**5a**)

The treatment of a 2:1 mixture of SiClMe<sub>2</sub>–SiClMe<sub>2</sub> and SiCl<sub>2</sub>Me–SiCl<sub>2</sub>Me with H<sub>2</sub>S and NEt<sub>3</sub> yielded, besides some **1**, the new bicyclic silthiane **5a**. No further products with the possible decaline like structures **5b** or **5c** could be observed by NMR spectroscopy (Scheme 6).

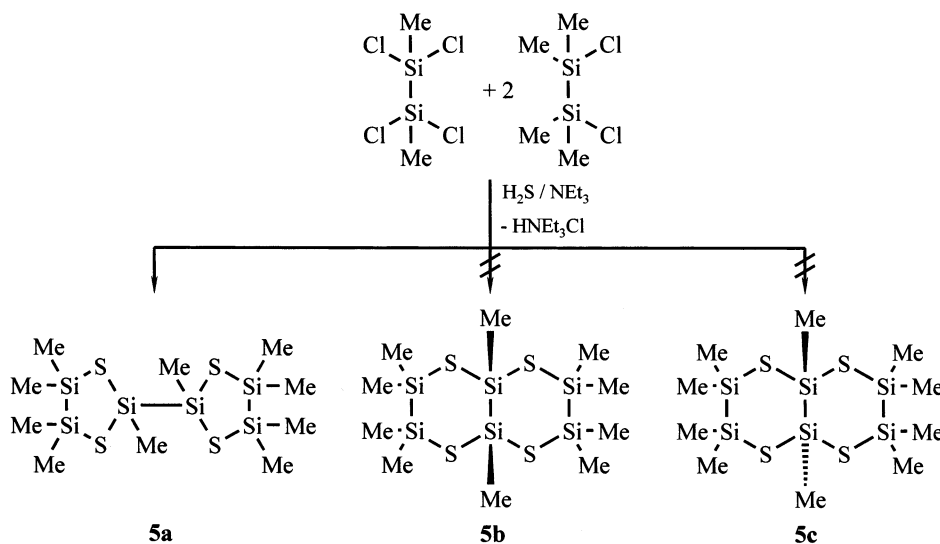
The assignment of **5a** as the five-membered ring isomer is supported by the <sup>29</sup>Si-NMR chemical shift of the SiMe<sub>2</sub> units, which is very close to the shift observed for the five-membered ring compounds **3a–c**, and also the Si-NMR shift at a relatively low field for the SiMe units. Furthermore, the splitting of the <sup>1</sup>H-

Table 4

Calculated geometry parameters and total energies (B3LYP/6-31G\*) of the compounds **4a**, **4b** and **4c**

| Compound  | d(SiSi) (Å)              | d(SiS) (Å)               | ∠ SiSSi (°)             | ∠ SSiS (°)               | Total energy (H) | Total energy with zero point corr. (H) |
|-----------|--------------------------|--------------------------|-------------------------|--------------------------|------------------|----------------------------------------|
| <b>4a</b> | 2.440                    | 2.180                    | 86.7                    | 103.5                    | –2910.69797      | –2910.53392                            |
| <b>4b</b> | 2.422                    | 2.190                    | 76.4                    | 94.8                     | –2910.66369      | –2910.50071                            |
| <b>4c</b> | 2.384/2.394 <sup>a</sup> | 2.174/2.177 <sup>b</sup> | 99.9/107.3 <sup>c</sup> | 114.1/109.2 <sup>d</sup> | –4366.07013      | –4365.82337                            |

<sup>a</sup> Si(2)–Si(3).<sup>b</sup> Si(2)–S and Si(3)–S.<sup>c</sup> Si(1)–Si(1)–Si(4) and Si(5)–Si(4)–Si(6).<sup>d</sup> S(2)–Si(2)–S(5) and S(3)–Si(3)–S(6).



Scheme 6.

and  $^{13}\text{C}$ -NMR signals of the diastereotopic  $\text{SiMe}_2$  units support the bicyclic structure **5a**.

#### 2.4. Bicyclo-[3,3,0]-octanes

If a 1:2 mixture of  $\text{SiCl}_2\text{Me}-\text{SiCl}_2\text{Me}$  and  $\text{Me}_2\text{SiCl}_2$  is treated with  $\text{H}_2\text{S}$  and  $\text{NEt}_3$ , the work-up results in an oily residue of 1,3,3,5,7,7-hexamethyl-1,3,5,7-tetrasil-2,4,6,8-tetrathiabicyclo-[3,3,0]-octane (**6**) together with some **2a**. Compound **4c**, which is probably also formed, is insoluble in hexane and was therefore removed together with the precipitated ammonium salt. In order to get **6** free of **2a**, the ratio of the chlorosilanes was changed to 1:1. This time **6** was found as the only hexane soluble product. Single crystals suitable for X-ray analysis were obtained from hexane solution, Fig. 2. Selected bond lengths and angles of **6** are summarized in Table 7.

The crystal structure analysis of **6** reveals the expected bicyclo-[3,3,0]-octane skeleton with  $\text{SiSSi}$  angles of  $99^\circ$  (Table 7), which is close to the  $\text{SiSSi}$  angles of the five-membered rings in **4c** ( $100$ – $100.5^\circ$ ) and approximately  $6^\circ$  smaller than the  $\text{SiSSi}$  angles in the six-membered rings of **4c** ( $105^\circ$ ) and published data for the six-membered ring compounds  $(\text{PhMeSiS})_3$ :  $106.2^\circ$  [12] and  $(\text{MeSiS}_{3/2})_4$ :  $104.5^\circ$  [13]. Both five-membered rings adopt an envelope conformation with angles between the two planes of  $50.39$  ( $0.05^\circ$ ) in the ring  $\text{Si}(1)-\text{Si}(1a)-\text{S}(1a)-\text{Si}(2)-\text{S}(1)$  and  $48.24$  ( $0.05^\circ$ ) in the ring  $\text{Si}(1)-\text{Si}(1a)-\text{S}(2a)-\text{Si}(3)-\text{S}(2)$ .

It is known from different  $\text{SiO}_2$  modifications that the  $\text{SiOSi}$  angle has a major influence on the  $^{29}\text{Si}$ -NMR shift [14,15] ranging from  $-107$  ppm in  $\alpha$ -quartz [16] (mean  $\text{SiOSi}$  angle:  $143.6^\circ$  [17]) to  $-128.2$  ppm in zunyite [18] ( $\text{SiOSi}$  angle:  $180^\circ$  [19]). The bond polarization theory has been applied to fit the  $^{29}\text{Si}$ -NMR shifts

with the molecular geometry of  $\text{SiO}_2$  networks [20]. From these results it seems likely that the  $\text{SiSSi}$  bond angle in cyclic silthianes also has an important influence on the  $^{29}\text{Si}$ -NMR shifts if silicon atoms with the same first coordination sphere are compared.

Because of the formation of five-membered rings, the  $^{29}\text{Si}$ -NMR signals in **6** (Table 8) show again the expected downfield shifts of 20.75 ppm ( $\text{SiMe}$ , part of two five-membered rings) and 10.5 ppm ( $\text{SiMe}_2$ ) compared with the same silyl units in the acyclic thiobutyl substituted compounds  $(\text{BuS})_2\text{SiMe}-\text{SiMe}(\text{SBu})_2$  and  $\text{Me}_2\text{Si}(\text{SBu})_2$  [8].

In comparison with the compounds **2a** and **4c** (the reaction products if  $\text{SiCl}_2\text{Me}-\text{SiCl}_2\text{Me}$  or  $\text{Me}_2\text{SiCl}_2$ , respectively, are treated separately with  $\text{H}_2\text{S}/\text{NEt}_3$ ) the formation of **6** is energetically preferred. According to Eq. (3):



three molecules of **6** are  $29.9 \text{ kJ mol}^{-1}$  lower in energy than **4c** and two molecules of **2a** (calculated energies,

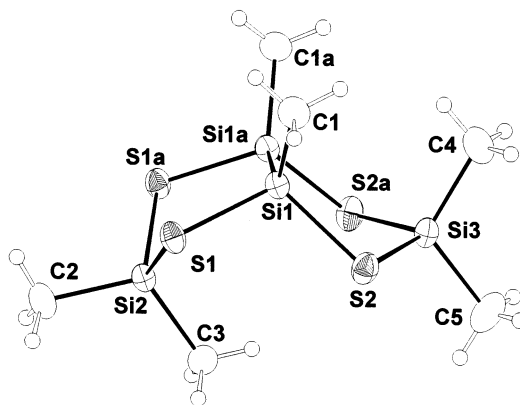
Fig. 2. The molecular structure of **6**.

Table 5  
Calculated geometry parameters and total energies (B3LYP/6-31G\*) of the compounds **6**, **10a–b** and **11**; for assignment of Si and S see Fig. 2, Scheme 8, and Eq. (4)

| Compound   | $d(\text{SiSi})$ and $d(\text{SiS})$ (Å)                                                                | Bond angles (°)                                                                                                                                                  | Total energy (H) | Total energy with zero point corr. (H) |
|------------|---------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------|----------------------------------------|
| <b>6</b>   | Si(1)–Si(1a): 2.381<br>Si(1)–S(1): 2.165<br>Si(2)–S(1): 2.184<br>Si(1)–S(2): 2.178<br>Si(3)–S(2): 2.178 | Si(1)–S(1)–Si(2): 100.4<br>Si(1)–S(2)–Si(3): 101.0<br>Si(1a)–Si(1)–S(1): 105.8<br>Si(1a)–Si(1)–S(2): 105.9<br>S(1)–Si(2)–S(1a): 110.3<br>S(2)–Si(3)–S(2a): 109.1 | –2990.56098      | –2990.32305                            |
| <b>10a</b> | Si(1)–Si(2): 2.370<br>Si(1)–S(1): 2.183<br>Si(1)–S(2): 2.182<br>Si(2)–S(2): 2.200                       | Si(1)–S(1)–Si(1): 89.1<br>Si(1)–S(2)–Si(2): 99.5<br>Si(1)–Si(2)–S(2): 102.1<br>Si(2)–Si(1)–S(2): 108.9<br>Si(2)–Si(1)–S(1): 101.2<br>S(1)–Si(1)–S(2): 109.2      | –2592.30580      | –2592.07037                            |
| <b>10b</b> | Si(1)–Si(2): 2.366<br>Si(1)–S(2): 2.186<br>Si(1)–S(2'): 2.192<br>Si(2)–S(1): 2.187                      | Si(2)–S(1)–Si(2): 113.1<br>Si(1)–S(2)–Si(1): 78.8/79.1<br>Si(1)–Si(2)–S(1): 109.5<br>Si(2)–Si(1)–S(2): 106.5/109.4<br>S(2)–Si(1)–S(2): 96.6                      | –2592.29259      | –2592.05752                            |
| <b>11</b>  | Si(1)–Si(2): 2.372<br>Si(1)–S(2): 2.201<br>Si(2)–S(2): 2.195<br>Si(3)–S(1): 2.170<br>Si(3)–S(2): 2.176  | Si(1)–S(1)–Si(3): 89.3<br>Si(2)–S(2)–Si(3): 100.0<br>Si(1)–Si(2)–S(2): 101.9<br>Si(2)–Si(1)–S(1): 99.4<br>S(1)–Si(3)–S(2): 108.2<br>S(2)–Si(3)–S(2): 111.5       | –2592.30320      | –2592.06758                            |

Table 6  
Calculated geometry parameters and total energies (B3LYP/6-31G\*) of the compounds **12a–b** and **14**; for assignment of Si and S see Scheme 9 and Eq. (5)

| Compound   | $d(\text{SiSi})$ and $d(\text{SiS})$ (Å)                                                                                                                                                     | Bond angles (°)                                                                                                                    | Total energy (H) | Total energy with zero point corr. (H) |
|------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------|------------------|----------------------------------------|
| <b>12a</b> | Si(1)–Si(2): 2.378<br>Si(1)–Si(3): 2.366<br>Si(4)–Si(5): 2.368<br>Si(1)–S(1): 2.197<br>Si(2)–S(2): 2.192<br>Si(3)–S(3): 2.186<br>Si(4)–S(1): 2.181<br>Si(4)–S(2): 2.180<br>Si(5)–S(3): 2.188 | Si(1)–S(1)–Si(4): 96.4<br>Si(2)–S(2)–Si(4): 102.0<br>Si(3)–S(3)–Si(5): 109.8<br>S(1)–Si(4)–S(2): 109.8<br>Si(2)–Si(1)–Si(3): 113.2 | –2961.65838      | –2961.34679                            |
| <b>12b</b> | Si(1)–Si(2): 2.369<br>Si(3)–Si(4): 2.368<br>Si(1)–S(1): 2.188<br>Si(2)–S(2): 2.194<br>Si(3)–S(2): 2.177<br>Si(4)–S(1): 2.192                                                                 | Si(1)–S(1)–Si(4): 104.8<br>Si(2)–S(2)–Si(3): 106.3<br>S(2)–Si(3)–S(2): 114.7<br>Si(2)–Si(1)–Si(2): 110.7                           | –2961.65709      | –2961.34571                            |
| <b>14</b>  | Si(1)–Si(2): 2.370<br>Si(2)–S(1): 2.195<br>Si(3)–S(1): 2.172                                                                                                                                 | Si(2)–S(1)–Si(3): 105.6<br>Si(1)–Si(2)–S(1): 107.0<br>S(1)–Si(3)–S(1): 112.4<br>Si(2)–Si(1)–Si(2): 105.7                           | –2961.65849      | –2961.34649                            |

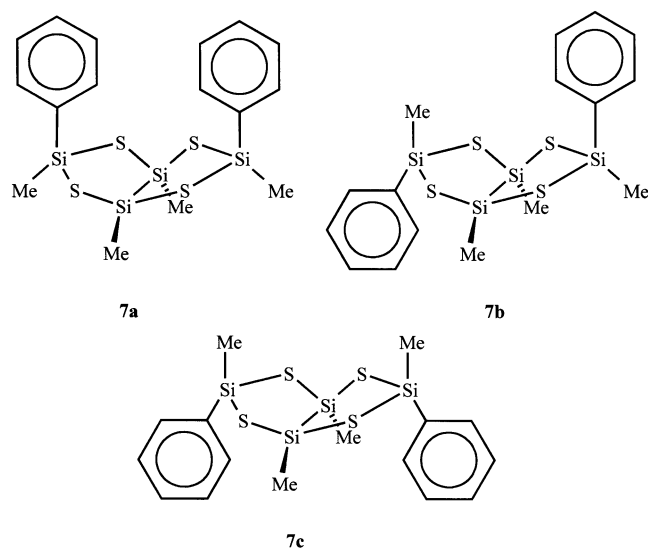
see Tables 4 and 5). The calculated geometry of **6** is in complete agreement with the result of the crystal structure analysis with envelope conformations of both five-membered rings and one  $\text{SiMe}_2$  unit in *exo*

and one in *endo* position. However, as for **4c** the calculated  $d_{\text{SiSi}}$  and  $d_{\text{SiS}}$  are 0.02–0.03 Å longer and the angles  $\text{SiSSi}$  are 1–2° larger than the observed data.

Three isomers of 3,7-diphenyl-1,3,5,7-tetramethyl-1,3,5,7-tetrasilol-2,4,6,8-tetrathiabicyclo-[3,3,0]-octane (**7a–c**) were obtained by a similar reaction of a mixture of  $\text{SiCl}_2\text{Me–SiCl}_2\text{Me}$  and two equivalents of  $\text{PhMeSiCl}_2$ . The three isomers differ in the spatial orientation of the two phenyl groups (Scheme 7):

Compound **7b** is formed with 49% yield and can be assigned unambiguously because it contains two different  $^{29}\text{Si}$ -NMR signals in this region. The isomer which is formed with a yield of only 9%, very likely corresponds to the structure of **7a**, because in **7a** the two phenyl rings hinder each other and make this isomer less favorable. Consequently the third isomer, which is formed with a yield of 42%, possesses the structure **7c**. Finally, the reaction of a mixture of  $\text{SiCl}_2\text{Me–SiCl}_2\text{Me}$  and two equivalents of  $\text{Ph}_2\text{SiCl}_2$  with  $\text{H}_2\text{S}$  and  $\text{NEt}_3$  resulted in the formation of 3,3,7,7-tetraphenyl-1,5-dimethyl-1,3,5,7-tetrasilol-2,4,6,8-tetrathiabicyclo-[3,3,0]-octane (**8**).

The  $^{29}\text{Si}$ -NMR shifts of the central  $\text{Si}_2\text{Me}_2$  units in **7a–c** and **8** are almost the same as those found for **6a** supporting



Scheme 7.

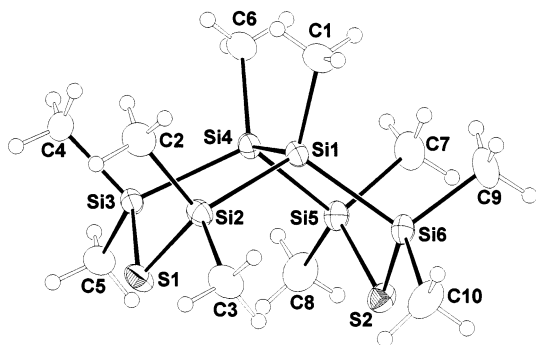


Fig. 3. The molecular structure of **9**.

Table 7  
Selected bond lengths and angles of **6**

| Atoms        | Bond lengths (Å) | Atoms             | Bond angles (°) |
|--------------|------------------|-------------------|-----------------|
| Si(1)–Si(1)  | 2.1343(7)        | Si(1)–S(1)–Si(2)  | 99.28(3)        |
| Si(1)–Si(2)  | 2.1563(7)        | Si(1)–S(2)–Si(3)  | 98.96(3)        |
| Si(2)–Si(1)  | 2.1460(7)        | S(1)–Si(1)–S(2)   | 109.76(3)       |
| Si(2)–Si(3)  | 2.1475(7)        | S(1)–Si(1)–Si(1a) | 104.92(2)       |
| Si(1)–C(1)   | 1.855(2)         | S(2)–Si(1)–Si(1a) | 105.40(2)       |
| Si(1)–Si(1a) | 2.3600(12)       | S(1)–Si(2)–S(1a)  | 106.67(4)       |
| Si(2)–C(2)   | 1.851(3)         | S(2a)–Si(3)–S(2)  | 109.15(4)       |
| Si(2)–C(3)   | 1.852(3)         | C(2)–Si(2)–C(3)   | 112.42(16)      |
| Si(3)–C(4)   | 1.846(3)         | C(4)–Si(3)–C(5)   | 112.86(19)      |
| Si(3)–C(5)   | 1.846(4)         |                   |                 |

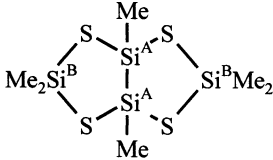
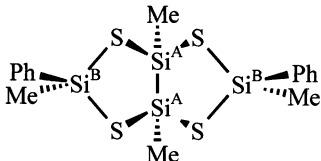
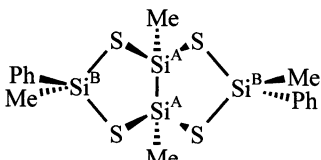
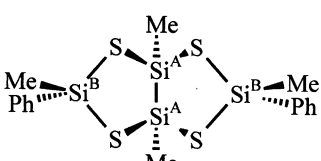
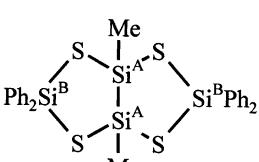
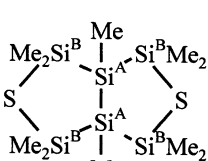
the bicyclo-[3,3,0]-octane structures of these compounds. Furthermore, the  $^{29}\text{Si}$ -NMR signals of the  $\text{SiPhMe}$  and  $\text{SiPh}_2$  units are very close to those of **3b** and **3c** and shifted by 7.4–8.6 ppm ( $\text{SiPhMe}$ ) and 5.4 ppm ( $\text{SiPh}_2$ ) downfield as compared with  $\text{PhMeSi}(\text{SBU})_2$  and  $\text{Ph}_2\text{Si}(\text{SBU})_2$  [8] as a result of the formation of five-membered rings.

Another silthiane with a bicyclo-[3,3,0]-octane skeleton was prepared by the reaction of 1,1,2,2-tetrakis(chlorodimethylsilyl)-1,2-dimethyldisilane with  $\text{H}_2\text{S}$  and  $\text{NEt}_3$ . The only observed silicon containing reaction product was the expected 1,2,2,4,4,5,6,6,8,8-decamethyl-1,2,4,5,6,8-hexasilol-3,7-dithiabicyclo-[3,3,0]octane (**9**). After sublimation, crystals of **9** suitable for crystal structure analysis could be obtained, Fig. 3.

The crystal structure analysis of **9** shows the expected bicyclo-[3,3,0]-octane skeleton with  $\text{SiSSi}$  angles of  $101–102^\circ$  (Table 9), which is again in the range of the  $\text{SiSSi}$  angles of the five-membered rings in **4c** and **6**. All  $\text{Si–Si}$  as well as  $\text{Si–S}$  bond lengths are in the usual ranges of 2.33–2.35 and 2.15–2.16 Å, respectively. The  $\text{SiSiSi}$  angles in the five-membered rings  $\text{Si}_4\text{S}$  are in the range  $102–103^\circ$ , whereas the angles  $\text{Si(6)–Si(1)–Si(4)}$  and  $\text{Si(5)–Si(4)–Si(3)}$  between the two rings are expanded to  $114–115^\circ$ . Both five-membered rings adopt an envelope conformation with angles of  $42.34(0.04)^\circ$  in the ring  $\text{Si(1)–Si(2)–S(1)–Si(3)–Si(4)}$  and  $44.35(0.03)^\circ$  in the ring  $\text{Si(1)–Si(6)–S(2)–Si(5)–Si(4)}$ . The angle between the planes  $\text{Si(1)–Si(2)–Si(3)–Si(4)}$  and  $\text{Si(1)–Si(4)–Si(5)–Si(6)}$  is  $119.06(0.02)^\circ$ . Compared with the  $^{29}\text{Si}$ -NMR shifts of the same hexasilane skeleton in the acyclic compound  $(\text{BuSM}_2\text{Si})_2\text{SiMe–SiMe–(SiMe}_2\text{SBU)}$  of  $-74.7$  ppm ( $\text{SiMe}$ ) and  $5.7$  ppm ( $\text{SiMe}_2$ ), the signals are shifted by  $3.4$  ( $\text{SiMe}$ ) and  $10.7$  ppm ( $\text{SiMe}_2$ ) to lower field in accordance with the formation of five-membered rings, although in this case  $\text{Si}_4\text{S}$  rings are present. The  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR shifts of the  $\text{SiMe}$  groups also differ significantly, see Section 3.10 and Table 8, but the  $^1J_{\text{SiC}}$  coupling constants remain almost unchanged.

Table 8

NMR chemical shifts (ppm) and  $^1J_{\text{SiC}}$  (Hz) data of silthianes **6**, **7a–c**, **8** and **9** with a bicyclo-[3,3,0]-octane skeleton

| compound                                                                                        | $\delta_{\text{Si}}$      | $^1J_{\text{SiC}}$                | $\delta_{\text{C}}$ (SiMe) | $\delta_{\text{H}}$ (SiMe) |
|-------------------------------------------------------------------------------------------------|---------------------------|-----------------------------------|----------------------------|----------------------------|
| <b>6</b><br>   | A: 29.85<br>B: 35.29      | 52.2<br>58.7                      | 5.24<br>8.19 / 7.48        | 0.91<br>0.66 / 0.73        |
| <b>7a</b><br>  | A: 30.6<br>B: 26.1        |                                   | 5.6<br>7.5                 |                            |
| <b>7b</b><br>  | A: 30.3<br>B: 26.8 / 26.0 |                                   | 5.1<br>7.7 / 6.1           |                            |
| <b>7c</b><br>  | A: 29.2<br>B: 25.6        |                                   | 4.5<br>6.4 <sup>a)</sup>   | 0.98<br>0.67               |
| <b>8</b><br>  | A: 28.7<br>B: 17.3        |                                   | 4.7                        | 0.69                       |
| <b>9</b><br> | A: -71.3<br>B: 16.4       | 45.2<br>$^1J_{\text{SiSi}}: 64.1$ | -12.05<br>3.78 / 4.36      | 0.28<br>0.49 / 0.54        |

<sup>a)</sup>: Ph,  $^{13}\text{C}$ : i: 133.15, o: 133.8, m: 128.0, p: 130.5

### 2.5. Bicyclo-[2,2,1]-heptanes (norbornanes)

The reaction of 1,1,2-trichlorotrimethyldisilane with  $\text{H}_2\text{S}$  and  $\text{NEt}_3$  yielded 1,2,2,4,5,5-hexamethyl-1,2,4,5-tetrasilol-3,6,7-trithianorbornane (**10a**) as the only product. The proposed structure is in agreement with the mass spectrum and with the presence of two  $^{29}\text{Si}$ -NMR and three  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR signals (Table 10) due to the splitting of the diastereotopic methyl groups in the  $\text{SiMe}_2$  units. The theoretically also possible structure **10b** bears only two different methyl groups which

would result in only two  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR signals (Scheme 8).

Furthermore, the Si-NMR shifts for **10a** are found 11.0 ppm (SiMe) and 11.3 ppm ( $\text{SiMe}_2$ ) downfield from the values for the acyclic thiobutyl substituted compound  $(\text{BuS})_2\text{SiMe-SiMe}_2(\text{SBu})$  [8], strongly supporting a structure with five-membered rings.

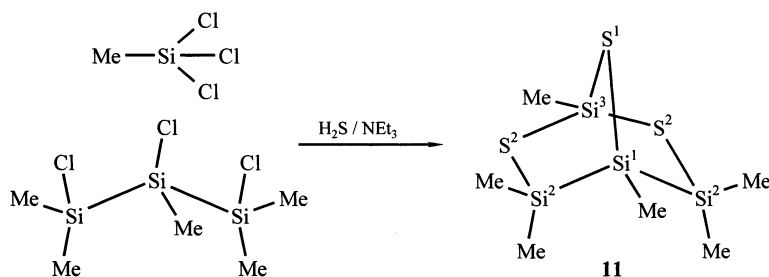
The calculated structure of **10a** (see Fig. 4) reveals a SiSSi angle at S(2) in the usual range for five-membered rings as well as a relatively small angle at S(1) of only  $89.1^\circ$ , which is even  $5^\circ$  smaller than the SiSSi angle

Table 9  
Selected bond lengths and angles of **9**

| Atoms       | Bond lengths (Å) | Atoms             | Bond angles (°) |
|-------------|------------------|-------------------|-----------------|
| Si(1)–Si(3) | 2.1541(8)        | Si(3)–Si(1)–Si(2) | 102.11(3)       |
| Si(1)–Si(2) | 2.1573(8)        | Si(5)–Si(2)–Si(6) | 101.31(3)       |
| Si(2)–Si(5) | 2.1509(8)        | Si(2)–Si(1)–Si(6) | 114.36(3)       |
| Si(2)–Si(6) | 2.1515(8)        | Si(2)–Si(1)–Si(4) | 102.45(3)       |
| Si(1)–Si(2) | 2.3443(8)        | Si(6)–Si(1)–Si(4) | 102.02(3)       |
| Si(1)–Si(6) | 2.3471(8)        | Si(1)–Si(2)–Si(1) | 106.56(3)       |
| Si(1)–Si(4) | 2.3512(8)        | Si(1)–Si(3)–Si(4) | 106.87(3)       |
| Si(3)–Si(4) | 2.3417(7)        | Si(5)–Si(4)–Si(3) | 115.26(3)       |
| Si(4)–Si(5) | 2.3371(8)        | Si(5)–Si(4)–Si(1) | 102.02(3)       |
| Si(1)–C(1)  | 1.890(2)         | Si(3)–Si(4)–Si(1) | 102.24(3)       |
| Si(4)–C(6)  | 1.888(2)         | S(2)–Si(5)–Si(4)  | 106.38(3)       |
|             |                  | S(2)–Si(6)–Si(1)  | 106.41(3)       |

found in decamethylhexasila-7-thianorbornane [7]. The calculations showed that the experimentally observed isomer **10a** is 33.7 kJ mol<sup>−1</sup> lower in energy than **10b** with a strained four-membered ring.

An isomeric compound, 1,2,2,4,6,6-hexamethyl-1,2,4,6-tetrasil-3,5,7-trithianorbornane (**11**), has been prepared by reacting a 1:1 molar mixture of 1,2,3-trichloropentamethyltrisilane and methyltrichlorosilane with H<sub>2</sub>S and NEt<sub>3</sub>. The mass spectrum and the three <sup>29</sup>Si-NMR signals detected at a relatively low field are in agreement with the norbornane structure **11**. The GC–MS spectra of **10a** and **11** differ only in the retention times and in the relative intensities of the parent peak and fragment peaks.



The <sup>29</sup>Si-NMR signals of the trisilane unit in **11** are shifted by 15.7 (Si<sup>A</sup>) and 6.4 ppm (Si<sup>B</sup>) to lower field compared with the acyclic derivative BuSSiMe<sub>2</sub>–SiMe(SBu)–SiMe<sub>2</sub>(SBu) [8]. The chemical shift of Si<sup>A</sup> is only 1.3 ppm upfield from value found for the bridgehead silicon atoms in decamethylhexasila-7-thianorbornane [7] with the same first coordination sphere. The calculated structure of **11** (Table 5) shows similar bond parameters as the isomeric compound **10a**. For instance, the bond angles SiSSi at S(1) and S(2) are almost identical. A comparison of the calculated total energies (with zero point correction) reveals that the norbornane **10a** is 7.3 kJ mol<sup>−1</sup> lower in energy than the isomer **11**.

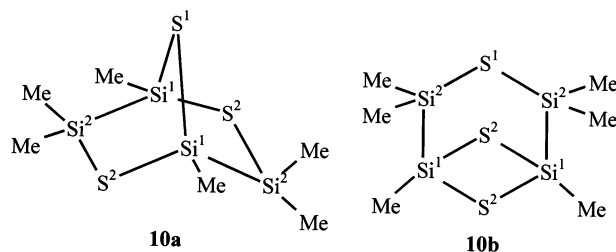
## 2.6. Bicyclo-[3,2,1]-octane and bicyclo-[3,3,1]-nonane

The treatment of a 1:1 mixture of 1,1,2-trichlorotrimethylidisilane and 1,2,3-trichloropentamethyltrisilane with H<sub>2</sub>S and NEt<sub>3</sub> resulted in the formation of 1,2,2,4,4,5,6,6-octamethyl-1,2,4,5,6-pentasila-3,7,8-trithiabicyclo-[3,2,1]-octane (**12a**). The structure is in agreement with the observed mass spectrum and the five <sup>29</sup>Si-NMR signals including two different <sup>1</sup>J<sub>SiSi</sub> coupling constants in the trisilane unit. As expected, eight different signals for the eight methyl groups are found by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. In the alternative structure **12b** (Scheme 9) with a bicyclo-[2,2,2]-octane skeleton the two SiMe<sub>2</sub> groups of the trisilane unit are equal, what should result in only four Si- and five C- and H-NMR signals.

The formation of **12a** containing a five-membered ring shows again that isomers with this ring size are preferred.

The calculated energies of the two isomers (Table 6) differ by only 2.8 kJ mol<sup>−1</sup>, the experimentally observed isomer **12a** being lower in energy than **12b**.

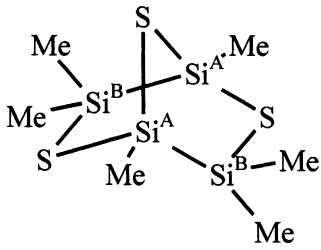
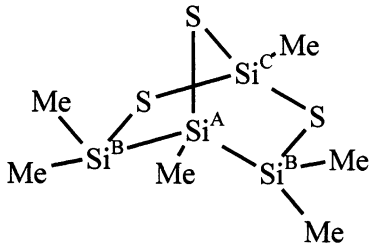
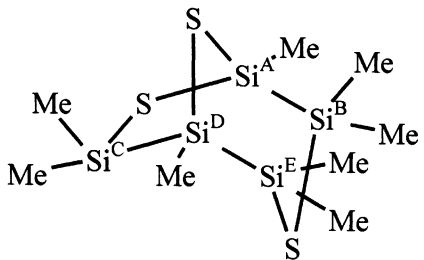
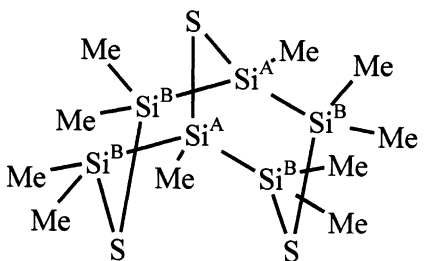
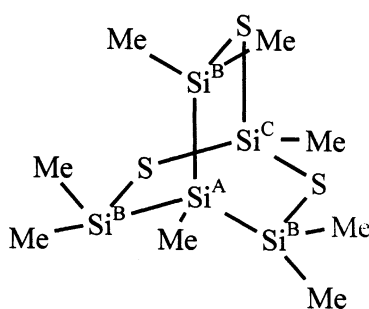
The DFT calculation of **12a** reveal that the six-membered ring adopts a chair conformation, while the five-membered ring has an envelope conformation. Due to the increased ring size of one cyclus, the angles SiSSi are larger than the calculated values for **10a** and **11**. The angle at S(2) is comparable with the angle in **3a**, and the angle at S(3) is similar to the angle in **1**, also containing a Si<sub>4</sub>S<sub>2</sub> six-membered ring. The geometry of



Scheme 8.

Table 10

NMR chemical shifts (ppm) and coupling constants  $^1J_{\text{SiC}}$  and  $^1J_{\text{SiSi}}$  (Hz) of the bicyclic silthianes **10a**, **11**, **12a**, **13a** and **14**

| compound                                                                                       | $\delta_{\text{Si}}$                                 | $^1J_{\text{SiC}}$                                        | $\delta_{\text{C}} (\text{SiMe})$                                                        | $\delta_{\text{H}} (\text{SiMe})$                      |
|------------------------------------------------------------------------------------------------|------------------------------------------------------|-----------------------------------------------------------|------------------------------------------------------------------------------------------|--------------------------------------------------------|
| <b>10a</b>    | A: 21.3<br>B: 10.5                                   | 47.6<br>46.6<br>$^1J_{\text{SiSi}}$ : 100.6               | 2.4<br>0.1 / 0.3                                                                         | 0.91<br>0.40 / 0.58                                    |
| <b>11</b>     | A: -8.9<br>B: 7.7<br>C: 28.1                         | $^1J_{\text{SiSi}}$ : 72.9                                | -7.8<br>1.16 / 1.28<br>7.2                                                               | 0.81<br>0.45 / 0.64<br>1.03                            |
| <b>12a</b>   | A: 22.1<br>B: -2.6<br>C: 12.9<br>D: -12.9<br>E: -2.1 | 44.7<br>$^1J_{\text{SiSi}}$ : 105.9<br>46.8<br>a)<br>46.6 | C: -3.7<br>A, B, D-E: 0.415, 0.465,<br>0.87, 1.74,<br>1.85, 1.92,<br>2.27 (2 C),<br>4.00 | A-E: 0.378,<br>0.527, 0.559,<br>0.609, 0.724,<br>0.740 |
| <b>13a</b>  | A: -27.5<br>B: -3.3                                  |                                                           | -2.1<br>2.35 / 2.82                                                                      | 0.46 / 0.58                                            |
| <b>14</b>   | A: -89.0<br>B: -1.0<br>C: 12.0                       | 36.9<br>$^1J_{\text{SiSi}}$ : 66.6<br>46.2<br>66.0        | -15.6<br>3.4<br>10.7                                                                     | 0.04<br>0.52<br>0.83                                   |

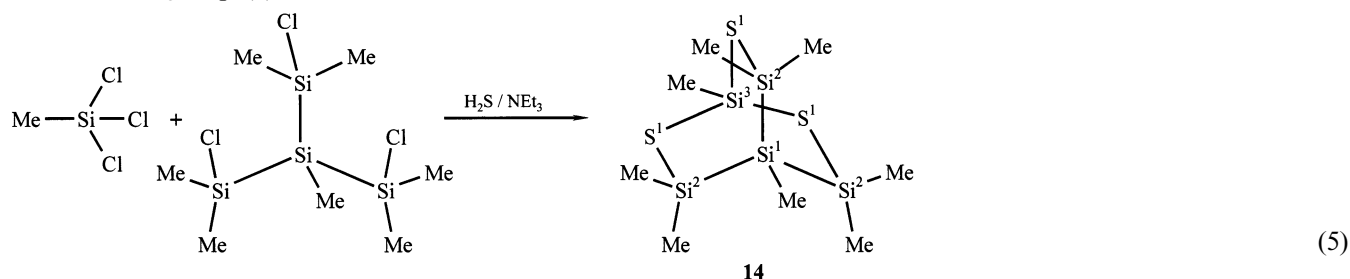
a)  $^1J_{\text{SiC SiD}}$ : 72.4,  $^1J_{\text{SiD SiE}}$ : 79.2

**12b** is very similar to the isomeric compound **14**. The calculated SiSSi angles of 104.8 and 106.3° are almost identical to the value of 105.6° in **14**.

If 1,2,3-trichloropentamethyltrisilane alone is reacted with H<sub>2</sub>S and NEt<sub>3</sub>, 1,2,2,4,4,5,6,6,8,8-decamethyl-1,2,4,5,6,8-hexasila-3,7,9-trithiabicyclo-[3,3,1]-nonane (**13a**) is formed. This bicyclus contains two six-membered rings Si<sub>4</sub>S<sub>2</sub> and can also be regarded as an adamantane structure with one missing corner. The only possible alternative structure **13b** is built up of only one six-membered ring and two seven-membered rings. **13b** should show three different <sup>29</sup>Si-NMR signals, but only two signals with a 2:1 ratio are observed, which is in agreement with structure **13a** (Scheme 10).

#### 2.7. 1,2,2,4,6,6,7,7-Octamethyl-1,2,4,6,7-pentasila-3,5,8-trithiabicyclo-[2,2,2]-octane (**14**)

Compound **14** is formed by the reaction of a 1:1 molar mixture of MeSi(SiMe<sub>2</sub>Cl)<sub>3</sub> and MeSiCl<sub>3</sub> with H<sub>2</sub>S and NEt<sub>3</sub>, Eq. (5):



Since this compound is built of six-membered rings, the <sup>29</sup>Si-NMR signals of all silyl groups are shifted to higher field (<sup>1</sup>SiMe: −9.6 ppm, SiMe<sub>2</sub>: −5.8 ppm, SiMe<sub>3</sub>: −17.5 ppm) compared with the acyclic compounds MeSi(SiMe<sub>2</sub>SBu)<sub>3</sub> and MeSi(SBu)<sub>3</sub> [8].

The DFT calculation of **14** (Table 6, Fig. 5) reveals SiSSi angles of 105.6° which are typical for six-membered rings. A comparison of the total energies (with zero point correction) of **14** with the isomeric com-

pound **12b** indicates a difference of only 2.0 kJ mol<sup>−1</sup>, **14** being the energetically preferred isomer.

### 3. Experimental

#### 3.1. NMR and GC–MS measurements

All NMR spectra were recorded on a Bruker DPX 400 in CDCl<sub>3</sub> solution and TMS as internal standard for <sup>1</sup>H-, <sup>13</sup>C- and <sup>29</sup>Si-NMR. In order to get a sufficient signal/noise ratio of <sup>29</sup>Si-NMR spectra for obtaining <sup>1</sup>J<sub>SiC</sub> or <sup>1</sup>J<sub>SiSi</sub> satellites, <sup>29</sup>Si INEPT spectra were also recorded. The assignment of *ipso* carbon atoms in phenyl substituents was simplified by recording <sup>13</sup>C APT spectra.

Mass spectra were measured on a Hewlett–Packard 5971 (ionization energy: 70 eV, column: 30 m × 0.25 mm × 0.25 μm, phenylmethylpolysiloxane, column temperature: 80°C (3 min)/20 K min<sup>−1</sup>, flow: He 0.5 ml min<sup>−1</sup>).

#### 3.2. Crystal structure analysis

X-ray structure analysis measurements were performed on a Bruker SMART CCD. Crystal data of **4c**, **6** and **9** as well as data collection and refinement details are given in Table 11.

All data were corrected for absorption using SADABS [21]. The structures were solved using direct methods (SHELX-97 [22]), refined using least-squares methods (SHELX-97) and drawn using ZORTEP [23].

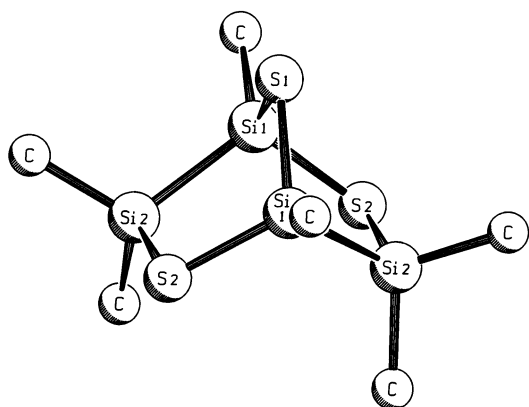
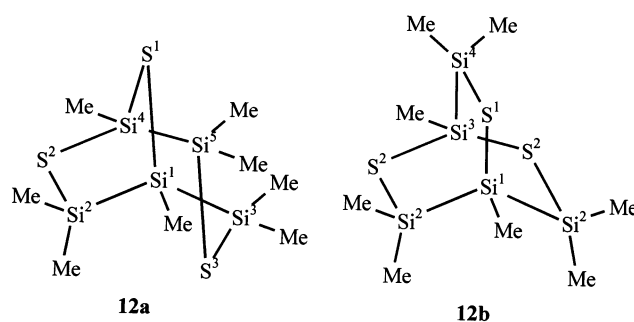
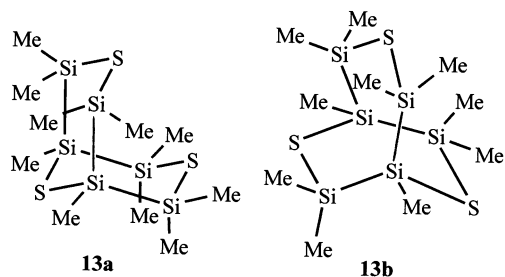


Fig. 4. Schakal plot of the optimized structure of **10a**, hydrogen atoms are omitted.



Scheme 9.



Scheme 10.

### 3.3. Theoretical methods

The *ab initio* molecular orbital calculations were carried out using the Gaussian 98 series of programs [24]. Geometries were fully optimized at the DFT level, using Becke's three-parameter hybrid exchange func-

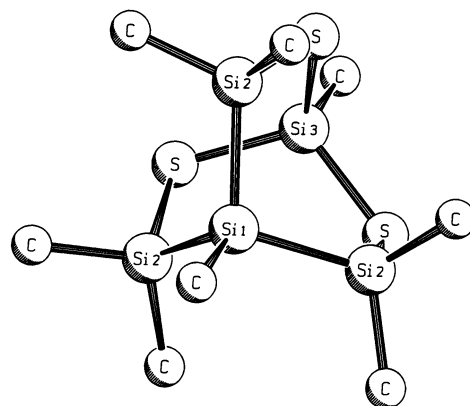


Fig. 5. Schakal plot of the optimized structure of **14**, hydrogen atoms are omitted.

tional and the correlation functional of Lee, Yang and Parr (B3LYP) [25]. Geometry optimizations, harmonic

Table 11

Crystal data of **4c**, **6** and **9** as well as data collection and refinement details

|                                                   | <b>4c</b>                          | <b>6</b>                           | <b>9</b>                           |
|---------------------------------------------------|------------------------------------|------------------------------------|------------------------------------|
| Crystal system                                    | Monoclinic                         | Orthorhombic                       | Monoclinic                         |
| Space group                                       | $P2_1/n$                           | $Pnma$                             | $P2_1/n$                           |
| Unit cell dimensions                              |                                    |                                    |                                    |
| $a$ (Å)                                           | 10.3954(4)                         | 12.1879(4)                         | 9.9221(2)                          |
| $b$ (Å)                                           | 8.1079(3)                          | 10.1585(4)                         | 12.5947(1)                         |
| $c$ (Å)                                           | 24.2696(9)                         | 13.5404(5)                         | 18.0410(3)                         |
| $\alpha$ (°)                                      | 90                                 | 90                                 | 90                                 |
| $\beta$ (°)                                       | 100.973(1)                         | 90                                 | 104.747(1)                         |
| $\gamma$ (°)                                      | 90                                 | 90                                 | 90                                 |
| Volume (Å <sup>3</sup> )                          | 2008.16(13)                        | 1676.45(11)                        | 2180.24(6)                         |
| $Z$                                               | 4                                  | 4                                  | 4                                  |
| $D_{\text{calc}}$ (g cm <sup>-3</sup> )           | 1.492                              | 1.311                              | 1.167                              |
| Linear absorption coefficient (mm <sup>-1</sup> ) | 1.022                              | 0.823                              | 0.561                              |
| Radiation used                                    | Mo-K $\alpha$                      | Mo-K $\alpha$                      | Mo-K $\alpha$                      |
| Temperature (K)                                   | 173(2)                             | 173(2)                             | 173(2)                             |
| Scan method                                       | $\omega$ scans                     | $\omega$ scans                     | $\omega$ scans                     |
| Absorption correction                             | Empirical                          | Empirical                          | Empirical                          |
| Max./min. transmission                            | 0.812213/0.580765                  | 0.867692/0.737513                  | 0.765533/0.376927                  |
| Measured reflections                              | 8945                               | 7891                               | 10 008                             |
| Independent reflections                           | 5386                               | 2369                               | 5408                               |
| Observed reflections                              | 3747                               | 1748                               | 4073                               |
| $R_{\text{int}}$                                  | 0.0336                             | 0.0435                             | 0.0339                             |
| $\theta$ Range for collection (°)                 | 1.71–30.29                         | 2.25–30.43                         | 1.99–30.35                         |
| Completeness to $\theta_{\text{max}}$ (%)         | 89.3                               | 88.6                               | 82.5                               |
| Refinement method                                 | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Final $R$ ( $I > 2\sigma(I)$ )                    | $R_1$ : 0.0392                     | $R_1$ : 0.0347                     | $R_1$ : 0.0393                     |
| $R$ (all data)                                    | $R_1$ : 0.0712                     | $R_1$ : 0.0610                     | $R_1$ : 0.0610                     |
| H-locating and refining                           | difmap/refall                      | difmap/refall                      | difmap/refall                      |
| Goodness-of-fit on $F^2$                          | 0.977                              | 1.025                              | 0.988                              |
| Max./min. e-density (e Å <sup>-3</sup> )          | 0.613/–0.557                       | 0.345/–0.359                       | 0.368/–0.718                       |
| Data collection program                           | SMART                              | SMART                              | SMART                              |
| Cell refinement program                           | SAINT                              | SAINT                              | SAINT                              |
| Data reduction program                            | XPREP                              | XPREP                              | XPREP                              |
| Absorption correction                             | SADABS                             | SADABS                             | SADABS                             |
| Structure solving program                         | SHELXS-97                          | SHELXS-97                          | SHELXS-97                          |
| Structure refining program                        | SHELXL-97                          | SHELXL-97                          | SHELXL-97                          |
| Structure drawing                                 | ZORTEP                             | ZORTEP                             | ZORTEP                             |

frequencies, and zero-point vibrational energies were calculated with the polarized 6-31G\* basis set [26]. All structures were identified as true local minima by their Hessian matrices.

### 3.4. Starting materials

H<sub>2</sub>S (N25, Air Liquide), triethylamine, BuSH, BuLi and all monosilanes Me<sub>x</sub>Ph<sub>y</sub>SiCl<sub>z</sub> are commercially available. The oligosilanes SiClMe<sub>2</sub>–SiClMe<sub>2</sub> [27], SiCl<sub>2</sub>Me–SiClMe<sub>2</sub> [28], SiCl<sub>2</sub>Me–SiCl<sub>2</sub>Me [29], SiClMe<sub>2</sub>–SiClMe–SiClMe<sub>2</sub> [30], SiMe(SiClMe<sub>2</sub>)<sub>3</sub> and [MeSi(SiClMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub> [31] were prepared as described previously.

### 3.5. 1,2,4-Trisila-3,5-dithiacyclopentanes

SiClMe<sub>2</sub>–SiClMe<sub>2</sub> (0.374 g, 2 mmol) and Me<sub>2</sub>SiCl<sub>2</sub> (0.258 g, 2 mmol) were dissolved in 20 ml *n*-hexane. H<sub>2</sub>S was bubbled through the stirred solution and at the same time triethylamine (1.11 ml, 8 mmol) were slowly added by a syringe. After 20 min the reaction mixture was filtered from precipitated triethylammonium chloride and the solvent was removed in vacuo yielding an oily residue which consisted of 55% **3a** as well as **1** and **2a** (determined by NMR).

**1**, GC–MS: *m/e* [relative intensity]: 296 [M<sup>+</sup>, 23], 281 [M – Me, 13], 237 [M – SiMe<sub>2</sub>H, 11], 116 [Si<sub>2</sub>Me<sub>4</sub>, 100], 73 [SiMe<sub>3</sub>, 92].

**2a**, GC–MS: 270 [M<sup>+</sup>, 21], 255 [M – Me, 100], 165 [Si<sub>2</sub>S<sub>2</sub>Me<sub>3</sub>, 73], 73 [SiMe<sub>3</sub>, 35].

**3a**, GC–MS: 238 [M<sup>+</sup>, 50], 223 [M – Me, 65], 165 [Si<sub>2</sub>S<sub>2</sub>Me<sub>3</sub>, 34], 163 [Si<sub>2</sub>Me<sub>3</sub>S, 30], 73 [SiMe<sub>3</sub>, 100].

The same reaction was repeated with PhMeSiCl<sub>2</sub> (0.382 g, 2 mmol) instead of Me<sub>2</sub>SiCl<sub>2</sub> and yielded a solid mixture of 55% **3b** as well as **1** and the two isomers of (PhMeSiS)<sub>3</sub>.

**3b**, GC–MS: 300 [M<sup>+</sup>, 36], 285 [M – Me, 22], 227 [Si<sub>2</sub>S<sub>2</sub>Me<sub>2</sub>Ph, 9], 209 (9), 195 [Si<sub>2</sub>SMe<sub>2</sub>Ph, 5], 165 [Si<sub>2</sub>S<sub>2</sub>Me<sub>3</sub>, 12], 135 [SiMe<sub>2</sub>Ph, 100], 105 [SiPh, 6], 73 [SiMe<sub>3</sub>, 20].

(PhMeSiS)<sub>3</sub>: <sup>29</sup>Si-NMR,  $\delta$ /ppm: 13.1 (2 Si), 12.95 (1 Si) [*cis,cis,trans*-isomer [12] (85%)] and 12.8 [all-*trans*-isomer (15%)].

Repetition of the same reaction with Ph<sub>2</sub>SiCl<sub>2</sub> (0.506 g, 2 mmol) instead of Me<sub>2</sub>SiCl<sub>2</sub> yielded a mixture of 55% **3c** as well as **1** and (Ph<sub>2</sub>SiS)<sub>3</sub> as solid residue.

**3c**, GC–MS: 362 [M<sup>+</sup>, 53], 347 [M – Me, 9], 289 [Si<sub>2</sub>S<sub>2</sub>MePh<sub>2</sub>, 5], 284 (15), 271 (12), 269 (7), 227 [Si<sub>2</sub>S<sub>2</sub>Me<sub>2</sub>Ph, 73], 209 (7), 197 [Si<sub>2</sub>S<sub>2</sub>Ph, 38], 135 [SiMe<sub>2</sub>Ph, 100], 105 [SiPh, 13], 77 [Ph, 8], 73 [SiMe<sub>3</sub>, 14].

### 3.6. Synthesis of 1,3,5,7,9,11-hexamethyl-1,3,5,7,9,11-hexasila-2,4,6,8,10,12-hexathiatetra-cyclo-[5,5,0,0<sup>3,11</sup>,0<sup>5,9</sup>]-dodecane (**4c**)

SiCl<sub>2</sub>Me–SiCl<sub>2</sub>Me (0.684 g, 3 mmol) was dissolved in 40 ml toluene and a stream of H<sub>2</sub>S was passed through the solution while NEt<sub>3</sub> (1.77 ml, 12.8 mmol) was added by syringe. The product was filtered from precipitated triethylammonium chloride and concentrated to a volume of 1 ml. Colorless crystals of **4c** (0.23 g, 51%, *F* > 190°C) crystallized from the solution. Since **4c** is almost insoluble in CDCl<sub>3</sub>, NMR spectra were taken in C<sub>6</sub>D<sub>6</sub>. Single crystals of **4c** suitable for X-ray analysis were obtained by slow cooling of a hot saturated solution in C<sub>6</sub>D<sub>6</sub>.

### 3.7. Synthesis of bis-(1,3,3,4,4-pentamethyl-1,3,4-trisila-2,5-dithiacyclopent-1-yl) (**5a**)

SiCl<sub>2</sub>Me–SiCl<sub>2</sub>Me (0.228 g, 1 mmol) and SiClMe<sub>2</sub>–SiClMe<sub>2</sub> (0.374 g, 2 mmol) were dissolved in 40 ml hexane 1.15 ml (8 mmol) NEt<sub>3</sub> were slowly added while H<sub>2</sub>S was bubbled through the solution. After filtration from the precipitated ammonium salt and removal of the solvent in vacuo a solid mixture of **5a** (60%) and **1** (40%) remained. Also formed **4c** is insoluble in hexane and was therefore removed by filtration.

### 3.8. Synthesis of 1,3,5,7-tetrasila-2,4,6,8-tetrathiabi-cyclo-[3,3,0]-octanes (**6**, **7a–c**, **8**)

SiCl<sub>2</sub>Me–SiCl<sub>2</sub>Me (0.342 g, 1.5 mmol) and Me<sub>2</sub>SiCl<sub>2</sub> (0.387 g, 3 mmol) were dissolved in 40 ml *n*-hexane. H<sub>2</sub>S was bubbled through the stirred solution while 1.66 ml (12 mmol) triethylamine were slowly added by a syringe. After 40 min the reaction mixture was filtered from precipitated triethylammonium chloride and the solvent was removed in vacuo yielding an oily residue which consisted of 78% **6** and 22% **2a** (determined by NMR). In order to get **6** free from **2a**, the molar ratio SiCl<sub>2</sub>Me–SiCl<sub>2</sub>Me:Me<sub>2</sub>SiCl<sub>2</sub> was changed from 1:2 to 1:1. The reaction was repeated with SiCl<sub>2</sub>Me–SiCl<sub>2</sub>Me (1.14 g, 5 mmol) and Me<sub>2</sub>SiCl<sub>2</sub> (0.65 g, 5 mmol) dissolved in 100 ml hexane and NEt<sub>3</sub> (4.15 ml, 30 mmol) was added while H<sub>2</sub>S passed through the solution. After filtration the solution was concentrated to 2 ml when colorless needles of **6** crystallized from the solution, *F* 75–77°C.

**6**, GC–MS: 330 [M<sup>+</sup>, 36], 315 [M – Me, 26], 165 [Si<sub>2</sub>S<sub>2</sub>Me<sub>3</sub>, 100], 73 [SiMe<sub>3</sub>, 20].

Analog reaction of a mixture of SiCl<sub>2</sub>Me–SiCl<sub>2</sub>Me (0.456 g, 2 mmol) and PhMeSiCl<sub>2</sub> (0.764 g, 4 mmol) dissolved in 50 ml hexane with H<sub>2</sub>S and NEt<sub>3</sub> (2.3 ml, 16 mmol) yielded, after work-up, a semicrystalline mixture of the three isomers **7a–c** as well as 15% of

the two isomers of  $(\text{PhMeSiS})_3$  (see Section 3.5). Repetition of this reaction with  $\text{Ph}_2\text{SiCl}_2$  (1.01 g, 4 mmol) instead of  $\text{PhMeSiCl}_2$  yielded a solid product which consisted of 45% **8** as well as 30%  $(\text{Ph}_2\text{SiS})_3$  ( $\delta_{\text{Si}}$ : 4.5 ppm, [9]) and 25%  $(\text{Ph}_2\text{SiS})_2$  ( $\delta_{\text{Si}}$ : –3.5 ppm, [9]).

### 3.9. Synthesis of 1,2,2,4,4,5,6,6,8,8-decamethyl-1,2,4,5,6,8-hexasila-3,7-dithiabicyclo-[3,3,0]-octane (**9**)

Through a solution of  $[\text{SiMe}(\text{SiClMe}_2)_2]_2$  (0.35 g, 0.76 mmol) in 25 ml hexane was bubbled  $\text{H}_2\text{S}$  while  $\text{NEt}_3$  (0.43 ml, 3.1 mmol) was added. After filtration and evaporation of the solvent, a viscous oil remained. Sublimation at 120°C/0.03 Torr yielded 0.2 g (69%) pure **9** as a crystalline product, F 75°C.

**9**, GC–MS: 382 [ $\text{M}^+$ , 73], 367 [ $\text{M} - \text{Me}$ , 38], 323 [ $\text{M} - \text{SiMe}_2\text{H}$ , 32], 309 [ $\text{M} - \text{SiMe}_3$ , 61], 277 [ $\text{Si}_5\text{SMe}_7$ , 13], 249 [ $\text{Si}_4\text{SMe}_7$ , 19], 131 [ $\text{Si}_2\text{Me}_5$ , 16], 73 [ $\text{SiMe}_3$ , 100], 59 [ $\text{SiMe}_2\text{H}$ , 15].

### 3.10. Synthesis of 1,1,2,2-tetrakis-(butylthiodimethylsilyl)-1,2-dimethyldisilane

$[\text{SiMe}(\text{SiClMe}_2)_2]_2$  (0.23 g, 0.5 mmol) was added to a BuSLi solution made from BuSH (0.18 g, 2 mmol) and BuLi (1.25 ml, 1.6 M, 2 mmol) in 10 ml dry THF. After stirring for 2 h and filtration from precipitated LiCl the solvent was removed in vacuo yielding  $[\text{SiMe}(\text{SiMe}_2\text{SBu})_2]_2$  (0.25 g, 0.37 mmol) as a colorless oily residue. NMR,  $\delta$ /ppm:  $^{29}\text{Si}$ : 5.7 ( $\text{SiMe}_2$ ,  $^1J_{\text{SiC}}$ : 44.7,  $^1J_{\text{SiSi}}$ : 64.6 Hz), –74.7 ( $\text{SiMe}$ );  $^{13}\text{C}$ : 2.21 ( $\text{SiMe}_2$ ), –8.5 ( $\text{SiMe}$ ), 26.85 ( $\text{SCH}_2$ ), 35.2 ( $\text{SCH}_2\text{CH}_2$ ), 22.0 ( $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 13.7 ( $\text{S} \sim \text{CH}_3$ );  $^1\text{H}$ : 0.545 ( $\text{SiMe}_2$ ), 0.400 ( $\text{SiMe}$ ), 2.53 ( $\text{SCH}_2$ ), 1.59 ( $\text{SCH}_2\text{CH}_2$ ), 1.42 ( $\text{SCH}_2\text{CH}_2\text{CH}_2$ ), 0.91 ( $\text{S} \sim \text{CH}_3$ ).

### 3.11. Synthesis of tetrasilatrithianorbornanes (**10a**, **11**)

1,2,2,4,5,5-Hexamethyl-1,2,4,5-tetrasil-3,6,7-trithianorbornane (**10a**) resulted from the reaction of a solution of  $\text{SiCl}_2\text{Me}-\text{SiClMe}_2$  (0.52 g, 2.5 mmol) in 20 ml hexane with  $\text{H}_2\text{S}$  and 1.04 ml (7.5 ml)  $\text{NEt}_3$  after filtration from the precipitated ammonium salt and evaporation of the solvent in vacuo as viscous oil, Kp 80°C/0.03 Torr.

**10a**, GC–MS: 298 [ $\text{M}^+$ , 47], 283 [ $\text{M} - \text{Me}$ , 40], 239 [ $\text{M} - \text{SiMe}_2\text{H}$ , 24], 223 [ $\text{Si}_3\text{S}_2\text{Me}_5$ , 22], 165 [ $\text{Si}_2\text{S}_2\text{Me}_3$ , 27], 73 [ $\text{SiMe}_3$ , 100].

The treatment of a mixture of 0.266 g (1 mmol)  $\text{SiClMe}(\text{SiClMe}_2)_2$  and 0.150 g (1 mmol)  $\text{MeSiCl}_3$  dissolved in 20 ml hexane with  $\text{H}_2\text{S}$  and 0.83 ml (6 mmol)  $\text{NEt}_3$  resulted after filtration and evaporation of the solvent in 0.25 g of an oily residue of 1,2,2,4,6,6-hexamethyl-1,2,4,6-tetrasil-3,5,7-trithianorbornane (**11**, 82%) besides 10%  $(\text{MeSiS}_{3/2})_4$  ( $\delta_{\text{Si}}$ : 17.2%, [9]) and 8% **13a**.

**11**, GC–MS: 298 [ $\text{M}^+$ , 38], 283 [ $\text{M} - \text{Me}$ , 34], 239 [ $\text{M} - \text{SiMe}_2\text{H}$ , 21], 223 [ $\text{Si}_3\text{S}_2\text{Me}_5$ , 19], 165 [ $\text{Si}_2\text{S}_2\text{Me}_3$ , 21], 73 [ $\text{SiMe}_3$ , 100].

### 3.12. Synthesis of 1,2,2,4,4,5,6,6-octamethyl-1,2,4,5,6-pentasil-3,7,8-trithiabicyclo-[3,2,1]-octane (**12a**)

$\text{SiClMe}(\text{SiClMe}_2)_2$  (0.266 g, 1 mmol) and  $\text{SiCl}_2\text{Me}-\text{SiClMe}_2$  (0.208 g, 1 mmol) were dissolved in 25 ml hexane and 0.83 ml (6 mmol)  $\text{NEt}_3$  were slowly added while  $\text{H}_2\text{S}$  was bubbled through the solution. After filtration from the ammonium salt and evaporation of the solvent 0.28 g of an oily residue remained which consisted of 65% **12a** besides 25% **10a** and 10% **13a**.

**12a**, GC–MS: 356 [ $\text{M}^+$ , 26], 341 [ $\text{M} - \text{Me}$ , 21], 297 [ $\text{M} - \text{SiMe}_2\text{H}$ , 13], 283 [ $\text{M} - \text{SiMe}_3$ , 13], 191 [ $\text{Si}_3\text{SMe}_5$ , 18], 176 [ $\text{Si}_3\text{SMe}_4$ , 18], 116 [ $\text{Si}_2\text{Me}_4$ , 21], 73 [ $\text{SiMe}_3$ , 100], 59 [ $\text{SiMe}_2\text{H}$ , 11].

### 3.13. Synthesis of 1,2,2,4,4,5,6,6,8-decamethyl-1,2,4,5,6,8-hexasila-3,7,9-trithiabicyclo-[3,3,1]-nonane (**13a**)

$\text{SiClMe}(\text{SiClMe}_2)_2$  (0.398 g, 1.5 mmol) was dissolved in 20 ml hexane and while  $\text{H}_2\text{S}$  passed through the solution  $\text{NEt}_3$  (0.63 ml, 4.5 mmol) was slowly added. After filtration and removal of the solvent an oily residue of **13a** remained. **13a** was also a by-product in the synthesis of **11** and **12a**.

**13a**, GC–MS: 414 [ $\text{M}^+$ , 7], 399 [ $\text{M} - \text{Me}$ , 4], 249 [ $\text{Si}_4\text{SMe}_7$ , 19], 234 [ $\text{Si}_4\text{SMe}_6$ , 27], 191 [ $\text{Si}_3\text{SMe}_5$ , 11], 131 [ $\text{Si}_2\text{Me}_5$ , 21], 116 [ $\text{Si}_2\text{Me}_4$ , 17], 73 [ $\text{SiMe}_3$ , 100], 59 [ $\text{SiMe}_2\text{H}$ , 12].

### 3.14. Synthesis of 1,2,2,4,6,6,7,7-octamethyl-1,2,4,6,7-pentasil-3,5,8-trithiabicyclo-[2,2,2]-octane (**14**)

A solution of  $\text{SiMe}(\text{SiClMe}_2)_3$  (0.34 g, 1.05 mmol) and  $\text{MeSiCl}_3$  (0.157 g, 1.5 mmol) in 25 ml hexane were reacted with  $\text{NEt}_3$  (0.87 ml, 6.3 mmol), while  $\text{H}_2\text{S}$  bubbled through the solution. After filtration and evaporation of the solvent 0.3 g of a semisolid residue of **14** remained.

**14**, GC–MS: 356 [ $\text{M}^+$ , 31], 341 [ $\text{M} - \text{Me}$ , 20], 297 [ $\text{M} - \text{SiMe}_2\text{H}$ , 12], 283 [ $\text{Si}_4\text{S}_3\text{Me}_5$ , 11], 191 [ $\text{Si}_3\text{SMe}_5$ , 14], 176 [ $\text{Si}_3\text{SMe}_4$ , 13], 131 [ $\text{Si}_2\text{Me}_5$ , 17], 116 [ $\text{Si}_2\text{Me}_4$ , 16], 73 [ $\text{SiMe}_3$ , 100], 59 [ $\text{SiMe}_2\text{H}$ , 13].

## 4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. **4c**: CCDC 141105, **6**:

CCDC 141106 and 9: CCDC 141107. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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## References

- [1] S.R. Bahr, P. Boudjouk, *Inorg. Chem.* 31 (1992) 712.
- [2] M. Unno, Y. Kawai, H. Shioyama, H. Matsumoto, *Organometallics* 16 (1997) 4428.
- [3] W. Ando, T. Kadowaki, A. Watanabe, N. Choi, Y. Kabe, T. Erata, M. Ishii, *Nippon Kagaku Kaishi* (1994) 214.
- [4] H. Stüger, M. Eibl, E. Hengge, *J. Organomet. Chem.* 431 (1992) 1.
- [5] U. Wannagat, O. Brandstätter, *Monatsh. Chem.* 94 (1963) 1090.
- [6] H. Nöth, H. Fußstädter, H. Pommerening, T. Taeger, *Chem. Ber.* 113 (1980) 342.
- [7] W. Wojnowski, B. Dreczewski, A. Herman, K. Peters, E.-A. Peters, H.G. v. Schnering, *Angew. Chem.* 97 (1985) 978.
- [8] U. Herzog, G. Roewer, *Main Group Met. Chem.* 22 (1999) 579.
- [9] H.-G. Horn, M. Hemeke, *Chem. Ztg.* 109 (1982) 263.
- [10] H.-G. Horn, *J. Prakt. Chem.* 334 (1992) 201.
- [11] E. Lukevics, O. Pudova, *Main Group Met. Chem.* 21 (1998) 123.
- [12] L. Pazdernik, F. Brisse, R. Rivest, *Acta Crystallogr. Sect. B* 33 (1977) 1780.
- [13] J.C.J. Bart, J.J. Daly, *J. Chem. Soc. Dalton Trans.* (1975) 2063.
- [14] U. Sternberg, *Mol. Phys.* 63 (1988) 249.
- [15] R.F. Pettifer, R. Dupree, I. Farnan, U. Sternberg, *J. Non-Cryst. Solids* 106 (1988) 408.
- [16] J.V. Smith, C.S. Blackwell, *Nature* 303 (1983) 223.
- [17] Y. LePage, G. Donnay, *Acta Crystallogr. Sect. B* 32 (1977) 2615.
- [18] M. Mägi, E. Lippmaa, A. Samoson, G. Engelhardt, A.-R. Grimmer, *J. Phys. Chem.* 88 (1984) 1518.
- [19] W.B. Kamb, *Acta Crystallogr.* 13 (1960) 15.
- [20] U. Sternberg, W. Priess, *J. Magn. Reson.* A102 (1993) 160.
- [21] SADABS: Area-Detector Absorption Correction, Siemens Industrial Auto-mation, Madison, WI, 1996.
- [22] SHELX-97 [includes SHELXS-97, SHELXL-97, CIFTAB], G.M. Sheldrick. SHELX-97. Programs for Crystal Structure Analysis (Release 97-2). University of Göttingen, Germany, 1997.
- [23] ZORTEP, L. Zsolnai, G. Huttner, University of Heidelberg, Germany, 1994.
- [24] Gaussian 98, Revision A.6, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, and J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.
- [25] (a) A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648. (b) P.J. Stevens, F.J. Devlin, C.F. Chabrowski, M.J. Frisch, *J. Phys. Chem.* 98 (1994) 11623.
- [26] (a) P.C. Hariharan, J.A. Pople, *Theor. Chim. Acta* 28 (1973) 213. (b) M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, *J. Chem. Phys.* 77 (1982) 3654.
- [27] H. Sakurai, K. Tominaga, T. Watanabe, M. Kumada, *Tetrahedron* 45 (1966) 5493.
- [28] H. Sakurai, T. Watanabe, M. Kumada, *J. Organomet. Chem.* 7 (1967) P15.
- [29] R. Lehnert, M. Höppner, H. Kelling, *Z. Anorg. Allg. Chem.* 591 (1990) 209.
- [30] U. Herzog, E. Brendler, G. Roewer, *J. Organomet. Chem.* 511 (1996) 85.
- [31] U. Herzog, Dissertation, TU Bergakademie Freiberg, 1997.