# Group 14 chalcogenides featuring a bicyclo[3.3.0]octane skeleton

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## Abstract

Reactions of mixtures of $Cl_2MeSiSiMeCl_2$ (**1**) and $Me_2MCl_2$ (M = Si, Ge, Sn) with either $H_2S/NEt_3$ or $Li_2E$ (E = Se, Te) yielded the bicyclo[3.3.0]octanes $Me_2M(E)_2Si_2Me_2(E)_2MMe_2$. A carbon containing analog, $(CH_2)_5C(S)_2Si_2Me_2(S)_2C(CH_2)_5$, was prepared from **1** and $(CH_2)_5C(SH)_2$. Crystal structures of three of these compounds were determined and the observed conformations of the bicyclo[3.3.0]octane skeletons compared with results of density functional theory calculations. Another class of silchalcogenides featuring a bicyclo[3.3.0]octane skeleton, $E(Me_2Si)_2Si_2Me_2(SiMe_2)_2E$, was formed from the doubly branched hexasilane $(ClMe_2Si)_2Si_2Me_2(SiMe_2Cl)_2$ and $H_2S/NEt_3$ or $Li_2E$. All products were characterized by multinuclear NMR ($^1H$, $^{13}C$, $^{29}Si$, $^{77}Se$, $^{119}Sn$, and $^{125}Te$). © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The reaction of organochlorosilanes with either $H_2E$ (E = S, Se) in the presence of a Lewis base or $Li_2E$ (E = S, Se, Te) yields silicon chalcogenides which usually form four- or six-membered heterocycles or polycycles with adamantane [1] or double-decker [2,3] structures depending on the functionality of the starting chlorosilane and the steric demand of the organic substituents.

In our previous report on cyclic and polycyclic silthianes containing Si–Si bonds [4] we have shown that in this class of compounds five-membered heterocycles consisting of three silicon and two sulfur atoms are most stable. The reaction of $Me_2SiCl_2$ with $H_2S/NEt_3$ yields the six-membered ring compound $(Me_2SiS)_3$ and the analogous reaction of the disilane $ClMe_2Si–SiMe_2Cl$ results in the formation of the six-membered heterocycle $S(SiMe_2SiMe_2)_2S$ without any acyclic by-products. If, however the reaction with $H_2S/NEt_3$ is carried out with a mixture of the two chlorosilanes, a five-membered heterocyclic compound is formed preferably:
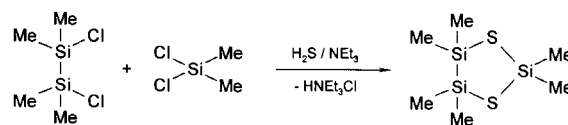


Density functional theory (DFT) calculations on the conversion reaction:
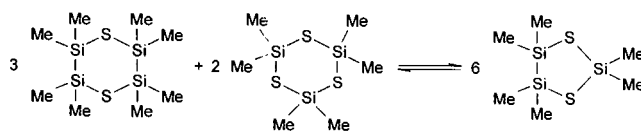


have indeed shown that the five-membered cyclic compound is 36 kJ mol$^{-1}$ more stable than the corresponding mixture of the two six-membered heterocycles. This tendency also applies to systems with heavier Group 14 elements like germanium and tin and the heavier chalcogens selenium and tellurium. For instance the reaction of equimolar mixtures of $Me_2MCl_2$ (M = Ge, Sn) and $ClMe_2Si–SiMe_2Cl$ with $Li_2Se$ or $Li_2Te$ resulted in a selective formation of the five-membered heterocycles $Me_2M(E)_2Si_2Me_4$ [5]:

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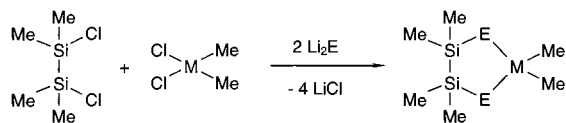
In continuation of these studies a mixture of the tetrafunctional disilane Cl₂MeSi–SiMeCl₂ (**1**) and Me₂SiCl₂ in a molar ratio of 1:2 is now shown to react with H₂S/NEt₃ yielding selectively 1,3,3,5,7,7-hexamethyl-2,4,6,8-tetrathiatetrasila-bicyclo[3.3.0]octane (**2a**):

The molecular structure of **2a** as determined by X-ray analysis revealed two fused five-membered rings adopting envelope conformations with one SiMe₂ unit in an *exo* and one in an *endo* position [4], see Fig. 1.
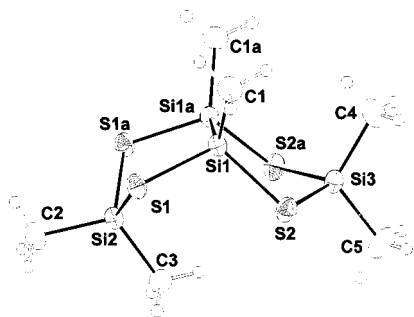


Fig. 1. ORTEP plot of the molecular structure of **2a** [4].

Table 1
NMR data (chemical shifts in ppm, coupling constants in Hz) of the bicyclo[3.3.0]octanes R₂M(S)₂Si₂Me₂(S)₂MR₂ (**2a–e**) (MR₂ = SiMe₂, GeMe₂, SnMe₂, SnPh₂, C(CH₂)₅)

| compound | group | $\delta_M$ | $\delta_C$ | $^1J_{MC}$ | $\delta_H$ |
|---|---|---|---|---|---|
| **2a** | SiMe | 29.85 | 5.2 | 52.2 | 0.91 |
| | SiMe₂ | 35.3 | 7.5 / 8.2 | 58.7 | 0.66 / 0.73 |
| **2b** | SiMe | 33.2 | 5.6 | 51.5 | 0.87 |
| | GeMe₂ | - | 10.4 / 10.5 | - | 0.95 / 1.03 |
| **2c** | SiMe | 29.8 | 6.4 | | 0.94 |
| | SnMe₂ | 181 | 3.5 / 4.8 | | 0.79 / 0.87 |
| | $^2J_{SiSn}$ 10.2 | | | | |
| **2d** | SiMe | 31.4 | 6.2 | 49.8 | 0.83 |
| | | | $^3J_{SnC}$ 16.8 | | |
| | SnPh₂ | 56 | [a] | | 7.35 (8 H), |
| | $^2J_{SiSn}$ 8.8 | | | | 7.58 (12 H) |
| **2e** | SiMe | 33.1 | 1.15 | | 0.92 |
| | C̲(CH₂)₅ | 74.4 | [b] | | [b] |

[a] Ph $^{13}$C: i 139.2 ($^1J_{SnC}$: 644.8) / 139.5 ($^1J_{SnC}$: 612.0), o 135.15 ($^2J_{SnC}$ 51.9) / 135.5 ($^2J_{SnC}$ 55.9), m 128.6 ($^3J_{SnC}$ 71.9) / 128.9 ($^3J_{SnC}$ 67.1), p 130.0 ($^4J_{SnC}$ 15.2) / 130.2 ($^4J_{SnC}$ 14.3),
[b] Cyclohexane rings $^{13}$C: o 44.2 / 47.7, m 23.9 / 24.1, p 24.9; $^1$H: o 2.03 / 2.26, m 1.65 / 1.70, p 1.42

The aim of this work is to extend these investigations to bicyclo[3.3.0]octanes also containing other Group 14 elements (C, Ge, Sn) and/or heavier chalcogens (Se, Te).

## 2. Results and discussion

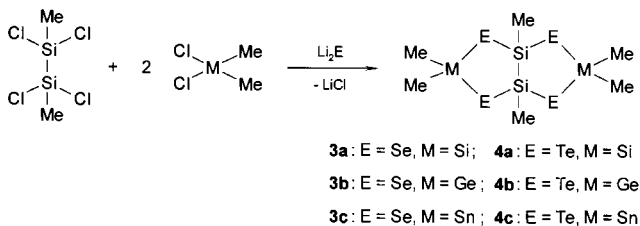### 2.1. Formation of 2,4,6,8-tetrachalcogena-bicyclo[3.3.0]octanes

Reacting 1:2 mixtures of **1** and the dichloro compounds Me₂MCl₂ (M = Ge, Sn) or Ph₂SnCl₂ with H₂S/NEt₃ the corresponding bicyclo[3.3.0]octanes **2b–d** are formed in high yields:



**2b** : MR₂ = GeMe₂

**2c** : MR₂ = SnMe₂

**2d** : MR₂ = SnPh₂
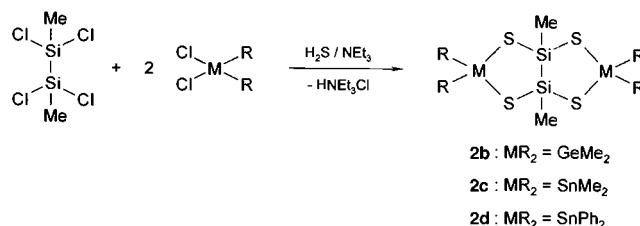
The carbon containing derivative **2e** could be prepared by treatment of **1** with two equivalents of cyclohexane-1,1-dithiol which had been prepared from cyclohexanone and H₂S according to Ref. [6]:
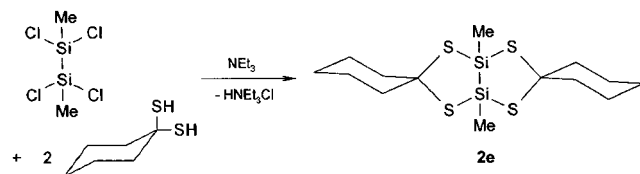


Analogous selenium and tellurium containing bicyclo[3.3.0]octanes (**3a–c**, **4a–c**) have been synthesized by analogous reactions of mixtures of **1** and Me₂MCl₂ (M = Si, Ge, Sn) with either Li₂Se or Li₂Te in THF solution:



**3a** : E = Se, M = Si;　**4a** : E = Te, M = Si

**3b** : E = Se, M = Ge ;　**4b** : E = Te, M = Ge

**3c** : E = Se, M = Sn ;　**4c** : E = Te, M = Sn

All newly prepared 2,4,6,8-tetrachalcogena-bicyclo[3.3.0]octanes are colorless solids. Their stability towards moisture and air decreases dramatically from the sulfur via the selenium to the tellurium heterocycles. Nevertheless all compounds could be characterized by multinuclear NMR spectroscopy, see Tables 1 and 2, and in some cases by GC–MS.

Table 2
NMR data (chemical shifts in ppm, coupling constants in Hz) of the bicyclo[3.3.0]octanes Me$_2$M(E)$_2$Si$_2$Me$_2$(E)$_2$MMe$_2$ (**3a**–**4c**) (M = Si, Ge, Sn; E = Se, Te)

| compound | $\delta_E$ | group | $\delta_M$ | $^1J_{ME}$ | $\delta_C$ | $^1J_{MC}$ | $\delta_H$ |
|---|---|---|---|---|---|---|---|
| **3a** | -208 | SiMe | 32.6 | 138.5 | 6.0 | | 1.07 |
| | | | | $^2J_{SiSe}$ 10.2 | | | |
| | | SiMe$_2$ | 28.7 | 128.3 | 7.7 / 9.3 | 53.9 | 0.88 / 0.95 |
| **3b** | -217 | SiMe | 35.8 | 144.3 | 5.9 | | 1.02 |
| | | | | $^2J_{SiSe}$ 9.7 | | | |
| | | GeMe$_2$ | | | 11.53 / 11.58 | - | 1.15 / 1.21 |
| **3c** | -378 | SiMe | 31.1 | 143.2 | 6.3 | | 1.04 |
| | | | | $^2J_{SiSe}$ 10 | | | |
| | | SnMe$_2$ | 114.4 | 1149 | 3.6 / 4.7 | 336.4 / 362.8 | 0.94 / 0.96 |
| | | | | $^2J_{SiSn}$ 14.1 | | | |
| **4a** | -650 | SiMe | 11.9 | 369.8 | 5.1 | | 1.30 |
| | | | | $^2J_{SiTe}$ 40.3 | | | |
| | | SiMe$_2$ | -23.7 | 345.0 | 9.5 / 10.8 | | 1.22 |
| **4b** | -645 | SiMe | 14.9 | 380.5 | 5.0 | | 1.22 |
| | | | | $^2J_{SiTe}$ 40.8 | | | |
| | | GeMe$_2$ | | | 11.5 / 12.5 | - | 1.47 / 1.50 |
| **4c** | -913 | SiMe | 7.8 | 372.7 | | | 1.23 |
| | | | | $^2J_{SiTe}$ 43.2 | | | |
| | | SnMe$_2$ | -72 | 2927 | | | 1.19 |
| | | | | $^2J_{SiSn}$ 8.7 | | | |

While the chemical shifts of M (C, Si, Sn) in the MR$_2$ units of **2a**–**4c** are similar to those of the corresponding five-membered monocyclic compounds Me$_4$Si$_2$(E)$_2$MR$_2$ [5] (in most cases slightly shifted to lower field), the selenium and tellurium resonances are observed by 60–105 ppm further downfield. Due to the bicyclic systems in **2a**–**4c** the two organic substituents at M are diastereotopic giving rise to two different $^1$H- and $^{13}$C-NMR signals.

### 2.2. Molecular structures of 2,4,6,8-tetrachalcogena-bicyclo[3.3.0]octanes

X-ray structure analyses have been carried out for **2b**, **2e** and **3c** while the molecular structure of **2a** has been reported previously [4]. Figs. 2–4 show the molecular structures. Compounds **2a** and **2b** crystallize in the same space group with almost identical unit cell parameters (Tables 3–5).

While the bicyclo[3.3.0]octane skeletons of **2a**, **2b** and **2e** adopt a bis-envelope conformation, it is obvious that a rather twisted conformation of both five-membered rings is observed for **3c**. The reasons for this different

conformation could be the larger bond lengths of Sn–Se as well as Se–Si whereas the central Si–Si bond remains the same.

Comparing the geometries of **2e**, **2a** and **2b** it can be seen that in this series of compounds with the ring atoms M (C, Si, Ge) the Si–Si bond length increases from 2.328(1) (**2e**) via 2.360(1) (**2a**) to 2.367(1) (**2b**). Consistently the average bond angles Si–S–M (101.99 ° in **2e**, 99.12 ° in **2a**, 98.72 ° in **2b**) and S–M–S (112.31 ° in **2e**, 107.91 ° in **2a**, 105.28 ° in **2b**)
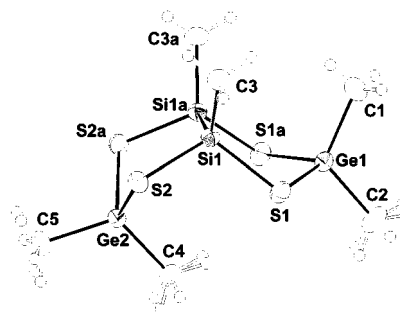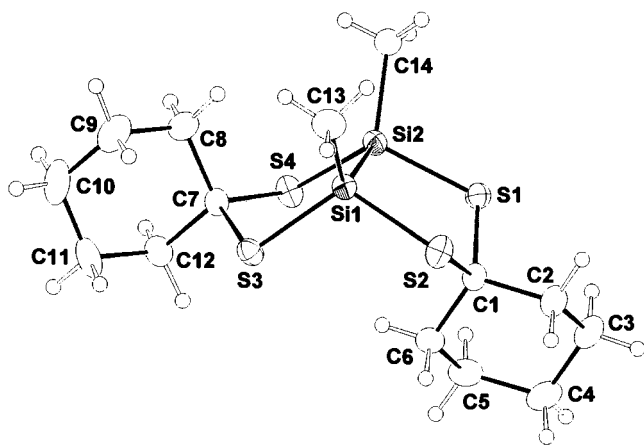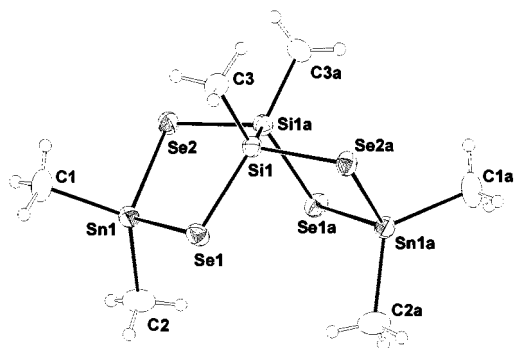


Fig. 2. Molecular structure of **2b**.

Fig. 3. Molecular structure of **2e**.



Fig. 4. Molecular structure of **3c**.

Table 3
Selected bond distances and angles of **2b**

| Atoms | Distances (Å) | Atoms | Angles (°) |
|---|---|---|---|
| Si(1)–Si(1a) | 2.3672(9) | S(1)–Si(1)–S(2) | 109.80(2) |
| S(1)–Si(1) | 2.1422(6) | S(1)–Si(1)–Si(1a) | 106.58(2) |
| S(2)–Si(1) | 2.1317(6) | S(2)–Si(1)–Si(1a) | 105.89(2) |
| S(1)–Ge(1) | 2.2360(5) | Si(1)–S(1)–Ge(1) | 98.87(2) |
| S(2)–Ge(2) | 2.2457(4) | Si(1)–S(2)–Ge(2) | 98.58(2) |
| Si(1)–C(3) | 1.859(2) | S(1)–Ge(1)–S(1a) | 106.77(2) |
| Ge(1)–C(1) | 1.928(3) | S(2)–Ge(2)–S(2a) | 103.79(2) |
| Ge(1)–C(2) | 1.931(3) | C(1)–Ge(1)–C(2) | 115.91(14) |
| Ge(2)–C(4) | 1.933(2) | C(4)–Ge(2)–C(5) | 115.31(11) |
| Ge(2)–C(5) | 1.929(2) | | |

decrease while the average angles Si–Si–S increase from 100.33 (**2e**) via 105.16 ° (**2a**) to 106.24 ° (**2b**). This is attributed to an increase in the bond lengths S–C, S–Si, S–Ge. The angles between the planes $Si_2S_2$ and $S_2M$ which characterize the envelope conformation of the related heterocycles vary only slightly between 49 and 50 °.

In order to get a better understanding of these differences we have performed DFT calculations on the bicyclo[3.3.0]octanes $Me_2C(S)_2Si_2Me_2(S)_2CMe_2$ (**2f**) as a model for **2e**, **2a**, **2b**, **2c** and **3c**. For **2f**, **2a** and **2b** two conformations were found as minima, one with the

experimentally observed bis-envelope conformation and one with a twisted conformation similar to that observed for **3c**. For the tin compounds (**2c** and **3c**) only one minimum corresponding to the twist conformation could be found. Whereas for **2f** the bis-envelope conformation is definitely more stable by 7.4 kJ mol$^{-1}$ the differences for **2a** are very small (0.4 kJ mol$^{-1}$, see also Table 6 and Fig. 5) and for **2b** the twist conformation is 3.65 kJ mol$^{-1}$ lower in energy.

These calculations suggest, that in solution both conformations of **2a** are present. Indeed, a $^{29}$Si-CP-MAS-NMR spectrum of the crystalline compound **2a** shows significant differences of the chemical shift values (27.0 ppm for the central $Si_2Me_2$ unit and 36.4/31.7 ppm for the two $SiMe_2$ units) from those obtained from solution (Table 1), even if one compares the average value of the two crystallographic different $SiMe_2$ units, see Fig. 6.

On the other hand, a $^{29}$Si-CP-MAS-NMR spectrum of $S(SiMe_2-SiMe_2)_2S$ revealed two signals at $-4.83$ and $-4.56$ ppm. This observation is in accordance with the crystal structure analysis [5] showing two crystallographically different silicon atoms while in solution a very similar $^{29}$Si-NMR chemical shift of $-4.76$ ppm was observed [5]. Here, the six-membered heterocycle adopts a chair conformation in solution as well as in the solid state.

Table 4
Selected bond distances and angles of **2e**

| Atoms | Distances (Å) | Atoms | Angles (°) |
|---|---|---|---|
| Si(1)–Si(2) | 2.3275(7) | S(1)–Si(2)–S(4) | 112.89(3) |
| S(1)–Si(2) | 2.1330(7) | S(2)–Si(1)–S(3) | 113.57(3) |
| S(2)–Si(1) | 2.1378(7) | Si(1)–Si(2)–S(1) | 100.58(3) |
| S(3)–Si(1) | 2.1463(7) | Si(1)–Si(2)–S(4) | 100.32(3) |
| S(4)–Si(2) | 2.1486(7) | Si(2)–Si(1)–S(3) | 100.17(3) |
| S(1)–C(1) | 1.863(2) | Si(2)–Si(1)–S(3) | 100.26(3) |
| S(2)–C(1) | 1.865(2) | Si(1)–S(2)–C(1) | 103.11(6) |
| S(3)–C(7) | 1.864(2) | Si(2)–S(1)–C(1) | 103.59(6) |
| S(4)–C(7) | 1.864(2) | Si(1)–S(3)–C(7) | 100.46(6) |
| Si(1)–C(13) | 1.863(2) | Si(2)–S(4)–C(7) | 100.79(6) |
| Si(2)–C(14) | 1.863(2) | S(1)–C(1)–S(2) | 112.37(10) |
| | | S(3)–C(7)–S(4) | 112.25(10) |

Table 5
Selected bond distances and angles of **3c**

| Atoms | Distances (Å) | Atoms | Angles (°) |
|---|---|---|---|
| Si(1)–Si(1a) | 2.333(2) | Se(1)–Si(1)–Se(2a) | 109.51(4) |
| Si(1)–Se(1) | 2.2802(10) | Si(1a)–Si(1)–Se(1) | 105.84(4) |
| Si(1)–Se(2a) | 2.2751(10) | Si(1)–Si(1a)–Se(2) | 106.88(6) |
| Sn(1)–Se(1) | 2.5546(5) | Si(1)–Se(1)–Sn(1) | 98.61(3) |
| Sn(1)–Se(2) | 2.5566(4) | Si(1a)–Se(2)–Sn(1) | 96.39(3) |
| Si(1)–C(3) | 1.861(4) | Se(1)–Sn(1)–Se(2) | 107.79(1) |
| Sn(1)–C(1) | 2.119(4) | C(1)–Sn(1)–C(2) | 120.3(2) |
| Sn(1)–C(2) | 2.126(4) | | |

Table 6
Results of the DFT calculations on $Me_2M(S)_2Si_2Me_2(S)_2MMe_2$ (**2f**, **a–c**; M = C, Si, Ge, Sn) and $Me_2Sn(Se)_2Si_2Me_2(Se)_2SnMe_2$ (**3c**)

| Compound M | **2f** C | | **2a** Si | | **2b** Ge | | **2c** Sn | **3c** Sn |
|---|---|---|---|---|---|---|---|---|
| Conformation | Bis-envelope | Twist | Bis-envelope | Twist | Bis-envelope | Twist | Twist | Twist |
| Total energy (H) | −2487.59397 | −2487.59096 | −2990.56098 | −2990.56125 | −2419.04330 | −2419.04480 | −2418.25497 | −862.39606 |
| Total energy with zero point correction (H) | −2487.34091 | −2487.33809 | −2990.32305 | −2990.32320 | −2418.80780 | −2418.80919 | −2418.02269 | −862.16696 |
| Si–Si (Å) | 2.352 | 2.326 | 2.381 | 2.353 | 2.393 | 2.360 | 2.365 | 2.371 |
| Si–S (Å) | 2.175, 2.158 | 2.160, 2.174 | 2.178, 2.165 | 2.180, 2.166 | 2.178, 2.163 | 2.180, 2.165 | 2.165, 2.185 | 2.333, 2.353 |
| M–S (Å) | 1.884, 1.884 | 1.875, 1.900 | 2.184, 2.178 | 2.189, 2.179 | 2.282, 2.289 | 2.297, 2.284 | 2.445, 2.455 | 2.631, 2.639 |
| Si–S–M (°) | 101.6, 102.8 | 107.1, 103.7 | 100.3, 101.0 | 105.0, 101.2 | 100.3, 101.8 | 104.4, 100.1 | 103.5, 99.1 | 100.8, 96.7 |

If both conformations of **2a** were present in solution, the NMR data of **2a** should be temperature dependent since lower temperature would favor the more stable conformation. Indeed, both the $^{29}Si$- and the $^1H$-NMR spectra show changes with temperature (Fig. 7a,b). Only one of the two $SiMe_2$ proton resonances (A) does not vary significantly with temperature, probably due to identical chemical shift values in both conformations.

For the germanium compound **2b** there is a contradiction between the results of the DFT calculation and the observed molecular structure. Here, crystal packing forces probably stabilize the bis-envelope conformation. On the other hand, the structure of the tin and selenium containing compound **3c** is again in accordance with the result of the calculations. However, it must be noted that there are additional but weak intermolecular contacts between selenium and tin atoms. The interatomic distances are, with values between 4.0 and 4.1 Å, slightly below the sum of the van-der-Waals radii of 4.2 Å, also see Fig. 8. These intermolecular contacts lead to the formation of wavy sheets of silicon, selenium and tin atoms perpendicular to the crystallographic $b$-axis.

Taking into account these intermolecular contacts the coordination number of selenium increases to three with a sum of the three bond angles of 322.6 ° at Se1 and 318.5 ° at Se2 and that of tin reaches six. The coordination sphere at tin can be regarded as a doubly capped tetrahedron characterized by Se1–Sn1–Se1b and Se2–Sn1–Se2b angles of 175.0 and 166.8 °, respectively. Such intramolecular contacts have already been reported for other tin selenium compounds, for example in $Me_2Sn(Se)_2Sn_2Me_4$, here the five-membered $Sn_3Se_2$ heterocycle adopts an envelope conformation and intermolecular Sn–Se contacts of 3.76–4.09 Å are
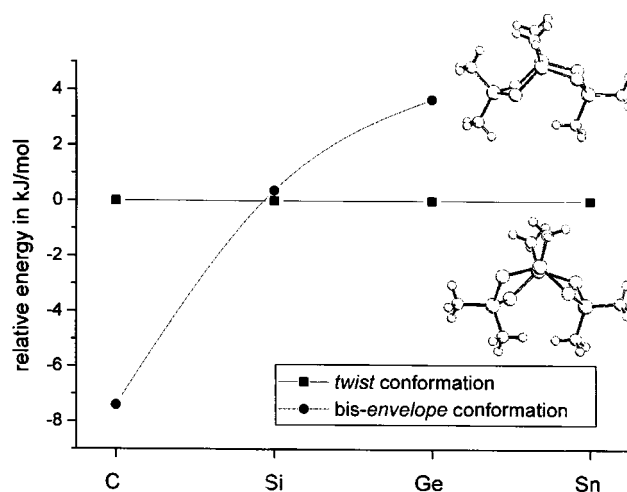


Fig. 5. Relative stabilities of the bis-envelope and twist conformations of $Me_2M(S)_2Si_2Me_2(S)_2MMe_2$, **2f**, **2a–c** (M = C, Si, Ge, Sn) as obtained from DFT calculations at the level B3LYP/6-31G*.
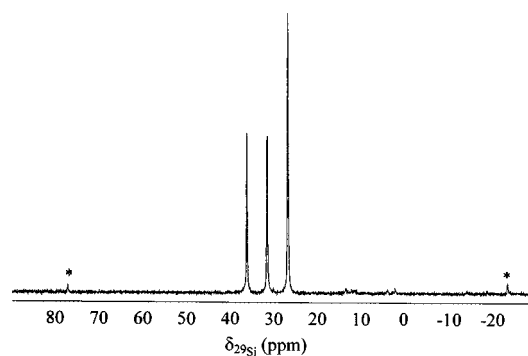


Fig. 6. $^{29}Si$-CP-MAS-NMR spectrum of the solid compound **2a** showing two different signals for the two crystallographically different $SiMe_2$ units and one for the central $Si_2Me_2$ unit.
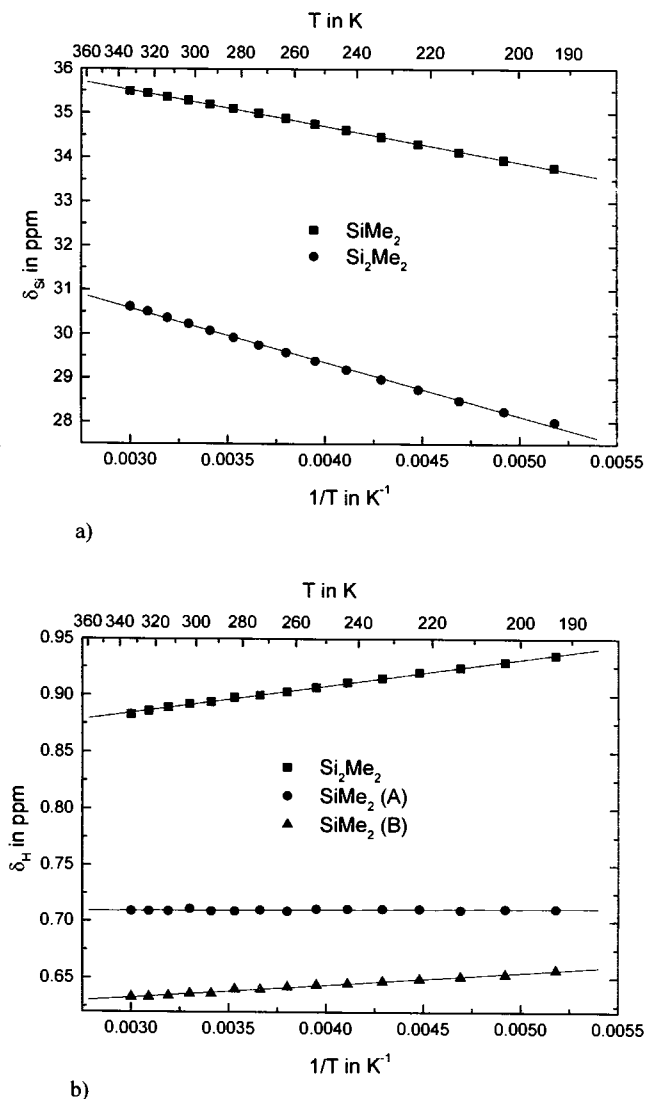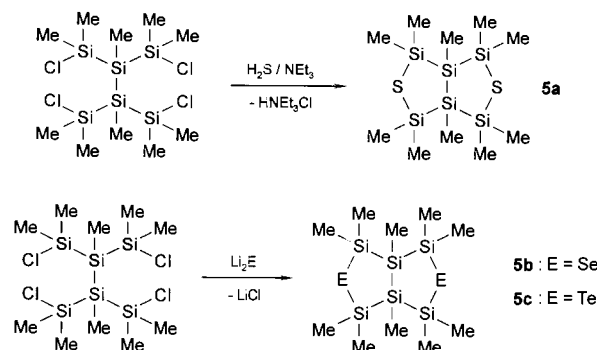
Fig. 7. (a) $^{29}$Si-NMR chemical shifts of **2a** as a function of temperature (−80 to +60 °C). (b) $^1$H-NMR chemical shifts of **2a** as a function of temperature (−80 to +60 °C).



These reactions are surprisingly clean, no other silicon containing by-products have been observed. These reactions show again the high stability of five-membered rings in these systems even though heterocycles with four silicon and one chalcogen atom are formed.

While we have already published the formation and the molecular structure of the sulfur compound **5a**, see Fig. 9 [4], we now succeeded in the preparation of the selenium (**5b**) and tellurium (**5c**) derivatives. The NMR data of **5a**–**c** are summarized in Table 7. Remarkable are the relatively drastic changes of the $^{29}$Si-NMR chemical shifts of the branching SiMe units from E = S to E = Te even though the first coordination sphere at these silicon atoms remains unchanged. As also observed for other silselenanes and -telluranes [5,9] the $^{125}$Te-NMR parameters ($\delta$ and $^1J_{ESi}$) follow the corresponding $^{77}$Se-NMR data of the analogous selenium compounds by a factor of 2.5–2.7.

## 3. Experimental

### 3.1. NMR and GC–MS measurements

All NMR spectra were recorded on a Bruker DPX 400 in CDCl$_3$ solution and with TMS as internal standard for $^1$H, $^{13}$C and $^{29}$Si. External Me$_4$Sn, Ph$_2$Se$_2$ ($\delta_{Se}$ 460 ppm) and Ph$_2$Te$_2$ ($\delta_{Te}$ 422 ppm) in CDCl$_3$ were used as standards for $^{119}$Sn, $^{77}$Se and $^{125}$Te.

In order to obtain a sufficient signal-to-noise ratio of $^{29}$Si-NMR spectra for resolving $^1J_{SiC}$, $^1J_{SiSi}$, $^{1,2}J_{SiSe}$ or $^{1,2}J_{SiTe}$ satellites $^{29}$Si INEPT spectra were also recorded. $^{77}$Se, $^{125}$Te and $^{119}$Sn spectra were determined using an IGATED pulse program.

Temperature dependent NMR spectra of **2a** were done in a solution of 60 vol% THF and 40 vol% CDCl$_3$ and TMS as internal standard. $^1$H- and $^{29}$Si-INEPT-NMR spectra were taken over a temperature range from −80 to +60 °C in steps of 10 °C.

$^{29}$Si-CP-MAS-NMR spectra were recorded on a Bruker MSL 300 using the CPCYCL pulse program, spinning frequency 3000 Hz, contact time 5 ms, calibration with external Q$_8$M$_8$.

Mass spectra were measured on a Hewlett–Packard 5971 (ionization energy 70 eV, column 30 m × 0.25

observed [7]. On the other hand, no intermolecular contacts are formed in the case of the five-membered tin chalcogen heterocycles $^tBu_2Sn(E)_2Sn^t_2Bu_4$ (E = S, Se, Te). The bulky $^tBu$ substituents prevent such contacts, force the five-membered ring into a planar (E = S) or almost planar (E = Se) conformation and increase the Sn−E bond lengths [8].

### 2.3. 3,7-Dichalcogena-1,2,4,5,6,8-hexasila-bicyclo[3.3.0]octanes (5a–c)

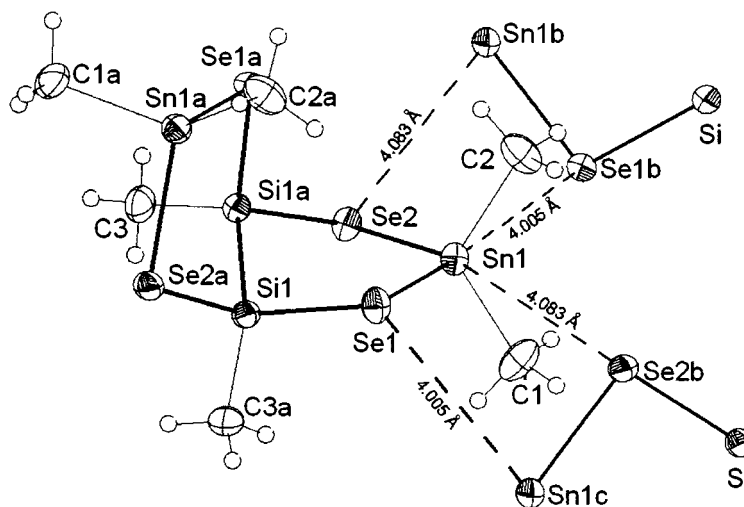A different class of silchalcogenanes is accessible from the doubly branched hexasilane (ClMe$_2$Si)$_2$-SiMeSiMe(SiMe$_2$Cl)$_2$:

Fig. 8. Intermolecular contacts between tin and selenium in **3c**.

mm × 0.25 μm, phenylmethylpolysiloxane, column temperature 80 °C (3 min)/20 K min$^{-1}$, He flow of 0.5 ml min$^{-1}$).

### 3.2. Crystal structure analyses

X-ray structure analysis measurements were performed on a Bruker SMART CCD. Crystal data of **2b**, **2e** and **3c** as well as data collection and refinement details are given in Table 8.

The unit cell dimensions were determined with the program SMART [10]. For data integration and refinement of the unit cell parameters the program SAINT [10] was used. The space group was determined with the aid of the programs XPREP [10] (**2e** and **3c**) and ABSEN [11] (**2b**). All data were corrected for absorption applying SADABS [12]. The structures were solved using direct methods (SHELX-97 [13] for **2e** and **3c**, SIR97 [14] for **2b**), refined using least-squares methods (SHELX-97) and drawn using ZORTEP [15]. The ellipsoids at the non-hydrogen atoms are at the 50% probability level. The protons of the methyl groups in **2b** could be located but not refined to sufficient quality. They have been generated using the FIX 137 command. Because of the mirror plane in **2b** the hydrogen positions at C2, C4 and C5 are duplicated.

### 3.3. Theoretical methods

The ab initio molecular orbital calculations were carried out using the GAUSSIAN 98 series of programs [16]. 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) [17,18]. Geometry optimizations, harmonic frequencies, and zero-point vibrational energies were

calculated with the polarized 6-31G* basis set for C, H and Si [19,20] and with effective core potentials for Ge, Sn and Se [21]. All structures were identified as true local minima by their Hessian matrices.

### 3.4. Starting materials

$H_2S$, Se, Te, triethylamine, 1 M LiBEt$_3$H in THF (super hydride), Me$_2$SiCl$_2$, Me$_2$GeCl$_2$, Me$_2$SnCl$_2$, Ph$_2$SnCl$_2$ were commercially available. Compound **1** [22], $(CH_2)_5C(SH)_2$ [6] and $(ClMe_2Si)_2Si_2Me_2(SiMe_2Cl)_2$ [23] were prepared as described previously. 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.

### 3.5. Preparation of $R_2M(S)_2Si_2Me_2(S)_2MR_2$ *(2a–d)* $(MR_2 = SiMe_2, GeMe_2, SnMe_2, SnPh_2)$

In a typical experiment 2 mmol of the corresponding dichloro compound (Me$_2$SiCl$_2$, Me$_2$GeCl$_2$, Me$_2$SnCl$_2$ or Ph$_2$SnCl$_2$) was dissolved in 40 ml of hexane (or toluene in the cases of the organotin chlorides) and 0.456 g (2
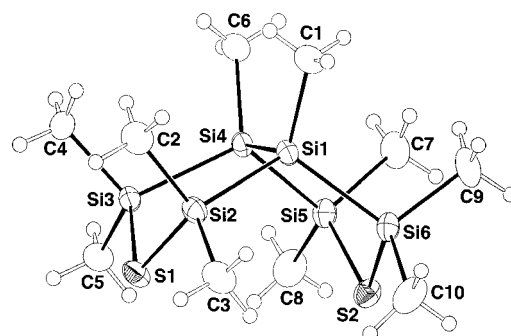


Fig. 9. Molecular structure of **5a** [4].

Table 7
NMR data (ppm, Hz) of the 3,7-dichalcogena-1,2,4,5,6,8-hexasilabicyclo[3.3.0]octanes $E(Me_2Si)_2Si_2Me_2(SiMe_2)_2E$ (E = S, Se, Te (**5a–c**)
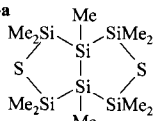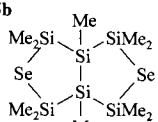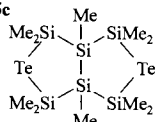
| compound | $\delta_E$ | group | $\delta_{Si}$ | $^1J_{SiSi}$ | $J_{SiE}$ | $\delta_C$ | $^1J_{SiC}$ | $\delta_H$ |
|---|---|---|---|---|---|---|---|---|
| **5a** | - | SiMe | -71.3 | 64.1 | - | -12.05 | | 0.28 |
| | | SiMe₂ | 16.4 | | - | 3.78 / 4.36 | 45.2 | 0.49 / 0.54 |
| **5b** | -278 | SiMe | -63.7 | 64.4 | $^2J$: 5.4 | -11.3 | 33.9 | 0.26 |
| | | SiMe₂ | 12.4 | | $^1J$ 107.9 | 3.81 / 3.95 | 43.0 | 0.59 / 0.65 |
| | | | | | $^3J$ 17.1 | | | |
| **5c** | -736 | SiMe | -49.8 | 58.8 | $^2J$ 21.4 | -10.3 | | 0.87 |
| | | SiMe₂ | -7.6 | | $^1J$ 270.2 | 3.42 / 3.91 | 42.5 | 1.24 |

Table 8
Crystal data of **2b**, **2e** and **3c** as well as data collection and refinement details

| | **2b** | **2e** | **3c** |
|---|---|---|---|
| Crystal system | Orthorhombic | Triclinic | Orthorhombic |
| Space group | $Pnma$ | $P\bar{1}$ | $Pbcn$ |
| Unit cell dimensions | | | |
| $a$ (Å) | 12.2673(9) | 6.92390(10) | 9.81560(10) |
| $b$ (Å) | 9.9225(8) | 9.4610(2) | 14.2553(2) |
| $c$ (Å) | 13.7735(10) | 15.6112(3) | 13.1109(2) |
| $\alpha$ (°) | 90 | 78.0530(10) | 90 |
| $\beta$ (°) | 90 | 85.9290(10) | 90 |
| $\gamma$ (°) | 90 | 71.0050(10) | 90 |
| Volume (Å³); $Z$ | 1676.5(2); 4 | 946.01(3); 2 | 1834.53(4); 4 |
| $D_{calc.}$ (g cm⁻³) | 1.663 | 1.330 | 2.533 |
| Linear absorption coefficient (mm⁻¹) | 4.196 | 0.618 | 10.762 |
| Radiation used | Mo–K$_\alpha$ | Mo–K$_\alpha$ | Mo–K$_\alpha$ |
| Temperature (K) | 173(2) | 173(2) | 173(2) |
| Scan method | ω scans | ω scans | ω scans |
| Absorption correction | Empirical | Empirical | Empirical |
| Max/min transmission | 0.519/0.487 | 0.902/0.693 | 0.119/0.052 |
| Measured reflections | 6286 | 7668 | 13047 |
| Independent reflections | 2517 | 5143 | 2715 |
| Observed reflections | 2171 | 3792 | 2170 |
| $R_{int}$ | 0.0206 | 0.0253 | 0.0516 |
| $\theta$ Range for collection (°) | 2.22–30.69 | 1.33–30.67 | 2.52–30.84 |
| Completeness to $\theta_{max}$ (%) | 91.9 | 88.0 | 93.9 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| Final $R_1$ $(I>2\sigma(I))$ | 0.0216 | 0.0349 | 0.0278 |
| $R_1$ (all data) | 0.0270 | 0.0591 | 0.0405 |
| H-locating and refining | DIFMAP/REFALL | DIFMAP/REFALL | DIFMAP/mixed |
| Goodness-of-fit on $F^2$ | 1.046 | 1.007 | 1.081 |
| Max/min e-density (e Å⁻³) | 0.436/−0.899 | 0.381/−0.273 | 0.961/−1.079 |

mmol) of compound **1** was added. With stirring, a stream of dried $H_2S$ was passed through the solution while 1.66 ml (12 mmol) of $NEt_3$ was slowly added by a syringe. A white precipitation of triethylammonium chloride appeared immediately. After stirring for 1 h the mixture was filtered and the solvent removed to yield the bicyclo[3.3.0]octanes as a white crystalline

residue. The products were recrystallized from hot saturated solutions in hexanes to give single crystals suitable for X-ray analysis.

**2a**: m.p. 75–77 °C, **2b**: m.p. 127 °C, **2c**: m.p. 184–187 °C, **2d**: m.p. 130 °C.

**2a**: GC–MS ($m/e$, rel. int.): 330 (M⁺, 36), 315 ($Me_5Si_4S_4$, 26), 165 ($Me_3Si_2S_2$, 100), 73 ($Me_3Si$, 20).

**2b**: GC–MS: 420 (M$^+$ ($^{74}$Ge$^{72}$Ge), 1.5), 405 (Me$_5$$^{74}$Ge$^{72}$GeSi$_2$S$_4$, 73), 301 (Me$_5$$^{74}$GeSi$_2$S$_3$, 30), 211 (Me$_3$$^{74}$GeSiS$_2$, 100), 181 (Me$^{74}$GeSiS$_2$, 21), 165 (Me$_3$Si$_2$S$_2$, 51), 135 (MeSi$_2$S$_2$, 10), 119 (Me$_3$$^{74}$Ge, 36), 105 (Me$_3$SiS, 24), 89 (Me$^{74}$Ge, 16), 73 (Me$_3$Si, 74). (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 [24].)

**2c**: Anal. Calc. for C$_6$H$_{18}$S$_4$Si$_2$Sn$_2$: C, 14.07; H, 3.54; S, 25.05; Found: C, 14.78; H, 3.59; S, 24.89%.

A molar ratio of Me$_2$MCl$_2$ to **1** of 1:1 instead of 2:1 was applied in order to prevent the formation of the six-membered heterocycles (Me$_2$MS)$_3$ as by-products. Under the reaction conditions excess **1** forms the tetracyclic cage compound Me$_6$Si$_6$S$_6$ [4], which is insoluble in hexane and can therefore be removed together with the ammonium salt by filtration.

### 3.6. (CH$_2$)$_5$C(S)$_2$Si$_2$Me$_2$(S)$_2$C(CH$_2$)$_5$ (2e)

A total of 0.228 g (1 mmol) of compound **1** was dissolved in 40 ml of hexane, 0.296 g (2 mmol) of (CH$_2$)$_2$C(SH)$_2$ and 0.55 ml (4 mmol) of NEt$_3$ were added under stirring. After 1 h the mixture was filtered from the precipitated ammonium salt and the solvent removed to yield **2e** as colorless crystals without any by-products. The product was recrystallized from hot hexane, m.p. 130 °C.

### 3.7. Me$_2$M(E)$_2$Si$_2$Me$_2$(E)$_2$MMe$_2$ (3a–4c) (M = Si, Ge, Sn; E = Se, Te)

#### 3.7.1. Selenium compounds (3a–c)

A total of 0.16 g (2 mmol) of black selenium powder was reacted with a mixture of 4 ml of a 1 M solution of Li[BEt$_3$H] in THF and an additional 5 ml of THF with stirring. The selenium dissolved within a few seconds with formation of a white suspension of Li$_2$Se. A mixture of 0.114 g (0.5 mmol) of **1** and 1 mmol of Me$_2$MCl$_2$ dissolved in 5 ml of hexane (or toluene in the case of Me$_2$SnCl$_2$) was added to the suspension. The precipitation of Li$_2$Se disappeared almost immediately. After stirring for 30 min at room temperature (r.t.) the solvents were removed in vacuo and replaced by 10 ml of hexane. The solution was separated from precipitated LiCl. Removal of the solvent produced **3a–c** as colorless crystalline powders. Crystals of **3c** were grown from toluene solution.

#### 3.7.2. Tellurium compounds (4a–c)

A total of 0.25 g (2 mmol) of tellurium powder (200 mesh) was added to a mixture of 4 ml of a 1 M solution of Li[BEt$_3$H] in THF and an additional 5 ml of THF under stirring. After 5 min the tellurium started to react with formation of a deep purple solution which became dark red after 1 h at r.t.

As described for the selenium compounds a mixture of 0.114 g (0.5 mmol) of **1** and 1 mmol of Me$_2$MCl$_2$ dissolved in 5 ml of hexane (or toluene in the case of Me$_2$SnCl$_2$) was added to the Li$_2$Te suspension. The analogous work-up yielded the tellurium containing bicyclo[3.3.0]octanes **4a–c** as light yellow crystalline residues which are extremely air sensitive and turn black within seconds but are stable under argon at r.t. for weeks.

### 3.8. 3,7-Dichalcogena-1,2,4,5,6,8-hexasilabicyclo[3.3.0]-octanes (5a–c)

The preparation of **5a** starting from the doubly branched hexasilane, H$_2$S and NEt$_3$ has already been described in Ref. [4]. The addition of 0.23 g (0.5 mmol) of (ClMe$_2$Si)$_2$Si$_2$Me$_2$(SiMe$_2$Cl)$_2$ to a suspension of 1 mmol Li$_2$Se or Li$_2$Te (prepared as described above) and work-up as described in Section 3.5 yielded the selenium compound **5b** as relatively low melting point crystalline needles (m.p. 60 °C) and the tellurium derivative **5c** as a light yellow, extremely air sensitive oil.

**5a**: GC–MS ($m/e$, relative intensity): 382 (M$^+$, 73), 367 (Me$_9$Si$_6$S$_2$, 38), 323 (Me$_7$Si$_5$S$_2$CH$_2$, 32), 309 (Me$_7$Si$_5$S$_2$, 61), 277 (Me$_7$Si$_5$S, 13), 249 (Me$_7$Si$_4$S, 19), 131 (Me$_5$Si$_2$, 16), 73 (Me$_3$Si, 100), 59 (Me$_2$SiH, 15).

**5b**: GC–MS: 478 (M$^+$, 19), 463 (Me$_9$Si$_6$$^{80}$Se$_2$, 15), 419 (Me$_7$Si$_5$$^{80}$Se$_2$CH$_2$, 9), 405 (Me$_7$Si$_5$$^{80}$Se$_2$CH$_2$, 13), 325 (Me$_7$Si$_5$$^{80}$Se, 14), 297 (Me$_7$Si$_4$$^{80}$Se,11), 267 (Me$_5$Si$_4$$^{80}$Se, 6), 239 (Me$_5$Si$_3$$^{80}$Se, 7), 159 (Me$_5$Si$_3$, 11), 131 (Me$_5$Si$_2$, 23), 73 (Me$_3$Si, 100), 59 (Me$_2$SiH, 12). (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 [24].)

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 163663 for compound **2b**, CCDC no. 163664 for compound **2e** and CCDC no. 163665 for compound **3c**. 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).

of Inorganic Chemistry, TU Chemnitz for the access to the X-ray facility used to determine the single-crystal structures.

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