Bis(oligosilanyl)chalcogenides $[(Me_3Si)_xMe_{3-x}Si]_2E$, alkalimetal oligosilanylchalcogenolates $(Me_3Si)_xMe_{3-x}Si–EM^I$ and oligosilanylchalcogenols $(Me_3Si)_xMe_{3-x}Si–EH$ (E = S, Se, Te) Syntheses and NMR study

Heike Lange, Uwe Herzog *

Institut für Anorganische Chemie, TU Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg, Germany

Abstract

Bis(oligosilanyl)chalcogenides $[(Me_3Si)_xMe_{3-x}Si]_2E$, alkalimetal oligosilanylchalcogenolates $(Me_3Si)_xMe_{3-x}Si–EM^I$ and oligosilanylchalcogenols $(Me_3Si)_xMe_{3-x}Si–EH$ (x = 1–3; E = S, Se, Te) were synthesized and characterized by [1]H-, [13]C-, ^{29}Si-, ^{77}Se- and [125]Te-NMR spectroscopy. Trends of NMR parameters (chemical shifts, coupling constants) are discussed. © 2002 Published by Elsevier Science B.V.

Keywords: Bis(oligosilanyl)chalcogenides; Alkalimetal oligosilanylchalcogenolates; NMR study

1. Introduction

The silicon–chalcogen chemistry is dominated by the formation of cyclic and polycyclic compounds. Apart from these species only a few acyclic compounds containing a Si–E–Si unit are known. Disilylchalcogenides such as $(Me_3Si)_2E$ (E = S [1], Se [2–4], Te [5]) have been prepared and utilized as chalcogen transfer reagents, e.g. by Fenske et al. in the preparation of nanosized copper chalcogenide clusters. Depending on the reaction conditions clusters containing up to 146 copper atoms have been isolated [6].

Several synthetic routes towards disilylchalcogenides have been described.

For instance, starting from the corresponding chlorosilane the reaction with Na_2Se or Li_2Te, prepared from the elements in liquid NH_3, furnished $(Me_3Si)_2Se$ in 83% yield [7] and $(Me_3Si)_2Te$ in 40% yield [8]. Disilylsulfides and selenides $(Me_nH_{3-n}Si)_2E$ have also been obtained by reaction of the corresponding silyliodides with complex thio- and selenoaluminates, prepared from $LiAlH_4$ and H_2E [9].

A more facile and high-yield approach to disilylchalcogenides starts from the elemental chalcogens and lithiumtriethylboranate [10], see Eq. (1).
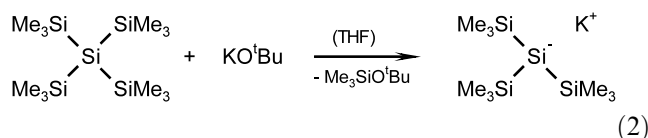
$$2\ Li[BEt_3H] + E \xrightarrow{\text{(THF)}} Li_2E + 2\ BEt_3 + H_2 \qquad (1)$$
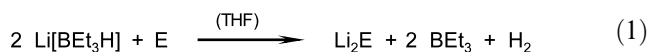
The thus formed lithium chalcogenides are partially soluble in THF and are therefore far more reactive. A convenient alternative route to $(Me_3Si)_2S$ starts from $(Me_3Si)_2NH$ and H_2S in the presence of 1% imidazole [11,12].

Arnold and coworkers [13] as well as Klinkhammer and coworkers [14] have shown that elemental tellurium inserts into the Si–Li bond of tris(trimethylsilyl)silyl lithium prepared from $Si(SiMe_3)_4$ and MeLi in THF with formation of the lithium tellurolate $(Me_3Si)_3SiTeLi$ which has also been characterized by a crystal structure analysis [15]. Treatment of the tellurolate with HOTf or HCl under controlled reaction conditions yielded the corresponding tellurol $(Me_3Si)_3SiTeH$ [14,16].

Marschner [17] showed tris(trimethylsilyl)silyl potassium to be prepared conveniently by the reaction of $Si(SiMe_3)_4$ with KO^tBu in THF; this is a convenient alternative route towards oligosilanyl anions (Eq (2)).

* Correspondong author. Tel.: +49-3731-394343; fax: +49-3731-394058

E-mail address: uwe.herzog@chemie.tu-freiberg.de (U. Herzog).

$$
\text{(Me}_3\text{Si)}_2\text{Si(SiMe}_3\text{)}_2 + \text{KO}^t\text{Bu} \xrightarrow[- \text{Me}_3\text{SiO}^t\text{Bu}]{\text{(THF)}} \text{(Me}_3\text{Si)}_2\text{Si}^-\text{K}^+\text{(SiMe}_3\text{)} \qquad (2)
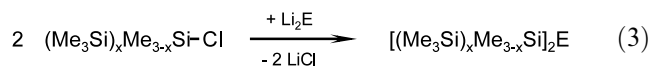$$

The aim of this work was to synthesize and characterize a series of acyclic bis(oligosilanyl)chalcogenides, alkalimetal oligosilanylchalcogenolates and oligosilanylchalcogenols because these compounds might serve as interesting synthons in the preparation of other chalcogenides. Furthermore, we are interested in the NMR data (chemical shifts, coupling constants) of these acyclic compounds. They may be compared with data of cyclic and polycyclic organosilicon chalcogenides [18–23] and conclusions with respect to the effects of ring formation on the NMR parameters can be drawn.

2. Results and discussion

2.1. Bis(oligosilanyl)chalcogenides, [(Me₃Si)ₓMe₃₋ₓSi]₂E (x = 0–3, E = S, Se, Te)

2.1. Bis(oligosilanyl)chalcogenides, [(Me$_3$Si)$_x$Me$_{3-x}$Si]$_2$E (x = 0–3, E = S, Se, Te)
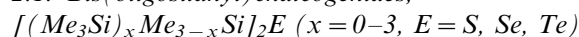
Bis(oligosilanyl)chalcogenides have been obtained by treatment of the corresponding chlorosilanes (Me$_3$Si)$_x$Me$_{3-x}$SiCl with a suspension of Li$_2$E in THF prepared in situ from Li[BEt$_3$H] and elemental E.

$$
2 \ (\text{Me}_3\text{Si})_x\text{Me}_{3-x}\text{Si-Cl} \xrightarrow[- \ 2 \ \text{LiCl}]{+ \ \text{Li}_2\text{E}} [(\text{Me}_3\text{Si})_x\text{Me}_{3-x}\text{Si}]_2\text{E} \qquad (3)
$$

In the case of E = S the chlorosilanes (Me$_3$Si)$_x$Me$_{3-x}$SiCl (x = 0, 1, 2) can alternatively be reacted with H$_2$S in the presence of NEt$_3$. While for x = 0 hexamethyldisilthiane was the only reaction product, for x = 1, a mixture of the disilthiane and pentamethyldisilanethiol emerged. For x = 2 heptamethyltrisilane-2-thiol [24] was formed exclusively (Scheme 1).

The different reaction products reflect an increase in steric shielding caused by the raising number of trimethylsilyl units attached. It prevents more or less the reaction of the initially formed thiol with a second molecule of the chlorosilane to give the bis(oligosilanyl)sulfide.
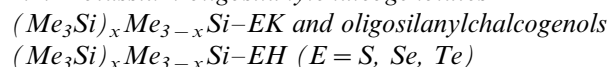
Apart from the mass spectrum the most significant proof of the presence of a thiol is the occurrence of an SH resonance in the ^{1}H-NMR spectra. The NMR data of all bis(oligosilanyl)chalcogenides prepared are sum-
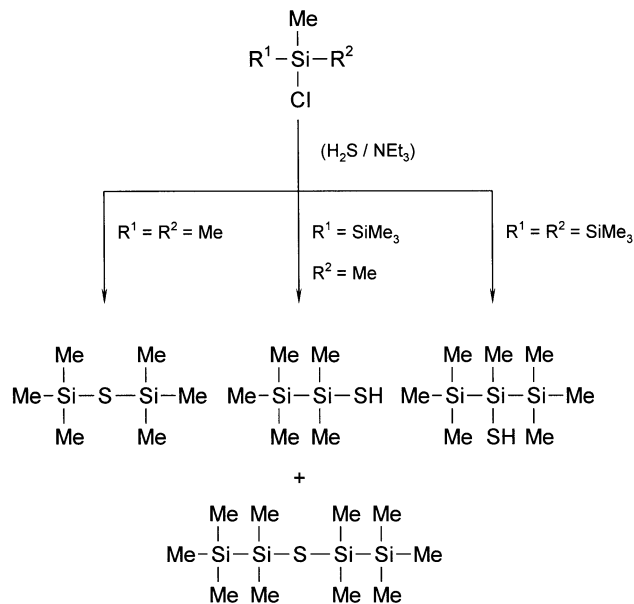
Scheme 1.

marized in Table 1. Remarkably the values of the $^1J_{\text{SiE}}$ coupling constants increase with number x of SiMe$_3$ units in each oligosilanyl unit whereas the $^2J_{\text{SiE}}$ coupling constants decrease significantly. As to be expected, δ_{Si} of the central silicon atoms as well as δ_{E} are shifted to higher field with increasing x.

2.2. Potassium oligosilanylchalcogenolates (Me₃Si)ₓMe₃₋ₓSi–EK and oligosilanylchalcogenols (Me₃Si)ₓMe₃₋ₓSi–EH (E = S, Se, Te)

2.2. Potassium oligosilanylchalcogenolates (Me$_3$Si)$_x$Me$_{3-x}$Si–EK and oligosilanylchalcogenols (Me$_3$Si)$_x$Me$_{3-x}$Si–EH (E = S, Se, Te)

The reactions of hypersilyl potassium prepared from (Me$_3$Si)$_4$Si and KO^{t}Bu with elemental chalcogens in THF afforded the related potassium hypersilylchalcogenolates, see Eq. (4).

$$
\text{(Me}_3\text{Si)}_3\text{Si}^-\text{K}^+ \xrightarrow{+ \ E \ \text{(THF)}} \text{(Me}_3\text{Si)}_3\text{Si–E}^-\ \text{K}^+ \qquad (4)
$$
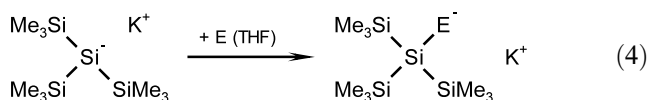
This type of reaction could also be applied to the branched tetrasilane MeSi(SiMe$_3$)$_3$ yielding the new heptamethyltrisilan-2-yl potassium and finally potassium heptamethyltrisilanylchalcogenolates:

The related silyl lithium derivative, (Me$_3$Si)$_2$SiMeLi has been reported previously, in THF solution it

$$
\text{(Me}_3\text{Si)}_2\text{Si(Me)(SiMe}_3\text{)} + \text{KO}^t\text{Bu} \xrightarrow[- \text{Me}_3\text{SiO}^t\text{Bu}]{\text{(THF)}} \text{(Me}_3\text{Si)}_2\text{Si}^-\text{K}^+\text{(Me)} \xrightarrow{+ \ E \ \text{(THF)}} \text{(Me}_3\text{Si)}_2\text{Si(Me)(E}^-\text{)}\ \text{K}^+ \qquad (5)
$$
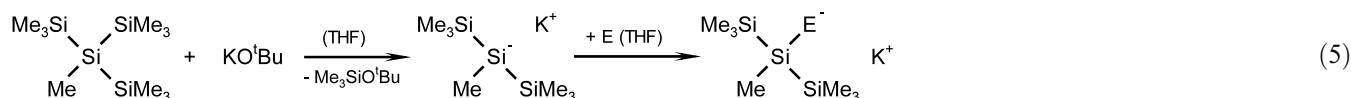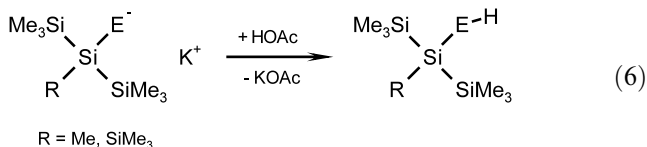
Table 1
NMR data of disilylchalcogenides $[(Me_3Si)_x Me_{3-x} Si]_2 E$ (E = S, Se, Te; x = 0, 1, 2, 3), chemical shifts in ppm, coupling constants in Hz
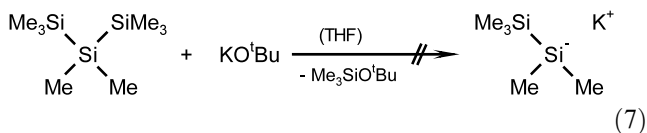
Compound	δ_E	δ_{Si}	$^nJ_{SiE}$	$^1J_{SiSi}$	δ_C	$^1J_{SiC}$	δ_H
$(Me_3Si)_2S$	–	14.65	–	–	4.12	53.9	0.353
$(Me_3Si^A Si^B Me_2)_2S$	–	A: −17.89	–	88.4	−2.80	46.6	0.139
		B: 0.22			1.35	44.4	0.382
$[(Me_3Si^A)_2Si^B Me]_2S$	–	A: −14.86	–	73.9	−1.55	46.5	0.154
		B: −20.98			−2.62	39.1	0.463
$[(Me_3Si^A)_3Si^B]_2S$	–	A: −10.65	–	60.4	0.96		0.240
		B: −49.91	–		–	–	–
$(Me_3Si)_2Se$	−337	11.76	107.4	–	4.56	52.5	0.452
$(Me_3Si^A Si^B Me_2)_2Se$	−405	A: −17.24	21.9	87.8	−2.46	45.2	0.133
		B: −3.26	129.3		1.99	42.0	0.512
$[(Me_3Si^A)_2Si^B Me]_2Se$	−555	A: −15.01	12.6	71.9	−1.27	46.0	0.172
		B: −27.47	135.6		−3.57		0.549
$[(Me_3Si^A)_3Si^B]_2Se$	−629	A: −10.96	9.5	57.6	1.24	45.4	0.256
		B: −60.47	151.2		–	–	–
$(Me_3Si)_2Te$	−852	−4.7	274.6	–	5.58	51.0	0.604
$[(Me_3Si^A Si^B Me_2)_2]Te$	−948	A: −16.48	45.2	84.1	−2.42		0.143
		B: −23.46	318.0		1.51	40.8	0.664
$[(Me_3Si^A)_2Si^B Me]_2Te$	−1158	A: −14.73	24.3	68.0	−0.97	45.5	0.196
		B: −54.53	324.1		−5.27	33.0	0.648
$[(Me_3Si^A)_3Si^B]_2Te$	−1240	A: −10.95	18.0	54.9	1.79		0.284
		B: −97.11	347.2		–	–	–

revealed very similar ^{29}Si NMR chemical shifts [25] suggesting that here too solvent separated ions $M(thf)_n^+$ and $Me_7Si_3^-$ are present.

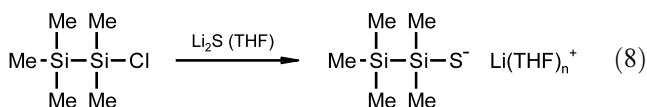Treatment of potassium oligosilanylchalcogenolates with anhydrous acetic acid afforded the corresponding thiols, selenols and tellurols, Eq. (6).

$$\begin{array}{c} Me_3Si \quad E^- \\ \diagdown \; Si \diagup \\ R \quad SiMe_3 \end{array} K^+ \xrightarrow[{- \; KOAc}]{+ \; HOAc} \begin{array}{c} Me_3Si \quad E{-}H \\ \diagdown \; Si \diagup \\ R \quad SiMe_3 \end{array} \quad (6)$$

R = Me, SiMe₃

Since the cleavage of octamethyltrisilane with potassium *tert*-butanolate in THF failed, the corresponding pentamethyldisilanylchalcogenolates could not be prepared via this route, Eq. (7).

$$\begin{array}{c} Me_3Si \quad SiMe_3 \\ \diagdown \; Si \diagup \\ Me \quad Me \end{array} + \; KO^tBu \xrightarrow[{- \; Me_3SiO^tBu}]{(THF)} \not\!\!\!\longrightarrow \begin{array}{c} Me_3Si \quad K^+ \\ \diagdown \; Si^- \diagup \\ Me \quad Me \end{array} \quad (7)$$

However, THF solutions of these compounds were obtained when chloropentamethyldisilane was reacted with excess Li_2E, see Eq. (8).

$$\begin{array}{c} Me \; Me \\ | \quad | \\ Me{-}Si{-}Si{-}Cl \\ | \quad | \\ Me \; Me \end{array} \xrightarrow{Li_2S \; (THF)} \begin{array}{c} Me \; Me \\ | \quad | \\ Me{-}Si{-}Si{-}S^- \; Li(THF)_n^+ \\ | \quad | \\ Me \; Me \end{array} \quad (8)$$

The NMR data of all alkalimetal oligosilanylchalcogenolates and the related thiols, selenols and tellurols synthesized so far are summarized in Tables 2 and 3. In these series of compounds (E = S, Se, Te) the differences between the δ_{Si} values of the central silicon atom in $[(Me_3Si)_x Me_{3-x} Si]_2 E$ and the corresponding $(Me_3Si)_x Me_{3-x} Si{-}EH$ increase with the number of Me_3Si groups x; this might be a result of the higher steric hindrance of *two* bulky silyl units in the bis(oligosilanyl)chalcogenides (Fig. 1). The increasing steric effect is also evident from a comparison of the ^{77}Se- and ^{125}Te-NMR shift values of the analogous selenium and tellurium compounds. NMR investigations on several classes of cyclic and polycyclic silselenanes and siltelluranes [19–21] as well as chalcogenobutyl substituted silanes [26] have shown that the ^{125}Te-NMR chemical shifts parallel the corresponding ^{77}Se-NMR values with a factor of 2.5–2.7. While the initial slope at $\delta_E \approx 0$ ppm for all pairs of compounds studied here varies between 2.7 and 3.1 (Fig. 2) it becomes flatter for larger x (more negative values of δ_{Se} and δ_{Te}).

The similarity of the NMR data observed for the potassium hypersilylchalcogenolates with those reported previously for lithium hypersilylthiolate, selenolate and tellurolate [14] suggests that these compounds should be regarded to exist as solvent separated ions in solution. This interpretation is in agreement with the increased $^1J_{SiSe}$ and $^1J_{SiTe}$ coupling constants—the coordination number of the chalcogen atoms decreases to one in the chalcogenolate ions. On the other hand, in the related selenols and tellurols much smaller $^1J_{SiSe}$ and $^1J_{SiTe}$ values are observed than in compounds with a Si–E–Si unit.

Table 2
NMR data of lithium and potassium oligosilanylchalcogenolates $(Me_3Si)_x Me_{3-x}Si-EM^I$ (E = S, Se, Te; x = 1, 2, 3) in THF solution, chemical shifts in ppm, coupling constants in Hz

Compound	δ_E	δ_{Si}	$^1J_{SiE}$	$^1J_{SiSi}$	δ_C	$^1J_{SiC}$	δ_H
$Me_3Si^A Me_2Si^B SLi$	–	A: −21.29	–	95.2	−1.81	41.3	−0.013
		B: −9.95			5.37	42.3	0.154
$(Me_3Si^A)_2MeSi^B SK$	–	A: −19.37	–	80.3	−1.40	39.8	0.016
		B: −31.85			−1.02		0.207
$(Me_3Si^A)_3Si^B SK$	–	A: −16.30	–	66.6	0.10	41.3	0.074
		B: −62.15			–	–	–
$Me_3Si^A Me_2Si^B SeLi$	−572	A: −21.87	164.7	91.9	−2.26		−0.011
		B: −17.79			4.79		0.289
$(Me_3Si^A)_2MeSi^B SeK$	−641	A: −20.16	172.6	77.5	−1.39		0.030
		B: −41.95			−1.4		0.349
$(Me_3Si^A)_3Si^B SeK$	−816	A: −18.20	170.6	64.1	0.30	42.3	0.096
		B: −77.55			–	–	–
$Me_3Si^A Me_2Si^B TeLi$	−1338	A: −21.67	429	87.5	−2.52		0.014
		B: −46.43			4.05		0.486
$(Me_3Si^A)_2MeSi^B TeK$	−1443	A: −20.11	424	73.4	−1.25	42.0	0.064
		B: −75.28			−3.52		0.568
$(Me_3Si^A)_3Si^B TeK$	−1652	A: −18.68	407	60.7	0.53	43.1	0.140
		B: −119.57			–	–	–

3. Experimental

3.1. NMR and GC–MS measurements

NMR spectra were recorded on a Bruker DPX 400 in $CDCl_3$ solution and with Me_4Si as internal standard for ^{1}H, ^{13}C and [29]Si. External $CDCl_3$ solutions of Ph_2Se_2 (δ_{Se} 460 ppm [27]) and Ph_2Te_2 (δ_{Te}: 422 ppm [28]) were used as standards for [77]Se and [125]Te.

THF solutions of $Me_7Si_3^- K^+$, $Me_9Si_4^- K^+$, $Me_5Si_2S^- Li^+$, $Me_7Si_3E^- K^+$ and $Me_9Si_4E^- K^+$ were sealed in 7 mm glass tubes and external $CDCl_3$ with

Me_4Si in a 10 mm sample tube was used for lock and calibration.

[29]Si INEPT spectra were also recorded in order to obtain a sufficient signal-to-noise ratio which allows the resolution of the $^1J_{SiC}$, $^{1,2}J_{SiSe}$, $^{1,2}J_{SiTe}$ or $^1J_{SiSi}$ satellites. [77]Se and [125]Te and spectra were determined using an IGATED pulse program. Coupled ^{77}Se- and [125]Te-NMR spectra of the selenols and tellurols prepared gave doublets with coupling constants identical to the values determined from the satellites in the ^{1}H-NMR spectra.

Mass spectra were measured on a Hewlett-Packard 5971 (ionization energy 70 eV, column 30 m × 0.25 mm × 0.25 μm, phenylmethylpolysiloxane, column tem-

Table 3
NMR data of oligosilanylchalcogenoles $(Me_3Si)_x Me_{3-x}Si-EH$ (E = S, x = 1, 2, 3; E = Se, Te, x = 2, 3), chemical shifts in ppm, coupling constants in Hz

Compound	δ_E	δ_{Si}	$^nJ_{SiE}$	$^1J_{SiSi}$	δ_C	$^1J_{SiC}$	δ_H (CH$_3$)	δ_H (EH)	$^1J_{EH}$
$Me_3Si^A Si^B Me_2-SH$	–	A: −17.66	–	90.9	−2.50	44.5	0.122	−0.28	–
		B: 0.73			2.29	42.8	0.408		
$(Me_3Si^A)_2MeSi^B SH$	–	A: −14.49	–	72.6	−1.96	45.2	0.166	−0.46	–
		B: −25.99			−2.56	35.9	0.388		
$(Me_3Si^A)_3Si^B SH$	–	A: −11.25	–	60.3	−0.27	45.2	0.213	−0.84	–
		B: −60.88							
$(Me_3Si^A)_2MeSi^B SeH$	−379	A: −14.12	7.9	70.8	−1.78	45.4	0.178	−2.73	41.0
		B: −31.71	94.5		−3.37	34.5	0.501		
$(Me_3Si^A)_3Si^B SeH$	−476	A: −11.4	< 7	57.8	−0.02	46.2	0.225	−3.22	36.8
		B: −69.9	87.1						
$(Me_3Si^A)_2MeSi^B TeH$	−814	A: −13.19	15.5	67.5	−1.43	46.2	0.197	−8.24	62.1
		B: −55.04	232.8		−4.95	32.6	0.675		
$(Me_3Si^A)_3Si^B TeH$	−950	A: −11.20	11.2	55.4	0.56	46.1	0.251	−8.96	74.3
		B: −100.15	209.0						
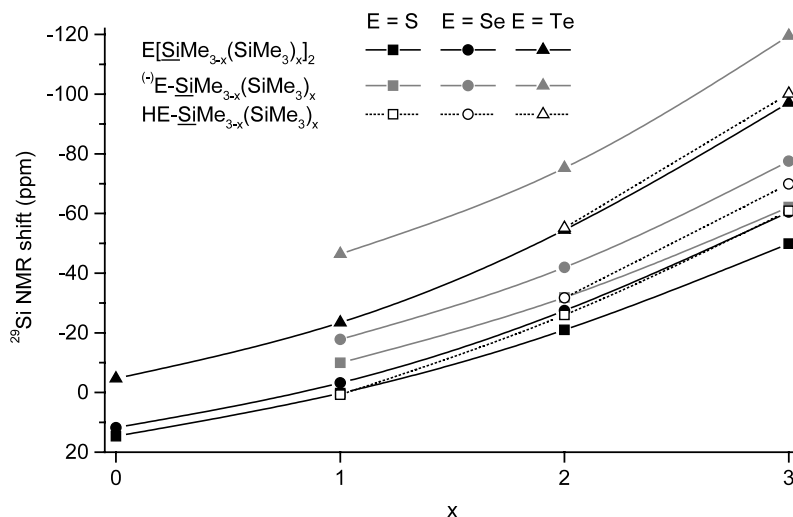
Fig. 1. ^{29}Si-NMR chemical shift of the central silicon atoms in $E[SiMe_{3-x}(SiMe_3)_x]_2$, $^{(-)}E[\underline{Si}Me_{3-x}(SiMe_3)_x]$ and $HE[\underline{Si}Me_{3-x}(SiMe_3)_x]$ as a function of x (E = S, Se, Te).

perature 80 °C (3 min)/20 K min^{-1}, He flow 0.5 ml min^{-1}).

3.2. Starting materials

Hydrogen sulphide (H_2S), sulfur, selenium, tellurium, Et_3N, 1 M LiBEt$_3$H in THF (Super Hydride), Me$_3$SiCl and HOAc are commercially available. ClSi$_2$Me$_5$ [29], (Me$_3$Si)$_2$SiClMe [30], (Me$_3$Si)$_3$SiCl [31], (Me$_3$Si)$_3$SiMe [32] and (Me$_3$Si)$_4$Si [33] were prepared as described. Except for THF, which was distilled from sodium potassium alloy prior to use, all solvents were dried over KOH or sodium wire. The reactions were carried out under an atmosphere of argon applying standard Schlenk techniques.

3.3. Reaction of chlorosilanes $(Me_3Si)_x Me_{3-x} SiCl$ $(x = 0, 1, 2)$ with H_2S–NEt_3

Chlorosilane $(Me_3Si)_x Me_{3-x} SiCl$ ($x = 0$, 1, 2, 2.0 mmol) were dissolved in 10 ml hexane and a stream of dried H_2S was bubbled through the stirred solution while 0.28 ml (2.0 mmol) of NEt$_3$ were slowly added by a syringe. After stirring for 30 min the reaction mixture was filtered from precipitated ammonium salts and the solvent was removed in vacuo. The products are (Me$_3$Si)$_2$S, a mixture of Me$_5$Si$_2$SH and (Me$_5$Si$_2$)$_2$S (35:65) and oily (Me$_3$Si)$_2$SiMeSH.

Me$_5$Si$_2$SH: GC–MS (m/e, relative intensity): 164 (M$^+$, 2), 149 (M–Me, 55), 133 (Me$_3$Si$_2$S, 2), 131 (Me$_5$Si$_2$, 2), 91 (Me$_2$SiSH, 8), 73 (Me$_3$Si, 100).
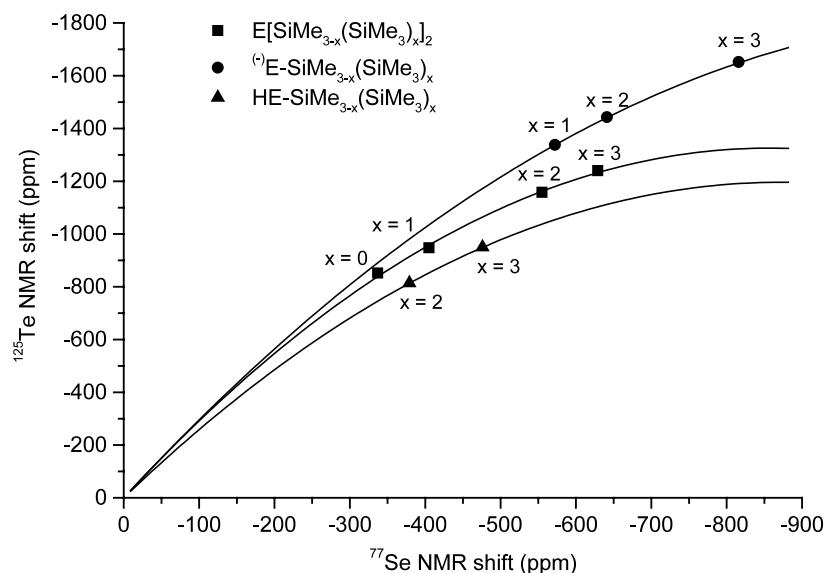
Fig. 2. Comparison of ^{125}Te- and ^{77}Se-NMR chemical shifts in $E[SiMe_{3-x}(SiMe_3)_x]_2$, $^{(-)}E[SiMe_{3-x}(SiMe_3)_x]$ and $HE[SiMe_{3-x}(SiMe_3)_x]$ (E = Se, Te). For all three classes of compounds, the initial slope varies between 2.7 and 3.1.

$(Me_5Si_2)_2S$: GC–MS: 294 (M$^+$, 1), 279 (M–Me, 3), 221 (Me$_7$Si$_3$S, 20), 191 (Me$_5$Si$_3$S, 4), 163 (Me$_5$Si$_2$S, 4), 131 (Me$_5$Si$_2$, 15), 116 (Me$_4$Si$_2$, 30), 73 (Me$_3$Si, 100).

Me$_7$Si$_3$SH: GC–MS: 222 (M$^+$, 11), 207 (M–Me, 5), 191 (Me$_5$Si$_3$S, 3), 148 (Me$_4$Si$_2$S, 23), 133 (Me$_3$Si$_2$S, 51), 119 (Me$_2$Si$_2$SH, 5), 73 (Me$_3$Si, 100).

3.4. Reaction of chlorosilanes $(Me_3Si)_xMe_{3-x}SiCl$ $(x = 0, 1, 2, 3)$ with Li_2E $(E = S, Se, Te)$

Chlorosilane $(Me_3Si)_xMe_{3-x}SiCl$ ($x = 0, 1, 2, 3, 2.0$ mmol) were added to a suspension of 1.0 mmol of Li$_2$E in THF at 0 °C prepared from 2.0 ml of a 1 M solution of LiBEt$_3$H in THF and 1.0 mmol of E. After stirring for 30 min the solvent THF was removed in vacuo and 10 ml of hexane was added. The suspension was filtered and the solvent removed from the filtrate in vacuo to furnish pure bis(oligosilanyl)chalcogenides [(Me$_3$Si)$_x$-Me$_{3-x}$Si]$_2$E as oily residues.

$(Me_7Si_3)_2S$: GC–MS: 410 (M$^+$, 4), 395 (M–Me, 5), 337 (Me$_{11}$Si$_5$S, 39), 249 (Me$_7$Si$_4$S, 34), 232 (Me$_8$Si$_4$, 54), 221 (Me$_7$Si$_3$S, 9), 191 (Me$_5$Si$_3$S, 13), 189 (Me$_7$Si$_3$, 10), 131 (Me$_5$Si$_2$, 40), 73 (Me$_3$Si, 100).

$(Me_5Si_2)_2Se$: GC–MS: 342 (M$^+$, 2), 327 (M–Me, 1), 269 (Me$_7$Si$_3$Se, 11), 239 (Me$_5$Si$_3$Se, 2), 181 (Me$_3$Si$_2$Se, 3), 131 (Me$_5$Si$_2$, 14), 116 (Me$_4$Si$_2$, 16), 73 (Me$_3$Si, 100).

3.5. Preparation of oligosilanyl potassium and reaction with chalcogens

MeSi(SiMe$_3$)$_3$ (1.0 g, 3.8 mmol) of was dissolved in 4 ml of THF and 0.50 g (4.4 mmol) of KO^{t}Bu was added. After stirring overnight NMR spectra of the reaction mixture revealed complete cleavage of the isotetrasilane and formation of Me$_3$SiO^{t}Bu [NMR (ppm, Hz): ^{29}Si: 6.7 ($^1J_{SiC}$: 58.8); ^{13}C: 31.7 (CMe_3), 2.11 (SiMe_3); ^{1}H: 1.21 (CMe$_3$), 0.06 (SiMe$_3$)] as well as (Me$_3$Si^A)$_2$Si^{B}Me K(thf)$_n$ [NMR (ppm, Hz): ^{29}Si: −6.72 (Si^A), −129.56 (Si^B, $^1J_{SiSi}$: 10.3), ^{13}C: 3.20 (Si^{A}Me$_3$, $^1J_{SiC}$: 33.7), −9.52 (Si^{B}Me); ^{1}H: −0.069 (Si^{A}Me$_3$), −0.283 (Si^{B}Me)].

Subsequent addition of 3.8 mmol of powdered sulfur, selenium or tellurium, respectively, yielded a THF solution of a potassium heptamethyltrisilan-2-ylchalco-genolate.

Analogously, 1.0 g (3.1 mmol) of Si(SiMe$_3$)$_4$ was dissolved in 4 ml of THF and 0.40 g (3.6 mmol) of KO^{t}Bu were added to give a THF solution of hypersi-lylpotassium [(Me$_3$Si^A)$_3$Si^B K(THF)$_n$ [NMR (ppm, Hz): ^{29}Si: −4.95 (A), −194.24 (B, $^1J_{SiSi}$: 8.9); ^{13}C: 6.81, ^{1}H: 0.144] and Me$_3$SiO^{t}Bu.

Subsequent addition of 3.1 mmol of powdered sulfur, selenium or tellurium, respectively, yielded a THF solution of a potassium hypersilylcogenolate ((Me$_3$-Si)$_3$SiE K(thf)$_n$).

3.6. Preparation of oligosilanylselenols and -tellurols

Oligosilanylchalcogenolate (1.0 mmol) in THF solution (see above) was cooled in an ice bath and reacted with 0.060 g (1.0 mmol) of anhydrous AcOH. The solvent was removed in vacuo and replaced by 10 ml hexane. After filtration the hexane was evaporated in vacuo to furnish the oligosilanylselenols and oligosila-nyltellurols as yellow oily residues.

3.7. Lithium pentamethyldisilanylchalcogenolates

Si$_2$Me$_5$Cl (0.17 g, 1.0 mmol) of was added to a THF solution of 1.2 mmol of Li$_2$E prepared from 2.4 ml of a 1 M LiBEt$_3$H solution and 1.2 mmol of E (E = S, Se, Te). The resulting reaction mixture was concentrated in vacuo to remove the by-product BEt$_3$ and the residue was dissolved in 1 ml of THF and analyzed by NMR revealing the formation of Me$_5$Si$_2$E Li(thf)$_n$.

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