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Synthesis and characterization of 2,5,7-trichalcogena-1,3,4,6-tetrasilanorbornanes $(RMeSiSiMe)_2E_3$ ($R = Me, Ph/E = S, Se, Te$)

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Abstract

The reactions of the trichlorodisilanes $ClRMeSi-SiMeCl_2$ ($R = Me, Ph$) with either H_2S/NEt_3 or Li_2E ($E = Se, Te$) result in the selective formation of 2,5,7-trichalcogena-1,3,4,6-tetrasilanorbornanes $(RMeSiSiMe)_2E_3$ ($R = Me, Ph/E = S, Se, Te$). In the cases of $R = Ph$, three stereoisomers with different spatial orientations of the phenyl substituents arise. The isomers with both phenyl substituents in equatorial positions are formed preferably. All products have been characterized by multinuclear NMR spectroscopy including $^1J_{SiSe}$ and $^1J_{SiTe}$ coupling constants. A crystal structure analysis of the isomer of $(PhMeSiSiMe)_2S_3$ with both phenyl substituents in equatorial positions reveals a very small bond angle at the bridging sulfur atom of 88.5° which is even 4.6° smaller than in the parent norbornane C_7H_{12}. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Norbornane; Silane; Silthiane; Selenium; Tellurium

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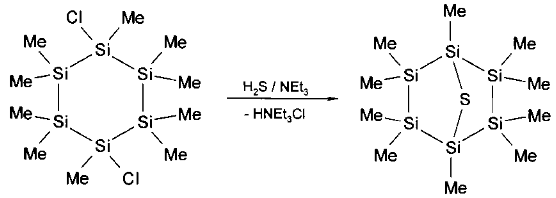
1. Introduction

Cyclic and polycyclic silthianes and related selenium and tellurium derivatives have been investigated for some time but only a small number of reports deals with structures containing Si–Si bonds [1–5]. In previous papers we could show that numerous new cyclic and polycyclic systems can be built starting from suitably substituted oligosilanes [6–9].

All these investigations also reveal that in these systems five membered rings Si_3E_2 ($E = S, Se, Te$) are the most favoured ring type.

One silthiane having a norbornane skeleton has already been published by Wojnowski et al. [10]. It is formed in a surprisingly clean reaction starting from 1,4-dichlorodecamethylcyclohexasilane:

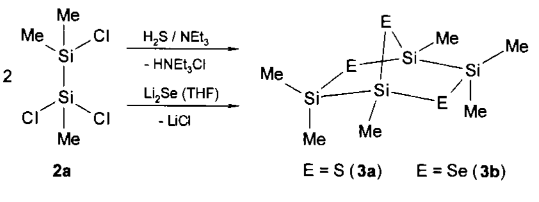


1

Remarkable is the relatively small angle at the sulfur atom in **1** of 94.9° while the bond lengths SiS (2.17 Å) and SiSi (2.34 Å) are in the usual range.

2. Results and discussion

The reactions of 1,1,2-trichlorotrimethyldisilane (**2a**) with either H_2S/NEt_3 or Li_2Se yield in clean reactions the norbornanes $(Si_2Me_3)_2E_3$, $E = S$ (**3a**), $E = Se$ (**3b**) while the reaction with Li_2Te failed:



2a

$E = S$ (**3a**) $E = Se$ (**3b**)

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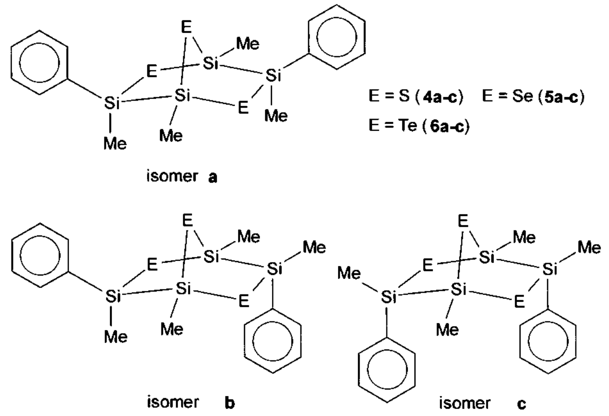
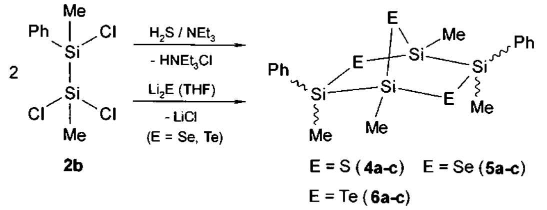


Scheme 1. Stereoisomers of $(Si_2Me_2Ph)_2E_3$, E = S (**4a**–**c**), Se (**5a**–**c**), Te (**6a**–**c**).

Both compounds are colourless liquids which could be identified by NMR spectroscopy and mass spectrometry.

In order to obtain crystalline norbornane derivatives **2a** was exchanged for 1-phenyl-1,2-dimethyltrichlorodisilane (**2b**). The reactions with H_2S/NEt_3 and Li_2E (E = Se, Te), respectively, yielded the expected norbornanes $(Si_2Me_2Ph)_2E_3$, E = S (**4a**–**c**), Se (**5a**–**c**), Te (**6a**–**c**).



Due to the different spatial orientations of the phenyl substituents three isomers are formed in each case, see Scheme 1.

Additionally all norbornanes discussed in this paper are chiral and consist of pairs of enantiomers. The NMR spectra of **4**–**6** show, that all three diastereomers **a**–**c** are formed but in different amounts. Isomer **b** gives raise to four different ^{29}Si-NMR chemical shifts and can therefore be identified unambiguously. The isomer, which is formed in relatively small amounts (8% for E = S, 10% for E = Se, 11.5% for E = Te) is likely to be the isomer **c** were both phenyl substituents are in axial positions, which is less favoured due to steric interactions. The longer Si–Se and Si–Te bonds in respect to Si–S bonds in **4a**–**c** increase the distance between the phenyl rings in the isomers **c** and hence, the content of this isomer raises from E = S to E = Te. Density functional theory (DFT) calculations of **3a** as well as the three isomers **4a–c** were carried out, see Table 1. Scheme 2 represents the calculated relative energies of **4a**–**c** confirming that **4a** is the most stable isomer.

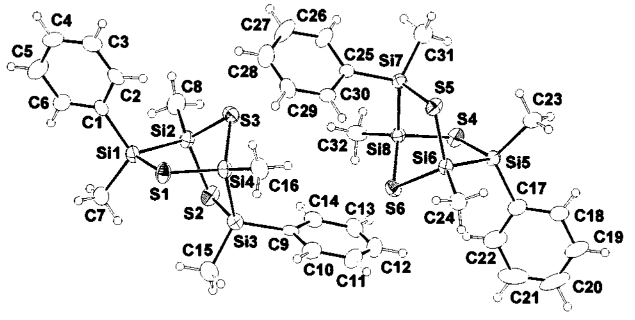
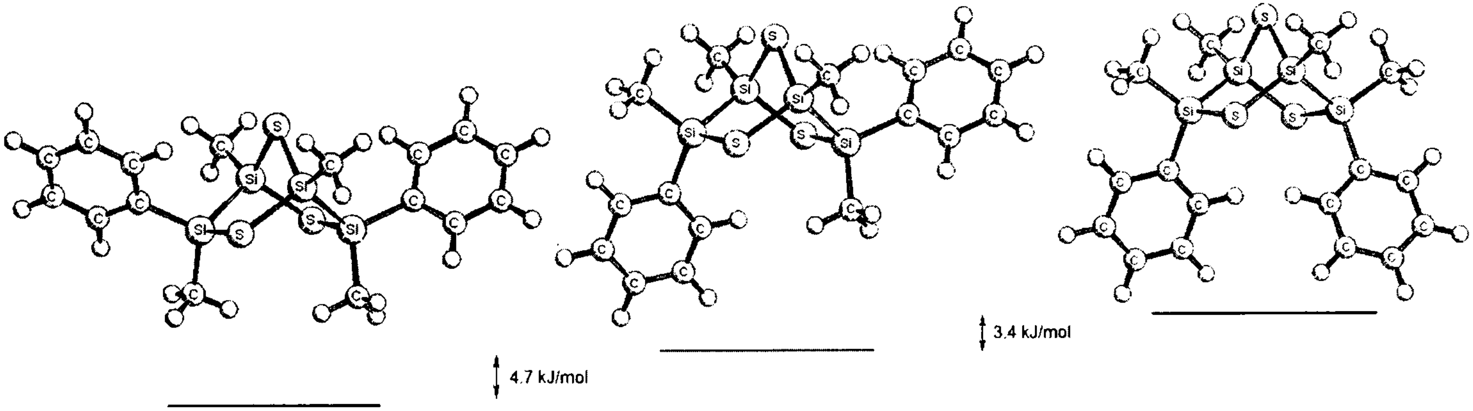


Fig. 1. ZORTEP plot of the two crystallographically independent molecules (A left, B right) in the crystal structure of racemic **4a**.

Fractional crystallization of **4a**–**c** from a $CDCl_3$–hexane solution yielded single crystals of **4a**, the isomer, which is formed in 53% amount. Fig. 1 shows the result of a crystal structure analysis. Both enantiomers of **4a** are present in the asymmetric unit because of crystallographic symmetry. The asymmetric unit contains two crystallographic independent molecules with almost identical bond lengths and angles. The largest differ-

Table 1
Calculated total energies and geometry parameters (B3LYP/6-31 G*) of the norbornanes **3a** and **4a–c** (numbering of Si1–Si4 and S1–S3 are in analogy to molecule A in Fig. 1)

	3a	4a	4b	4c
Total energy (H)	−2592.30580	−2975.77342	−2975.77183	−2975.77070
Total energy with zero point correction (H)	−2592.07037	−2975.42954	−2975.42776	−2975.42647
d(Si1–Si2) (Å)	2.370	2.372	2.368/2.370	2.368
d(Si1–S1) (Å)	2.187	2.196	2.199/2.201	2.204
d(Si4–S1) (Å)	2.182	2.186	2.184/2.185	2.184
d(Si2–S3) (Å)	2.183	2.182	2.183/2.184	2.186
∠(Si2–S3–Si4) (°)	89.1	88.9	89.1	89.3
∠(Si1–S1–Si4) (°)	99.5	99.5	99.7/100.2	100.2
∠(Si2–Si1–S1) (°)	102.1	102.1	101.5	101.1
∠(Si1–Si2–S2) (°)	108.9	108.9/109.3	107.8/111.8	110.8
∠(Si1–Si2–S3) (°)	101.2	101.7/101.9	99.6/101.6	99.2
∠(S2–Si2–S3) (°)	109.2	108.5	108.5/109.3	109.2



Scheme 2. Calculated (B3LYP/6-31G*) geometries and relative energies of the stereoisomers **4a**–**c**.

ences occur in the orientations of the phenyl rings, what can be described by the dihedral angles C–C–Si–Si. While the dihedral angles C(22)–C(17)–Si(5)–Si(6) and C(30)–C(25)–Si(7)–Si(8) of molecule B are relatively similar (+ 63.42 and + 76.74°, respectively) the angles C(2)–C(1)–Si(1)–Si(2) and C(10)–C(9)–Si(3)–Si(4) in molecule A are quite different (− 71.07 and + 73.39°, respectively). Some important bond lengths and angles are summarized in Table 2. The most interesting feature of the structure are the angles at the sulfur bridges S3 and S6 which are with 88.5° by 6.4° smaller than in **1** and also 4.6° smaller than the angle of 93.1° at the bridging methylene unit in the parent hydrocarbon norbornane C_7H_{12} [11]. A result of these small angles at S3 and S6 are also small Si–Si distances (Si2–Si4 and Si6–Si8), which are with 3.01 Å only 28% larger than a normal Si–Si single bond [12]. Nevertheless there is no indication of a Si–Si bond by means of NMR spectroscopy.

On the other hand the angles at the other sulfur atoms (S1, S2, S4 and S5) are with 98–99° in the usual range for five-membered rings Si_3S_2 in polycyclic silthianes.

Table 2
Selected bond lengths (Å) and angles (°) of (a) molecule A and (b) molecule B in the X-ray structure of **4a**

Atoms	Bond length (Å)	Atoms	Bond angle (°)
(a)			
Si(1)–Si(2)	2.351(3)	Si(1)–S(1)–Si(4)	98.1(1)
Si(3)–Si(4)	2.352(3)	Si(3)–S(2)–Si(2)	98.3(1)
Si(1)–S(1)	2.164(3)	Si(2)–S(3)–Si(4)	88.6(1)
Si(3)–S(2)	2.166(3)	Si(1)–Si(2)–S(2)	109.2(1)
Si(2)–S(2)	2.152(3)	Si(3)–Si(4)–S(1)	108.4(1)
Si(4)–S(1)	2.141(3)	Si(2)–Si(1)–S(1)	103.1(1)
Si(2)–S(3)	2.148(3)	Si(4)–Si(3)–S(2)	102.8(1)
Si(4)–S(3)	2.155(3)	Si(1)–Si(2)–S(3)	101.4(1)
Si(1)–C(1)	1.867(8)	Si(3)–Si(4)–S(3)	102.3(1)
Si(3)–C(9)	1.853(7)	S(1)–Si(4)–S(3)	109.2(1)
Si(1)–C(7)	1.841(7)	S(2)–Si(2)–S(3)	109.0(1)
Si(3)–C(15)	1.872(8)	C(1)–Si(1)–C(7)	111.6(3)
Si(2)–C(8)	1.853(8)	C(9)–Si(3)–C(15)	110.1(3)
Si(4)–C(16)	1.863(6)		
(b)			
Si(5)–Si(6)	2.353(3)	Si(5)–S(4)–Si(8)	99.0(1)
Si(7)–Si(8)	2.337(3)	Si(7)–S(5)–Si(6)	98.7(1)
Si(5)–S(4)	2.164(3)	Si(6)–S(6)–Si(8)	88.5(1)
Si(7)–S(5)	2.162(3)	Si(5)–Si(6)–S(5)	107.1(1)
Si(6)–S(5)	2.148(3)	Si(7)–Si(8)–S(4)	108.7(1)
Si(8)–S(4)	2.147(3)	Si(6)–Si(5)–S(4)	102.4(1)
Si(6)–S(6)	2.155(2)	Si(8)–Si(7)–S(5)	102.9(1)
Si(8)–S(6)	2.163(3)	Si(5)–Si(6)–S(6)	102.0(1)
Si(5)–C(17)	1.861(8)	Si(7)–Si(8)–S(6)	101.8(1)
Si(7)–C(25)	1.868(7)	S(4)–Si(8)–S(6)	109.0(1)
Si(5)–C(23)	1.852(7)	S(5)–Si(6)–S(6)	109.9(1)
Si(7)–C(31)	1.843(8)	C(17)–Si(5)–C(23)	109.8(3)
Si(6)–C(24)	1.870(7)	C(25)–Si(7)–C(31)	111.6(3)
Si(8)–C(32)	1.852(6)		

The calculated geometry of **4a** (see Table 1) is in a good agreement with the result of the X-ray structure analysis, especially in terms of the unusual angle at the bridging sulfur atom. As the calculations show, this angle as well as the whole symmetry within the norbornane skeleton remains almost unchanged in the other isomers **4b**–**c** as well as in the permethylated norbornane **3a**. The values of the calculated dihedral angles C(2)–C(1)–Si(1)–Si(2) and C(10)–C(9)–Si(3)–Si(4) are with + 68.0 and + 74.6° similar to the observed angles in molecule B in the crystal structure, see above. These dihedral angles allow a maximal distance between the phenyl rings and the methyl groups at Si2 and Si4, respectively. Crystal packing forces may be responsible for the different dihedral angles found for molecule A in the crystal structure.

As for other silicon sulfur compounds, calculated previously with the same method [6,9,13], the calculated SiS as well as SiSi bonds are in average 0.02 Å longer than the values found by X-ray analysis.

Tables 3–6 summarize the ^{1}H-, ^{13}C-, ^{29}Si-, ^{77}Se- and ^{125}Te-NMR data of the prepared norbornanes. The assignment of the coupling constants $^{1}J_{SiSe}$ and $^{1}J_{SiTe}$ was possible unambiguously by observing the satellites in the ^{29}Si- as well as in the ^{77}Se- and ^{125}Te-NMR spectra, respectively.

Compared with the ^{29}Si-NMR chemical shifts of the related acyclic chalcogenobutyl substituted disilanes $(BuE)_2Si^AMe–Si^BMe_2(EBu)$, E = S: δ_A: 10.3 ppm, δ_B: − 0.8 ppm [14]; E = Se: δ_A: 0.8 ppm, δ_B: − 6.0 ppm [15] having the same first coordination spheres at silicon, the chemical shifts in the norbornanes **3a** and **3b** are shifted by some 11 ppm (E = S) and 14–20 ppm (E = Se) to lower field. This confirms the general trends of δ_{Si} in five-membered rings Si_3E_2 as discussed in detail in [7]. On the other hand the coupling constants $^{1}J_{SiSi}$ in the norbornanes are close to the values in the acyclic disilanes $(BuE)_2SiMe–SiMe_2(EBu)$ with the same E. A comparison of δ_{Se} and δ_{Te} of analogous E atoms in **5a**–**c** and **6a**–**c** is shown in Fig. 2.

A linear correlation of δ_{Se} and δ_{Te} with a slope of 2.44 are found for the positions of E^B and E^C (assignment see Tables 3 and 4). This is in good agreement with observations in other cyclic and polycyclic silselenides and -tellurides where a slope of 2.49 has been found [7] whereas the slope increases to 3.16 for the bridging E^A atoms in **5a**–**c** and **6a**–**c**.

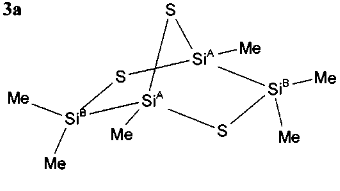
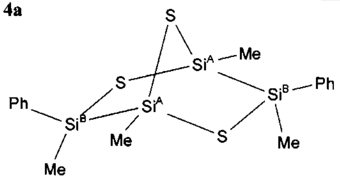
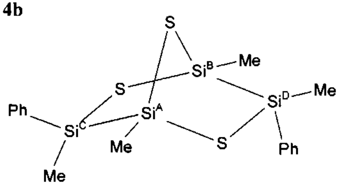
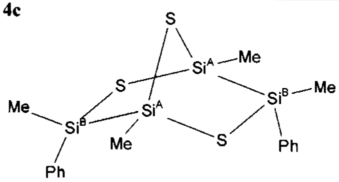
3. Experimental

3.1. NMR and GC–MS measurements

All NMR spectra in solution were recorded on a Bruker DPX 400 in $CDCl_3$ solution and TMS as internal standard for ^{1}H, ^{13}C and ^{29}Si. External Ph_2Se_2 (δ_{Se}:

Table 3

^{29}Si-, ^{13}C- and ^{1}H-NMR data of the norbornanes $(MeSiSiMeR)_2S_3$ (R = Me (**3a**), Ph (**4a–c**))

compound	δ_{Si}	δ_C	δ_H
3a 	A: 21.3 B: 10.5 $^1J_{SiSi}$: 100.6	A Me: 2.4, $^1J_{SiC}$: 48.6 B Me: 0.1 / 0.3	A: 0.91 B: 0.40 / 0.58
4a 	A: 21.64 B: 0.71 $^1J_{SiSi}$: 101.1	A Me: -2.07 B Me: 0.14 i: 135.60, o: 134.10, m: 128.02, p: 129.75	A: 0.92 B: 0.83 Ph: o: 7.35, m: 7.61, p: 7.39
4b 	A: 22.45 B: 19.59 C: 1.16 D: 3.12 $^1J_{SiASiC}$: 102.0 $^1J_{SiBSiD}$: 101.6	A Me: -2.39 B Me: 1.71 C/D Me: 0.40 / 0.46 C i: 134.28, o: 134.06, m: 128.0, p: 129.70 D i: 135.74, o: 134.49 m: 128.0, p: 129.96	A: 0.92 B: 1.01 C: 0.82 D: 0.67
4c 	A: 20.74 B: 3.73	A Me: 1.77 B Me: 0.67 i: 133.81, o: 134.64, m: 128.0, p: 129.83	A: 0.99 B: 0.64

460 ppm) and Ph_2Te_2 (δ_{Te}: 422 ppm) in $CDCl_3$ were used as standards for ^{77}Se and ^{125}Te.

In order to get a sufficient signal/noise ratio of ^{29}Si NMR spectra for obtaining $^1J_{SiC}$, $^1J_{SiSi}$, $^1J_{SiSe}$ or $^{1,2}J_{SiTe}$ satellites ^{29}Si INEPT spectra were also recorded. ^{77}Se and ^{125}Te spectra were recorded using an igated pulse program.

GC–MS spectra were measured on a Hewlett–Packard 5971 (ionization energy: 70 eV, column: 30 m × 0.25 mm × 0.25 μm, phenylmethylpolysiloxane, column temperature: 100°C (3 min)/20 K min^{-1}, flow: He 0.5 ml min^{-1}).

3.2. Crystal structure analysis

X-ray structure analysis measurements were performed on a Bruker smart CCD. Crystal data of **4a** as well as data collection and refinement details are given in Table 7.

The unit cell was determined with the program smart [16]. For data integration and refinement of the unit cell the program SAINT [10] was used. The space group was determined using the program absen [17]. All data were corrected for absorption using sadabs [18]. The structure was solved using direct methods (SIR-97 [19]), refined using least-squares methods (SHELX-97) and drawn using ZORTEP [20].

3.3. Theoretical methods

The ab initio molecular orbital calculations were carried out using the GAUSSIAN-98 series of programs [21]. Geometries were fully optimized at the DFT level, using Becke's three-parameter hybrid exchange functional and the correlation functional of Lee et al. (B3LYP) [22,23]. Geometry optimizations, harmonic frequencies, and zero-point vibrational energies were calculated with the polarized 6-31G* basis set for C, H, S and Si [24,25]. All structures were identified as true local minima by their Hessian matrices.

3.4. Starting materials

H_2S (N25, Air Liquide), Se, Te, triethylamine, 1 M $LiBEt_3H$ in THF (Super Hydride) were commercially available. Complex **2a** was prepared as described previously [26]. THF was distilled from sodium potassium alloy prior to use. The other solvents were dried over

Table 4
^{29}Si- and ^{77}Se-NMR data of the norbornanes $(MeSiSiMeR)_2Se_3$ (R = Me (**3b**), Ph (**5a–c**))

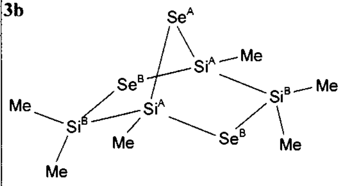
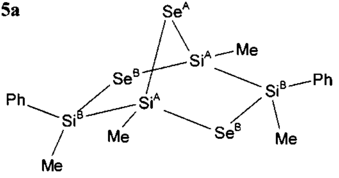
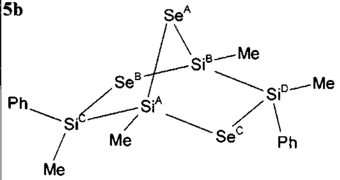
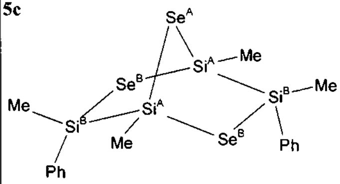
compound	δ_{Se}	δ_{Si}	$^1J_{SiSe}$
3b 	A: -219.5 B: -319.1	A: 15.11 B: 14.33	Si^ASe^A: 125.4 Si^ASe^B: 135.1 Si^BSe^B: 103.0
5a 	A: -185.9 B: -297.1	A: 15.56 B: 3.83 $^1J_{SiSi}$: 91.1	Si^ASe^A: 127.3 Si^ASe^B: 133.6 Si^BSe^B: 108.8
5b 	A: -199.7 B: -303.4 C: -335.2	A: 16.62 B: 12.65 C: 4.49 D: 7.11 $^1J_{SiBSiD}$: 92.3	Si^ASe^A: 127.3 Si^ASe^C: 134.1 Si^BSe^A: 124.4 Si^BSe^B: 138.0 Si^CSe^B: 109.8 Si^DSe^C: 107.9
5c 	A: -207.9 B: -335.8	A: 13.93 B: 7.65	Si^ASe^A: 124.4 Si^ASe^B: 138.0 Si^BSe^B: 107.9

Table 5
^{29}Si- and ^{125}Te-NMR data of the norbornanes $(MeSiSiMePh)_2Te_3$ (**6a–c**)

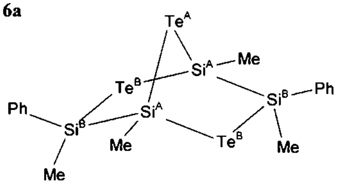
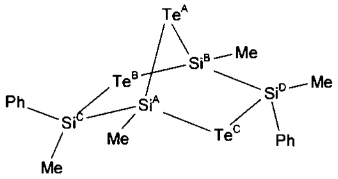
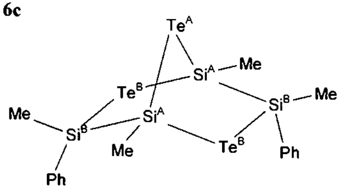
compound	δ_{Te}	δ_{Si}	$^nJ_{SiTe}$
6a 	A: -593 B: -741	A: -22.44 B: 3.55	$^1J_{Si^ATe^A}$: 337.1 $^1J_{Si^ATe^B}$: 331.9 $^2J_{Si^ATe}{}^B$: 31.6 $^1J_{Si^BTe^B}$: 302.7 $^2J_{Si^BTe}$: 20.4
6b 	A: -627 B: -749 C: -807	A: -20.70 B: -26.75 C: 4.48 D: 8.69	$^1J_{Si^ATe^A}$: 335.5 $^1J_{Si^ATe^C}$: 326.3 $^2J_{Si^ATe^B}$: 32.6 $^1J_{Si^BTe^A}$: 326.3 $^1J_{Si^BTe^B}$: 319.4 $^2J_{Si^BTe^C}$: 29.6 $^1J_{Si^CTe^B}$: 299.7 $^2J_{Si^CTe}$: 19.4 $^1J_{Si^DTe^C}$: 295.5 $^2J_{Si^DTe}$: 17.5
6c 	A: -654 B: -809	A: -24.86 B: 9.21	$^1J_{Si^ATe^A}$: 318.8 $^1J_{Si^ATe^B}$: 308.1 $^1J_{Si^BTe^B}$: 295.5

Table 6
^{13}C- and ^{1}H-NMR data of the norbornanes $(MeSiSiMeR)_2E_3$ (R = Me, E = Se (**3b**); R = Ph, E = Se (**5a–c**), E = Te (**6a–c**)) (for assignment of the silyl units A–D see Tables 4 and 5)

Compound	δ_C (SiMe)		δ_C (SiPh)		δ_H	
	E = Se	E = Te	E = Se	E = Te	E = Se	E = Te
3b	A: 1.97 B: −0.04/0.14	– –	–	–	A: 1.11 B: 0.70/0.48	– –
5a/6a	A: −2.18 B: −0.08	A: −2.65 B: −1.22	i: 135.15 o: 134.17 m: 127.92 p: 129.59	i: 134.66 o: 134.54 m: 127.89 p: 129.39	A: 1.03 B: 0.97 Ph: o: 7.30 m: 7.65 p: 7.35	A: 1.09 B: 0.99
5b/6b	A: −2.48 B: 0.67 C/D: 0.09/0.06	A: −2.83 B: −1.73 C/D: −1.31/−1.33	C: i: 135.18 o: 134.2 m: 127.9 p: 129.60 D: i: 133.64 o: 134.68 m: 127.9 p: 129.87	i: o: 134.60 m: 127.9 p: 129.40 i: o: 135.25 m: 127.9 p: 129.80	A: 1.02 B: 1.11 C: 0.97 D: 0.76	A: 1.07 B: 1.11 C: 1.01 D: 0.80
5c/6c	A: 0.75 B: 0.27	A: −1.90 B: −1.26	i: 133.57 o: 135.03 m: 127.9 p: 129.83	i: o: 135.22 m: 127.9 p: 129.79	A: 1.11 B: 0.74	

KOH or sodium wire. All reactions were carried out under argon applying standard Schlenk techniques.

*3.5. Preparation of 1-phenyl-1,2-dimethyltrichlorodisilane (**2b**)*

A solution of 0.1 mol phenylmagnesium bromide in 100 ml of diethyl ether (prepared from 16 g (0.10 mol) PhBr and 2.5 g (0.11 mol) Mg) was slowly added under stirring to a solution of 27.4 g (0.12 mol) of 1,1,2,2-tetrachlorodimethyldisilane in 50 ml of diethyl ether. The solvent was removed in vacuo and replaced by 100 ml of hexane. The mixture was filtered from precipitated magnesium salts and distilled under reduced pressure to give 16.55 g (0.061 mol) **2b**, Kp_1: 110°C.

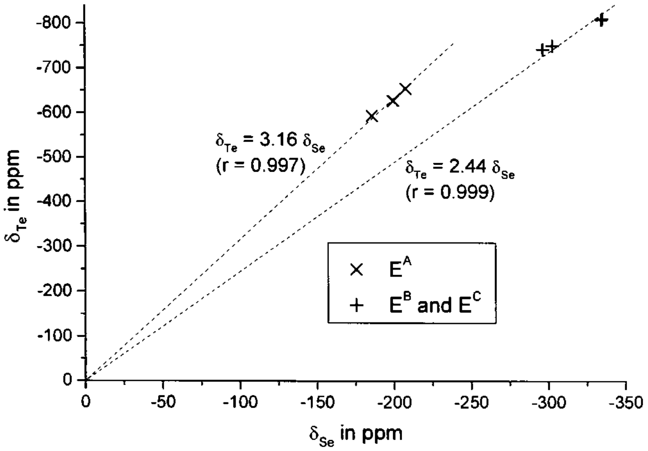


Fig. 2. Comparison of δ_{Se} and δ_{Te} in the norbornanes **5a**–**c** (E = Se) and **6a**–**c** (E = Te) (for assignment of A, B and C see Tables 4 and 5).

Table 7
Crystal data of **4a** as well as data collection and refinement details

	4a
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	16.483(2)
b (Å)	33.464(5)
c (Å)	8.036(1)
β (°)	100.078(3)
Volume (Å^3)	4364.2(11)
Z	8
$D_{calc.}$ (g cm^{-3})	1.287
Linear absorption coefficient (mm^{-1})	0.556
Radiation used	Mo–K$_\alpha$
Temperature (K)	173(2)
Scan method	ω-scans
Absorption correction	Empirical
Max./min. transmission	0.957/0.851
Measured reflections	21 353
Independent reflections	10 306
Observed reflections ($>2\sigma_I$)	3525
R_{int}	0.1608
θ Range for collection (°)	1.25–30.65
Completeness to θ_{max} (%)	76.3
Refinement method	Full-matrix least-squares on F^2
Final R_1 ($I > 2\sigma(I)$)	0.0724
R_1 (all data)	0.2645
H-locating and refining	difmap/refall
Goodness-of-fit on F^2	0.926
Max./min. e-density (e Å^{-3})	0.476/−0.522

*3.5.1. PhMeClSi^A–Si^{B}Cl$_2$Me (**2b**)*

^{29}Si-NMR: δ_A: 3.80 ppm, δ_B: 23.53 ppm, $^1J_{SiSi}$: 127.8 Hz; ^{13}C-NMR: δ_{MeA}: −0.61 ppm ($^1J_{SiC}$: 53.7 Hz), δ_{MeB}: 5.81 ppm ($^1J_{SiC}$: 54.4 Hz), Ph: δ_i: 131.49 ppm, δ_o: 133.68 ppm, δ_m: 128.44 ppm, δ_p: 131.07 ppm; ^{1}H-NMR: δ_{MeA}: 0.86 ppm, δ_{MeB}: 0.89 ppm, Ph: 7.65 ppm (2 H), 7.41 (3 H).

GC–MS: 268/270 (M$^+$, 4), 253 (M–Me, 1), 233 (M–Cl, 1), 175 (PhSiCl$_2$, 1), 155 (MePhSiCl, 100), 135 (Me$_2$PhSi, 2), 120 (PhSi, 3), 105 (PhSi, 5), 77 (Ph, 3).

Due to the use of phenylmagnesium bromide the product contained also small amounts (10% each) of the two 1-phenyl-1,2-dimethylbromodichlorosilanes PhMeBrSi^A–Si^{B}Cl$_2$Me (δ_{SiA}: −1.5 ppm, δ_{SiB}: 22.3 ppm) and PhMeClSi^A–Si^{B}ClBrMe (δ_{SiA}: 3.68/3.64 ppm, δ_{SiB}: 18.25/18.05 ppm, two diastereomers in equal amounts) but this had no consequences for the further reactions of **2b**.

The distillation residue (1.5 g) consisted of PhMeXSi–SiXMePh (X = Cl, Br): PhMeClSi–SiClMePh (40%, δ_{Si}: 6.47/6.25 ppm, two diastereomers in equal amounts), PhMeClSi^A–Si^{B}BrMePh (40%, δ_{SiA}: 5.86/5.59 ppm, δ_{SiB}: 1.48/1.17 ppm, two diastereomers in equal amounts), PhMeBrSi–SiBrMePh (20%, δ_{Si}: 0.83/0.43 ppm, two diastereomers in equal amounts).

PhMeClSi–SiClMePh GC–MS: 310 (M$^+$, 2), 275 (M–Cl, 1), 217 (Ph$_2$SiCl, 1), 197 (MePh$_2$Si, 100), 155 (MePhSiCl, 43), 120 (PhSi, 25), 105 (PhSi, 22) (two GC peaks with identical MS due to the two diastereomers).

*3.6. Preparation of 1,3,3,4,6,6-hexamethyl-2,5,7-trithia-1,3,4,6-tetrasilanorbornane (**3a**)*

A total of 0.52 g (2.5 mmol) of **2a** was diluted with 20 ml of hexane and a stream of dried H$_2$S was bubbled through the stirred solution while 1.04 ml (7.5 mmol) of NEt$_3$ was slowly added. After filtration from the precipitated ammonium salt the solvent was removed in vacuo and the colourless oily residue, already pure **3a**, could be distilled at 80°C/0.03 Torr without decomposition.

3a GC–MS (*m*/*e*, rel. int.): 298 (M$^+$, 47), 283 (M–Me, 40), 239 (M–SiMe$_2$H, 24), 223 (Me$_5$S$_2$Si$_3$, 22), 165 (Me$_3$S$_2$Si$_2$, 27), 73 (Me$_3$Si, 100).

*3.7. Preparation of 1,3,3,4,6,6-hexamethyl-2,5,7-triselena-1,3,4,6-tetrasilanorbornane (**3b**)*

A total of 0.42 g (2 mmol) of **2a** was added at 0°C to a suspension of 3 mmol Li_2Se, prepared from 0.24 g (3 mmol) of selenium powder and 6 ml of a 1 M $LiBEt_3H$ solution in THF. The solvent was removed in vacuo and replaced by 10 ml of hexane. The mixture was filtered from precipitated lithium salts and the solvent removed in vacuo to give pure **3b** as an oily liquid in approximately 60% yield.

3b GC–MS: 440 (M^+, 18), 425 (M–Me, 14), 381 (M–$SiMe_2H$, 4), 365 (M–$SiMe_3$, 1), 319 ($Me_5^{80}Se_2Si_3$, 10), 303 ($Me_3^{80}Se_2Si_3CH_2$, 3), 289 ($Me_3^{80}Se_2Si_3$, 2), 261 ($Me_3^{80}Se_2Si_2$, 9), 231 ($Me^{80}Se_2Si_2$, 2), 211 (Me_5SeSi_2, 8), 195 ($Me_3SeSi_2CH_2$, 9), 281 (Me_3SeSi_2, 8), 123 (MeSeSi, 7), 73 (Me_3Si, 100). The isotopic patterns of all fragments fitted the natural abundance of $^{76}Se:^{77}Se:^{78}Se:^{80}Se:^{82}Se = 9.2:7.6:23.7:49.8:8.8$ [27].

*3.8. Preparation of 3,6-diphenyl-1,3,4,6-hexamethyl-2,5,7-trithia-1,3,4,6-tetrasilanorbornane (**4a**–**c**, mixture of stereoisomers)*

A total of 0.54 g (2 mmol) of **2b** was dissolved in 40 ml of hexane and dried H_2S was bubbled through the stirred reaction mixture while 0.83 ml (6 mmol) of NEt_3 was slowly added by a syringe. The mixture was filtered from precipitated triethylammonium salts (chloride and some bromide due to the content of bromodichlorophenyl-1,2-dimethyldisilanes, see Section 3.5) and the solvent was removed from the filtrate in vacuo to get **4a**–**c** as crystalline product. A ^{29}Si-NMR spectrum of a solution in $CDCl_3$ revealed a composition of 53% **4a**, 39% **4b** and 8% **4c**. No by-products have been detected. Single crystals of **4a** could be obtained by slow concentration of a solution of **4a**–**c** in hexane–$CDCl_3$.

*3.9. Preparation of 3,6-diphenyl-1,3,4,6-hexamethyl-2,5,7-triselena-1,3,4,6-tetrasilanorbornane (**5a**–**c**, mixture of stereoisomers) and 3,6-diphenyl-1,3,4,6-hexamethyl-2,5,7-tritellura-1,3,4,6-tetrasilanorbornane (**6a**–**c**, mixture of stereoisomers)*

A total of 0.54 g (2 mmol) of **2b** was added to a suspension of 3 mmol Li_2E (E = Se or Te) prepared from 0.24 g (3 mmol) of Se or 0.38 g (3 mmol) of Te powder and 6 ml of a 1 M solution of $LiBEt_3H$ in THF. In the case of E = Te the reaction was carried out at −30°C to prevent Si–Si bond cleavage. After 20 min the solvent was replaced by 10 ml of toluene and the product was filtered from precipitated lithium halogenides. Removal of the solvent led to **5a**–**c** and **6a**–**c**, respectively, as microcrystalline residues. ^{29}Si-NMR spectra of the products revealed compositions of 50% **5a**, 40% **5b** and 10% **5c** and 44.5% **6a**, 44% **6b** and 11.5% **6c**, respectively.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 156569. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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