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Journal of Organometallic Chemistry 627 (2001) 23–36

Journal of Organometallic Chemistry

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Five- and six-membered ring Group 14 chalcogenides of the types $(Me_2ME)_3$ (M = Si, Ge, Sn), $E(Si_2Me_4)_2E$, $Me_4Si_2(E)_2MR_x$ ($MR_x = C(CH_2)_5$, $SiMe_2$, $GeMe_2$, $SnMe_2$, $SnPh_2$, BPh) and $[Me_4Si_2(E)_2SiMe–]_2$ (E = S, Se, Te)

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Received 8 September 2000; accepted 14 December 2000

Abstract

The reactions of Me_2MCl_2 (M = Si, Ge, Sn) with either H_2S/NEt_3 or Li_2E (E = Se, Te) yielded the six-membered-ring compounds $(Me_2ME)_3$. Similarly the treatment of $ClMe_2SiSiMe_2Cl$ (**1**) with H_2S/NEt_3 or Li_2E resulted in the formation of $E(Si_2Me_4)_2E$. Mixed species $E(Si_2Me_4)_2E'$ could be obtained by reaction with mixtures of Li_2E and Li_2E' or in the presence of traces of moisture (E′ = O). Reactions of 1:1 mixtures of Me_2MCl_2 and **1** with Li_2E resulted in exclusive or at least preferred formation of five-membered rings $Me_4Si_2(E)_2MMe_2$. A carbon analogue, $Me_4Si_2(S)_2C(CH_2)_5$, was obtained from **1** and $(HS)_2C(CH_2)_5$. Boron could also be introduced in these ring systems, starting from $PhBCl_2$ and **1** the compounds $PhB(E)_2Si_2Me_4$ (E = S, Se) could be synthesized. Mixtures of **1** and $Cl_2MeSiSiMeCl_2$ yielded, on treatment either with H_2S/NEt_3 or Li_2E (E = Se, Te), the bis(cyclopentyl) compounds $[Me_4Si_2(E)_2SiMe–]_2$.

All products have been characterized by multinuclear NMR (^1H, ^{11}B, ^{13}C, ^{29}Si, ^{77}Se, ^{119}Sn, ^{125}Te) measurements including coupling constants. Trends of chemical shifts and coupling constants are discussed. The crystal structures of $E(Si_2Me_4)_2E$ (E = S, Se) and $[Me_4Si_2(S)_2SiMe–]_2$ are reported.

Keywords: Silthianes; Selenides; Tellurides; Germanium; Tin

1. Introduction

In the course of our systematic investigations on silicon (and other Group 14) chalcogenides [1–4] we report in this paper on five- and six-membered ring chalcogenides of Group 14 elements (Si, Ge, Sn). Some compounds like $(Me_2SiE)_3$ (E = S [5], Se [6]), $(Me_2SnE)_3$ (E = S, Se, Te) [7], $E(Si_2Me_4)_2E$ (E = S, Se) [8], $Me_4Si_2(S)_2SiMe_2$ [1,9] or $Me_4Sn_2(E)_2SnMe_2$ (E = S, Se, Te) [7] have been reported previously (including some NMR chemical shifts) but there has not been any systematic investigation of this class of compounds so far allowing us to conclude, e.g. trends of NMR data (chemical shifts, coupling constants) in series like $(Me_2ME)_3$, M = Si, Ge, Sn, E = (O), S, Se, Te. On the other hand, especially a comparison of NMR data of the same building blocks in five- and six-membered ring compounds seems to be very interesting. Previous investigations, for instance, have shown, that the formation of five-membered rings is accompanied by a strong down field shift of the ^{29}Si-NMR signals in comparison with acyclic compounds or six-membered rings containing the same first coordination sphere at silicon.

DFT calculations on the equilibrium have shown that the formation of the five-membered ring according to Eq. (1) lowers the total energy (including vibrational zero point correction) of the system by 36.0 kJ mol^{-1} [1]. This means that five-membered rings seem to be the most stable ring size in these systems.

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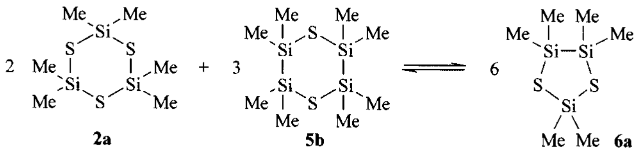


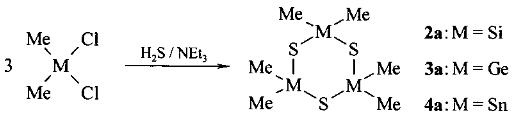
(1)

Crystal structures of $(R_2ME)_3$ are only known for some cyclotrisilthianes with larger substituents R, e.g. *trans*-$(PhMeSiS)_3$ (twisted boat conformation, d_{SiS}: 2.13–2.15 Å, ∠SiSSi: 104.7–108.0°, ∠SSiS: 112.2–112.6° [10]) and for the tin chalcogenides $(Me_2SnS)_3$ (two modifications reported: tetragonal: d_{SnS}: 2.41 Å, ∠SnSSn: 103°, ∠SSnS: 107.7° [11]; monoclinic: d_{SnS}: 2.41–2.44 Å, ∠SnSSn: 102.0–104.4° ∠SSnS: 106.1–108.7° [12]), $(Me_2SnSe)_3$ (d_{SnSe}: 2.52–2.54 Å, ∠SnSeSn: 100.6, 101.1°, ∠SeSnSe: 107.8, 110.6°) [13], and $(Me_2SnTe)_3$ (d_{SnTe}: 2.72–2.77 Å, ∠SnTeSn: 94.9–97.4°, ∠TeSnTe: 111.3–113.6°) [14] which also adopt unusual twisted boat conformations. Furthermore the molecular structures of the five-membered heterocyclic tin compounds $Me_4Sn_2^A(Se)_2Sn^BMe_2$ (envelope conformation, d_{SnSn}: 2.77–2.78 Å, d_{Sn^ASe}: 2.56–2.58 Å, d_{Sn^BSe}: 2.52–2.55 Å, ∠SnSeSn: 93.3–96.7°, ∠SeSn^{B}Se: 106.5–107.2°) [15] and $^tBu_4Sn_2^A(E)_2Sn^{B\,t}Bu_2$ (E = S: planar, d_{SnSn}: 2.88 Å, d_{Sn^AS}: 2.40–2.43 Å, d_{Sn^BS}: 2.40–2.42 Å, ∠SnSSn: 107.9–108.3°, ∠SSn^{B}S: 115.3; E = Se: planar, d_{SnSn}: 2.88 Å, d_{Sn^ASe}: 2.52–2.53 Å, d_{Sn^BSe}: 2.52–2.53 Å, ∠SnSeSn: 106.3–106.5°, ∠SeSn^{B}Se: 115.1; E = Te: twisted, d_{SnSn}: 2.84 Å, d_{Sn^ATe}: 2.75 Å, d_{Sn^BTe}: 2.74 Å, ∠SnTeSn: 101.6–102.3°, ∠TeSn^{B}Te: 114.0–114.3) [16]; have been reported. The conformations of the latter are obviously determined by the steric demand of the ^{t}butyl substituents at the tin atoms.

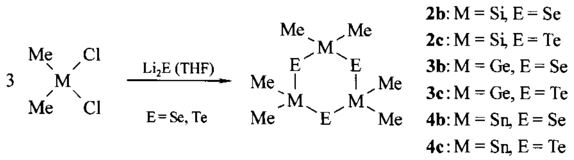
2. Results and discussion

2.1. Six-membered ring compounds $(Me_2ME)_3$ (M = Si, Ge, Sn; E = S, Se, Te)

All compounds of this class could be synthesized starting from the dichlorodimethyl derivatives either by reaction with H_2S/NEt_3 or Li_2E (E = Se, Te) Eqs. (2) and (3):



(2)



(3)

All products were characterized by multinuclear NMR spectroscopy, in the cases of E = S MS spectra could also be recorded. Table 1 summarizes the observed NMR parameters. NMR data of **2a**, **2b** and **4a**–**c**, as far as they have been published, are in good agreement with these data. In comparison with the acyclic compounds $Me_2Si(SBu)_2$ (δ_{Si}: 24.8 ppm) [17], $Me_2Si(SMe)_2$ (δ_{Si}: 28.14 ppm) [18], $Me_2Si(SeBu)_2$ (δ_{Si}: 18.1 ppm) [19] and $Me_2Si(TeBu)_2$ (δ_{Si}: −24.6 ppm) [20] the formation of a six-membered ring is accompanied by a high field shift of about 3 ppm (compared to the EBu-derivatives with the same E). Similar effects can also be observed for the tin compounds. The acyclic derivatives $Me_2Sn(SMe)_2$ and $Me_2Sn(SeMe)_2$ exhibit

Table 1
NMR data of the six-membered rings $(Me_2ME)_3$; M = Si, Ge, Sn; E = S, Se, Te (chemical shifts in ppm, coupling constants in Hz)

Compound	δ_E	δ_M	$^1J_{ME}$	δ_C	$^1J_{MC}$	δ_H
$(Me_2SiS)_3$ (**2a**)		21.1		7.95	59.6	0.69
$(Me_2SiSe)_3$ (**2b**)	Se: −244	15.2	130.7	8.7	55.4	0.91
$(Me_2SiTe)_3$ (**2c**)	Te: −618	−23.7	344.5	8.8	49.5 $^2J_{TeC}$: 18.4	1.26 $^3J_{TeH}$: 8.8
$(Me_2GeS)_3$ (**3a**)				10.6		0.97
$(Me_2GeSe)_3$ (**3b**)	Se: −182			11.1		1.15
$(Me_2GeTe)_3$ (**3c**)	Te: −476			10.3	 $^2J_{TeC}$: 9.6	1.42 $^3J_{TeH}$: 7.3
$(Me_2SnS)_3$ (**4a**)		133 $^2J_{SnSn}$: 193 [a]		4.8	405.1	0.86
$(Me_2SnSe)_3$ (**4b**)	Se: −360	46 $^2J_{SnSn}$: 231 [a]	1217	4.4	363.5	0.99 $^2J_{SnH}$: 57.8
$(Me_2SnTe)_3$ (**4c**)	Te: −859	−192 $^2J_{SnSn}$: 239 [a]	3098	1.9	298	1.17 $^2J_{SnH}$: 52

[a] $^2J_{119Sn117Sn}$.

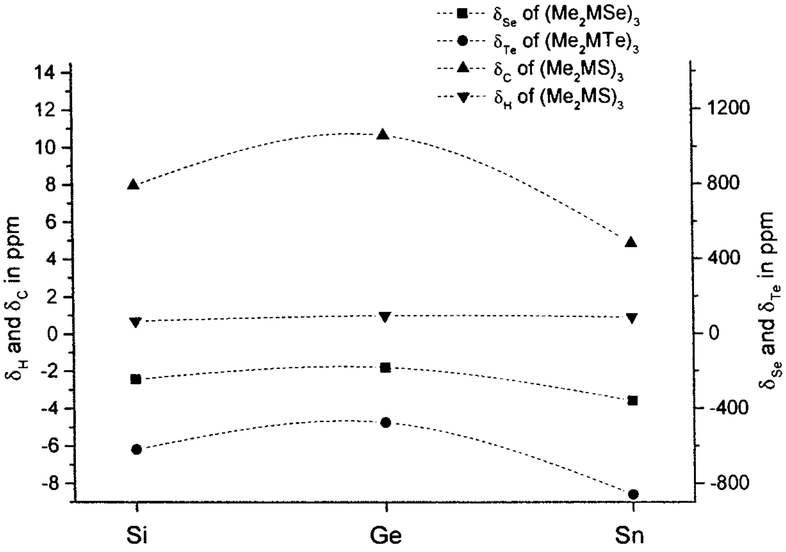


Fig. 1. NMR chemical shifts in six-membered rings $(Me_2ME)_3$ (M = Si, Ge, Sn; E = S, Se, Te).

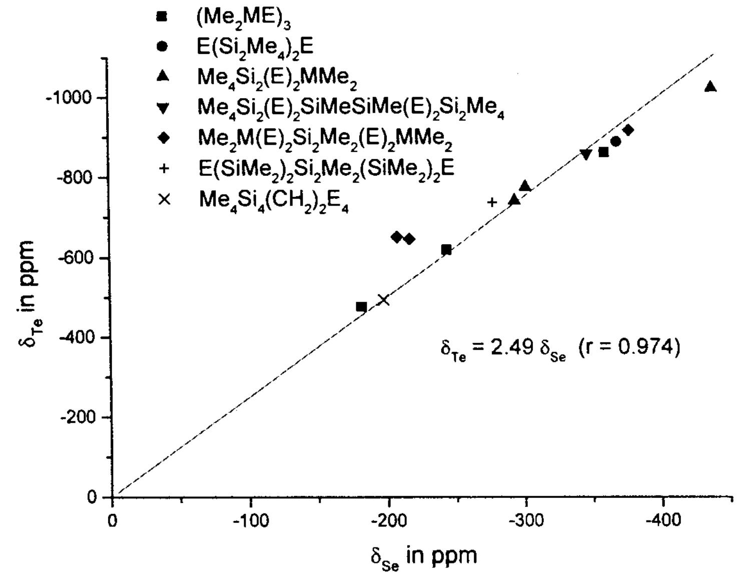


Fig. 2. Correlation of δ_{Se} and δ_{Te} in different kinds of silselenanes and siltelluranes and related germanium and tin derivatives (M = Si, Ge, Sn; E = Se, Te) reported here and in Refs. [3,4] (r = regression coefficient).

^{119}Sn-NMR shifts of 144 [21] and 57 ppm [22], respectively, which are in both cases at a lower field by 11 ppm than the corresponding $(Me_2SnE)_3$ derivatives. On the other hand, the ^{29}Si-NMR signal of $Me_2Si(TeBu)_2$ (δ_{Si}: -24.6 ppm) [20] is by 0.9 ppm at a higher field than in the case of the corresponding six-membered ring **2c**.

If several NMR parameters, such as δ_E, δ_C or δ_H of analogous derivatives of silicon, germanium and tin are compared, see Fig. 1, it is obvious, that the values of the germanium compounds do not lie between those of the silicon and tin derivatives but are shifted in all cases to a lower field. This trend can also be found in five-membered rings discussed in Section 2.3.

It can be explained with the higher electronegativity (2.02) of germanium (values according to Allred and Rochow [23]) in comparison with those of silicon (1.74) and tin (1.72).

Concerning the chemical shifts of selenium and tellurium it has already been stated, that in equivalent compounds the chemical shifts run closely parallel. A plot of δ_{Te} against δ_{Se} for a variety of organic derivatives has been found to be linear with a slope of about 1.6 [24,25]. As can be seen from Figs. 2 and 3 again a linear relationship between δ_{Se} and δ_{Te} as well as $^1J_{SiSe}$ and $^1J_{SiTe}$ could be observed but with a steeper slope of app. 2.6 in both cases. In order to show that this observation is more general other types of Group 14

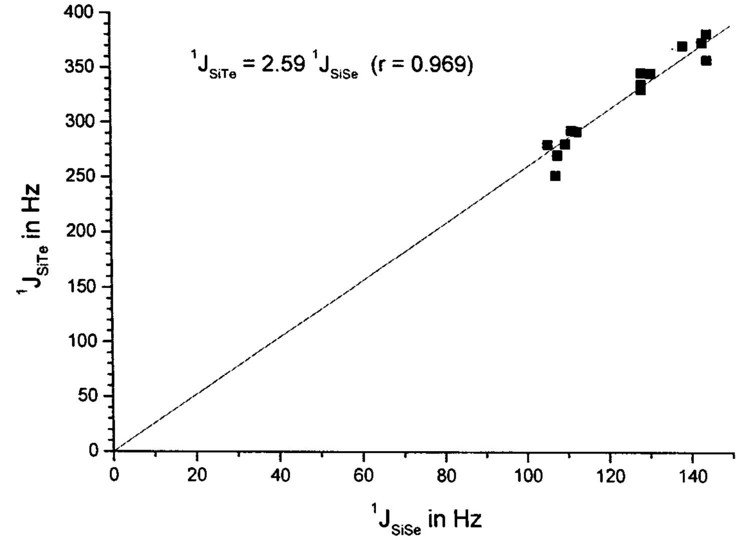


Fig. 3. Correlation of $^{1}J_{SiSe}$ and $^{1}J_{SiTe}$ in different kinds of silselenanes and siltelluranes reported here and in Refs. [3,4] (same compounds as in Fig. 2).

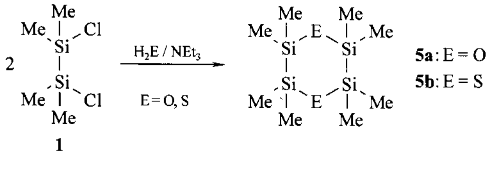
selenides and tellurides have been included into the figures, too.

Some deviations in Fig. 2 may arise from the fact that compounds like $(Me_2SiSe)_3$ and $(Me_2SiTe)_3$ have been compared, but to be correct, δ_{Se} of $(Me_2SiSe)_3$ should be compared with the δ_{Te} of $Me_6Si_3Se_2Te$.

An equivalent correlation like that in Fig. 3 can also be observed by comparing $^{1}J_{SnSe}$ with $^{1}J_{SnTe}$ of equivalent compounds (**4b**/**4c**, **6i**/**6n** or the bicyclic compounds $Me_2Sn(E)_2Si_2Me_2(E)_2SnMe_2$ [3]) yielding a slope of 2.54.

2.2. Six-membered rings $E(Si_2Me_4)_2E'$; E, E' = O, S, Se, Te

Starting from **1** the six-membered rings $E(Si_2Me_4)_2E$ (E = O (**5a**), S (**5b**), Se (**5c**) and Te (**5d**)) were formed without any acyclic by-products by reaction with either H_2E/NEt_3 or Li_2E (Eqs. (4) and (5)):



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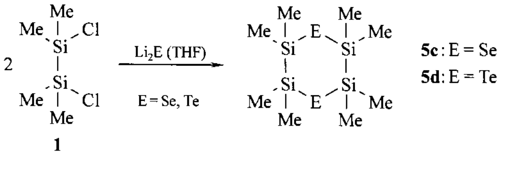


(5)

In the synthesis of **5d** it is crucial to add **1** to the THF solution of Li_2Te at a temperature below 0°C, otherwise the five-membered ring $Me_4Si_2(Te)_2SiMe_2$ (**6l**) is formed exclusively by the cleavage of one Si–Si bond.

The mixed species $O(Si_2Me_4)_2E$ (E = S (**5e**), Se (**5f**), Te (**5g**)) have been observed as by-products if the reactions (Eqs. (4) and (5)) were carried out in the presence of traces of moisture. Besides NMR-spectroscopic evidence also a mass spectrum of **5e** could be recorded. Finally the mixed substituted compounds $S(Si_2Me_4)_2Se$ (**5h**), $S(Si_2Me_4)_2Te$ (**5i**) and $Se(Si_2Me_4)_2Te$ (**5k**) were prepared together with the homosubstituted cycles **5b**–**d** upon treatment of **1** with 1:1 mixtures of Li_2E and Li_2E' (E = S, Se; E′ = Se, Te).

While **5a** is a well known compound [26] (a ^{29}Si-NMR chemical shift of 2.3 ppm has been reported in Ref. [27]), the sulfur and selenium derivatives **5b** and **5c** have been synthesized by the insertion of elemental sulfur or selenium (red modification) into the five-membered rings $(Me_2Si)_4E$ (obtained from $(Me_2Si)_4$ and E_8) [8]. In contrast to observations reported in Ref. [8] we found both compounds to give relatively stable colorless crystals in an inert atmosphere but they hydrolyze on contact with air (**5c** more rapidly than **5b**). The ^{29}Si-NMR shifts given in Ref. [8] differ somewhat from our results, especially for **5c** and the also reported mixed sulfur selenium compound **5h**.

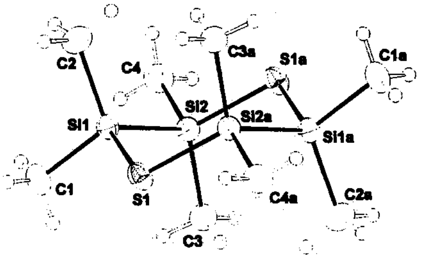


Fig. 4. ZORTEP plot of the molecular structure of **5b**.

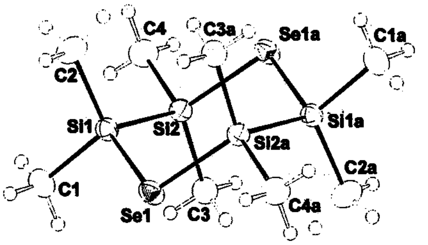


Fig. 5. ZORTEP plot of the molecular structure of **5c**.

Crystal structure analyses of **5b** and **5c** have been carried out, and Figs. 4 and 5 show the molecular structures. In contrast to the reported twisted boat conformations of $(MePhSiS)_3$ [10] and **4a**–**c** [11–14] in both molecules the six-membered ring adopts a chair conformation. Some important bond parameters are summed up in Table 2. Both compounds crystallize in the same space group with almost identical lattice constants.

The Si–S as well as Si–Se bond lengths found are relatively large in comparison with reported values of other silthianes and silselenanes. But in general the Si–S bond distances decrease with the number of S substituents at silicon [28] and in **5b** there is only one sulfur atom connected to each silicon atom. The same might also hold for the Si–Se bond lengths but fewer data of crystal structures are available. Furthermore, the bond angles at sulfur and selenium are smaller than the tetrahedral angle but larger than values found previously in other cyclic silthianes or selenanes or related germanium and tin compounds. These observations are confirmed by previously performed DFT calculations on **5b** (B3LYP/6-31G*) which also yielded a relatively large bond length Si–S of 2.187 Å and an angle Si–S–Si of 109.2° [1].

Table 2
Important bond distances and angles of **5b** and **5c**

Atoms	Bond length		Atoms	Angles	
	5b (E = S)	**5c** (E = Se)		**5b** (E = S)	**5c** (E = Se)
Si(1)–Si(2)	2.3373(4)	2.3306(10)	Si(1)–E(1)–Si(2a)	106.45(1)	105.14(3)
Si(1)–E(1)	2.1562(4)	2.2908(8)	E(1)–Si(1)–Si(2)	111.90(2)	111.37(4)
Si(2a)–E(1)	2.1545(4)	2.2883(8)	E(1a)–Si(2)–Si(1)	113.29(2)	112.27(3)
Si(1)–C(1)	1.8713(11)	1.870(3)	C(1)–Si(1)–C(2)	109.21(6)	110.17(16)
Si(1)–C(2)	1.8869(11)	1.863(8)	C(3)–Si(2)–C(4)	109.68(5)	110.65(15)
Si(2)–C(3)	1.8666(11)	1.871(3)	E(1)–Si(1)–Si(2)–E(1a)	−59.65(2)	−62.40(4)
Si(2)–C(4)	1.8709(11)	1.867(3)	Si(2a)–E(1)–Si(1)–Si(2)	55.74(2)	58.17(4)

Table 3
NMR data of the six-membered ring compounds $E(SiMe_2SiMe_2)_2E$ (E = O, S, Se, Te)

Compound	δ_E	δ_{Si}	$^1J_{SiE}$	δ_C	$^1J_{SiC}$	δ_H
$O(Si_2Me_4)_2O$ (**5a**)		3.7		2.8		0.21
$S(Si_2Me_4)_2S$ (**5b**)		−4.8		1.94	45.4	0.44
$Se(Si_2Me_4)_2Se$ (**5c**)	−369	−9.1	109.8	1.40	44.1	0.55
$Te(Si_2Me_4)_2Te$ (**5d**)	−885	−28.9	280.2 $^2J_{SiTe}$: 13	1.00	42.3	0.72

Table 4
NMR data of the six-membered ring compounds $E(Si^AMe_2Si^BMe_2)_2E'$ (E, E′ = O, S, Se; E ≠ E′)

Compound	δ_E	$^1J_{SiE}$	δ_{SiA}	$^1J_{SiC}$	δ_{SiB}	$^1J_{SiC}$	$^1J_{SiSi}$	δ_C	δ_{HA}	δ_{HB}
$O(Si_2Me_4)_2S$ (**5e**)			4.7	58.3	−8.4	43.7	100.1	2.31, 1.88	0.26	0.38
$O(Si_2Me_4)_2Se$ (**5f**)	Se: −317	103	4.1		−13.6	43.2	98	1.85, 1.75	0.26	0.48
$O(Si_2Me_4)_2Te$ (**5g**)	Te: −902	255.1	3.8	[a]	−35.6	40.8	95.7	1.48, 1.12	0.26	0.64
$S(Si_2Me_4)_2Se$ (**5h**)	Se: −370	107.9	−3.9	45.7	−10.1	45.7	92.8	1.81, 1.52	0.45	0.54
$S(Si_2Me_4)_2Te$ (**5i**)	Te: −916	267.2	−2.5	[b]	−32.8	43.7	89.4	1.73, 0.97	0.47	0.70
$Se(Si_2Me_4)_2Te$ (**5k**)	Se: −366	112.2	−7.3	44.5	−31.5	41.8	88.0	1.37, 0.93	0.57	0.71
	Te: −890	273.1		[c]						

[a] $^2J_{SiTe}$: 10.2.
[b] $^2J_{SiTe}$: 8.3.
[c] $^2J_{SiTe}$: 8.7.

The observed NMR parameters of **5a**–**k** are given in Tables 3 and 4. In the row **5a**–**d** (E = O, S, Se, Te) the ^{29}Si- and ^{13}C-NMR signals are shifted to higher field and the values of the $^{1}J_{SiC}$ coupling constants decrease which is consistent with the decreasing electronegativity of E. On the other hand, δ_H of the methyl groups increases, but this trend parallels the increasing deshielding effect of heavier halogen substituents at silicon towards methyl protons [29].

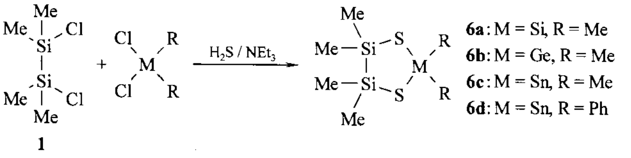
Compared with the acyclic disilane derivatives BuS–SiMe$_2$–SiMe$_2$–SBu [17], BuSe–SiMe$_2$–SiMe$_2$–SeBu [19] and BuTe–SiMe$_2$–SiMe$_2$–TeBu [20] the ^{29}Si-NMR signals of the six-membered rings are more shielded by 3.2 (**5b**), 2.4 (**5c**) and 2.9 ppm (**5d**) whereas the δ_C values of the methyl carbon atoms are shifted by 2–3 ppm to a lower field and δ_H and $^{1}J_{SiC}$ remain almost unchanged.

In the mixed six-membered ring compounds **5e**–**k** δ_{Si} of the SiMe$_2$ units attached to the more electronegative E atom is shifted to a lower field while δ_{Si} of the other SiMe$_2$ units are shifted to a higher field in comparison with δ_{Si} in the comparable compounds **5a**–**d**. This effect increases with increasing difference in the electronegativities of E and E′ and can also be observed for other unsymmetrically substituted disilanes.

In the mixed six-membered rings it has also been possible to obtain $^{1}J_{SiSi}$ coupling constants. As expected, the values increase with the electronegativities of the two chalcogen atoms E and E′ and fall in the expected range.

2.3. *Five-membered rings Me$_4$Si$_2$(E,E′)$_2$MR$_x$; E (E′ = S, Se, Te; MR$_x$ = BPh, C(CH$_2$)$_5$, SiMe$_2$, GeMe$_2$, SnMe$_2$, SnPh$_2$)*

As already reported in Ref. [1], the reaction of **1** in mixture with Me$_2$SiCl$_2$ yields the five-membered ring Me$_4$Si$_2$(S)$_2$SiMe$_2$ (**6a**) as the preferred product. This reaction can also be used to prepare the corresponding germanium (**6b**), tin (**6c**,**d**) and boron (**6e**) containing cycles (Eqs. (6) and (7)):



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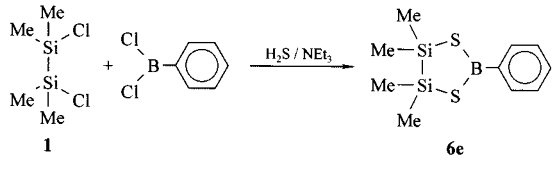
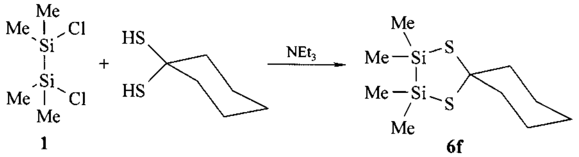


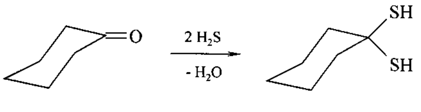
(7)

A carbon analog (**6f**) has been obtained in a clean reaction by treatment of **1** with cyclohexane-1,1-dithiol (Eq. (8)):



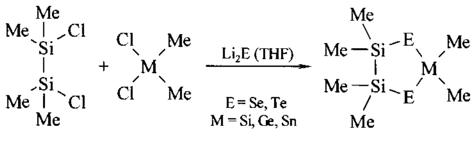
(8)

1,1-Dithiols are accessible from ketones and H$_2$S according to [30] (Eq. (9)):



(9)

The selenium and tellurium containing five-membered rings **6g**–**n** have been prepared by reaction with Li$_2$Se or Li$_2$Te. In these cases the reactions yield only the expected five-membered ring compounds without six-membered rings (Me$_2$ME)$_3$ and **5c**,**d** as by-products (Eq. (10)).



(10)

As stated above, pure Me$_4$Si$_2$(Te)$_2$SiMe$_2$ (**6l**) is also observed in the reaction of pure **1** with Li$_2$Te at room temperature under the cleavage of the Si–Si bonds.

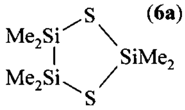
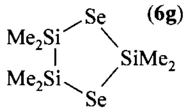
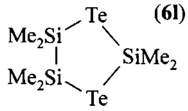
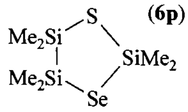
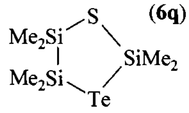
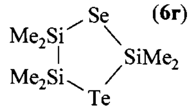
Mixed sulfur selenium (**6p**), sulfur tellurium (**6q**) as well as selenium tellurium (**6r**) five-membered rings could be detected in the product mixtures besides **6a**, **6g** and **6l**, if 1:1 mixtures of **1** and Me$_2$SiCl$_2$ were reacted with 1:1 mixtures of Li$_2$E and Li$_2$E′ in THF.

No oxygen containing five-membered rings, but the O-substituted six-membered rings **5e**–**g** were observed as by-products when the reactions were carried out in the presence of traces of moisture. The larger bond angle SiOSi prevents the formation of the smaller five-membered rings in this case.

The NMR data of all prepared five-membered rings are given in Tables 5 and 6. **6e** has been synthesized before in a different route [9], but only the ^{11}B- and ^{1}H-NMR shifts were given. The strongly deshielded selenium NMR signal in **6k** compared to all other selenium compounds of this paper is remarkable. In contrast to other ^{77}Se-NMR spectra this signal is much more broadened due to the contact with the quadrupolar nuclei ^{10}B and ^{11}B. The same reason is responsible for the problems in detecting the ipso carbon atoms of the phenyl rings in **6e** and **6k**.

Compared with the six-membered heterocycles discussed before, the ^{29}Si-NMR signals of the same silyl units in five-membered rings are shifted significantly to

Table 5
NMR data of five-membered rings $Me_4Si_2(E)_2SiMe_2$ (E = S, Se, Te)

compound	δ_E	group	δ_{Si}	$^1J_{SiE}$	$^2J_{SiE}$	δ_C	$^1J_{SiC}$	δ_H
 **(6a)**	-	Si_2Me_4	11.0	-	-	1.09	46.5	0.48
		$SiMe_2$	34.1	-	-	8.46	58.3	0.62
 **(6g)**	Se: -302	Si_2Me_4	14.0	105.5	$^2J_{SeC}$: 6	0.7	45.2	0.58
		$SiMe_2$	24.8	128.3	-	9.8	54.0	0.85
 **(6l)**	Te: -774	Si_2Me_4	10.2	279.9	28.7	0.3	42.8	0.71
					$^2J_{TeC}$: 19.8			
		$SiMe_2$	-22.8	334.3	$^2J_{TeC}$: 17.1	11.0	47.6	1.20
 **(6p)**	Se: -312	$SSiMe_2$	14.5	-		0.9	45.6	0.49
		$SeSiMe_2$	10.3	104.0	-	0.8	44.7	0.58
		E_2SiMe_2	29.9	125.4	-	9.2	56.4	0.73
 **(6q)**	Te:-827	$SSiMe_2$	21.2	-	24.4	0.5	45.2	0.49
		$TeSiMe_2$	-2.1	268.2	$^1J_{SiSi}$: 84.6	0.5	43.7	0.71
		E_2SiMe_2	10.5	329.0	$^2J_{TeC}$: 16.0	10.5	53.5	0.89
 **(6r)**	Se: -288	$SeSiMe_2$	21.1	109.3	$^2J_{SiTe}$: 25.8	0.5	44.7	0.58
		$TeSiMe_2$	2.0	272.7	$^2J_{SiSe}$: 6	0.4	42.8	0.71
	Te: -806	E_2SiMe_2	3.1	Se: 129.3	-	10.8	50.0	1.01
				Te: 334.3	$^1J_{SiSi}$: 84.0			

a lower field. A closer look reveals that this low field shift increases within the disilanyl unit (in comparison with **5b**–**d**), if one goes down the row of S, Se and Te, whereas the opposite is observed for the monosilyl units $Me_2Si(E–)_2$ (in comparison with **2a**–**c**), see Fig. 6.

In the three tin derivatives $Me_4Si_2(E)_2SnMe_2$ (E = S (**6c**), Se (**6i**), Te (**6n**)) the ^{119}Sn-NMR signals are shifted downfield by about 50 ppm in comparison with **4a**–**c**.

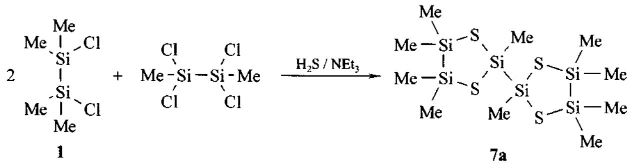
The values of δ_{Se} and δ_{Te} in the five-membered rings $Me_4Si_2(E)_2MMe_2$ (M = Si, Ge, Sn), where the E atoms are placed between one disilanyl and one MMe_2 unit, are almost exactly the average between the shifts found in the comparable six-membered rings **5c**,**d**, **2b**–**4b** and **2c**–**4c** for M = Si, while for M = Ge and Sn the deviations towards higher field increase up to 146 ppm in **6n**.

Other NMR parameters do not show significant changes due to the change in ring size, at best it seems, that $^1J_{SiSi}$ in analogous units $E–SiMe_2–SiMe_2–E'$ are in five-membered rings by 4–5 Hz smaller than in six-membered rings.

In five-membered rings with two different E atoms (**6p**–**r**) δ_{Si} of the unit $E–Me_2Si–E'$ is almost the average of the chemical shifts of the monosilyl unit in the rings $Si_2Me_4(E)_2SiMe_2$ and $Si_2Me_4(E')_2SiMe_2$ while the ^{29}Si-NMR shifts of the disilanyl units behave like those already discussed for **5e**–**k** but to a larger extent.

2.4. *Bis(cyclopentyl) compounds $Me_4Si_2(E)_2SiMe–SiMe(E)_2Si_2Me_4$ (E = S (**7a**), Se (**7b**), Te (**7c**))*

In a previous paper [1] we have already reported the formation and the NMR data of the sulfur compound **7a** according to (Eq. (11))

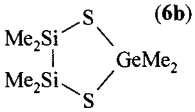
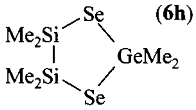
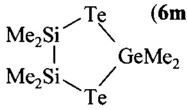
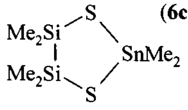
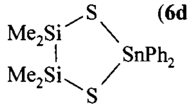
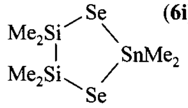
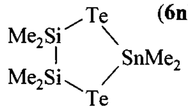
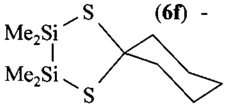
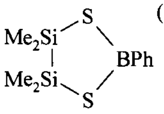
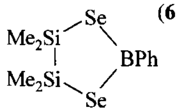


(11)

By changing the starting molar ratio of $MeCl_2Si–SiCl_2Me$:**1** from 1:2 to 1:1 the amount of the by-product **5b** could be reduced to 20%. Upon treatment with H_2S and NEt_3 excess $MeCl_2Si–SiCl_2Me$ forms $Me_6Si_6S_6$ [1], which is insoluble in hexane and can therefore be removed very easily.

The selenium and tellurium compounds **7b**,**c** are formed in the reaction of Li_2E with a 1:2 mixture of $MeCl_2Si–SiCl_2Me$ and **1** in THF as main products besides smaller amounts of **5c**,**d** and the noradamantane $Me_4Si_4Se_5$ in the case of selenium [4] (Eq. (12)):

Table 6
NMR data of five-membered ring compounds $Me_4Si_2(E)_2MR_x$ (E = S, Se, Te; MR_x: $GeMe_2$, $SnMe_2$, $SnPh_2$, $C(CH_2)_5$, BPh)

compound	δ_E	group	δ_M	$^1J_{ME}$	δ_C	$^1J_{MC}$	δ_H
 **(6b)**	-	Si_2Me_4	12.2	-	1.1	46.2	0.46
		$GeMe_2$	-	-	10.6	-	0.90
 **(6h)**	Se: -294	Si_2Me_4	14.8	111.3 $^2J_{SiSe}$: 6.3	0.6	44.7	0.55
		$GeMe_2$	-	-	11.8	-	1.09
 **(6m)**	Te: -740	Si_2Me_4	10.8	292.5 $^2J_{SiTe}$: 28.7	0.3 $^2J_{TeC}$: 17.6	42.3	0.67
		$GeMe_2$	-	-	12.2	-	1.40
 **(6c)**	-	Si_2Me_4	10.6	$^2J_{SiSn}$: 10.2	1.6		0.42
		$SnMe_2$	183		3.5		0.80
 **(6d)**	-	Si_2Me_4	11.7	$^2J_{SiSn}$: 10.2	1.5 $^3J_{SnC}$: 16.8		0.42
		$SnPh_2$	68		a)		a)
 **(6i)**	Se: -439	Si_2Me_4	12.2	112.6 $^2J_{SiSe}$: 7.2,	1.1 $^3J_{SnC}$: 14.4		0.52
		$SnMe_2$	98.3	1170 $^2J_{SiSn}$: 13.0	3.3	349.5	0.89
 **(6n)**	Te: -1018	Si_2Me_4	6.7	291.5 $^2J_{SiTe}$: 31.1	0.9		0.67
		$SnMe_2$	-139	2966	7.7		1.1
 **(6f)**	-	Si_2Me_4	10.5	-	-0.1	47.1	0.49
		C^i	70.7		b)		b)
 **(6e)**	-	Si_2Me_4	17.0	-	-0.4	46.6	0.54
		BPh	64.1		c)		c)
 **(6k)**	Se: +33	Si_2Me_4	18.1	97.2	-0.5	45.2	0.65
		BPh	70.0		d)		d)

a): Ph ^{13}C: i: 140.0 ($^1J_{SnC}$: 620.0), o: 135.2 ($^2J_{SnC}$: 51.9), m: 128.7 ($^3J_{SnC}$: 67.1), p: 129.9 ($^4J_{SnC}$: 13.6); ^1H: 7.32 (6H), 7.63 (4H)

b): cyclohexane ring: ^{13}C: o: 46.65, m: 24.2, p: 25.0; ^1H: o: 2.02 ($^3J_{HH}$: 5.7), m: 1.68, p: 1.41 ($^3J_{HH}$: 6.6)

c): Ph ^{13}C: o: 134.1, m: 127.6, p: 131.7; ^1H: o: 8.04, m: 7.35, p: 7.43

d): Ph ^{13}C: o: 133.9, m: 127.7, p: 131.7; ^1H: o: 8.24 ($^3J_{HH}$: 6.6), m: 7.34, p: 7.45 ($^3J_{HH}$: 7.3)

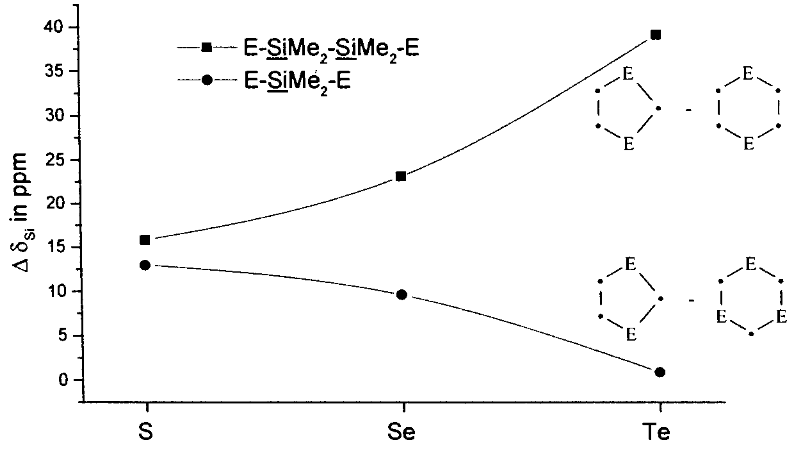
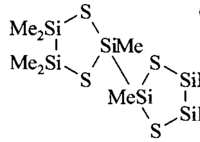
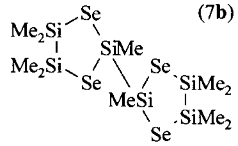
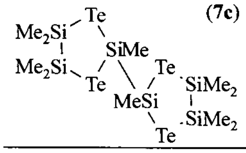
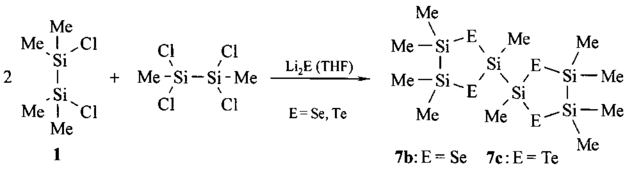


Fig. 6. Comparison of δ_{Si} of mono and disilyl units in five- and six-membered ring silicon chalcogenides (**2a**–**c**, **5b**–**d** and **6a**, **6g**, **6l**).

Table 7
NMR data of the compounds $Me_4Si_2(E)_2SiMe$–$SiMe(E)_2Si_2Me_4$ (E = S, Se, Te (**7a**–**c**))

compound	δ_E	group	δ_{Si}	$^1J_{SiE}$	$^2J_{SiE}$	δ_C	$^1J_{SiC}$	δ_H
 (**7a**)	-	SiMe	20.25	-	-	7.17	48.6	0.73
		$SiMe_2$	12.55	-	-	0.90 / 1.41	46.2	0.49 / 0.50
 (**7b**)	-347	SiMe	8.42	144.3	19.9	6.9		0.96
		$SiMe_2$	15.91	107.4	6.3	0.6 / 1.0	43.2	0.57 / 0.58
 (**7c**)	-856	SiMe	-42.80	356.7	34.0	5.35		1.30
		$SiMe_2$	11.97	251.7	29.6	0.52 / 0.88		0.67 / 0.71



(12)

The NMR data of the compounds **7a**–**c** are given in Table 7.

While the δ_{Si} of the Si_2Me_4 units can be compared with the disilanyl units of the five-membered rings **6a**, **6f** and **6l** and show only small additional down field shifts of 1.5–2 ppm the chemical shifts of the central Si_2Me_2 units could at best be compared with the compounds $C_2H_4(S)_2SiMe$–$SiMe(S)_2C_2H_4$ (δ_{Si}: 23.8 ppm) and $C_6H_4(S)_2SiMe$–$SiMe(S)_2C_6H_4$ (δ_{Si}: 20.8 ppm) [2], which are indeed similar to **7a**. But no related selenium or tellurium compounds are known. In contrast to the monocyclic five-membered rings the methyl groups in the $SiMe_2$ units of **7a**–**c** are diastereotopic giving rise to two different carbon and hydrogen NMR signals. But the averages of the two signals are close to the values found in **6a**, **6f** and **6l**, respectively.

Fig. 7 shows the result of the crystal structure analysis of **7a** confirming the expected bis(cyclopentyl) skeleton. Some important bond lengths and angles are given in Table 8. The five-membered rings adopt a twisted

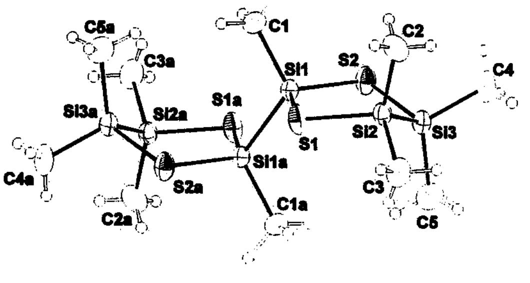


Fig. 7. ZORTEP plot of the molecular structure of **7a**.

Table 8
Important bond distances (Å) and angles (°) of **7a**

Atoms	Distances	Atoms	Angles
Si(1)–Si(1a)	2.323(2)	Si(1)–S(1)–Si(2)	104.38(5)
Si(1)–S(1)	2.1458(12)	Si(1)–S(2)–Si(3)	103.85(5)
Si(1)–S(2)	2.1409(12)	S(1)–Si(1)–S(2)	112.65(5)
Si(2)–S(1)	2.1551(12)	S(1)–Si(2)–Si(3)	103.05(5)
Si(3)–S(2)	2.1539(13)	S(2)–Si(3)–Si(2)	103.65(5)
Si(2)–Si(3)	2.3310(13)	Si(1a)–Si(1)–C(1)	111.22(14)
Si(1)–C(1)	1.853(4)	C(2)–Si(2)–C(3)	110.5(2)
Si(2)–C(2)	1.848(4)	C(4)–Si(3)–C(5)	109.1(2)
Si(2)–C(3)	1.860(4)		
Si(3)–C(4)	1.865(4)		
Si(3)–C(5)	1.874(4)		

conformation. Si(2) and Si(3) are 0.382(2) Å above and 0.461(2) Å below the plane defined by the atoms Si(1), S(1) and S(2). The angles at the sulfur atoms are larger than in other silthianes containing five-membered rings Si_3S_2 [1] but in this case the five-membered rings are not incorporated into bi- or polycyclic ring systems, and the angles are close to the calculated Si–S–Si angle of 103.8° in **6a** (B3LYP/6-31G*, [1]). Also the calculated angles S–Si–S and Si–Si–S of 111.6° and 102.2° for **6a** are mirrored well in the observed angles in **7a**. The bond lengths Si–Si, Si–S and Si–C are in the expected range. As already observed in other silthianes the Si–S bond length decreases with increasing number of S substituents at Si. Therefore the Si–S bonds at Si(1) are slightly shorter than the Si–S bonds at Si(2) and Si(3).

3. Experimental

3.1. NMR and GC–MS 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/noise ratio of the ^{29}Si-NMR spectra for obtaining $^1J_{SiC}$, $^1J_{SiSi}$, $^{1,2}J_{SiSe}$ or $^{1,2}J_{SiTe}$ satellites also ^{29}Si INEPT spectra were recorded. ^{77}Se, ^{125}Te and ^{119}Sn spectra were recorded using an IGATED pulse program.

External $BF_3{\cdot}OEt_2$, Me_4Sn, Ph_2Se_2 (δ_{Se}: 460 ppm) and Ph_2Te_2 (δ_{Te}: 422 ppm) in $CDCl_3$ were used as standards for ^{11}B, ^{119}Sn, ^{77}Se and ^{125}Te.

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^{-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 **5b**, **5c** and **7a** as well as data collection and refinement details are given in Table 9.

The unit cells were determined with the program SMART [31]. For data integration and refinement of the unit cells the program SAINT [31] was used. The space groups were determined using the programs XPREP [31] (**5a**, **5b**) and ABSEN [32]. All data were corrected for absorption using SADABS [33]. The structures were solved using direct methods (**5a**, **5b**: SHELX-97 [34], **7a**: SIR-97 [35]), refined using least-squares methods (SHELX-97) and drawn using ZORTEP [36]. The ellipsoides at the nonhydrogen atoms are at the 50% probability level.

3.3. Starting materials

H_2S (N25, Air Liquide), Se, Te, triethylamine, 1 M $Li[BEt_3H]$ in THF (Super Hydride), Me_2SiCl_2, Me_2GeCl_2, Me_2SnCl_2, Ph_2SnCl_2, $PhBCl_2$ were commercially available. **1** and $SiCl_2Me$–$SiCl_2Me$ were prepared as described previously [37,38]. THF was distilled from sodium potassium alloy prior to use. The other solvents were dried over KOH or sodium wire. All reactions were carried out under argon applying standard Schlenk techniques.

3.4. Preparation of the six-membered ring compounds $(Me_2ME)_3$ (M = Si, Ge, Sn; E = S, Se, Te) (**2a–4c**)

3.4.1. Sulfur compounds (**2a–4a**)

In a typical reaction 2 mmol Me_2MCl_2 (M = Si, Ge, Sn) was dissolved in 20 ml hexane and a stream of dried H_2S was passed through the stirred solution while 0.55 ml (4 mmol) NEt_3 were slowly added by a syringe. A white precipitate of Et_3NHCl was formed. After filtration the solvent was removed in vacuo yielding pure **2a–3a** as colorless oils and **4a** as a semicrystalline residue in ca. 60% yield.

2a GC–MS *m/e* (rel. int.): 270 (M^+, 21), 255 ($Me_5Si_3S_3$, 100), 165 ($Me_3Si_2S_2$), 73 (Me_3Si, 35).

3a GC–MS 404 ($Me_6{}^{72}Ge_2{}^{74}GeS_3$, 13), 389 ($Me_5{}^{72}Ge_2{}^{74}GeS_3$, 92), 255 ($Me_3{}^{72}Ge{}^{74}GeS_2$, 100), 225 ($Me{}^{72}Ge{}^{74}GeS_2$, 12), 151 ($Me_3{}^{74}GeS$, 5), 119 ($Me_3{}^{74}Ge$, 48), 89 ($Me{}^{74}Ge$, 14). (The isotopic patterns of all fragments fitted the natural abundance of ^{70}Ge:^{72}Ge:^{73}Ge:^{74}Ge:^{76}Ge = 20.5:27.4:7.8:36.5:7.8 [39].)

4a GC–MS 527 ($Me_5{}^{118}Sn{}^{120}Sn_2S_3$, 16), 497 ($Me_3{}^{118}Sn{}^{120}Sn_2S_3$, 4), 362 ($Me_4{}^{118}Sn{}^{120}SnS_2$, 20), 347 ($Me_3{}^{118}Sn{}^{120}SnS_2$, 100), 317 ($Me{}^{118}Sn{}^{120}SnS_2$, 63), 302 ($^{118}Sn{}^{120}SnS_2$, 19), 270 ($^{118}Sn{}^{120}SnS$, 10), 197 ($Me_3{}^{120}SnS$, 35), 165 ($Me_3{}^{120}Sn$, 31), 135 ($Me{}^{120}Sn$, 19), 120 ($^{120}Sn$, 15) (The isotopic patterns of all fragments fitted the natural abundance of ^{116}Sn: ^{117}Sn:^{118}Sn:^{119}Sn:^{120}Sn:^{122}Sn:^{124}Sn = 14.53:7.68:24.22:8.58:32.59:4.63:5.79 [39].)

3.4.2. Selenium compounds (**2b–4b**)

Black selenium powder (0.16 g, 2 mmol) was reacted with a mixture of 4 ml 1 M solution of Li[BEt_3H] ("Super Hydride") in THF and 5 ml THF under stirring. The selenium dissolved within a few seconds with the formation of a white suspension of Li_2Se in THF. Me_2MCl_2 (2 mmol) dissolved in 1 ml THF was added to this mixture. The precipitation of Li_2Se disappeared almost immediately. After stirring for 30 min at room temperature the THF was removed in vacuo and replaced by 10 ml hexane. The solution was separated from precipitated LiCl. Removal of the solvent produced **2b** and **3b** as colorless oils and **4b** as a white solid in ca. 50% yield.

3.4.3. Tellurium compounds (**2c–4c**)

Tellurium powder (0.25 g, 2 mmol (200 mesh)) was added to a mixture of 4 ml 1 M solution of Li[BEt_3H] ("Super Hydride") in THF and 5 ml THF under stirring. After 5 min the tellurium started to react under the formation of a deep purple solution which became dark red after 1 h at room temperature.

Dichloride Me_2MCl_2 (2 mmol) dissolved in 1 ml THF was added to this "Li_2Te"-solution under stirring, which turned light orange. Work-up as described for the selenium compounds **2b–4b** yielded the tellurium compounds as light yellow viscous oils in ca. 40% yield.

3.5. Preparation of the six-membered ring compounds $E(SiMe_2SiMe_2)_2E$ ($E = O$, S, Se, Te) (**5a–d**) and mixed compounds $E(SiMe_2SiMe_2)_2E'$ ($E \neq E)'$

3.5.1. Synthesis of $S(SiMe_2SiMe_2)_2S$ (**5b**)

1,2-$Si_2Me_4Cl_2$ (**1**) (2.5 g, 13.3 mmol) was dissolved in 100 ml hexane and 3.7 ml (26.6 mol) NEt_3 was slowly added while a stream of dried H_2S passed through the stirred solution. After 1 h the reaction mixture was filtered from precipitated Et_3NHCl and most of the solvent was removed in vacuo when **5b** crystallized in colorless needles from the solution in yield of 1.6 g (81%).

If the reaction is carried out with H_2S, which was not dried with $CaCl_2$ prior to use, besides **5b** the monooxygen and dioxygen six-membered ring compounds **5e** and **5a** were formed as by-products, which could also be proved by GC–MS:

5b GC–MS: 296 (M^+, 23), 281 ($Me_7Si_4S_2$, 13), 237 ($Me_5Si_3S_2CH_2$, 11), 116 (Me_4Si_2, 100), 73 (Me_3Si, 92).

Table 9
Crystal data of **5b**, **5c** and **7a** as well as data collection and refinement details

	5b	**5c**	**7a**
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	6.8132(5)	6.8672(10)	6.6431(5)
b (Å)	12.1869(9)	12.2988(17)	12.4055(11)
c (Å)	10.1091(8)	10.2087(15)	14.7678(12)
α (°)	90	90	90
β (°)	91.006(2)	1.852(3)	96.962(2)
γ (°)	90	90	90
Volume (Å^3)	839.25(11)	861.8(2)	1208.1(2)
Z	2	2	2
Density (calc.) in g cm^{-3}	1.174	1.505	1.229
Linear absorption coefficient (mm^{-1})	0.575	4.541	0.682
Radiation used	Mo–K_α	Mo–K_α	Mo–K_α
Temperature	173(2) K	173(2) K	173(2) K
Scan method	ω scans	ω scans	ω scans
Absorption correction	Empirical	Empirical	Empirical
Max/min transmission	0.8465/0.6960	0.6118/0.2917	0.9602/0.8756
Measured reflections	5581	4267	5306
Independent reflections	2404	2033	2619
Observed reflections	2078	1628	1520
R(int)	0.0192	0.0254	0.0547
Theta range for collection (°)	2.62–30.74	2.59–31.16	2.15–29.55
Completeness to θ_{max} (%)	92.0	73.2	77.3
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_1 ($I>2\sigma(I)$)	0.0215	0.0292	0.0410
R_1 (all data)	0.0263	0.0422	0.0989
H-locating and refining	difmap/refall	difmap/refall	difmap/refall
Goodness-of-fit on F^2	1.028	1.000	0.908
Max/min e-density (e Å^{-3})	0.258/−0.261	0.558/−0.715	0.354/−0.298

5e GC–MS: 280 (M^+, 22), 265 (Me_7Si_4OS, 16), 221 (Me_7Si_3S, 14), 205 (Me_7Si_3O, 13), 147 (Me_5Si_2O, 24), 116 (Me_4Si_2, 100), 101 (Me_3Si_2, 7), 73 (Me_3Si, 57).

5a GC–MS: 264 (M^+, 32), 249 ($Me_7Si_4O_2$, 41), 221 ($Me_7Si_3O_2$, 7), 205 (Me_7Si_3O, 97), 191 ($Me_5Si_3O_2$, 57), 175 (Me_5Si_3O, 15), 147 (Me_5Si_2O, 27), 131 (Me_5Si_2, 12), 117 (Me_3Si_2O, 18), 91 (35), 73 (Me_3Si, 100).

*3.5.2. Synthesis of $Se(SiMe_2SiMe_2)_2Se$ (**5c**)*

1 (2 mmol) was added at room temperature to Li_2Se suspension prepared from 2 mmol Se powder, 4 ml 1 M $Li[BEt_3H]$ solution and 5 ml THF and the mixture was stirred for 1 h before the solvent was removed and replaced by 10 ml hexane. The hexane solution was separated from precipitated LiCl and concentrated in vacuo until needles of **5c** crystallized from the solution in 64% yield (0.25 g).

If this reaction is carried out with THF, which was not dried very carefully, the monooxygen compound **5f** was obtained as by-product as confirmed by GC–MS.

5c GC–MS: 392 (M^+, 2), 377 ($Me_7Si_4{}^{80}Se_2$, 1), 333 ($Me_5Si_3Se_2CH_2$, 2), 319 ($Me_5Si_3Se_2$, 0.5), 239 (Me_5Si_3Se, 3), 211 (Me_5Si_2Se, 2), 195 ($Me_3Si_2SeCH_2$, 5), 131 (Me_5Si_2, 8), 116 (Me_4Si_2, 100), 101 (Me_3Si_2, 8), 73 (Me_3Si, 74).

5f GC–MS: 328 (M^+, 3), 313 (Me_7Si_4OSe), 269 (Me_7Si_3Se, 4), 255 (Me_5Si_3OSe), 205 (Me_7Si_3O, 7), 189 (Me_7Si_3, 2), 175 (Me_5Si_3O, 3), 147 (Me_5Si_2O, 32), 131 (Me_5Si_2, 12), 116 (Me_4Si_2, 91), 101 (Si_2Me_3, 9), 73 (Me_3Si, 100). (The isotopic patterns of all fragments fitted the natural abundance of ^{76}Se:^{77}Se:^{78}Se:^{80}Se:$^{82}Se = 9.2:7.6:23.7:49.8:8.8$ [39].)

*3.5.3. Synthesis of $Te(SiMe_2SiMe_2)_2Te$ (**5d**)*

The tellurium compound was synthesized essentially via the same procedure as the selenium compound **5c**, but the disilane **1** was added while the Li_2Te suspension was cooled to the range −40 to −30°C and further work-up was carried out in an ice bath (0°C). Colorless, very thin needles of **5d** could be obtained which decompose very rapidly, if the sample is heated above room temperature, but in solid state under Ar they are stable at 20°C for at least several weeks.

Again, if the reaction is carried out with THF containing traces of moisture, the monooxygen compound **5g** could be obtained as by-product.

If the addition of **1** to the Li_2Te suspension is done at room temperature, pure **6l** was obtained as a colorless oil after work-up.

The six-membered rings containing two different chalcogen atoms ($E = S$, Se; $E' = Se$, Te) were prepared via the same route than **5c** and **5d** but 2 mmol of **1** was added to a mixture of Li_2E and Li_2E' prepared from 1 mmol E, 1mmol E′ and 4 ml 1 M $Li[BEt_3H]$ in 5 ml THF. **5h**, **5i** and **5k** were detected by NMR in a mixture with two of the already known compounds **5b**, **5c** and **5d** and in the case of **5h** also by GC–MS.

5h GC–MS: 344 (M^+, 2), 329 (Me_7Si_4SSe, 1), 285 ($Me_5Si_3SSeCH_2$, 2), 239 (Me_5Si_3Se, 2), 211 (Me_5Si_2Se, 1), 191 (Me_5Si_3S, 3), 147 ($Me_3Si_2SCH_2$, 6), 131 (Me_5Si_2, 9), 116 (Me_4Si_2, 100), 101 (Me_3Si_2, 8), 73 (Me_3Si, 66).

3.6. Preparation of the five-membered ring compounds $Me_4Si_2(E)_2MR_x$

*3.6.1. Sulfur derivatives $Me_4Si_2(S)_2MMe_2$ ($M = Si$, Ge, Sn (**6a–c**)) and $Me_4Si_2(S)_2SnPh_2$ (**6d**)*

1 (0.28 g, 1.5 mmol) and 1.5 mmol Me_2MCl_2 ($M =$ Si, Ge or Sn) or 1.5 mmol Ph_2SnCl_2 were dissolved in 40 ml hexane (or 25 ml toluene in the cases of the tin compounds) and 0.83 ml (6 mmol) NEt_3 was slowly added while a stream of dried H_2S was bubbled through the stirred solution. After 1 h the mixture was filtered from precipitated ammonium salt and the solvent removed in vacuo yielding an oily residue of ca. 55–65% of the desired five-membered ring compound **6a–d** besides a mixture of the six-membered rings **2–4a** and **5b**.

6a GC–MS: 238 (M^+, 50), 223 ($Me_5Si_3S_2$, 65), 165 ($Me_3Si_2S_2$, 34), 163 (Me_5Si_2S, 30), 73 (Me_3Si, 100).

6b GC–MS: 284 (M^+, 7), 269 ($Me_5GeSi_2S_2$, 12), 209 (Me_5GeSiS; 1), 181 ($MeGeSiS_2$, 2), 163 (Me_5Si_2S, 10), 119 (Me_3Ge, 4), 89 (MeGe, 5), 73 (Me_3Si, 100).

6c GC–MS: 330 (M^+, 2), 315 ($Me_5Si_2SnS_2$, 25), 227 ($MeSiSnS_2$, 14), 195 (MeSiSnS, 2), 165 (Me_3Sn, 3), 135 (MeSn, 13), 73 (Me_3Si, 100).

*3.6.2. Preparation of $Me_4Si_2(S)_2BPh$ (**6e**)*

$PhBCl_2$ (0.32 g, 2 mmol) and 0.37 g (2 mmol) **1** were dissolved in 40 ml hexane and 1.11 ml (8 mmol) NEt_3 was slowly added while a stream of H_2S was passed through the stirred solution. After 1 h the product mixture was filtered and the solvent was removed yielding pure **6e** as very thin needles unsuitable for X-ray analysis. The observed ^{11}B- and ^1H-NMR signals were in good agreement with the ^1H- and ^{11}B-NMR data of **6e** published in Ref. [9].

*3.6.3. Preparation of $Me_4Si_2(S)_2C(CH_2)_5$ (**6f**)*

According to the procedure described in Ref. [30] 10.2 g (0.104 mol) cyclohexanone and 0.86 g (0.01 mol) morpholine were dissolved in 40 ml methanol and H_2S was bubbled through the mixture for 3 h. The resulting product was treated with diluted sulfuric acid until two phases occurred. The oily organic phase was separated, the solvents were removed in vacuo at room temperature and the product was dried over $CaCl_2$. ^1H- and ^{13}C-NMR spectra revealed that the product is pure cyclohexane-1,1-dithiol which was used without further purification, yield: 6.3 g (0.043 mol, 41%).

^{1}H-NMR (ppm): 2.53 (SH), 1.87 (*ortho*-CH$_2$, $^3J_{HH}$ = 5.9 Hz), 1.52 (*meta*-CH$_2$), 1.32 (*para*-CH$_2$, $^3J_{HH}$ = 5.7 Hz). ^{13}C-NMR (ppm): 53.3 (*C*(SH)$_2$), 45.7 (*ortho*-CH$_2$), 23.6 (*meta*-CH$_2$), 24.9 (*para*-CH$_2$).

Cyclohexane-1,1-dithiol (0.22 g, 1.5 mmol) and 0.28 g (1.5 mmol) **1** were dissolved in 25 ml hexane and 0.42 ml (3 mmol) NEt$_3$ was slowly added under stirring. After filtration from precipitated Et$_3$NHCl and removal of the solvent 0.29 g (74%) pure **6f** remained as an oily residue.

GC–MS: 262 (M$^+$, 3), 247 (M − Me, 2), 181 (Me$_4$Si$_2$S$_2$H, 10), 180 (Me$_4$Si$_2$S$_2$, 11), 165 (Me$_3$Si$_2$S$_2$, 100), 149 (Me$_4$Si$_2$SH, 17), 133 (Me$_3$Si$_2$S, 10), 73 (Me$_3$Si, 23).

*3.6.4. Selenium and tellurium derivatives Me$_4$Si$_2$(Se)$_2$MMe$_2$ (M = Si, Ge, Sn (**6g–i**)) and Me$_4$Si$_2$(Te)$_2$MMe$_2$ (**6l–n**)*

Selenium (0.16 g, 2 mmol) or 0.25 g (2 mmol) tellurium powder reacted at room temperature with a solution of 4 mmol Li[BEt$_3$H] ("Super hydride") in 10 ml THF. The selenium dissolved very rapidly and the initially dark brown solution became a white suspension of Li$_2$Se within a few minutes. But it took 1–2 h until the tellurium was completely dissolved and the initially deep purple solution became a light red suspension of Li$_2$Te.

A mixture of 0.187 g (1 mmol) **1** and 1 mmol of the dichlorides Me$_2$MMe$_2$ were dissolved in 2 ml THF and added to the Li$_2$E suspension under stirring. After 30 min the solvent was removed and exchanged with 10 ml hexane. The clear solution was separated and the solvent removed to yield the five-membered ring compounds as oils in a 50–70% yield. Only in the case of **6n** some **6l** occurred as the by-product as determined by NMR. **5f** or **5g**, respectively, were detected as by-products, if the reactions were not carried out under absolute exclusion from oxygen and moisture.

6g GC–MS: 334 (M$^+$, 6), 319 (Me$_5$Si$_3^{80}$Se$_2$, 8), 261 (Me$_3$Si$_2$Se$_2$, 3), 246 (Me$_2$Si$_2$Se$_2$, 1), 211 (Me$_5$Si$_2$Se, 17), 195 (Me$_3$Si$_2$SeCH$_2$, 7), 181 (Si$_2$Me$_3$Se, 5), 123 (MeSiSe, 7), 73 (Me$_3$Si, 100).

*3.6.5. Mixed five-membered rings Me$_4$Si$_2$(E)(E′)SiMe$_2$ (E = S, E′ = Se (6p), E = S, E′ = Te (6q), E = Se, E′ = Te (**6r**))*

E (1 mmol) (S or Se) and 1 mmol E′ (Se or Te) were mixed and added to a solution of 4 mmol Li[BEt$_3$H] in 10 ml THF. A mixture of 0.187 g (1 mmol) 1 and 0.129 g (1 mmol) Me$_2$SiCl$_2$ in 2 ml THF was added to the stirred suspension of Li$_2$E and Li$_2$E′. After work-up as described in Section 3.6.4 an oily mixture was obtained, which contained 45–50% **6p**, **6q** or **6r**, respectively, besides a mixture of two of the homocycles **6a**, **6g** and **6l**.

6p GC–MS: 286 (M$^+$, 11), 271 (Me$_5$Si$_3$SSe, 16), 213 (Me$_3$Si$_2$SSe, 10), 211 (Me$_5$Si$_2$Se, 9), 181 (Me$_3$Si$_2$Se, 2), 163 (Me$_5$Si$_2$S, 18), 147 (Me$_3$Si$_2$SCH$_2$, 8), 133 (Me$_3$Si$_2$S, 6), 123 (MeSiSe, 4), 73 (Me$_3$Se, 100).

*3.7. Preparation of the bis(cyclopentyl) compounds Me$_4$Si$_2$(E)$_2$Si$_2$Me$_2$(E)$_2$Si$_2$Me$_4$ (E = S, Se, Te (**7a–c**))*

1 (0.37 g, 2 mmol) and 0.46 g (2 mmol) SiCl$_2$Me–SiCl$_2$Me were dissolved in 50 ml hexane and H$_2$S was bubbled through the solution while 1.66 ml (12 mmol) NEt$_3$ was added by a syringe. After 1 h the mixture was filtered and the solvent removed to yield a crystalline residue of 75% **7a** besides **5b**. Single crystals of **7a** were obtained from hexane solution.

7b and **7c** were obtained by reacting a mixture of 0.187 g (1 mmol) **1** and 0.114 g (0.5 mmol) SiCl$_2$Me–SiCl$_2$Me dissolved in 1 ml THF with a suspension of 2 mmol Li$_2$E (E = Se, Te, prepared from E and LiBEt$_3$H as described above) in 5 ml THF at room temperature (E = Se) or at −20°C (E = Te). After reacting for 30 min the THF was exchanged for hexane and the clear hexane solution was separated and the solvent removed to yield **7b** as a semicrystalline residue and **7c** (which contained **5d** and **6l** as by-products) as an oily residue.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 154132, 154133 and 154134 for **5b**, **5c** and **7a**, respectively. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223336033 or e-mail: deposit@ccdc.cam.ac.uk or http:// www.ccdc.cam.ac.uk).

Acknowledgements

The authors wish to thank the 'Deutsche Forschungsgemeinschaft' for financial support. Special thanks are given to Prof. H. Lang, Chair of Inorganic Chemistry, TU, Chemnitz for the access to the X-ray facility used to determine the single crystal structures.

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