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Dimeric and trimeric diorganosilicon chalcogenides $(PhRSiE)_{2,3}$ (E = S, Se, Te; R = Ph, Me)

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Abstract

Ph_2SiCl_2 and $PhMeSiCl_2$ react with Li_2E (E = S, Se, Te) under formation of trimeric diorganosilicon chalcogenides $(PhRSiE)_3$ (R = Ph: **1a**–**3a**, R = Me: *cis*/*trans*-**4a** (E = S), *cis*/*trans*-**5a** (E = Se)). In case of E = S, Se dimeric four-membered ring compounds $(PhRSiE)_2$ (R = Ph: **1b**–**2b**, R = Me: *cis*/*trans*-**4b** (E = S), *cis*/*trans*-**5b** (E = Se)) have been observed as by-products. **1a**–**5b** have been characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{29}Si, ^{77}Se, ^{125}Te). Four- and six-membered ring compounds differ significantly in ^{29}Si and ^{77}Se chemical shifts as well as in the value of $^1J_{SiSe}$.

The molecular structures of **2a**, **3a** and *trans*-**5a** reported in this paper are the first examples of compounds with unfused six-membered rings Si_3E_3 (E = Se, Te). The Si_3E_3 rings adopt twisted boat conformations. The crystal structure of **3a** reveals an intermolecular Te–Te contact of 3.858 Å which yields a dimerization in the solid state.

Keywords: Hypersilyl; Silicon; Chalcogenides

1. Introduction

In the course of our investigations on cyclic and polycyclic organosilicon chalcogenides (sulfides, selenides and tellurides) we became in interested in the NMR data and molecular structures of cyclic dimeric and trimeric diorganosilicon chalcogenides $(R_2SiE)_2$ and $(R_2SiE)_3$. Despite several early investigations especially on the sulfur compounds [1,2] until now only one crystal structure analysis of a six-membered ring compound $(R_2SiE)_3$ has been reported. The molecular structure of *trans*-$(PhMeSiS)_3$ reveals a central Si_3S_3 six-membered ring in a twisted boat conformation [3].

Recently Kawaguchi and coworkers [4,5] have demonstrated the potential of $(Me_2SiS)_3$ as starting material in the preparation of several types of sulfide clusters of transition metals with S–$SiMe_2$–S and S–$SiMe_2$–S–$SiMe_2$–S ligands.

On heating the trimeric six-membered ring compounds $(R_2SiE)_3$ (E = S, Se) interconvert to the dimeric four-membered rings $(R_2S{:}E)_2$ [2,6–9]. Several studies have shown [10–12] that this conversion proceeds via an elimination of a silathione $R_2Si{=}S$ or silaselenone $R_2Si{=}Se$ which could be trapped by several reagents.

Starting from dichlorosilanes with more bulky substituents reactions with H_2S/amine, $(Me_3Si)_2S$ or M^I_2E (M^I = alkaline) yield the four-membered ring compounds $(R_2SiE)_2$ [13,14]. Several compounds of this type have also been obtained by reactions of silylenes with elemental chalcogens or chalcogen transfer reagents

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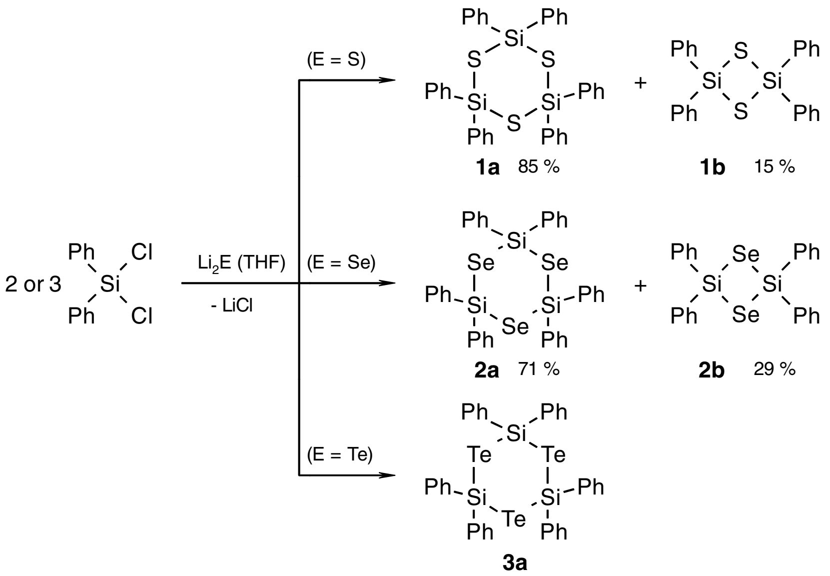


Scheme 1. Reaction of Ph_2SiCl_2 with Li_2E (E = S, Se, Te).

[15–18]. The molecular structures of $(R_2SiE)_2$ always show planar four-membered rings Si_2E_2 with small bond angles (81–85°) at the chalcogen atoms [14–16,19]. In case of E = S this leads to short transannular Si···Si contacts of 2.8–2.9 Å.

2. Results and discussion

2.1. Perphenylated compounds $(Ph_2SiE)_3$ (1a–3a) and $(Ph_2SiE)_2$ (1b–2b) (E = S, Se, Te)

Hexaphenylcyclotrisilthiane (**1a**), hexaphenylcyclotrisilselenane (**2a**) and hexaphenylcyclotrisiltellurane (**3a**) have been obtained by reaction of Ph_2SiCl_2 with Li_2E (E = S, Se, Te) in THF. While in case of the tellurium compound only the trimeric six-membered ring compound **3a** was obtained, in case of E = S and Se the product contained also the dimeric four-membered ring compounds $(Ph_2SiE)_2$ (**1b**, **2b**) Scheme 1.

The NMR data of the perphenylated four- and six-membered ring compounds $(Ph_2SiE)_{2,3}$ (**1a**–**3a**, **1b**–**2b**) are summarized in Table 1.

A comparison of the ^{29}Si NMR chemical shifts of $(Ph_2SiE)_3$ and $(Ph_2SiE)_2$ with those of acyclic chalcogenobutyl-substituted-silanes $Ph_2Si(EBu)_2$ (E = S [20], Se [21], Te [22]) with the same first coordination sphere at the silicon atoms is illustrated in Fig. 1.

Table 1
^1H, ^{13}C, ^{29}Si, ^{77}Se and ^{125}Te NMR data of **1**–**5** $(PhRSiE)_x$ ($x = 2, 3$; E = S, Se, Te; R = Me, Ph) (assignment of Si^A, Si^B and Se^A, Se^B; see Scheme 2)

Compound	δ_E	$^1J_{SiE}$	δ_{Si}	δ_C					δ_H
				Me	*ipso*	*ortho*	*meta*	*para*	*Me*
$(Ph_2SiS)_3$ (**1a**)	–	–	4.48	–	135.02	134.66	127.68	130.11	–
$(Ph_2SiS)_2$ (**1b**)	–	–	–3.55	–					–
$(Ph_2SiSe)_3$ (**2a**)	Se: –294	137.8	3.77	–	135.26	135.03	127.73	130.11	–
$(Ph_2SiSe)_2$ (**2b**)	Se: –211	99.1	–22.30	–					–
$(Ph_2SiTe)_3$ (**3a**)	Te: –673	373.2	–19.56	–	133.33	135.66	127.82	130.18	–
trans-$(PhMeSiS)_3$	–	–	A: 13.05	7.49	136.77	133.73	127.87	130.25	0.879
(*trans*-**4a**)			B: 12.92	6.76	137.13	133.62	127.95	130.33	0.591
cis-$(PhMeSiS)_3$ (*cis*-**4a**)	–	–	12.73	7.80	136.93	133.63	127.84		0.976
$(PhMeSiS)_2$ (**4b**)	–	–	6.13/	7.65					
(*cis*/*trans*-**4b**)			6.11						
trans-$(PhMeSiSe)_3$	Se^A: −262	135.1	A: 9.00	7.93	136.37	133.93	127.85	130.30	
(*trans*-**5a**)	Se^B: −264	134.6	B: 8.80	7.00	136.67	133.81	128.00	130.44	
cis-$(PhMeSiSe)_3$ (*cis*-**5a**)	Se: −266	135.1	8.73	8.60	136.87	133.86	127.85		
$(PhMeSiS)_2$ (**5b**)	Se: −199/	96.2	−15.31/	8.19/		133.23/	127.95/	130.44	
(*cis*/*trans*-**5b**)	Se: −200	96.2	−15.40	8.21		133.27	128.00		

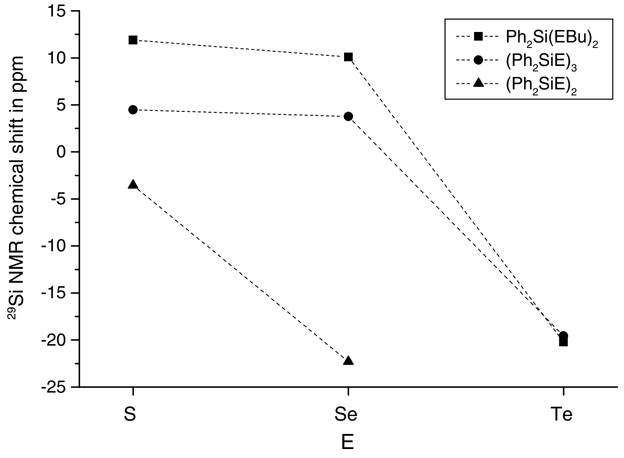


Fig. 1. Comparison of the ^{29}Si NMR chemical shifts of $Ph_2Si(EBu)_2$ with cyclic $(Ph_2SiE)_2$ and $(Ph_2SiE)_3$.

It reveals that for E = S (**1a**) and Se (**2a**) the six-membered ring compounds show additional high field shifts of 7.4 and 6.3 ppm, respectively, while for E = Te (**3a**) the ^{29}Si NMR chemical shifts are almost identical. On the other hand the four-membered ring compounds $(Ph_2SiE)_2$ (**1a**, **2a**) exhibit additional high field shifts of the ^{29}Si NMR signals in comparison with the corresponding six-membered ring compounds which increase from 8.0 ppm (E = S) to 26.1 ppm (E = Se).

Furthermore, the significant difference of the values of the $^1J_{SiSe}$ coupling constants between the four-membered ring **2b** and the six-membered ring compound **2a** is remarkable despite the fact that the first as well as the second coordination spheres at both the silicon and the selenium atom are identical. The value of $^1J_{SiSe}$ in **2b** is in the range of the previously reported values of 106 and 87.5 Hz in the four-membered ring compounds $^tBu_2Si(Se)_2Si^tBu_2$ [18], and $(Me_3Si)_2Si(Se)_2Si(SiMe_3)_2$ [14]. On the other hand the value of $^1J_{SiSe}$ in **2a** fits to the values of 128.3 Hz in $Me_2\mathit{Si}(\mathit{Se})_2Si_2Me_4$ (five-membered ring) [23], 133.6 Hz in $Me_2\mathit{Si}(\mathit{Se})_2Si_3Me_6$, 138.5 Hz in $PhMe\mathit{Si}(\mathit{Se})_2Si_3Me_6$, and 141.5 Hz in $Ph_2\mathit{Si}(\mathit{Se})_2Si_3Me_6$ (six-membered rings) [24].

The smaller value of the coupling constants $^1J_{SiSe}$ in the four-membered rings may be explained by an increased bond length Si–Se to reduce the steric repulsion of the two $SiPh_2$ units or by an increased p-character of the Si–Se bond orbitals as a result of the smaller bond angles Si–Se–Si and Se–Si–Se in the four-membered rings. While several crystal structure analyses of compounds with a Si_2Se_2 four-membered ring have been carried out ($(C_6H_4(NCH_2CMe_3)_2Si(Se)_2Si(NCH_2CMe_3)_2C_6H_4$: Si–Se: 2.255 and 2.294 Å, Se–Si–Se: 96.98°, Si–Se–Si: 83.02° [16]; $^tBu_2Si(Se)_2Si^tBu_2$: Si–Se: 2.304 and 2.305 Å, Se–Si–Se: 96.73°, Si–Se–Si: 83.27° [18], $C_2H_2(N^tBu)_2Si(Se)_2Si(N^tBu)_2C_2H_2$: Si–Se: 2.263 and 2.365 Å, Se–Si–Se: 95.21°, Si–Se–Si: 84.79° [15]) we succeeded in the crystal structure analysis of the first example of a molecule with an unfused six-membered ring Si_3Se_3. The molecular structure of $(Ph_2SiSe)_3$ (**2a**) is shown in Fig. 2.

$(Ph_2SiSe)_3$ is isomorphous with the corresponding tin compounds $(Ph_2SnSe)_3$ [25] and $(Ph_2SnS)_3$ [26,27]. As expected the central six-membered ring Si_3Se_3 adopts a twisted boat conformation. This can also be seen from the sequence of the torsion angles given in Table 3 which follow the order $+\varphi_1$, $+\varphi_2$, $-(\varphi_1 + \varphi_2)$, $+\varphi_1$, $+\varphi_2$, $-(\varphi_1 + \varphi_2)$. Important bond lengths and angles are given in Table 2. The average bond length Si–Se in **2a** is 2.283 Å, that is 0.02 Å shorter than the average bond length Si–Se in the four-membered ring $^tBu_2Si(Se)_2Si^tBu_2$ (with the same first coordination sphere at silicon). The bond angles Si–Se–Si and Se–Si–Se in **2a** are in average 104.15° and 113.28°, respectively. This is close to the corresponding angles Sn–Se–Sn and Se–Sn–Se in the isomorphic tin compound $(Ph_2SnSe)_3$.

The tellurium compound $(Ph_2SiTe)_3$ (**3a**) has also been characterized by a crystal structure analysis. This is the first example of a structurally characterized molecule with a Si_3Te_3 six-membered ring. The molecular structure of **3a** is shown in Fig. 3. Selected bond lengths, bond angles and dihedral angles are summarized in Tables 4 and 5.

The average bond length Si–Te of 2.494 Å is in the range of typical Si–Te single bonds. As for the selenium compound the average bond length Si–Te is 0.04 Å

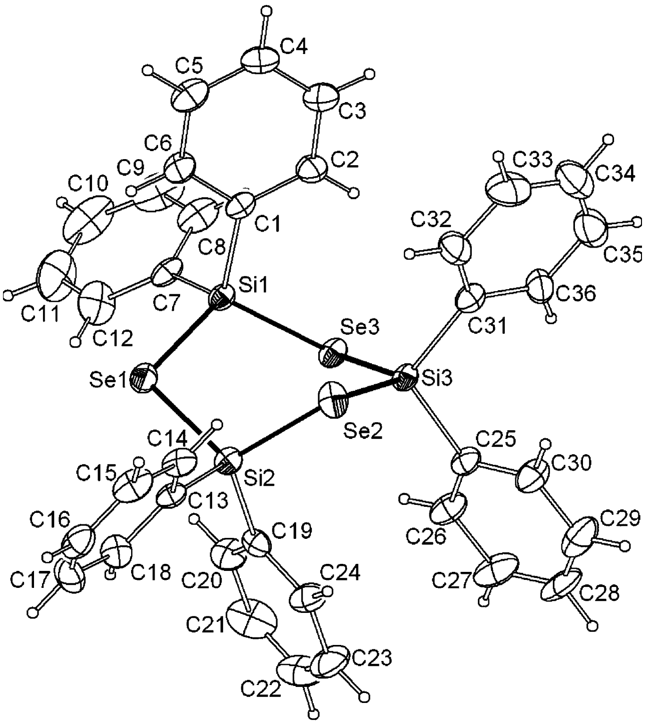


Fig. 2. Molecular structure of $(Ph_2SiSe)_3$ (**2a**).

Table 2
Selected bond length and angles of $(Ph_2SiSe)_3$ (**2a**)

Atoms	Bond length (Å)	Atoms	Bond angles (°)
Si1–Se1	2.283(2)	Si1–Se1–Si2	104.04(8)
Se1–Si2	2.285(2)	Si2–Se2–Si3	102.26(9)
Si2–Se2	2.270(2)	Si1–Se3–Si3	106.16(8)
Se2–Si3	2.281(2)	Se1–Si1–Se3	113.62(9)
Si3–Se3	2.300(3)	Se1–Si2–Se2	112.12(9)
Se3–Si1	2.279(2)	Se2–Si3–Se3	114.11(9)
Si1–C1	1.870(8)	C1–Si1–C7	107.3(3)
Si1–C7	1.867(8)	C13–Si2–C19	111.0(3)
Si2–C13	1.884(8)	C25–Si3–C31	108.6(3)
Si2–C19	1.866(8)		
Si3–C25	1.867(7)		
Si3–C31	1.855(8)		

Table 3
Dihedral angles of $(Ph_2SiSe)_3$ (**2a**)

Atoms	Dihedral angle (°)
Se3–Si1–Se1–Si2	30.18(11)
Si1–Se1–Si2–Se2	42.64(11)
Se1–Si2–Se2–Si3	−77.33(11)
Si2–Se2–Si3–Se3	34.34(11)
Se2–Si3–Se3–Si1	29.34(11)
Si3–Se3–Si1–Se1	−67.69(11)

Table 4
Selected bond length and angles of $(Ph_2SiTe)_3$ (**3a**)

Atoms	Bond length (Å)	Atoms	Bond angles (°)
Si1–Te1	2.481(5)	Si1–Te1–Si2	101.7(2)
Te1–Si2	2.484(5)	Si2–Te2–Si3	102.4(2)
Si2–Te2	2.496(5)	Si1–Te3–Si3	100.6(2)
Te2–Si3	2.506(5)	Te1–Si1–Te3	116.0(2)
Si3–Te3	2.490(5)	Te1–Si2–Te2	112.3(2)
Te3–Si1	2.508(5)	Te2–Si3–Te3	113.3(2)
Si1–C1	1.89(2)	C1–Si1–C7	109.3(7)
Si1–C7	1.90(2)	C13–Si2–C19	109.2(7)
Si2–C13	1.88(2)	C25–Si3–C31	110.0(7)
Si2–C19	1.89(2)		
Si2–C25	1.88(2)		
Si2–C31	1.89(2)		

Table 5
Dihedral angles of $(Ph_2SiTe)_3$ (**3a**)

Atoms	Dihedral angle (°)
Te3–Si1–Te1–Si2	13.1(2)
Si1–Te1–Si2–Te2	−72.3(2)
Te1–Si2–Te2–Si3	53.8(2)
Si2–Te2–Si3–Te3	21.1(2)
Te2–Si3–Te3–Si1	−71.3(2)
Si3–Te3–Si1–Te1	50.4(2)

shorter than in the four-membered ring compound ${}^{t}Bu_2Si(Te)_2Si{}^{t}Bu_2$ (Si–Te: 2.529 and 2.535 Å, Te–Si–Te: 97.55°, Si–Te–Si: 82.45°) [18] with the same first coordination sphere at silicon.

As can be seen from Fig. 3 and from the sequence of the dihedral angles in Table 5 the central six-membered ring Si_3Te_3 adopts an only slightly twisted boat conformation (ideal boat conformation: $+\varphi$, $-\varphi$, 0, $+\varphi$, $-\varphi$, 0). The crystal structure of **3a** is not isomorphous with that of the corresponding tin compound $(Ph_2SnTe)_3$ [25]. This is likely to result of an intermolecular Te···Te contact of 3.858 Å which leads to a dimerization of $(Ph_2SiTe)_3$ in the crystal structure, see Fig. 4. Such intermolecular Te···Te contacts are known from the structure of elemental tellurium (Te···Te: 3.495 Å) or telluroethers like MeTeC≡CC≡CTeMe (Te···Te: 3.74 and 3.82 Å) [28,29] but have not been observed before in structures of organosilicon or organotin tellurides. Calculations have shown that np(E)···σ*(E–C) interactions increase in the series E = S, Se, Te. For E = Te an Te···Te–C(sp^3) interaction decreases the total energy by about 2.8 kJ mol^{-1}, an Te···Te–C(sp) interaction by about 9.2 kJ mol^{-1} [29]. On the other hand our calculations on different conformations of $(Ph_2SnS)_3$ have revealed that a twisted boat conformation of the Sn_3S_3 six-membered ring represents the global minimum, a geometry with an almost ideal boat conformation is approximately 3.4 kJ mol^{-1} higher in energy while a sterically less favored chair conformation is 7.9 kJ mol^{-1} above the global minimum [25]. Hence, it seems possible that the formation of an intermolecular Te···Te contact can compensate the higher energy of a less twisted boat conformation of the Si_3Te_3 ring to allow this interaction.

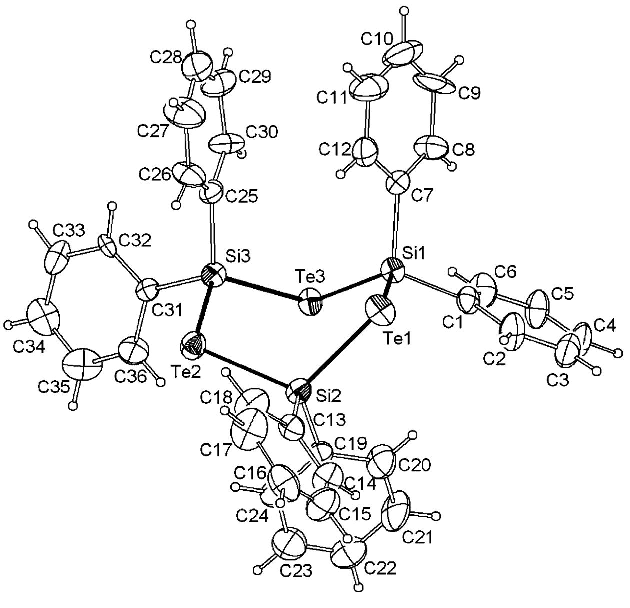


Fig. 3. Molecular structure of $(Ph_2SiTe)_3$ (**3a**).

2.2. *Phenylmethyl substituted compounds $(PhMeSiE)_3$ (**4a**, **5a**) and $(PhMeSiE)_2$ (**4b**, **5b**) (E = S, Se)*

Starting from $PhMeSiCl_2$ reactions with Li_2E (E = S, Se) yield a mixture of cyclic trimers $(PhMeSiE)_3$ (**4a**, **5a**, 92% in case of E = S (**4a**), 83% in case of E = Se(**5a**)) and

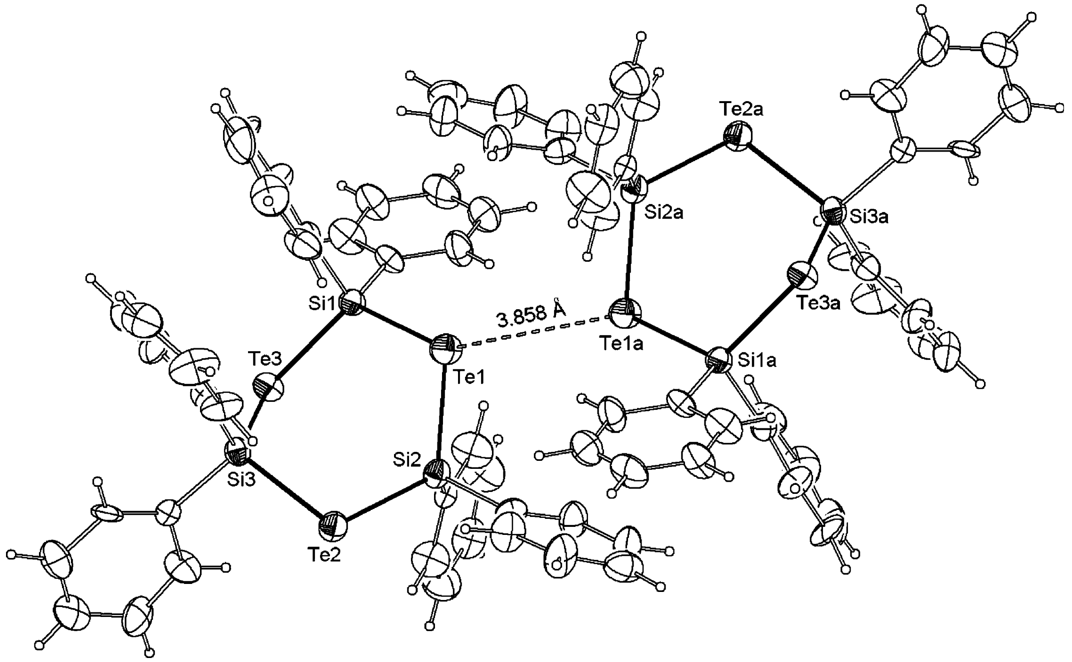
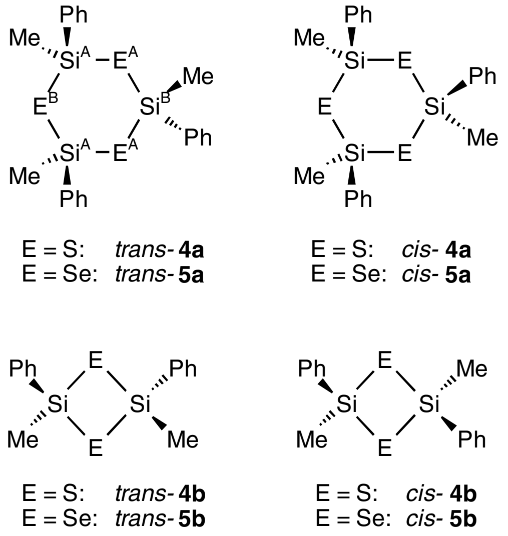


Fig. 4. Molecular structure of $(Ph_2SiTe)_3$ (**3a**) with the intermolecular Te1···Te1a interaction that leads to a dimerization in the crystal structure.

cyclic dimers $(PhMeSiE)_2$ (**4b**, **5b**). Both exist as a mixture of two stereoisomers as shown in Scheme 2.

In the *cis*-isomers of $(PhMeSiE)_3$ (*cis*-**4a**, *cis*-**5a**) all silicon as well as sulfur or selenium atoms are equivalent which give rise to only one ^{29}Si or ^{77}Se NMR signal. Because all phenyl substituents are on the same side of the Si_3E_3 six-membered ring this isomer is less favored than the *trans*-isomer with one phenyl substituent at the other side of the Si_3E_3 six-membered ring. In *trans*-**4a** and *trans*-**5a** two different silicon as well as selenium sites can be distinguished resulting in two ^{29}Si or ^{77}Se NMR signals in the ratio 2:1. This makes an unequivocal assignment of the NMR signals possible.



Scheme 2. Stereoisomers of $(PhMeSiE)_3$ and $(PhMeSiE)_2$ (E = S, Se).

The NMR spectra of the products reveal that the *trans*-isomer is the main constituent (81% in case of E = S, 82% in case of E = Se).

As for the perphenylated compounds discussed above a comparison with the acyclic chalcogenobutyl substituted silanes $PhMeSi(SBu)_2$ (δ_{Si} 18.2 ppm) and $PhMeSi(SeBu)_2$ (δ_{Si} 13.0 ppm) reveals high field shifts of 6 or 4 ppm, respectively, in the six-membered ring compounds $(PhMeSiE)_3$ (**4a**, **5a**).

The four-membered ring compounds $(PhMeSiE)_2$ (**4b**, **5b**) are only minor by-products (8% in case of E = S (**4b**), 17% in case of E = Se(**5b**)). The NMR spectra reveal that the *cis*- and *trans*-isomers are formed in equal amounts. Since both isomers give rise to one ^{29}Si and one ^{77}Se NMR signal an assignment of the signals to the *cis*- or *trans*-isomer was not possible.

As in case of the perphenylated cycles **1a**–**1b** and **2a**–**2b** the ^{29}Si NMR signals of the four-membered ring compounds $(PhMeSiE)_2$ (**4b**, **5b**) are shifted to higher field in comparison with the corresponding six-membered ring compounds **4a** and **5a** (7 ppm in case of E = S, 24 ppm in case of E = Se). Again the value of the $^1J_{SiSe}$ coupling constant in both isomers of the four-membered ring compound **5b** is significantly smaller than in the isomers of **5a**.

From a saturated hexane solution of a product mixture of **5a** and **5b** single crystals of *trans*-**5a** have been obtained. The result of the crystal structure analysis is shown in Fig. 5. Selected bond lengths and angles are given in Tables 6 and 7.

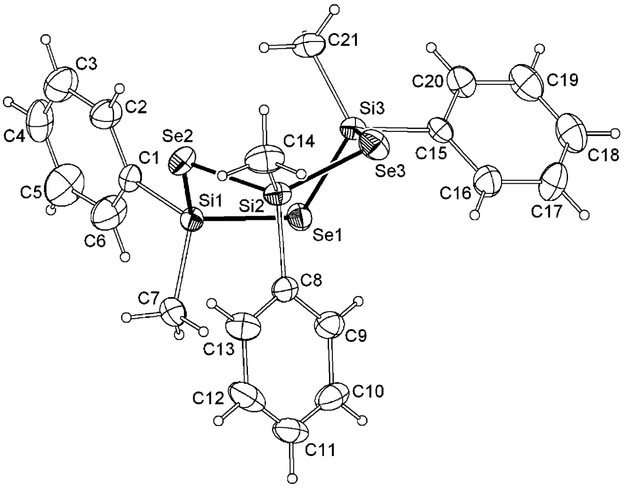


Fig. 5. Molecular structure of *trans*-$(PhMeSiSe)_3$ (*trans*-**5a**).

Table 6
Selected bond length and angles of *trans*-$(PhMeSiSe)_3$ (*trans*-**5a**)

Atoms	Bond length (Å)	Atoms	Bond angles (°)
Se1–Si1	2.282(2)	Si1–Se1–Si3	105.91(7)
Si1–Se2	2.275(5)	Si1–Se2–Si2	102.42(8)
Se2–Si2	2.278(2)	Si2–Se3–Si3	103.24(7)
Si2–Se3	2.245(2)	Se1–Si1–Se2	113.39(8)
Se3–Si3	2.278(2)	Se2–Si2–Se3	113.91(8)
Si3–Se1	2.260(2)	Se1–Si3–Se3	114.18(8)
Si1–C1	1.865(7)	C1–Si1–C7	111.0(3)
Si1–C7	1.857(7)	C8–Si2–C14	110.7(3)
Si2–C8	1.871(7)	C15–Si3–C21	112.4(3)
Si2–C14	1.871(7)		
Si3–C15	1.863(7)		
Si3–C21	1.857(7)		

Table 7
Dihedral angles of *trans*-$(PhMeSiSe)_3$ (*trans*-**5a**)

Atoms	Dihedral angle (°)
Si3–Se1–Si1–Se2	18.30(10)
Se1–Si1–Se2–Si2	43.89(10)
Si1–Se2–Si2–Se3	−75.36(10)
Se2–Si2–Se3–Si3	30.86(11)
Si2–Se3–Si3–Se1	41.43(10)
Se3–Si3–Se1–Si1	−68.42(10)

trans-**5a** is isomorphous with *trans*-**4a**, the only molecular structure reported for a compound with an unfused six-membered ring Si_3S_3 [3].

The molecular structure of *trans*-**5a** reveals a central six-membered ring Si_3Se_3 in a twisted boat conformation. Bond length Si–Se and Si–C as well as bond angles Si–Se–Si and Se–Si–Se are comparable with the data of **2a** given in Table 2. In comparison with the sulfur compound *trans*-**4a** [3] the bond angles Si–E–Si are in average 2.4° smaller for E = Se reflecting the higher p-character of the bond orbitals at the heavier chalcogen.

The dihedral angles in the central six-membered ring Si_3Se_3 of *trans*-**5a** (Table 7) are similar to the values found in *trans*-**4a**. Deviations from the values in **2a** result from the different steric demand of phenyl and methyl substituents in $(PhMeSiE)_3$.

3. Experimental

3.1. NMR measurements

All NMR spectra were recorded on a Bruker DPX 400 in $CDCl_3$ solution and TMS as internal standard for ^1H, ^{13}C and ^{29}Si. In order to get a sufficient signal to noise ratio of ^{29}Si NMR spectra for obtaining $^1J_{SiSe}$ or $^1J_{SiTe}$ satellites ^{29}Si INEPT spectra were also recorded. ^{77}Se and ^{125}Te NMR spectra were obtained using an IGATED pulse program.

External $CDCl_3$ solutions of Ph_2Se_2 (δ_{Se}: 460 ppm [30]) and Ph_2Te_2 (δ_{Te}: 422 ppm [31]) were used as standards for ^{77}Se and ^{125}Te.

3.2. Crystal structure analyses

X-ray structure analysis measurements of **2a** and *trans*-**5a** were performed on a Bruker Smart CCD, while a Rigaku AFC7 with Mercury CCD was used for **3a**. Crystal data of **2a**, **3a** and *trans*-**5a** as well as data collection and refinement details are given in Table 8.

The unit cell of **2a** and *trans*-**5a** were determined with the program SMART [32]. For data integration and refinement of the unit cell the program SAINT [32] was used. The space group was determined using the program XPREP [32]. All data were corrected for absorption using SADABS [33]. For the data collection, unit cell refinement and data reduction of **3a** the program package CRYSTAL CLEAR [34] was used. The structures were solved using direct methods (SIR-97 [35]), refined using least-squares-methods (SHELX-97 [36]) and drawn using DIAMOND [37]. The ellipsoides of the non-hydrogen atoms are shown at the 30% probability level.

3.3. Starting materials

Sulfur, selenium, tellurium, 1 M solution of Li[BEt_3H] in THF (Super-Hydride®), Ph_2SiCl_2 and $PhMeSiCl_2$ were commercially available. THF was distilled from sodium potassium alloy prior to use. Hexane was dried over KOH. All reactions were carried out under argon applying standard Schlenk techniques.

3.4. Synthesis of $(Ph_2SiE)_3$ (E = S (**1a**), Se (**2a**) and Te (**3a**))

In a typical experiment sulfur, selenium or tellurium powder (3.0 mmol) were reacted with 6.0 mL of a 1 M solution of Li[BEt_3H] in THF yielding a light yellow solution of Li_2S, white suspension of Li_2Se or pink suspension of Li_2Te, respectively.

Table 8
Crystal data of **2a**, **3a** and *trans*-**5a** as well as data collection and refinement details

Compound	**2a**	**3a**	*trans*-**5a**
Empirical formula	$C_{36}H_{30}Se_3Si_3$	$C_{36}H_{30}Te_3Si_3$	$C_{21}H_{24}Se_3Si_3$
Formula weight	783.75	929.67	597.55
Crystal shape	Block	Column	Block
Temperature (K)	298(2)	295(2)	298(2)
Crystal color	Colorless	Red	Colorless
Crystal size (mm^3)	0.40 × 0.30 × 0.20	0.29 × 0.11 × 0.11	0.40 × 0.30 × 0.30
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions			
a (Å)	11.968(8)	9.684(1)	9.549(2)
b (Å)	21.457(11)	20.828(2)	11.022(3)
c (Å)	13.371(8)	18.031(2)	12.347(3)
α (°)	90	90	103.924(4)
β (°)	94.851(8)	101.704(5)	99.398(5)
γ (°)	90	90	99.875(5)
Volume (Å^3); Z	3421(4); 4	3561.2(6); 4	1213.9(5); 2
Density (calc., g/cm^3)	1.522	1.734	1.635
Linear absorption coefficient (mm^{-1})	3.355	2.566	4.698
Scan method	ω scans	φ scans	ω scans
Absorption correction	Empirical	Multiscan	Empirical
Measured reflections	29,861	20,236	12,169
Independent reflections	7211	4925	4949
Observed reflections	3835	4148	2854
R_{int}	0.1614	0.0751	0.0710
θ range for collection (°)	1.80–26.48	1.96–23.00	1.74–26.44
Index ranges	$-14 \leqslant h \leqslant 14$	$-9 \leqslant h \leqslant 10$	$-11 \leqslant h \leqslant 11$
	$0 \leqslant k \leqslant 26$	$-17 \leqslant k \leqslant 22$	$-13 \leqslant k \leqslant 13$
	$0 \leqslant l \leqslant 16$	$-19 \leqslant l \leqslant 19$	$0 \leqslant l \leqslant 15$
Completeness to θ_{max} (%)	99.0	99.4	99.2
Number of parameters	379	380	247
Final R_1/wR_2 $[I > 2\sigma(I)]$[a]	0.0710/0.1531	0.1042/0.1820	0.0572/0.1171
Final R_1/wR_2 (all data)[a]	0.1491/0.1877	0.1242/0.1890	0.1227/0.1372
Goodness-of-fit (S)[b] on F^2	0.963	1.289	1.022
H-locating and refining	Geom./mixed	Geom./mixed	Geom./mixed
Max./min. e-density (e/Å^3)	1.356/−1.017	0.741/−0.728	0.920/−0.772

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum||F_o|$, $wR^2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^2)]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

[b] $S = [\sum w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$, where n = number of reflections and p = parameters used.

Ph_2SiCl_2 (3.0 mmol, 0.62 mL) were added at 0 °C (−30 °C in the case of Li_2Te) with stirring. After stirring for 1 h the solvent was removed in vacuo and replaced by 10 mL C_6H_6. After filtration from precipitated lithium salts evaporation of the solvent yielded white crystalline residues of $(Ph_2SiS)_3$ (**1a**), $(Ph_2SiSe)_3$ (**2a**) or a red–brown residue of $(Ph_2SiTe)_3$ (**3a**).

Characterization of the products by NMR spectroscopy revealed that **1a** contained 15% $(Ph_2SiS)_2$ (**1b**, δ_{Si}: −2.90 ppm [38]) and **2a** contained 29% $(Ph_2SiSe)_2$ (**2b**) while no formation of four-membered ring compounds was observed in the case of **3a**.

Single crystals of **2a** and **3a** have been obtained from saturated solutions in hexane.

3.5. Synthesis of $(PhMeSiE)_3$ (E = S (**4a**) and Se (**5a**))

$PhMeSiCl_2$ (3.0 mmol, 0.49 g) were added at 0 °C to 3.0 mmol Li_2S or Li_2Se in THF prepared as described in 3.4. After stirring for 1 h the solvent was removed in vacuo and replaced by 20 mL hexane. After filtration from precipitated lithium salts evaporation of the solvent yielded white crystalline residues of mixtures of *cis*- and *trans*-**4a** plus *cis*- and *trans*-**4b** or *cis*- and *trans*-**5a** plus *cis*- and *trans*-**5b**, respectively. The compositions of the product mixtures were examined by ^{29}Si and ^{77}Se NMR spectroscopy. Single crystals of *trans*-**5a** were obtained from a saturated solution in hexane.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. 252700 for **2a**, 252701 for **3a** and 252702 for *trans*-**5a**.

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 www: http://www.ccdc.cam.ac.uk).

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