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# Heteronoradamantanes $Me_2Si_2(RM)_2E_5$ ($RM = MeGe, PhSn; E = S, Se$)

Uwe Herzog [a,*], Horst Borrmann [b]

[a] *Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Str. 29, D-09596 Freiberg, Germany*
[b] *Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, D-01187 Dresden, Germany*

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## Abstract

The reaction of a 1:2 molar mixture of 1,2-$Me_2Si_2Cl_4$ and $MeGeCl_3$ with $H_2S/NEt_3$ yielded $Me_2Si_2(MeGe)_2S_5$ (**1**), the first mixed silicon–germanium chalcogenide with a noradamantane-like structure, while the treatment of a 1:2 mixture of 1,2-$Me_2Si_2Cl_4$ and $PhSnCl_3$ with $Li_2Se$ resulted in the formation of the first silicon- and tin-containing noradamantane $Me_2Si_2(PhSn)_2Se_5$ (**2**). Both compounds have been characterized by NMR spectroscopy ($^1H$, $^{13}C$, $^{29}Si$, $^{77}Se$ and $^{119}Sn$). The molecular structure of **1** in the solid state is reported.

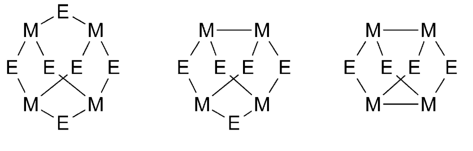
*Keywords:* Disilane; Chalcogen; Adamantane; Noradamantane

## 1. Introduction

Adamantane-like structures are frequently observed in the chemistry of inorganic and organometallic compounds [1]. Silsesquithianes [2,3] and selenanes [4] as well as related germanium [5,6] and tin [7–9] compounds $(RM)_4E_6$ ($M = Si, Ge, Sn; E = S, Se$) which usually adopt adamantane-like structures can easily be obtained by reaction of an organotrichloro derivative $RMCl_3$ with either $H_2S$/base or an alkaline chalcogenide $M^I_2E$. Furthermore, several chalcogenosilicates [10–12], germanates [13–17] and stannates [18,19] with adamantane-like structures $M^I_4[M_4E_{10}]$ ($M^I = Na, K, NR_4$; $M = Si, Ge, Sn$; $E = S, Se, Te$) have been reported. When one chalcogen atom is removed from the adamantane structure the resulting cage $(RM)_4E_5$ is called noradamantane while removal of two chalcogen atoms results in bis-noradamantanes $(RM)_4E_4$ (Scheme 1).

Ando et al. [20] reported first examples of such cages by reaction of 1,2-$^tBu_2M_2Cl_4$ ($M = Si, Ge$) with $Li_2E$ ($E = S, Se$). While the expected bis-noradamantane $(^tBuGe)_4S_4$ could be isolated for $M = Ge$ and $E = S$, reactions for $M = Si$ and $E = S$ or Se resulted in the cleavage of one Si–Si bond and the formation of noradamantanes $(^tBuSi)_4S_5$ in low yield. A similar observation was made in the reaction of 1,2-$Me_2Si_2Cl_4$ with $Li_2Se$, which exclusively yielded the noradamantane $(MeSi)_4Se_5$ (**4**) [21], while the reaction of $Me_2Si_2Cl_4$ with $H_2S/NEt_3$ yielded the tetracyclic cage compound $Me_6Si_6S_6$ formed by three disilane units [22]. In a more straightforward reaction the treatment of a 1:2 molar mixture of 1,2-$Me_2Si_2Cl_4$ and $MeSiCl_3$ with $H_2S/NEt_3$ resulted in the formation of $(MeSi)_4S_5$ (**3**) [21]. The first silicon-containing bis-noradamantane, $(RSi)_4S_4$, was isolated by reaction of $R_2Si_2(NH_2)_4$ ($R = CH(SiMe_3)_2$) with $H_2S$ [23].

However, no examples with two different Group 14 elements in the noradamantane or bis-noradamantane cages are known so far.



Scheme 1.

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* Corresponding author. Tel.: +49-3731-394343; fax: +49-3731-394058.
*E-mail address:* uwe.herzog@chemie.tu-freiberg.de (U. Herzog).

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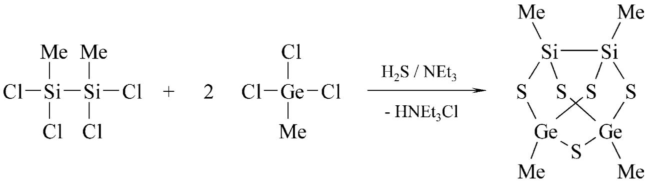
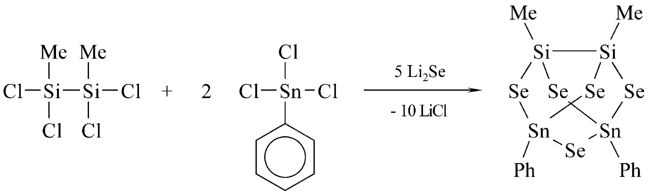
## 2. Results and discussion

The reaction of a mixture of 1,2-$Me_2Si_2Cl_4$ and $MeGeCl_3$ with $H_2S$ and $NEt_3$ yielded the expected silicon–germanium noradamantane (**1**) (see Eq. (1)):



(1)

A similar reaction with $MeSnCl_3$ instead of $MeGeCl_3$ did not yield the corresponding tin-containing noradamantane; however, treatment of a 1:2 molar mixture of 1,2-$Me_2Si_2Cl_4$ and $PhSnCl_3$ with $Li_2Se$ in THF gave yellow crystals of **2**, a silicon–tin noradamantane (see Eq. (2)):



(2)

Several attempts to produce the corresponding sulfur compound via reactions of 1,2-$Me_2Si_2Cl_4+PhSnCl_3$ with either $Li_2S$ or $H_2S/NEt_3$ have been performed without success. These observations show that formation of the heteronoradamantanes by these methods strongly depends on the relative reactivities of the two chlorocompounds used. If one of the two starting materials reacts much faster with $H_2S/NEt_3$ or $Li_2E$, the expected heteronoradamantanes will not be formed.

The molecular structure of **1** was determined, as depicted in Fig. 1. **1** crystallizes in the orthorhombic space group *Pbcn* ($Z = 4$). The molecule contains a $C_2$ axis through S1, which intersects the bond Si1–Si1a. Selected bond lengths and angles are given in Table 1.

Despite different crystal symmetry, the molecular geometry of **1** is similar to that of **3** as reported in Ref. [21]. Like in **3** the Si1–Si1a bond is slightly longer than the average Si–Si bond length of 2.33–2.34 Å in disilanes like $Si_2Me_6$ or $Si_2Cl_6$ [24]. The Si–S–Ge angles, which are part of five-membered rings, are 10° smaller than the angle Ge1–S1–Ge1a which is only part of six-membered rings of the noradamantane cage. The dihedral angles S2–Si1–Si1a–S3a (1.52°) and C2–Si1–Si1a–C2a (2.01°) reveal that both five-membered rings $Si_2S_2Ge$ adopt almost an envelope conformation. The arrangement of the five sulfur atoms is approximated by a tetragonal pyramid with S1 in the apical position. S2, S3, S2a and S3a form an almost ideal square (S2–S3: 3.512 Å, S2–S3a: 3.557 Å, S3–S2–S3a: 89.81°, S2–S3–S2a: 90.18°).

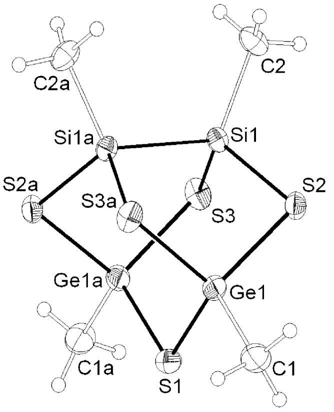


Fig. 1. Molecular structure of **1**. Thermal ellipsoids are at the 30% probability level.

Table 1
Selected bond distances and angles of **1**

| | |
|---|---|
| *Bond length (Å)* | |
| Si1–Si1a | 2.3648(12) |
| Si1–S2 | 2.1464(8) |
| Si1–S3 | 2.1489(8) |
| Ge1–S1 | 2.2333(7) |
| Ge1–S2 | 2.2236(7) |
| Ge1–S3a | 2.2201(7) |
| Ge1–C1 | 1.930(2) |
| Si1–C2 | 1.849(3) |
| *Bond angle (°)* | |
| Si1a–Si1–S2 | 106.89(4) |
| Si1a–Si1–S3 | 105.33(4) |
| S2–Si1–S3 | 109.69(4) |
| Ge1–S1–Ge1a | 105.10(4) |
| Si1–S2–Ge1 | 94.77(3) |
| Si1–S3–Ge1a | 95.14(3) |
| S1–Ge1–S2 | 110.44(2) |
| S1–Ge1–S3a | 111.54(2) |
| S2–Ge1–S3a | 106.34(3) |

Both new heteronoradamantanes were characterized by multinuclear NMR spectroscopy. Especially for **2** the NMR spectra provide additional information about connectivities in the noradamantane cage through the occurrence of several satellites due to $^1J_{SiSe}$, $^2J_{SiSe}$, $^2J_{SiSn}$, $^2J_{SnSn}$ and $^1J_{SnSe}$ (see Figs. 2–4). As expected for a noradamantane cage, there are two $^{77}$Se-NMR resonances in a 4:1 intensity ratio, in which the lower signal corresponds to the selenium atom which connects the two tin atoms.

The NMR data of **1** and **2** including all observed coupling constants are given in Table 2 and may be compared with those of the silicon-based noradamantanes $Me_4Si_4E_5$ (**3**, **4**). The NMR data of the disilane units in **1** and **2** are similar to the values found in **3** and **4**

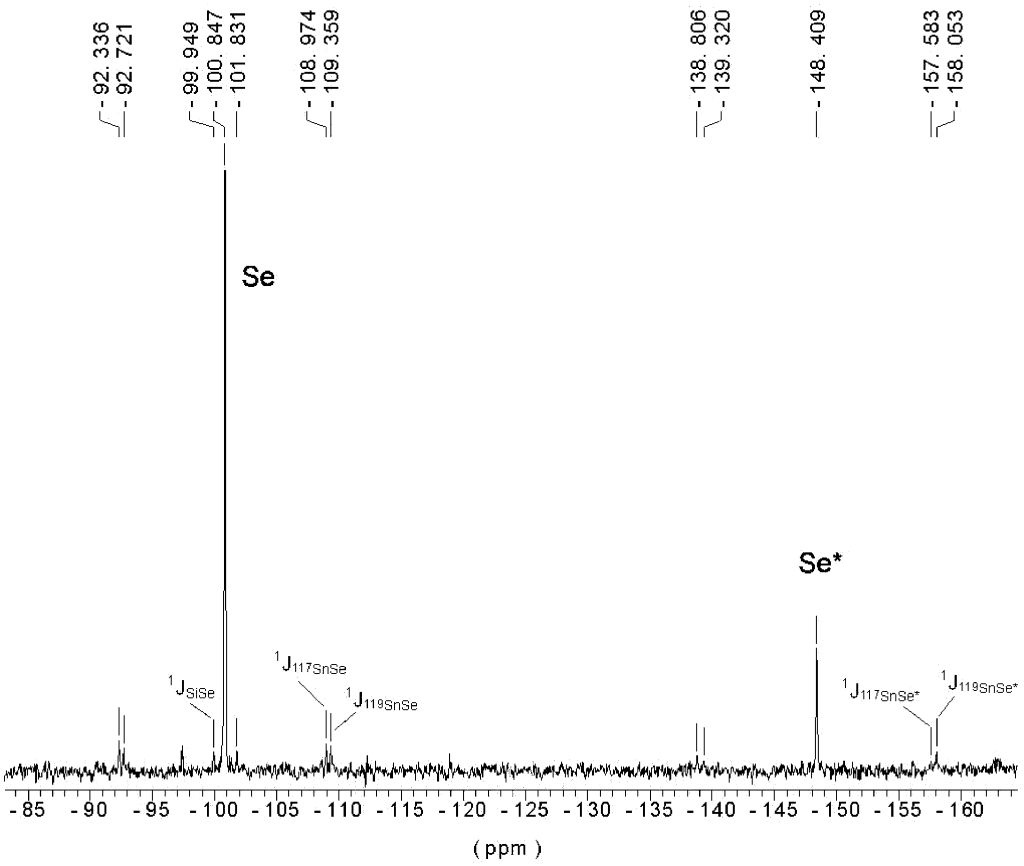


Fig. 2. $^{77}$Se-NMR spectrum of **2** showing the two different selenium sites. The satellites are caused by couplings with $^{119/117}$Sn and $^{29}$Si nuclei.

for the same element E. As observed previously for other mixed silicon–germanium and silicon–tin chalcogenides, the $^{29}$Si-NMR resonances show a low-field shift when germanium is introduced into the ring system instead of silicon, while a high-field shift is observed for tin [25,26].

The $^{77}$Se-NMR signal of the Si–Se–Sn linkage in **2** is shifted by about 50 ppm to higher field with respect to $-53$ ppm as observed in **4**, while more than twice this effect is observed for the Sn–Se*–Sn linkage in comparison with Si–Se*–Si in **4**. The observed $^1J_{SnSe}$ coupling constants are by a factor of 9 larger than the corresponding $^1J_{SiSe}$ in **4**.

## 3. Experimental

### 3.1. NMR and GC–MS measurements

All NMR spectra were recorded in 10-mm sample tubes on a Bruker DPX 400 in $CDCl_3$ solution and with TMS as internal standard for $^1$H, $^{13}$C and $^{29}$Si. External $Me_4Sn$ and $Ph_2Se_2$ ($\delta_{Se}$ 460 ppm) in $CDCl_3$ were used as standards for $^{119}$Sn and $^{77}$Se.

$^{29}$Si spectra were recorded using a refocused INEPT experiment. $^{77}$Se and $^{119}$Sn spectra were obtained applying an IGATED pulse sequence. The assignment of the ipso carbon atoms in the phenyl rings in **2** was simplified by recording a $^{13}$C APT spectrum.

Mass spectra were measured on a Hewlett-Packard 5971 (ionization energy: 70 eV, column: 30 m $\times$ 0.25 mm $\times$ 0.25 μm, phenylmethylpolysiloxane, column temperature: 80 °C (3 min)/20 K min$^{-1}$, He flow: 0.5 ml min$^{-1}$).

### 3.2. Crystal structure analysis

The X-ray structure analysis measurements of **1** were performed on a Rigaku AFC7 with Mercury CCD at room temperature. Crystal data—size: $0.40 \times 0.08 \times 0.05$ mm$^3$; formula weight: 421.84 g mol$^{-1}$; space group: *Pbcn* (orthorhombic); unit cell: $a = 11.5972(10)$ Å, $b = 12.0210(10)$ Å, $c = 10.7856(9)$ Å; volume: 1503.6(2) Å$^3$; density (calc.): 1.863 g cm$^{-3}$; and linear absorption coefficient: 4.813 mm$^{-1}$.

For data collection, unit cell refinement and data reduction of **1**, the program package Crystal Clear [27] was used. The structure was solved using direct methods (SHELXS-97 [28]), refined using least-squares methods

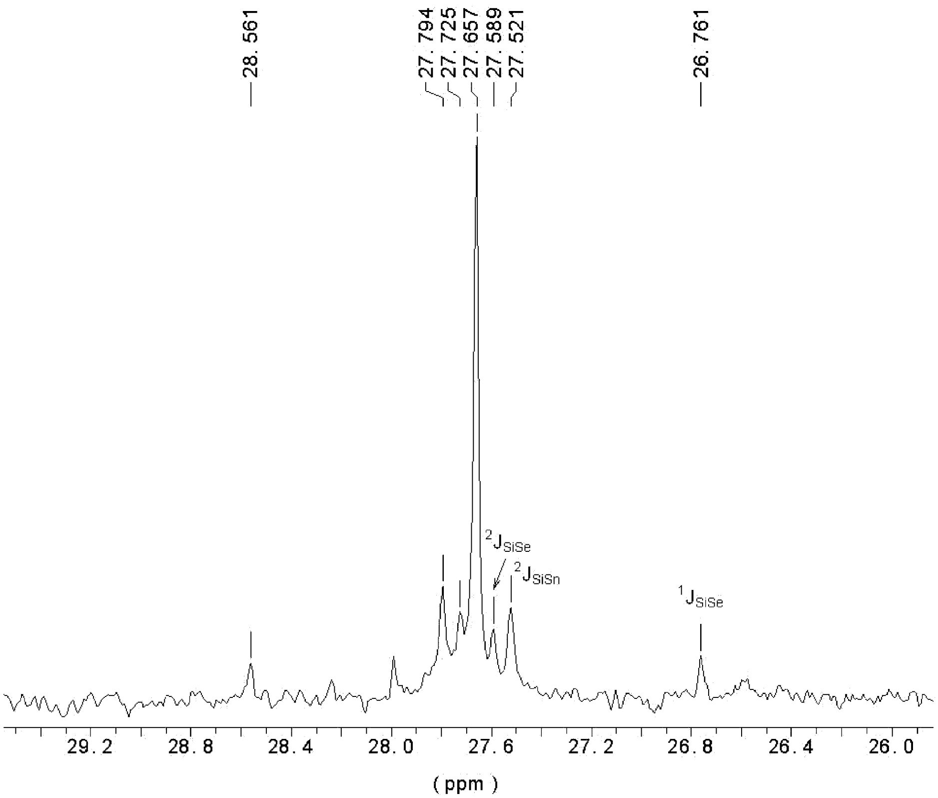


Fig. 3. ${}^{29}$Si-NMR spectrum of **2** with the satellites caused by coupling with ${}^{77}$Se (${}^1J_{SiSe}$ and ${}^2J_{SiSe}$) and ${}^{119/117}$Sn (${}^2J_{SiSn}$).

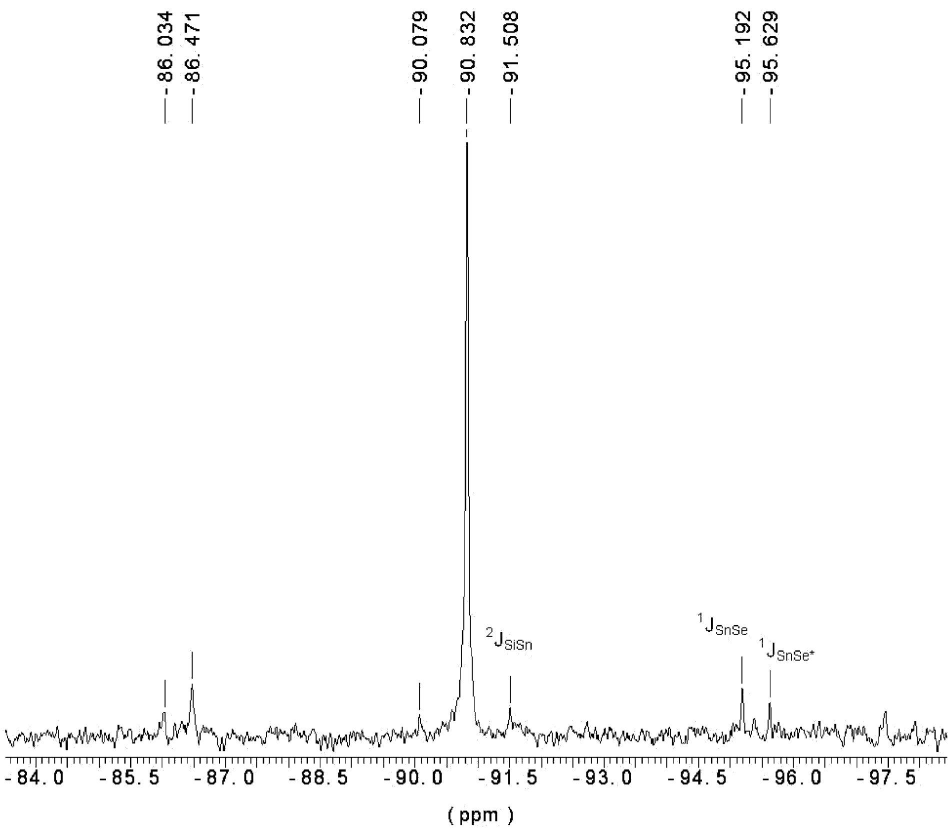
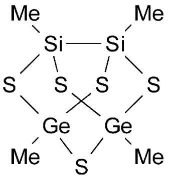
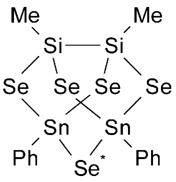
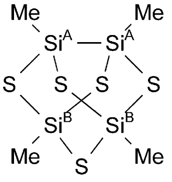
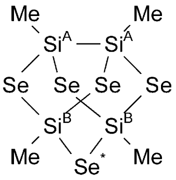


Fig. 4. ${}^{119}$Sn-NMR spectrum of **2** showing two sets of coupling satellites for ${}^{77}$Se (${}^1J_{SnSe}$ and ${}^1J_{SnSe*}$) and satellites caused by ${}^{29}$Si (${}^2J_{SiSn}$).

Table 2
Nmr data of Noradamantanes $Me_2Si_2(E)_4(MR)_2E$

| | compound | $\delta_{Se}$ | $\delta_{Si}$ / $\delta_{Sn}$ | $^nJ_{SiSe}$ $^nJ_{SnSe}$ | $\delta_C$ | $^1J_{SiC}$ | $\delta_H$ |
|---|---|---|---|---|---|---|---|
| **1** |  | - | Si: 29.93 | - | 2.95 | 52.2 | 1.04 |
| | | | Ge: - | | 12.96 | - | 1.39 |
| **2** |  | | Si: 27.66 | $^1J_{SiSe}$: 143.1 | 7.03 | | 1.20 |
| | | Se: -101 | | $^2J_{SiSe}$: 10.9 | | | |
| | | Se*: -148 | Sn: -90.8 | $^1J_{SnSe}$: 1300 | i: 139.07 | | |
| | | | $^2J_{SiSn}$: 22.1 | $^1J_{SnSe*}$: 1432 | o: 134.23 | | o: 7.62 |
| | | | $^2J_{SnSn}$: 213 | | m: 129.46 | | m+p: 7.47 |
| | | | | | p: 131.26 | | |
| **3** |  | - | $Si^A$: 23.9 | - | 1.8 | 53.0 | 1.05 |
| | | | $Si^B$: 27.7 | | 8.8 | 65.6 | 1.06 |
| **4** |  | Se: -53 | $Si^A$: 28.9 | $^1J_{SiSe}$: 134.1 | 2.6 | | 1.22 |
| | | Se*: -12 | | $^2J_{SiSe}$: 9.2 | | | |
| | | | $Si^B$: 3.5 | $^1J_{SiSe}$: 147.7 | 10.4 | | 1.34 |
| | | | | $^1J_{SiSe*}$: 156.5 | | | |

(E = S, Se; MR = SiMe, GeMe, SnPh).

(SHELXL-97 [28]) and drawn using DIAMOND [29]. The ellipsoids of non-hydrogen atoms are shown at the 30% probability level. All hydrogen atoms were localized from Fourier difference maps.

Absorption correction: numerical, measured reflections: 10 993, independent reflections: 1779, observed reflections: 1412 ($I > 2\sigma_I$), $R_{int}$: 0.0316, index ranges: $-15 \le h \le 15$, $-14 \le k \le 15$, $-13 \le l \le 12$, number of parameters: 62, final $R_1$: 0.0268 ($I > 2\sigma_I$), $R_1$: 0.0431 (all data), $wR_2$: 0.0600 ($I > 2\sigma_I$), $wR_2$: 0.0633 (all data), goodness-of-fit: 1.031, max./min. residual electron density: +0.665/−0.267 e Å$^{-3}$.

### 3.3. Starting materials

$H_2S$, Se, triethylamine, 1 M $LiBEt_3H$ in THF (Super Hydride®), $MeGeCl_3$, $MeSnCl_3$ and $PhSnCl_3$ were commercially available. 1,2-$Me_2Si_2Cl_4$ was prepared as described previously [30]. 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. 1,3,5,7-Tetramethyl-2,4,6,8,9-pentathia-3,7-disila-1,5-digermatricyclo[3.3.1.0$^{3,7}$]nonane (1)

0.23 g (1.0 mmol) 1,2-$Si_2Me_2Cl_4$ and 0.20 g (1.0 mmol) $MeGeCl_3$ were dissolved in 30 ml hexane and dried $H_2S$ was bubbled through the stirred solution while 0.97 ml (7.0 mmol) $NEt_3$ was slowly added. After stirring for 1 h, the mixture was filtered from precipitated $HNEt_3Cl$ and the solvent was removed in vacuo yielding colorless crystals of **1** (0.12 g, 57%); m.p.: 176 °C. Excess 1,2-$Si_2Me_2Cl_4$ reacts with $H_2S/NEt_3$ to form $Me_6Si_6S_6$ [22] which is almost insoluble in hexane and is easily removed by filtration together with the ammonium salt.

**1** GC–MS (*m/e*, rel. int.): 422 ($M^+$, 7), 407 (M − Me, 40), 347 ($Me_3SiGe_2S_4$, 1), 303 ($Me_3Si_2GeS_4$, 100), 288 ($Me_2Si_2GeS_4$, 5), 182 ($Me_2Si_2S_3$, 21), 167 ($MeSi_2S_3$, 13), 75 (MeSiS, 31); elemental analysis: $C_4H_{12}Ge_2S_5Si_2$

($M = 421.84$ g mol$^{-1}$, Calc./Found): C, 11.39/11.86; H, 2.87/3.02%.

An analogous reaction with $MeSnCl_3$ instead of $MeGeCl_3$ in either hexane or toluene as a solvent yielded no product after filtration and removal of the solvent in vacuo.

### *3.5. 1,5-Diphenyl-3,7-dimethyl-2,4,6,8,9-pentaselena-3,7-disila-1,5-distannatricyclo[3.3.1.0$^{3,7}$]nonane (**2**)*

0.14 g (0.6 mmol) 1,2-$Si_2Me_2Cl_4$ and 0.36 g (1.2 mmol) $PhSnCl_3$ were dissolved in 1 ml THF and this mixture was added to a $Li_2Se$ solution prepared from 0.24 g (3.0 mmol) selenium powder and 6.0 ml 1 M $LiBEt_3H$ in THF at 0 °C. After stirring for 30 min, the solvent was removed in vacuo and the residue was dissolved in 10 ml toluene. After filtration from the lithium salts, the solvent was removed to yield 0.25 g (0.28 mol, 47%) **2** as yellow microcrystalline powder (m.p.: $>160$ °C (decomposition)), insoluble in hexane but soluble in toluene and $CDCl_3$.

An analogous reaction with a $Li_2S$ solution (prepared from sulfur and 1 M $LiBEt_3H$ in THF) did not give an isolable product.

## 4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 201354 for **1**. Copies of the data can be obtained free of charge on application to 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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## References

[1] J.J. Vittal, Polyhedron 15 (1996) 1585.
[2] J.C.J. Bart, J.J. Daly, J. Chem. Soc. Dalton Trans. (1975) 2063.
[3] A. Haas, R. Hitze, C. Krüger, K. Angermund, Z. Naturforsch. Teil B 39 (1984) 890.
[4] J.A. Forstner, E.L. Muetterties, Inorg. Chem. 5 (1966) 552.
[5] R.H. Benno, C.J. Fritchie, J. Chem. Soc. Dalton Trans. (1973) 543.
[6] A. Haas, H.-J. Kutsch, C. Krüger, Chem. Ber. 120 (1987) 1045.
[7] D. Kobelt, E.F. Paulus, H. Scherer, Acta Crystallogr. Sect. B 28 (1972) 2323.
[8] C.-W. Park, M.A. Pell, J.A. Ibers, Inorg. Chem. 35 (1996) 4555.
[9] A. Blecher, M. Dräger, B. Mathiasch, Z. Naturforsch. Teil B 36 (1981) 1361.
[10] M. Ribes, J. Oliver-Fourcade, E. Philippot, M. Maurin, J. Solid State Chem. 8 (1973) 195.
[11] B. Eisenmann, J. Hansa, H. Schäfer, Z. Naturforsch. Teil B 40 (1985) 450.
[12] B. Eisenmann, H. Schäfer, Z. Anorg. Allg. Chem. 491 (1982) 67.
[13] G. Eulenberger, Acta Crystallogr. Sect. B 32 (1976) 3059.
[14] B. Krebs, S. Pohl, Z. Anorg. Allg. Chem. 424 (1976) 265.
[15] S.S. Dhingra, R.C. Haushalter, Polyhedron 13 (1994) 2775.
[16] W.S. Sheldrick, B. Schaaf, Z. Naturforsch. Teil B 50 (1995) 1469.
[17] K.O. Klepp, F. Fabian, Z. Naturforsch. Teil B 54 (1999) 1499.
[18] J. Campbell, D.P. DiCiommo, H.P.A. Mercier, A.M. Pirani, G.J. Schrobilgen, M. Willuhn, Inorg. Chem. 34 (1995) 6265.
[19] A. Fehlker, R. Blachnik, Z. Anorg. Allg. Chem. 627 (2001) 1128.
[20] W. Ando, T. Kadowaki, A. Watanabe, N. Choi, Y. Kabe, T. Erata, M. Ishii, Nippon Kagaku Kaishi (1994) 214.
[21] U. Herzog, G. Rheinwald, J. Organomet. Chem. 628 (2001) 133.
[22] U. Herzog, U. Böhme, G. Roewer, G. Rheinwald, H. Lang, J. Organomet. Chem. 602 (2000) 193.
[23] C. Ackerhans, H.W. Roesky, M. Noltemeyer, Organometallics 20 (2001) 1282.
[24] E. Lukevics, O. Pudova, Main Group Met. Chem. 21 (1998) 123.
[25] U. Herzog, G. Rheinwald, J. Organomet. Chem. 627 (2001) 23.
[26] U. Herzog, U. Böhme, E. Brendler, G. Rheinwald, J. Organomet. Chem. 630 (2001) 139.
[27] Rigaku Corp., 2000.
[28] G.M. Sheldrick, SHELX-97 (includes SHELXS-97, SHELXL-97, CIFTAB), Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, 1997.
[29] M. Berndt, K. Brandenburg, H. Putz, DIAMOND 2.1: Crystal Impact GbR, http://www.crystalimpact.de, Bonn, Germany, 1999.
[30] R. Lehnert, M. Höppner, H. Kelling, Z. Anorg. Allg. Chem. 591 (1990) 209.