

Organosilicon chalcogenides with trisilane units — adamantanes and noradamantanes

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Abstract

1,1,3,3-Tetrachlorotetramethyltrisilane (1b) has been prepared from Ph_2MeSiCl and Me_2SiCl_2 via $\text{Ph}_2\text{MeSi-SiMe}_2\text{-SiMePh}_2$ (1a). Reaction of 1b with Li_2E (E = S, Se) furnishes the new tricyclic organosilicon chalcogenides $(\text{Me}_2\text{Si})_2(\text{MeSi})_4\text{E}_4$ (E = S (2a), Se (2b)) with adamantane structures. If a mixture of 1b and $\text{Cl}_2\text{MeSi-SiMeCl}_2$ is reacted with $\text{H}_2\text{S}/\text{NEt}_3$, $(\text{Me}_2\text{Si})(\text{MeSi})_4\text{S}_4$ (3a), a noradamantane with a trisilane and a disilane unit is formed. The molecular structures of 2a and 3a are reported. All new compounds are characterized by NMR spectroscopy (^1H , ^{13}C , ^{29}Si , ^{77}Se).

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1. Introduction

Adamantane cages are a structural motif frequently observed in inorganic as well as organometallic chemistry [1].

Adamantanes-like $\text{Si}_4\text{E}_{104}$ ions (E = S, Se, Te) have been observed in several chalcogenosilicates [2–5], while silsesquichalcogenides $(\text{RM})_4\text{E}_6$ (I; E = S, Se; M = Si, Ge, Sn) which usually adopt adamantane-like structures have been prepared starting from organotrichlorosilanes, germanes or stannanes by reactions with alkalimetal chalcogenides or other chalcogen transfer reagents [6–8].

However, in case of bulky substituents (R = tBu [9], 1,1,2-trimethylpropyl [10]), the reactions of RMCl_3 (M = Si, Ge) with $(\text{NH}_4)_2\text{S}_5$ or Li_2E (E = S, Se) resulted in the formation of sesquichalcogenides with double-decker-like structures $[(\text{RME})_2\text{E}]_2$ (II).

Recently, we were able to show [11] that reactions of tetrachlorodisilylmethane $\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$ with either $\text{H}_2\text{S}/\text{NEt}_3$ or Li_2E (E = Se, Te) led to the

formation of adamantane-like cages $(\text{CH}_2)_2(\text{SiMe})_4\text{E}_4$ (III; E = S, Se, Te).

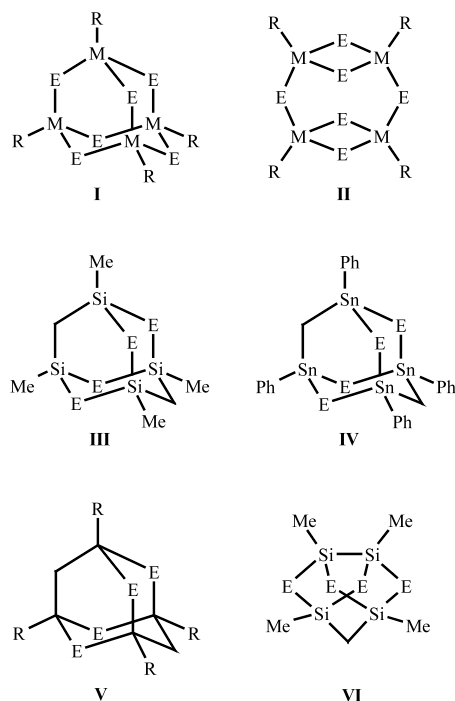
The molecular structures of the three compounds revealed an increasingly distorted geometry of the adamantane cage with growing size of the chalcogen atoms as a result of the difference of the bond lengths Si–C and Si–E. Related adamantane cages with tin atoms instead of silicon and E = S, Se have (IV) been prepared by Jurkschat and coworkers [12] by the reaction of a corresponding distannylmethane with Na_2E while compounds with carbon atoms at the positions of silicon (V) are known to be formed starting from β -diketones with H_2S [13–15] or H_2Se [16] in acid reaction mixtures (HCl, $\text{ZnCl}_2/\text{HOAc}$).

By reaction of a 1:1 molar mixture of the tetrachlorodisilylmethane $\text{Cl}_2\text{MeSi-CH}_2\text{-SiMeCl}_2$ and $\text{Cl}_2\text{MeSi-SiMeCl}_2$ with either $\text{H}_2\text{S}/\text{NEt}_3$ or Li_2Se , we have also succeeded in the preparation of noradamantanes $(\text{CH}_2)(\text{SiMe})_4\text{E}_4$ (VI; E = S, Se) (Scheme 1) [11].

In the course of our investigations of the reaction products of several chlorofunctionalized trisilanes with chalcogen transfer reagents such as $\text{H}_2\text{S}/\text{NEt}_3$ or Li_2E , we became interested in the nature of the reaction products of the trisilane $\text{Cl}_2\text{MeSi-SiMe}_2\text{-SiMeCl}_2$ (1b).

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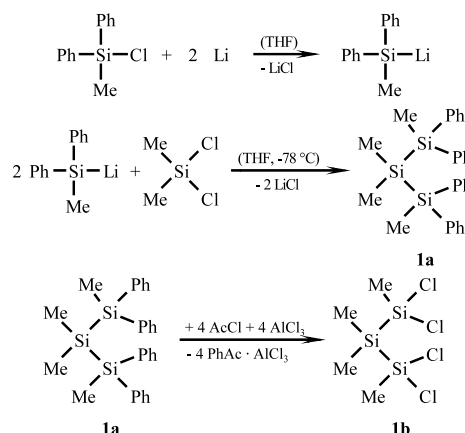
Scheme 1. Structures of sesquichalcogenides (RM)₄E₆ of Group 14 elements (M = C, Si, Ge, Sn) and related compounds (RM)₄(CH₂)_xE₄ (x = 1, 2).

The questions arise whether it would be possible to prepare compounds of the types (Me₂Si)₂(MeSi)₄E₄ and (Me₂Si)(MeSi)₄E₄ and whether these compounds also exhibit adamantane (or noradamantane)-like structures.

2. Results and discussion

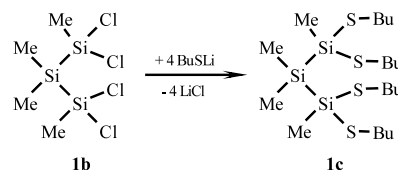
2.1. Preparation of Me₂Si(SiMeCl₂)₂ and Me₂Si[SiMe(SBu)₂]₂

The starting trisilane Cl₂MeSi–SiMe₂–SiMeCl₂ (**1b**) has been synthesized in three steps from Ph₂MeSiCl and Me₂SiCl₂:



In order to compare the NMR chemical shifts of the

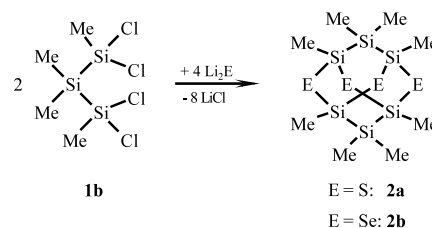
polycyclic target molecules with a related acyclic compound, we reacted the trisilane **1b** with BuSLi and obtained an acyclic thiobutyl-substituted trisilane **1c** with the same substitution pattern, i.e. the same first coordination sphere at the silicon atoms:



The NMR data of all synthesized trisilanes are given in Table 1.

2.2. Adamantanes (Me₂Si)₂(SiMe)₄E₄ (E = S (**2a**), Se (**2b**))

Reactions of the trisilane Me₂Si(SiMeCl₂)₂ (**1b**) with Li₂E (E = S, Se) led to the formation of (Me₂Si)₂(SiMe)₄E₄ (**2a** and **2b**).



The adamantane-like structure of **2a** could be proven unambiguously by a crystal structure analysis. Fig. 1 shows the molecular structure, and selected bond distances and angles are given in Table 2.

All bond lengths are in the ranges of typical single bonds. Even though all angles Si–Si–Si and Si–S–Si are somewhat smaller and all angles S–Si–S are larger than the ideal tetrahedral angle of 109.5°, in contrast to the adamantane-like compounds (CH₂)₂(SiMe)₄E₄ described previously [11], the Si₆S₄ core represents an almost undisturbed adamantane cage. This is also evident from a comparison of the lengths of the

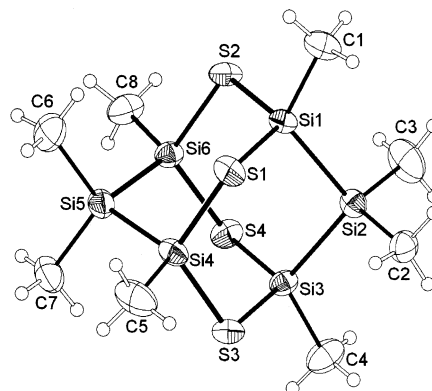


Fig. 1. Molecular structure of (Me₂Si)₂(SiMe)₄S₄ (**2a**).

Table 1
NMR data (Hz, ppm) of the trisilanes Me₂Si(SiMeR₂)₂ (R = Ph (1a), Cl (1b), SBU (1c))

Compound	δSi	1JSiSi	δC	1JSiC	δH
Me ₂ SiB(SiAMePh ₂) ₂ (1a)	A: -19.05	72.6	SiAMe: -4.24 ^a	38.6	0.441 ^b
	B: -47.23		SiBMe ₂ : -5.03		0.276
Me ₂ SiB(SiAMeCl ₂) ₂ (1b)	A: 32.74	95.7	SiAMe: 7.83	52.1	0.955
	B: -35.59		SiBMe ₂ : -7.77		0.450
Me ₂ SiB[SiAMe(SBU) ₂] ₂ (1c)	A: 14.27	80.0	SiAMe: 0.80 ^c	41.4	0.657 ^d
	B: -38.98		SiBMe ₂ : -4.72		0.355

^a SiA₂Ph₂: 137.01 (i), 134.82 (o), 127.75 (m), 128.68 (p).

^b SiA₂Ph₂: 7.36 (o), 7.22 (m+p).

^c SC₁H₂C₂H₂C₃H₂C₄H₃: 27.0 (C₁), 34.7 (C₂), 22.1 (C₃), 13.8 (C₄).

^d SC₁H₂C₂H₂C₃H₂C₄H₃: 2.68 (C₁H₂), 1.65 (C₂H₂), 1.43 (C₃H₂), 0.92 (C₄H₂).

diagonals Z–Z and E–E (Z = SiMe₂, CH₂) as well as the bond angles Si–Z–Si and Si–E–Si (see Table 3). While for 2a both ratios are almost equal to unity, deviations increase for Z = CH₂ with the size of the chalcogen.

The NMR data of 2a and 2b are summarized in Table 4. A comparison with the ²⁹Si-NMR chemical shifts of the sulfur compound 2a with those of the acyclic thiobutyl derivative 1c reveals a significant high field shift of SiB despite the same first and second coordination spheres while SiA is only slightly shifted to a higher field in the adamantane 2a. This is in agreement with observations made previously for other cyclic and polycyclic organosilicon chalcogenides. The incorporation of a silicon atom into a six-membered ring is always accompanied by a high field shift of the ²⁹Si-NMR signal [17]. In oligosilanes, this high field shift is even

Table 3
Geometric parameters of the adamantanes Z₂(SiMe)₄E₄ (Z = SiMe₂, CH₂; E = S, Se, Te)

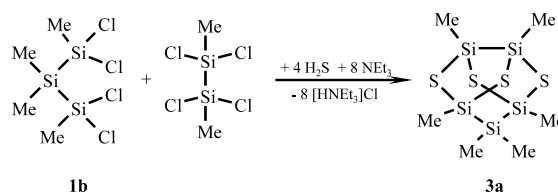
Parameter	Z = SiMe ₂ ; E = S	Z = CH ₂ ; E = S	Z = CH ₂ ; E = Se	Z = CH ₂ ; E = Te
E–E ^a (a)	5.13	4.97	5.30	5.78
Z–Z (b)	5.16	4.31	4.35	4.43
a/b	0.99	1.15	1.22	1.30
∠ Si–Z–Si (c)	104.0	118.9	122.6	127.6
∠ Si–E–Si (d)	107.5	101.3	98.3	93.9
c/d	0.97	1.17	1.25	1.36

^a Average distance E₁–E₄ and E₂–E₃.

more pronounced for the silicon atoms not directly bound to the sulfur atoms [18].

2.3. Noradamantane (Me₂Si)(SiMe)₄S₄ (3a)

If a 1:1 molar mixture of the trisilane 1b and 1,1,2,2-tetrachlorodimethyldisilane is reacted with H₂S/NEt₃, a noradamantane with a trisilane and a disilane unit connected by four sulfur atoms is formed:



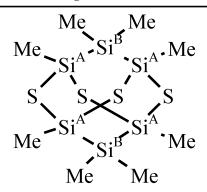
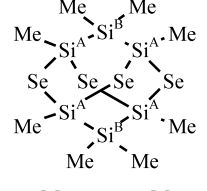
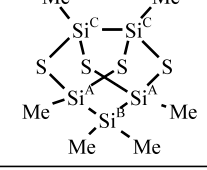
The NMR data of this new noradamantane 3a are given in Table 2. In comparison with the acyclic thiobutyl-substituted oligosilanes 1c and (BuS)₂MeSi–SiMe(SBU)₂ (δSi: 9.1 ppm) [19] containing the same oligosilanyl units, the NMR signals of SiA and SiC in 3a are shifted by 12–18 ppm to a lower field as a consequence of the incorporation into five-membered rings.

Merely SiB of 3a, which is part of six-membered rings only, shows an NMR signal high field from the

Table 2
Selected bond lengths and bond angles of (Me₂Si)₂(SiMe)₄S₄ (2a)

Atoms	Bond length (Å)	Atoms	bond angle (°)
Si1–Si2	2.316(2)	Si1–Si2–Si3	103.81(6)
Si2–Si3	2.317(2)	Si4–Si5–Si6	104.09(6)
Si4–Si5	2.326(2)	Si1–Si1–Si4	106.93(6)
Si5–Si6	2.321(2)	Si1–Si2–Si6	108.10(6)
Si1–Si1	2.144(2)	Si3–S3–Si4	107.85(6)
Si1–Si2	2.145(2)	Si3–S4–Si6	106.94(6)
Si3–S3	2.145(2)	S1–Si1–S2	115.69(7)
Si3–S4	2.150(2)	S3–Si3–S4	114.93(7)
Si4–S1	2.145(2)	S1–Si4–S3	116.06(7)
Si4–S3	2.151(2)	S2–Si6–S4	113.90(7)
Si6–S2	2.148(2)	S1–Si1–Si2	108.06(6)
Si6–S4	2.143(2)	S2–Si1–Si2	109.47(6)
Si1–C1	1.866(5)	S3–Si3–Si2	108.34(6)
Si2–C2	1.888(5)	S4–Si3–Si2	110.03(7)
Si2–C3	1.884(5)	S1–Si4–Si5	109.19(7)
Si3–C4	1.861(5)	S3–Si4–Si5	107.48(7)
Si4–C5	1.864(5)	S2–Si6–Si5	108.29(6)
Si5–C6	1.882(5)	S4–Si6–Si5	110.50(7)
Si5–C7	1.882(5)	C2–Si2–C3	111.7(3)
Si6–C8	1.865(5)	C6–Si5–C7	112.1(3)

Table 4
NMR data (Hz, ppm) of the adamantanes (Me₂Si)₂(SiMe)₄E₄ (E = S (2a), Se (2b)) and the noradamantane (Me₂Si)(SiMe)₄S₄ (3a)

compound	δ_{Se}	δ_{Si}	δ_{C}	$^1J_{\text{SiC}}$	δ_{H}
 2a	–	A: 13.2 B: –56.2 $^1J_{\text{SiSi}}: 86.5$	5.36 –8.34	43.2	0.71 0.41
 2b	–161 $^1J_{\text{SiSe}}: 137.0$	A: –1.4 B: –61.3 $^1J_{\text{SiSi}}: 81.4$	5.03 –9.33		0.88 0.42
 3a	–	A: 26.2 B: –49.4 C: 25.6 $^1J_{\text{Si}^{\text{A}}\text{Si}^{\text{B}}}: 85.0$	3.3 –8.1 2.2	45.2 41.8 51.0	0.80 0.33 0.95

resonance of SiB in 1c; however, it is 7 ppm low field shifted from the signal of SiB in the adamantane 2a.

This noradamantane has also been characterized by a crystal structure analysis. The asymmetric unit contains two independent molecules with almost identical geometries. Molecule A is shown in Fig. 2. Important bond lengths and angles are summarized in Table 5. Like in 2a, the four chalcogen atoms span an almost ideal square with S–S distances of 3.48–3.56 Å and angles S–S–S between 89.6° and 90.3°.

Due to the smaller ring size, the Si–S–Si angles in 3a are in average 11.5° smaller than in 2a.

The most striking difference to the geometry of the related noradamantane (H₂C)(SiMe)₄S₄ [11] is the bond angle Si–Si–Si of the trisilane unit which is 104.8° (average of the two independent molecules). It is almost 17° smaller than the angle Si–C–Si of the

disilylmethane unit and results from the larger bond length Si–Si in comparison with Si–C.

3. Experimental

3.1. NMR and GC/MS measurements

All NMR spectra were recorded on a Bruker DPX 400 in CDCl₃ solution and TMS as internal standard for ¹H, ¹³C and ²⁹Si. In order to get a sufficient signal to noise ratio of ²⁹Si-NMR spectra for obtaining ¹J_{SiC}, ¹J_{SiSi} or ¹J_{SiSe} satellites, ²⁹Si INEPT spectra were also recorded. ⁷⁷Se-NMR spectra were obtained using an IGATED pulse program.

External Ph₂Se₂ (δ_{Se} : 460 ppm [20]) in CDCl₃ was used as standard for ⁷⁷Se.

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}/200 °C, flow: He 0.5 ml min^{–1}).

3.2. Crystal structure analyses

X-ray structure analysis measurements of 2a and 3a were performed on a Rigaku AFC7 with Mercury CCD. Crystal data of 2a and 3a as well as data collection and refinement details are given in Table 6.

For the data collection, unit cell refinement and data reduction of 2a and 3a the program package Crystal Clear [21] was used. The structures were solved using direct methods, refined using least-squares methods

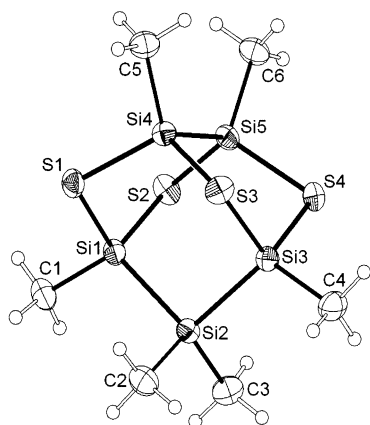


Fig. 2. Molecular structure of (Me₂Si)(SiMe)₄S₄ (3a), molecule A.

Table 5
Selected bond lengths and bond angles of (Me₂Si)(SiMe)₄S₄ (3a), molecules A and B

Atoms	Bond length (Å)	Atoms	Bond angle (°)
Si1–Si2	2.345(2)	Si1–Si2–Si3	105.11(7)
Si2–Si3	2.338(2)	Si1–Si1–Si4	95.85(7)
Si1–S1	2.160(2)	Si1–S2–Si5	96.09(7)
Si1–S2	2.145(2)	Si3–S3–Si4	95.70(7)
Si3–S3	2.158(2)	Si3–S4–Si5	95.91(8)
Si3–S4	2.149(2)	S1–Si1–S2	107.89(8)
Si4–S1	2.136(2)	S3–Si3–S4	108.55(8)
Si4–S3	2.134(2)	S1–Si4–S3	112.61(9)
Si5–S2	2.145(2)	S2–Si5–S4	112.49(8)
Si5–S4	2.143(2)	Si1–Si1–Si2	108.70(7)
Si4–Si5	2.359(2)	S2–Si1–Si2	109.56(8)
Si1–C1	1.855(5)	S3–Si3–Si2	108.89(8)
Si2–C2	1.860(5)	S4–Si3–Si2	109.07(7)
Si2–C3	1.881(5)	S1–Si4–Si5	105.44(7)
Si3–C4	1.848(5)	S3–Si4–Si5	105.60(7)
Si4–C5	1.844(4)	S2–Si5–Si4	104.93(8)
Si5–C6	1.841(5)	S4–Si5–Si4	105.24(7)
		C2–Si2–C3	111.6(2)0
Si6–Si7	2.343(2)	Si6–Si7–Si8	104.52(7)
Si7–Si8	2.344(2)	Si6–S5–Si9	96.32(7)
Si6–S5	2.144(2)	Si6–S6–Si10	96.31(8)
Si6–S6	2.152(2)	Si8–S7–Si9	95.90(8)
Si8–S7	2.146(2)	Si8–S8–Si10	95.88(7)
Si8–S8	2.150(2)	S5–Si6–S6	108.51(8)
Si9–S5	2.140(2)	S7–Si8–S8	108.56(8)
Si9–S7	2.145(2)	S5–Si9–S7	111.89(8)
Si10–S6	2.141(2)	S6–Si10–S8	111.39(9)
Si5–S4	2.143(2)	S5–Si6–Si7	108.20(8)
Si9–Si10	2.358(2)	S6–Si6–Si7	109.54(7)
Si6–C7	1.857(5)	S7–Si8–Si7	108.85(8)
Si7–C8	1.879(6)	S8–Si8–Si7	109.70(8)
Si7–C9	1.877(5)	S5–Si9–Si10	105.43(8)
Si8–C10	1.859(5)	S7–Si9–Si10	105.03(7)
Si9–C11	1.855(5)	S6–Si10–Si9	105.15(7)
Si10–C12	1.852(5)	S8–Si10–Si9	105.55(8)
		C8–Si7–C9	110.9(3)0

(shelx-97 [22]) and drawn using Diamond [23]. The ellipsoids at the non-hydrogen atoms are shown at the 30% probability level.

3.3. Starting materials

Sulfur, selenium, 1.0 M Li[BET₃H] in THF (Super Hydride®), Me₂SiCl₂, Ph₂MeSiCl, lithium powder, H₂S and NEt₃ were commercially available. Cl₂MeSi–SiMeCl₂ was prepared as described in [24]. THF was distilled from sodium potassium alloy prior to use. Hexane was dried over KOH. All reactions were carried out under argon applying standard Schlenk techniques.

3.4. Synthesis of Me₂Si(SiMePh₂)₂ (1a)

Ph₂MeSiCl (7.7 g, 33 mmol) was dissolved in 30 ml THF and lithium powder (0.78 g, 0.11 mol) was added.

Table 6
Crystal data of 2a and 3a as well as data collection and refinement details

	2a	3a
Empirical formula	C ₈ H ₂₄ S ₄ Si ₆	C ₆ H ₁₈ S ₄ Si ₅
Formula weight	417.05	358.89
Crystal shape	block	block
Temperature (K)	295(2)	293(2)
Crystal color	colorless	colorless
Crystal size (mm ³)	0.37 × 0.25 × 0.16	0.17 × 0.11 × 0.07
Crystal system	monoclinic	monoclinic
Space group	P21/n	P21/c
Unit cell dimensions		
a (Å)	12.827(2)	8.2255(5)
b (Å)	10.897(1)	15.820(1)
c (Å)	16.449(2)	27.722(2)
β (°)	96.187(7)	90.502(4)
V (Å ³), Z	2285.8(5), 4	3607.3(4), 8
Density (calc., g cm ^{−3})	1.212	1.322
Linear absorption coeff. (mm ^{−1})	0.717	0.833
Scan method	φ-scans	φ-scans
Absorption correction	numerical	numerical
Measured reflections	19 502	21 471
Independent reflections	3987	5628
Observed reflections	3270	3481
Rint	0.0406	0.1008
θ range for collection (°)	1.92–25.00	1.95–24.00
Index ranges	−15 ≤ h ≤ 12, −12 ≤ k ≤ 12, −18 ≤ l ≤ 19	−9 ≤ h ≤ 8, −18 ≤ k ≤ 18, −31 ≤ l ≤ 18
Completeness to θ _{max} (%)	99.2	99.3
Number of parameters	171	283
Final R1/wR2 [I > 2σ(I)] ^a	0.0786/0.1668	0.1195/0.1046
Final R1/wR2 (all data) ^a	0.0632/0.1572	0.0521/0.0909
Goodness-of-fit (S) ^b on F ₂	1.098	0.994
H-locating and refining	geom./mixed	geom./mixed
Max./min. e-density (e Å ^{−3})	0.492/−0.342	0.268/−0.333

^a R1 = Σ(|Fo| − |Fc|)/Σ|Fo|, wR2 = [Σw(Fo₂ − Fc₂)²/Σ(wFo₂)]^{1/2}, w = 1/[σ²(Fo₂) + (aP)² + bP] where P = (Fo₂ + 2Fc₂)/3.

^b S = [Σw(Fo₂ − Fc₂)²]/(n − p)^{1/2}, n = number of reflections, p = parameters used.

After some time, the stirred reaction mixture started to turn green. After reaction overnight, the deep-green solution of Ph₂MeSiLi was slowly transferred by a cannula into a solution of Me₂SiCl₂ (2.12 g, 16.5 mmol) in THF (20 ml) at −80 °C. After complete addition, the reaction mixture was brought to room temperature and the THF was removed in vacuo. After addition of n-hexane (50 ml), the mixture was filtered from precipitated LiCl and the solvent was removed in vacuo

yielding 6.4 g (14 mmol, 85%) pure Me₂Si(SiMePh₂)₂ (1a) as an oily residue.

3.5. Synthesis of Me₂Si(SiMeCl₂)₂ (1b)

1a (6.25 g, 13.8 mmol) was dissolved in 20 ml hexane and AlCl₃ (8.3 g, 62 mmol) was added. Acetyl chloride (4.4 ml, 62 mmol) was slowly added to this mixture with stirring. After reaction overnight, the upper layer was isolated and the residue extracted with n-hexane (2 × 10 ml). The combined hexane solutions were concentrated in vacuo at room temperature to yield 2.9 g (10 mmol) pure Me₂Si(SiMeCl₂)₂ (1b) which was checked by NMR spectroscopy.

1b: GC/MS (m/e, rel. int.): 286 (Me₄Si₃Cl₃Si₃Cl₃ [M⁺], 1), 271 ([M⁺ – Me], 1), 249/251 ([M⁺ – Cl], 2), 171 ([Me₃Si₂Cl₂], 18), 156 ([Me₂Si₂Cl₂], 17), 113 ([MeSiCl₂], 6), 93 ([Me₂SiCl], 29), 73 ([Me₃Si], 100).

3.6. Synthesis of Me₂Si[SiMe(SBu)₂]₂ (1c)

Sulfur (64 mg, 2.0 mmol) was added to a mixture of a 1.6-M BuLi solution in hexane (1.25 ml) and THF (2 ml). The sulfur dissolves immediately under formation of BuSLi. 1b (0.14 g, 0.5 mmol) was added to this BuSLi solution. After stirring for 30 min, the solvents were removed in vacuo and the residue was dissolved in hexane (10 ml). After filtration from precipitated lithium chloride evaporation of the solvent yielded pure Me₂Si[SiMe(SBu)₂]₂ (1c, 0.16 g, 0.32 mmol) which was characterized by NMR spectroscopy (see Table 1).

3.7. Adamantanes (Me₂Si)₂(SiMe)₄E₄ (E = S (2a), Se (2b))

1b (0.29 g, 1.0 mmol) was added at 0 °C to a solution of 2.0 mmol Li₂E (E = S, Se), prepared from 2.0 mmol elemental E and 4.0 ml of a 1.0 M solution of Li[BET₃H] in THF (Super-Hydride®). After stirring for 20 min, the solvents were removed in vacuo and the residue dissolved in 10 ml hexane. After filtration from precipitated lithium salts, the removal of the solvent in vacuo yielded the adamantanes 2a and 2b as colorless crystals (60–70% yield, 2a: m.p.: 174 °C).

The sulfur compound 2a can also be prepared by reaction of 1b with H₂S/NEt₃ in hexane solution.

2a: GC/MS: 416 ([M⁺], 68), 401 ([M⁺ – Me], 100), 357 ([Me₅Si₅S₄CH₂], 20), 343 ([Me₅Si₅S₄], 17), 311 ([Me₅Si₅S₃], 24), 283 ([Me₅Si₄S₃], 18), 266 ([Me₆Si₄S₂], 10), 251 ([Me₅Si₄S₂], 35), 223 ([Me₅Si₃S₂], 9), 191 ([Me₅Si₃S], 21), 176 ([Me₄Si₃S], 9), 165 ([Me₃Si₂S₂], 11), 163 ([Me₅Si₂S], 8), 131 ([Me₅Si₂], 24), 116 ([Me₄Si₂], 18), 73 ([Me₃Si], 94).

3.8. Noradamantane (Me₂Si)(SiMe)₄S₄ (3a)

1b (0.29 g, 1.0 mmol) and Cl₂MeSi–SiMeCl₂ (0.23 g, 1.0 mmol) were dissolved in 40 ml hexane and H₂S was bubbled through the solution while NEt₃ (1.7 ml, 12 mmol) was added slowly. After 1 h, the mixture was filtered from precipitated [HNEt₃]Cl and the solvent was removed in vacuo to yield colorless crystalline 3a in 55% yield, m.p.: 169 °C.

3a: GC/MS: 358 ([M⁺], 43), 343 ([M⁺ – Me], 41), 283 ([Me₅Si₄S₃], 20), 239 ([Me₆Si₃S₂H], 4), 225 ([Me₃–Si₃S₃], 7), 223 ([Me₅Si₃S₂], 9), 208 ([Me₄Si₃S₂], 14), 193 ([Me₃Si₃S₂], 5), 165 ([Me₃Si₂S₂], 26), 133 ([Me₃–Si₂S], 12), 73 ([Me₃Si], 100).

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 199979 for 2a and 199980 for 3a. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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References

- [1] J.J. Vittal, Polyhedron 15 (1996) 1585.
- [2] M. Ribes, J. Olivier-Fourcade, E. Philippot, M. Maurin, J. Solid State Chem. 8 (1973) 195.
- [3] C. Köster, A. Lindemann, J. Kuchinke, C. Mück-Lichtenfeld, B. Krebs, Solid State Sci. 4 (2002) 641.
- [4] B. Eisenmann, J. Hansa, H. Schäfer, Z. Naturforsch. B 40 (1985) 450.
- [5] B. Eisenmann, H. Schäfer, Z. Anorg. Allg. Chem. 491 (1982) 67.
- [6] J.C.J. Bart, J.J. Daly, J. Chem. Soc. Dalton Trans. (1975) 2063.
- [7] A. Haas, R. Hitze, C. Krüger, K. Angermund, Z. Naturforsch. B 39 (1984) 890.
- [8] S.R. Bahr, P. Boudjouk, Inorg. Chem. 31 (1992) 712.
- [9] (a) W. Ando, T. Kadowaki, Y. Kabe, M. Ishii, Angew. Chem. 104 (1992) 84; (b) W. Ando, T. Kadowaki, Y. Kabe, M. Ishii, Angew. Chem. Int. Ed. Engl. 31 (1992) 59.
- [10] M. Unno, Y. Kawai, H. Shioyama, H. Matsumoto, Organometallics 16 (1997) 4428.
- [11] U. Herzog, G. Rheinwald, J. Organomet. Chem. 628 (2001) 133.
- [12] D. Dakternieks, K. Jurkschat, H. Wu, E.R.T. Tiekink, Organometallics 12 (1993) 2788.
- [13] K. Olsson, Arkiv. Kemi. 26 (1967) 435.

- [14] K. Olsson, *Arkiv. Kemi.* 26 (1967) 465.
- [15] J.E. Barnes, J.A.W. Dalziel, S.D. Ross, *Spectrochim. Acta A* 27 (1971) 1247.
- [16] K. Olsson, S.-O. Almqvist, *Acta Chem. Scand.* 23 (1969) 3271.
- [17] U. Herzog, G. Rheinwald, *J. Organomet. Chem.* 627 (2001) 23.
- [18] U. Herzog, G. Rheinwald, *Organometallics* 20 (2001) 5369.
- [19] U. Herzog, G. Roewer, *Main Group Met. Chem.* 22 (1999) 579.
- [20] M. Lardon, *J. Am. Chem. Soc.* 92 (1970) 5063.
- [21] crystal clear, Rigaku Corp., 2000.
- [22] G.M. Sheldrick, shelx97 (includes shelxs97, shelxl97, ciftab): programs for crystal structure analysis, Release 97-2, University of Göttingen, Germany, 1997.
- [23] M. Berndt, K. Brandenburg, H. Putz, diamond 2.1: crystal impact GbR, www.crystalimpact.de, Bonn, Germany, 1999.
- [24] R. Lehnert, M. Höppner, H. Kelling, *Z. Anorg. Allg. Chem.* 591 (1990) 209.