

# Synthesis and NMR Investigation of Selenobutyl Substituted Silanes and Oligosilanes

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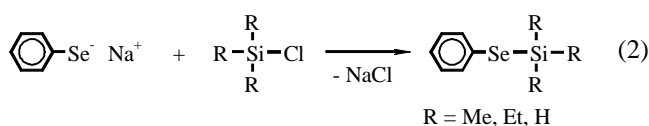
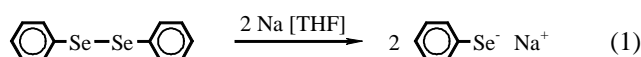
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**Abstract.** The reaction of BuSeLi, made from BuLi and elemental selenium, with chlorosilanes  $\text{Me}_x\text{Ph}_y\text{SiCl}_{4-x-y}$  led to selenobutyl substituted derivatives. In the cases of polychlorosilanes formation of the completely substituted products  $\text{Me}_x\text{Ph}_y\text{Si}(\text{SeBu})_{4-x-y}$  are favoured. Higher yields of partially substituted products could be obtained by reaction of chlorosilanes with BuSeH/NEt<sub>3</sub>. Besides monosilanes the reac-

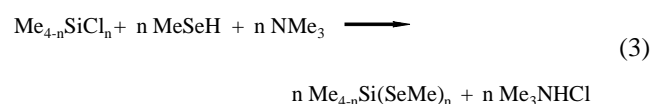
tions of several methylchlorodi-, tri- and isotetrasilanes with BuSeLi and BuSeH/NEt<sub>3</sub> were also investigated. In SiClMe(SiClMe<sub>2</sub>)<sub>2</sub> the chlorine substituent at the middle silicon atom is substituted by BuSeH/NEt<sub>3</sub> at first selectively. All products were characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si and <sup>77</sup>Se NMR and trends of chemical shifts and coupling constants (<sup>1</sup>J<sub>SiSi</sub>, <sup>1</sup>J<sub>SiSe</sub>, <sup>2</sup>J<sub>SiSe</sub>) with the substitution pattern were investigated.

Recently we have investigated trends of NMR parameters in thiobutyl substituted mono- and oligosilanes [1]. These investigations will be extended in this work to selenobutyl substituted silanes. There are only very few reports in the literature about organoseleno substituted silanes. Most of these publications deal with phenylselenotrimethylsilane. Phenylselenosilanes have been prepared by dehydrogenative coupling of trialkylsilanes with phenylselenol in the presence of Rh(Ph<sub>3</sub>P)<sub>3</sub>Cl or by reduction of diphenyldiselenide with sodium and subsequent reaction with a chlorosilane [2]:



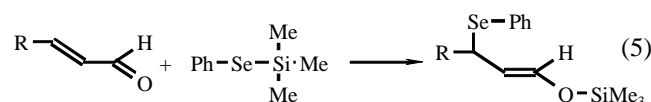
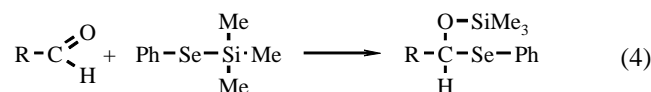
Elemental selenium inserts in THF solution into the carbon-metal bond of organolithium or Grignard compounds, yielding R-Se-Li or R-Se-Mg-X. But attempts to isolate Ph-Se-SiMe<sub>3</sub> by treatment of a Ph-Se-MgBr solution in diethyl ether with Me<sub>3</sub>SiCl yielded only (Me<sub>3</sub>Si)<sub>2</sub>Se [3].

Another approach to organoseleno substituted silanes is the reaction of chlorosilanes with selenols (R-SeH) in the presence of a Lewis base like NMe<sub>3</sub> [4]:

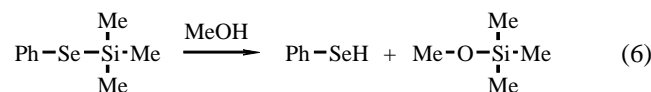


But unlike mercaptans, selenols are commercially not available and decompose easily under formation of diselenides. Nevertheless the series Me<sub>x</sub>Si(SeMe)<sub>4-x</sub> has been prepared *via* this route and <sup>1</sup>H NMR and IR data were reported [4].

Phenylselenotrimethylsilane has been used in organic synthesis. It reacts with aldehydes under formation of phenylseleno substituted silyl ethers,  $\alpha,\beta$ -unsaturated aldehydes yield the 1,4-addition products [5]:



The Si-Se bond in PhSeSiMe<sub>3</sub> can also be cleaved by methanol yielding phenylselenol [6]:



## Results and Discussion

### I. Monosilanes

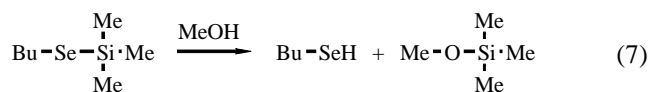
The insertion of elemental selenium into BuLi in THF solution and subsequent reaction with Me<sub>3</sub>SiCl should yield Me<sub>3</sub>Si-SeBu. If this reaction is carried out at room

temperature the product is mainly an equimolar mixture of  $\text{Bu}_2\text{Se}$  and  $(\text{Me}_3\text{Si})_2\text{Se}$  besides some  $\text{Me}_3\text{SiSeBu}$ . In this case the mixture can not be separated by distillation because all three products have almost the same boiling point of 53–54 °C at 1 kPa.  $\text{Me}_2\text{SiCl}_2$  or  $\text{MeSiCl}_3$ , respectively, yielded besides the desired  $\text{Me}_x\text{Si}(\text{SeBu})_{4-x}$  ( $x = 1, 2$ ) dibutylselenide and the known silselenides cyclo- $(\text{Me}_2\text{SiSe})_3$  and  $(\text{MeSi})_4\text{Se}_6$ , respectively [7]. For that reason it is crucial that the reaction of Se with BuLi has to be carried out at 0 °C.

Even if the BuSeLi solution was added slowly to an excess of a polychlorosilane,  $\text{R}_{4-x}\text{SiCl}_x$  ( $x > 1$ ), the completely substituted silane was obtained as main product. For instance the addition of one equivalent BuSeLi to  $\text{MeSiCl}_3$  yielded after removal of all volatile products including residual  $\text{MeSiCl}_3$  a mixture of 13%  $\text{MeSiCl}_2(\text{SeBu})$ , 20%  $\text{MeSiCl}(\text{SeBu})_2$  and 70%  $\text{MeSi}(\text{SeBu})_3$ . The reaction of two equivalents of BuSeLi to  $\text{SiCl}_4$  resulted in a mixture of 7%  $\text{SiCl}_3(\text{SeBu})$ , 4%  $\text{SiCl}_2(\text{SeBu})_2$ , 14%  $\text{SiCl}(\text{SeBu})_3$  and 75%  $\text{Si}(\text{SeBu})_4$ .

In order to get higher yields of partially selenobutyl substituted silanes it has been necessary to prepare butylselenol, BuSeH, which reacts with chlorosilanes in the presence of an amine, e.g.  $\text{NEt}_3$ , analogously to the formation of thiobutyl substituted silanes from chlorosilanes, thiobutanol and triethylamine. In the case of thiobutyl substituted silanes this reaction led to relatively high yields of partially substituted products [1], whereas in reactions of alkali metal thiophenolate with chlorosilanes like  $\text{Me}_2\text{SiCl}_2$  or  $\text{MeSiCl}_3$  the completely substituted products dominate [8].

In analogy to the preparation of phenylselenol by methanolysis of  $\text{PhSeSiMe}_3$  [6] butylselenol was prepared by reaction of BuSeSiMe<sub>3</sub> with methanol and fractional distillation:



The reaction of  $\text{MeSiCl}_3$  or  $\text{SiCl}_4$  with BuSeH and  $\text{NEt}_3$  in molar ratios 1:1:1 yielded after filtration from the precipitated triethylammonium chloride mixtures which consisted mainly of partially substituted products. In the case of  $\text{MeSiCl}_3$  a mixture of 37%  $\text{MeSiCl}_2(\text{SeBu})$ , 57%  $\text{MeSiCl}(\text{SeBu})_2$  and only 6%  $\text{MeSi}(\text{SeBu})_3$  was obtained,  $\text{SiCl}_4$  yielded a mixture of 5%  $\text{SiCl}_3(\text{SeBu})$ , 32%  $\text{SiCl}_2(\text{SeBu})_2$ , 56%  $\text{SiCl}(\text{SeBu})_3$  and 7%  $\text{Si}(\text{SeBu})_4$ . The dependence of the product mixture composition of the reaction of  $\text{PhSiCl}_3$  with HSeBu/ $\text{NEt}_3$  is illustrated in fig. 1.

Finally, all possible compounds  $\text{Me}_{4-x-y-z}\text{SiPh}_x\text{Cl}_y(\text{SeBu})_z$  could be detected and characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{77}\text{Se}$  NMR. In some cases of more volatile

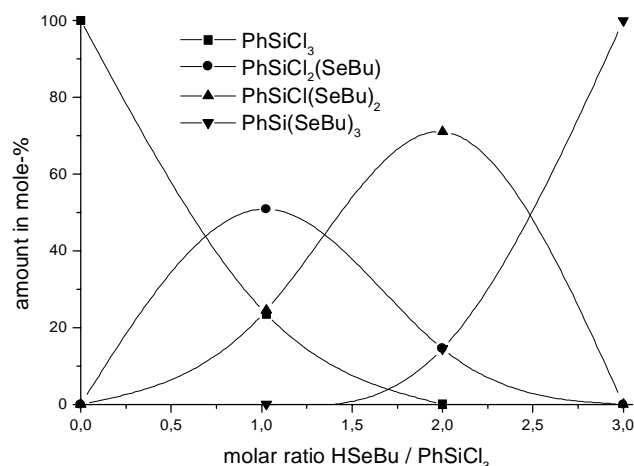


Fig. 1 Product composition of the reaction of  $\text{PhSiCl}_3$  with HSeBu/ $\text{NEt}_3$

products also mass spectra could be obtained. But because of the weakness of the Si–Se bond the GC-MS spectra of all compounds bearing more than one BuSe substituent indicated only the decomposition product BuSeSeBu.

The NMR data of the series  $\text{Me}_{4-x-y-z}\text{SiPh}_x\text{Cl}_y(\text{SeBu})_z$  are summarized in tables 1 and 2. In order to make changes of the NMR parameters versus the substitution pattern more clearly all parameters which change significantly with the substitution pattern were correlated with the number of chlorine, selenobutyl and phenyl substituents (table 3). Linear correlations were found in the cases of  $^{77}\text{Se}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR shifts as well as the coupling constants  $^1J_{\text{SiSe}}$  and  $^1J_{\text{SiC}}$ .

It should be noticed, that the  $^{77}\text{Se}$  chemical shift changes by more than 200 ppm from +63 ppm in  $\text{Cl}_3\text{SiSeBu}$  to –145 ppm in  $\text{Ph}_3\text{SiSeBu}$  despite of the fact that the first coordination sphere is always the same (Si–Se–C) and only the substituents at the silicon atom vary.

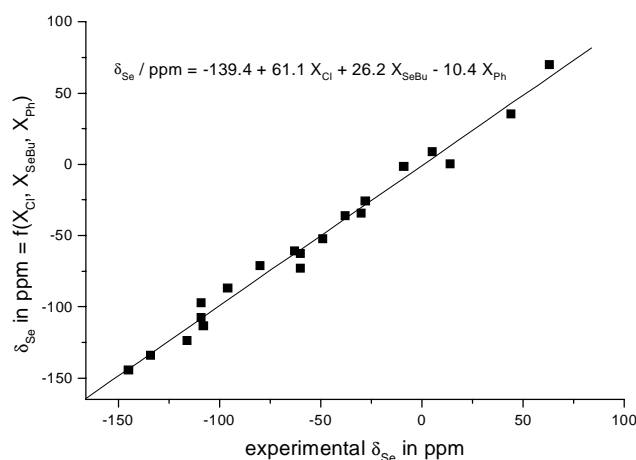
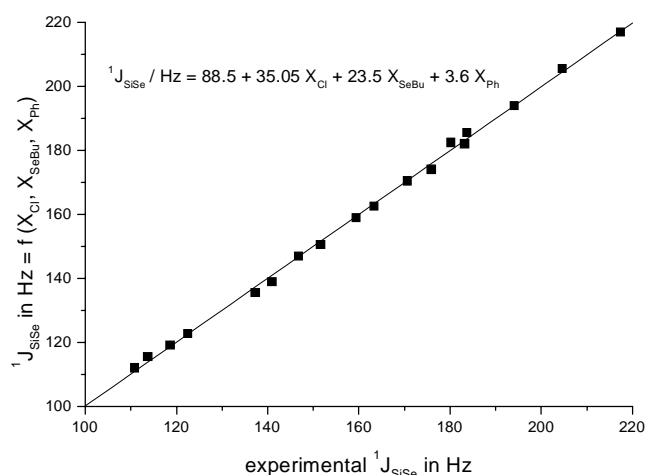


Fig. 2  $\delta_{\text{Se}}$  in monosilanes  $\text{Me}_x\text{Ph}_y\text{SiCl}_{4-x-y-z}(\text{SeBu})_z$  as function of the numbers of chlorine, selenobutyl and phenyl substituents

Furthermore, the very good linear correlation of the  $^1J_{\text{SiSe}}$  versus the substitution pattern is remarkable and might provide diagnostic values also for other selenium substituted silanes. The correlation of  $\delta_{\text{Se}}$  and  $^1J_{\text{SiSe}}$  with the substitution pattern is illustrated in fig. 2 and 3.

In general the values of A1 and A3, which indicate the effects of chlorine and phenyl substituents, are close to the observed values in thiobutyl substituted silanes [1].

But compared with thiobutyl substituted silanes [1], deviations of  $^{13}\text{C}$  NMR shifts of Si-CH<sub>3</sub> groups from a linear fit with the substitution pattern increase (standard deviation for SBU: 0.235 ppm, for SeBu 0.49 ppm). Whereas the effects of a SeBu substituent and a SBU substituent towards  $\delta_{\text{C}}$  of the carbon atoms in the phenyl rings and  $\delta_{\text{C}2-4(\text{SeBu})}$  are very similar, a SeBu substituent causes a much higher low field shift of  $\delta_{\text{C}(\text{SiMe})}$  (2.36 ppm instead of 1.31 ppm) and  $\delta_{\text{H}(\text{SiMe})}$  (0.354 ppm instead of 0.235 ppm). The greater effect of selenium compared with sulfur substituents towards  $\delta_{\text{C}}$  and  $\delta_{\text{H}}$  of



**Fig. 3**  $^1J_{\text{SiSe}}$  in monosilanes  $\text{Me}_x\text{Ph}_y\text{SiCl}_{4-x-y-z}(\text{SeBu})_z$  as function of the numbers of chlorine, selenobutyl and phenyl substituents

Si-Me groups parallels the increasing effects of heavier halogenes (I > Br > Cl > F) [9]. On the other hand

**Table 1**  $^{29}\text{Si}$ ,  $^{77}\text{Se}$  and  $^1\text{H}$  NMR chem. shifts (in ppm) and  $^1J_{\text{SiSe}}$  (in Hz) of  $\text{Me}_x\text{Ph}_y\text{SiCl}_{4-x-y-z}(\text{SeBu})_z$ , SeBu:  $\text{Se}-\text{C}^1\text{H}_2-\text{C}^2\text{H}_2-\text{C}^3\text{H}_2-\text{C}^4\text{H}_3$

compound	$\delta_{\text{Si}}$	$\delta_{\text{Se}}$	$^1J_{\text{SiSe}}$	$\delta_{\text{H}}$ SiMe	SiPh (o)	SiPh (m+p)	$\text{C}^1\text{H}_2$	$\text{C}^2\text{H}_2$	$\text{C}^3\text{H}_2$	$\text{C}^4\text{H}_3$
$\text{Me}_3\text{SiCl}$	29.8	–	–	0.35	–	–	–	–	–	–
$\text{Me}_3\text{Si}(\text{SeBu})$	11.3	–108	110.8	0.38	–	–	2.45	1.63	1.41	0.90
$\text{Me}_2\text{SiCl}_2$	32.0	–	–	0.71	–	–	–	–	–	–
$\text{Me}_2\text{SiCl}(\text{SeBu})$	28.7	–49	146.8	0.77	–	–	2.66	1.67	1.42	0.91
$\text{Me}_2\text{Si}(\text{SeBu})_2$	18.1	–96	137.3	0.71	–	–	2.59	1.67	1.42	0.91
$\text{MeSiCl}_3$	12.7	–	–	1.05	–	–	–	–	–	–
$\text{MeSiCl}_2(\text{SeBu})$	18.4	5	183.2	1.11	–	–	2.81	1.74	1.43	0.93
$\text{MeSiCl}(\text{SeBu})_2$	20.3	–28	170.6	1.09	–	–	2.732/ 2.726 <sup>a)</sup>	1.73	1.43	0.92
$\text{MeSi}(\text{SeBu})_3$	13.5	–63	159.4	1.06	–	–	2.67	1.71	1.42	0.92
$\text{SiCl}_3(\text{SeBu})$	–12.1	63	217.4	–	–	–	2.92	–	–	–
$\text{SiCl}_2(\text{SeBu})_2$	–3.1	44	204.6	–	–	–	2.84	1.78	1.44	0.93
$\text{SiCl}(\text{SeBu})_3$	1.7	14	194.0	–	–	–	2.80	1.77	1.43	0.93
$\text{Si}(\text{SeBu})_4$	1.9	–30	180.2	–	–	–	2.76	1.74	1.42	0.92
$\text{Me}_2\text{PhSiCl}$	20.3	–	–	0.61	7.58	7.33	–	–	–	–
$\text{Me}_2\text{PhSi}(\text{SeBu})$	6.2	–116	113.7	0.63	7.61	7.30	2.34	1.51	1.29	0.79
$\text{MePh}_2\text{SiCl}$	10.3	–	–	0.87	7.60	7.32	–	–	–	–
$\text{MePh}_2\text{Si}(\text{SeBu})$	2.2	–134	118.6	0.89	7.64	7.29	2.35	1.49	1.25	0.75
$\text{Ph}_3\text{SiCl}$	1.2	–	–	–	7.64	p 7.45, m 7.40	–	–	–	–
$\text{Ph}_3\text{Si}(\text{SeBu})$	–1.3	–145	122.5	–	7.71	7.27	2.39	1.45	1.22	0.69
$\text{MePhSiCl}_2$	18.8	–	–	0.92	7.65	7.35	–	–	–	–
$\text{MePhSiClSeBu}$	20.0	–60	151.6	0.92	–	–	–	–	–	–
$\text{MePhSi}(\text{SeBu})_2$	13.0	–109	140.9	0.93	7.71	7.33	2.553/ 2.541 <sup>a)</sup>	1.60	1.34	0.82
$\text{Ph}_2\text{SiCl}_2$	6.0	–	–	–	7.70	p 7.34, m 7.29	–	–	–	–
$\text{Ph}_2\text{SiCl}(\text{SeBu})$	12.4	–60	156.2	–	–	–	2.55	1.52	1.26	0.77
$\text{Ph}_2\text{Si}(\text{SeBu})_2$	10.1	–109	144.6	–	–	–	2.58	1.54	1.36	0.82
$\text{PhSiCl}_3$	–0.6	–	–	–	7.76	p 7.51, m 7.43	–	–	–	–
$\text{PhSiCl}_2(\text{SeBu})$	8.1	–9	183.7	–	–	–	2.75	1.68	1.37	0.87
$\text{PhSiCl}(\text{SeBu})_2$	12.9	–38	175.9	–	–	–	2.69	1.66	1.36	0.86
$\text{PhSi}(\text{SeBu})_3$	11.3	–80	163.3	–	7.81	7.37	2.63	1.63	1.36	0.83

<sup>a)</sup> diastereotopic H atoms

**Table 2**  $^{13}\text{C}$  NMR chem. shifts (in ppm) and  $^1J_{\text{SiC}}$  (in Hz) of  $\text{Me}_x\text{Ph}_y\text{SiCl}_{4-x-y-z}(\text{SeBu})_z$ ; SeBu:  $\text{Se}-\text{C}^1\text{H}_2-\text{C}^2\text{H}_2-\text{C}^3\text{H}_2-\text{C}^4\text{H}_3$ 

compound	SiMe	SeBu C <sup>1</sup>	C <sup>2</sup>	C <sup>3</sup>	C <sup>4</sup>	SiPh <i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>	$^1J_{\text{SiC}}$ (Me)
Me <sub>3</sub> SiCl	3.2	–	–	–	–	–	–	–	–	57.7
Me <sub>3</sub> SiSeBu	1.8	18.2 <sup>c)</sup>	35.2	22.8	13.5	–	–	–	–	52.1
Me <sub>2</sub> SiCl <sub>2</sub>	6.6	–	–	–	–	–	–	–	–	64.7
Me <sub>2</sub> SiClSeBu	5.7	21.5	34.4	22.8	13.5	–	–	–	–	–
Me <sub>2</sub> Si(SeBu) <sub>2</sub>	3.8	21.3	34.5	22.9	13.5	–	–	–	–	53.6
MeSiCl <sub>3</sub>	9.7	–	–	–	–	–	–	–	–	80.0
MeSiCl <sub>2</sub> SeBu	9.9	23.9	33.9	22.7	13.5	–	–	–	–	–
MeSiCl(SeBu) <sub>2</sub>	8.9	23.8	34.1	22.8	13.5	–	–	–	–	–
MeSi(SeBu) <sub>3</sub>	6.3	23.6	34.3	22.9	13.5	–	–	–	–	–
SiCl <sub>3</sub> (SeBu)	–	–	–	–	–	–	–	–	–	–
SiCl <sub>2</sub> (SeBu) <sub>2</sub>	–	25.9	33.6	22.7	13.4	–	–	–	–	–
SiCl(SeBu) <sub>3</sub>	–	26.0	33.8	22.8	13.5	–	–	–	–	–
Si(SeBu) <sub>4</sub>	–	25.7	33.8	22.9	13.6	–	–	–	–	–
Me <sub>2</sub> PhSiCl	2.0	–	–	–	–	136.05	133.0	128.0	130.25	59.1
Me <sub>2</sub> PhSiSeBu	0.4	19.1	34.7	22.8	34.7	136.9	133.7	127.8	129.55	53.9 <sup>a)</sup>
MePh <sub>2</sub> SiCl	0.85	–	–	–	–	134.25	134.0	128.05	130.45	–
MePh <sub>2</sub> SiSeBu	–0.8	19.9	34.5	22.7	13.4	135.1	134.6	127.9	129.8	55.4 <sup>b)</sup>
Ph <sub>3</sub> SiCl	–	–	–	–	–	132.7	135.1	128.1	130.7	–
Ph <sub>3</sub> SiSeBu	–	20.6	34.2	22.6	13.3	133.5	135.7	127.9	129.9	–
Ph <sub>2</sub> Si	–	–	–	–	–	134.2	136.4	127.9	129.6	–
MePhSiCl <sub>2</sub>	5.3	–	–	–	–	133.2	132.9	128.3	131.6	–
MePhSiClSeBu	4.8	22.0	34.0	22.7	13.4	134.3	133.4	128.1	130.8	–
MePhSi(SeBu) <sub>2</sub>	2.8	21.8	34.2	22.8	13.5	135.1	133.9	128.0	130.2	–
Ph <sub>2</sub> SiCl <sub>2</sub>	–	–	–	–	–	131.8	133.95	128.25	131.65	–
Ph <sub>2</sub> SiCl(SeBu)	–	22.0	33.9	22.6	13.3	133.0	134.45	128.2	131.0	–
Ph <sub>2</sub> Si(SeBu) <sub>2</sub>	–	22.4	34.0	22.8	13.45	133.8	134.9	128.05	130.4	–
PhSiCl <sub>3</sub>	–	–	–	–	–	131.4	133.1	128.5	132.7	–
PhSiCl <sub>2</sub> SeBu	–	23.6	33.7	22.6	13.35	132.9	133.5	128.4	132.1	–
PhSiCl(SeBu) <sub>2</sub>	–	24.2	33.8	22.7	13.4	133.7	133.9	128.2	131.4	–
PhSi(SeBu) <sub>3</sub>	–	24.0	33.9	22.8	13.5	134.0	134.3	128.0	130.7	–

<sup>a)</sup>  $^1J_{\text{SiC}}(\text{SiPh})$ : 69.0 Hz, <sup>b)</sup>  $^1J_{\text{SiC}}(\text{SiPh})$ : 70.9 Hz, <sup>c)</sup>  $^1J_{\text{SeC}}$ : 53.5 Hz

**Table 3** Multiple linear regression results of  $^{77}\text{Se}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR parameters in  $\text{Me}_x\text{Ph}_y\text{SiCl}_{4-x-y-z}(\text{SeBu})_z$ 

parameter	A0 (ppm)	A1 (ppm)	A2 (ppm)	A3 (ppm)	r	sd (ppm)
$\delta_{\text{Se}}$	–139.4	61.1	26.2	–10.4	0.992	7.8
$\delta_{\text{C}} \text{Si}-\text{CH}_3$	– 0.4	3.62	2.36	–1.30	0.991	0.49
$\delta_{\text{C}} \text{Se}-\text{CH}_2-$	16.3	2.43	2.40	0.56	0.993	0.29
$\delta_{\text{C}} \text{Se}-\text{CH}_2-\text{CH}_2-$	35.4	–0.53	–0.39	–0.29	0.974	0.098
$\delta_{\text{C}} \textit{ipso}$ (Ph)	139.4	–2.18	–1.28	–1.44	0.974	0.35
$\delta_{\text{C}} \textit{ortho}$ (Ph)	132.05	–0.06	0.41	1.06	0.995	0.11
$\delta_{\text{C}} \textit{meta}$ (Ph)	127.7	0.26	0.11	0.05	0.963	0.04
$\delta_{\text{C}} \textit{para}$ (Ph)	128.8	1.24	0.57	0.19	0.999	0.05
$\delta_{\text{H}} \text{Si}-\text{CH}_3$	0.015	0.349	0.354	0.244	0.996	0.03
$\delta_{\text{H}} \text{Se}-\text{CH}_2-$	2.346	0.160	0.106	–0.026	0.977	0.04
$^1J_{\text{SiSe}}$	88.5 Hz	35.05 Hz	23.5 Hz	3.6 Hz	0.999	1.4 Hz
$^1J_{\text{SiC}}(\text{Me})$	48.4 Hz	9.72 Hz	3.00 Hz	1.94 Hz	0.985	2.0 Hz

parameter = A0 + A1 \* X<sub>Cl</sub> + A2 \* X<sub>SeBu</sub> + A3 \* X<sub>Ph</sub>

X<sub>Cl</sub> = number of chlorine substituents, X<sub>SeBu</sub> = number of selenobutyl substituents

X<sub>Ph</sub> = number of phenyl substituents

because of the lower electronegativity of selenium the introduction of a selenobutyl substituent increases the coupling constant  $^1J_{\text{SiC}}$  by 3.0 Hz, whereas a thiobutyl substituent causes an increase of 4.3 Hz [1].

More complicated is a correlation of  $\delta_{\text{Si}}$  with the substitution pattern. In general a “sagging” pattern of  $\delta_{\text{Si}}$  is

observed in the series  $\text{R}_x\text{SiX}_{4-x}$  with R = alkyl or aryl and X = heteroelement like F, Cl, Br, OR, SR, NR<sub>2</sub>. In these cases a quadratic fit of the type  $\delta_{\text{Si}}$  (in ppm) = A0 + A1 \* [X] + A2 \* [X]<sup>2</sup> can be used to correlate the chemical shifts with the number of X- substituents [X]. The  $^{29}\text{Si}$  NMR shifts of the series  $\text{Me}_x\text{Si}(\text{SeBu})_{4-x}$  can

be fitted with:

$$\delta_{\text{Si}} \text{ (in ppm)} = -0.41 + 16.94 * [\text{X}] - 4.09 * [\text{X}]^2; r = 0.995, \text{sd} = 1.11 \text{ ppm}$$

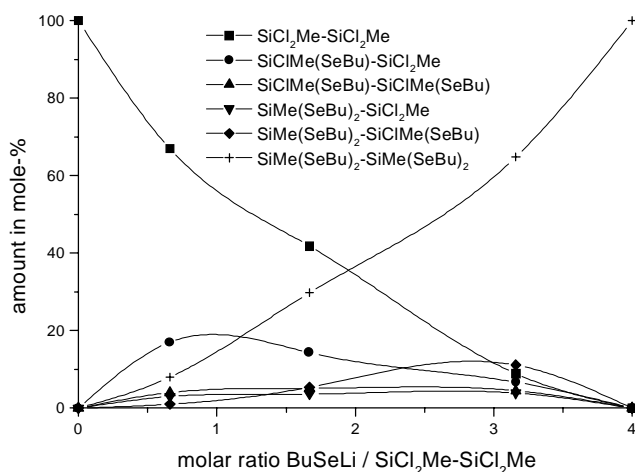
[X] = number of SeBu substituents

More interesting is a comparison of the  $^{29}\text{Si}$  NMR shifts of  $\text{Me}_{4-x-y-z}\text{SiPh}_x\text{Cl}_y(\text{SeBu})_z$  with the analogously substituted thiobutyl silanes  $\text{Me}_{4-x-y-z}\text{SiPh}_x\text{Cl}_y(\text{SBU})_z$ . In general the signals of the selenobutyl substituted compounds are shifted to higher field. The difference  $\Delta\delta = \delta_{(\text{SBU})} - \delta_{(\text{SeBU})}$  increases with the number of EBU (E = S or Se) and chlorine substituents but decreases with the number of phenyl substituents. It can be fitted with:

$$\Delta\delta \text{ (in ppm)} = -5.9 + 2.60 * [\text{Cl}] + 7.66 * [\text{SeBu}] - 1.76 * [\text{Ph}]; r = 0.937, \text{sd} = 3.03 \text{ ppm}$$

## II. Disilanes

The reaction of chloropentamethyldisilane with a THF solution of BuSeLi yielded after filtration from LiCl and removal of the solvents pure  $\text{Si}_2\text{Me}_5\text{SeBu}$ . Similar reaction of 1,2-dichlorotetramethyldisilane yielded with one equivalent BuSeLi a mixture of 45%  $\text{ClMe}_2\text{Si-SiMe}_2(\text{SeBu})$  besides equal amounts of 1,2- $\text{Si}_2\text{Me}_4(\text{SeBu})_2$  and residual  $\text{Si}_2\text{Me}_4\text{Cl}_2$ . The reaction with two equivalents BuSeLi yielded pure 1,2- $\text{Si}_2\text{Me}_4(\text{SeBu})_2$  after work-up. The treatment of 1,1,2,2-tetrachlorodimethyldisilane with BuSeLi using several molar ratios yielded product mixtures which contained only small amounts of partially substituted disilanes  $\text{Si}_2\text{Me}_2\text{Cl}_x(\text{SeBu})_{4-x}$  besides starting  $\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$  and the final substitution product  $\text{SiMe}(\text{SeBu})_2\text{-SiMe}(\text{SeBu})_2$ , see fig. 4.



**Fig. 4** Product composition of the reaction of  $\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$  with BuSeLi

On the other hand, addition of two equivalents BuSeH and  $\text{NEt}_3$  to a solution of 1,1,2,2-tetrachlorodimethyld-

isilane in *n*-hexane yielded a mixture of 2%  $\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$ , 21%  $\text{SiClMe}(\text{SeBu})\text{-SiCl}_2\text{Me}$ , 29%  $\text{SiClMe}(\text{SeBu})\text{-SiClMe}(\text{SeBu})$  (both diastereomers), 28%  $\text{SiMe}(\text{SeBu})_2\text{-SiCl}_2\text{Me}$ , 17%  $\text{SiMe}(\text{SeBu})_2\text{-SiClMe}(\text{SeBu})$  and 4%  $\text{SiMe}(\text{SeBu})_2\text{-SiMe}(\text{SeBu})_2$ . Finally, the addition of two equivalents BuSeH/ $\text{NEt}_3$  to a solution of  $\text{SiCl}_2\text{Me-SiClMe}_2$  produced mainly  $\text{SiMe}(\text{SeBu})_2\text{-SiClMe}_2$ . This indicates, that the  $\text{SiCl}_2\text{Me}$  group is preferred substituted as it was also observed in the reaction of  $\text{SiCl}_2\text{Me-SiClMe}_2$  with BuSH/ $\text{NEt}_3$  [1].

The NMR data of all observed selenobutyl substituted disilanes are summarized in tables 4 and 5. It was again possible to correlate some of the observed parameters with the substitution pattern, see table 6, but in disilanes one has to distinguish between substituents at  $\text{Si}^1$  and the neighbour  $\text{Si}^2$ .

In the case of  $\delta_{\text{H}(\text{SiMe})}$  substituents at  $\text{Si}^2$  exhibit approximately  $1/4$  the effect of substituents at  $\text{Si}^1$ . Compared with monosilanes chlorine substituents at  $\text{Si}^1$  cause greater but SeBu substituents at  $\text{Si}^1$  smaller downfield shifts of  $\delta_{\text{H}} \text{SiMe}$ ,  $\delta_{\text{C}} \text{SiMe}$  and  $\delta_{\text{Se}}$  in disilanes. Remarkable are the very good correlations of  $\delta_{\text{Se}}$  and  $^1J_{\text{SiSe}}$  in disilanes. The measured values of the coupling constant  $^1J_{\text{SiSi}}$  can be fitted with the quadratic equation:

$$^1J_{\text{SiSi}} = 81.3 \text{ Hz} + 10.7 \text{ Hz} * X_{\text{Cl}} + 1.73 \text{ Hz} * (X_{\text{Cl}})^2 + 3.9 \text{ Hz} * X_{\text{SeBu}}; r = 0.998, \text{sd} = 1.62$$

$X_{\text{Cl}}$  = number of chlorine substituents,  $X_{\text{SeBu}}$  = number of SeBu substituents

No simple method could be found to fit the observed  $^{29}\text{Si}$  NMR chemical shifts with the substitution pattern. But if the silicon chemical shifts are compared with those ones of the analogously SBU substituted disilanes in [1] it can be seen that all silyl groups bearing EBU (E = S, Se) substituents are shifted to higher field by approximately 5 ppm per EBU substituent.

## III. Tri- and Isotetrasilanes

The reaction of 1,3-dichlorohexamethyltrisilane with 1 equivalent HSeBu/ $\text{NEt}_3$  yielded the monosubstituted product  $\text{ClSiMe}_2\text{-SiMe}_2\text{-SiMe}_2\text{SeBu}$  in 52% amount besides starting  $\text{SiMe}_2(\text{SiMe}_2\text{Cl})_2$  and disubstituted trisilane  $\text{SiMe}_2(\text{SiMe}_2\text{SeBu})_2$ .

1,2,3-Trichloropentamethyltrisilane bears chlorine substituents at the terminal as well as at the middle silicon atom. Therefore, the stepwise reaction with BuSeH/ $\text{NEt}_3$  can follow two different pathways depending on the higher or lower reactivity of the chlorine substituent at the middle silicon atom. For instance the Lewis-base catalyzed hydrogenation with one equivalent  $\text{Me}_3\text{SnH}$  yields exclusively  $(\text{SiClMe}_2)_2\text{SiMeH}$  [10] whereas in the reaction with  $\text{HNEt}_2$  the terminal chlorine substituents are substituted by  $\text{NEt}_2$  first [11]. In analogy to the reaction with  $\text{HSBu}/\text{NEt}_3$  [1] 1,2,3-

**Table 4**  $^{29}\text{Si}$  and  $^{77}\text{Se}$  NMR chem. shifts (in ppm) and coupling constants  $^1J_{\text{SiSi}}$ ,  $^1J_{\text{SiC}}$ ,  $^1J_{\text{SiSe}}$  and  $^2J_{\text{SiSe}}$  (in Hz) in disilanes  $\text{Si}_2\text{Me}_{6-x-y}\text{Cl}_x(\text{SeBu})_y$ 

compound	$\delta_{\text{SiA}}$	$^1J_{\text{SiC}}$	$\delta_{\text{SiB}}$	$^1J_{\text{SiC}}$	$^1J_{\text{SiSi}}$	$\delta_{\text{Se}}$	$^1J_{\text{SiSe}}$	$^2J_{\text{SiSe}}$
$\text{Si}^{\text{A}}\text{Me}_3\text{-Si}^{\text{B}}\text{Me}_2\text{Cl}$	-18.2	46.1	22.9	44.8	94.0	-	-	-
$\text{Si}^{\text{A}}\text{Me}_3\text{-Si}^{\text{B}}\text{Me}_2\text{SeBu}$	-17.5	45.2	-5.6	42.8	86.1	-128	119.5	14.6
$\text{SiMe}_2\text{Cl-SiMe}_2\text{Cl}$	17.4	48.8	-	-	-	-	-	-
$\text{Si}^{\text{A}}\text{Me}_2\text{Cl-Si}^{\text{B}}\text{Me}_2\text{SeBu}$	20.0	41.8	-8.3	45.2	97.2	-136	121.5	16.0
$\text{SiMe}_2(\text{SeBu})\text{-SiMe}_2(\text{SeBu})$	-6.7	44.7	-	-	-	-125	122.2	15.1
$\text{Si}^{\text{A}}\text{Me}_2\text{Cl-Si}^{\text{B}}\text{MeCl}_2$	15.0	52.0	24.7	54.0	127.0	-	-	-
$\text{Si}^{\text{A}}\text{Me}_2\text{Cl-Si}^{\text{B}}\text{Me}(\text{SeBu})_2$	18.6	-	-1.4	-	100.6	-122	150.2	17.0
$\text{Si}^{\text{A}}\text{Me}_2(\text{SeBu})\text{-Si}^{\text{B}}\text{Me}(\text{SeBu})_2$	-6.0	-	0.8	-	93.3	A: -119 B: -113	124.9 150.6	15.5 14.1
$\text{SiMeCl}_2\text{-SiMeCl}_2$	17.6	57.5	-	-	-	-	-	-
$\text{Si}^{\text{A}}\text{MeCl}_2\text{-Si}^{\text{B}}\text{MeCl}(\text{SeBu})$	20.4	-	11.7	-	135.6	-60	168.6	-
$\text{SiMeCl}(\text{SeBu})\text{-SiMeCl}(\text{SeBu})$	13.7/ 14.0 <sup>a)</sup>	-	-	-	-	-45.9/ -46.7 <sup>a)</sup>	166.7 <sup>a)</sup>	14.6/ 14.1 <sup>a)</sup>
$\text{Si}^{\text{A}}\text{MeCl}_2\text{-Si}^{\text{B}}\text{Me}(\text{SeBu})_2$	22.4	-	-3.9	-	118.1	-123	154.5	20.4
$\text{Si}^{\text{A}}\text{MeCl}(\text{SeBu})\text{-Si}^{\text{B}}\text{Me}(\text{SeBu})_2$	15.3	-	-2.1	-	104.0	A: -35 B: -113.7/ -114.0 <sup>b)</sup>	168.1 153.6	17.7 12
$\text{SiMe}(\text{SeBu})_2\text{-SiMe}(\text{SeBu})_2$	-1.1	45.2	-	-	-	-106	154.1	16.0

<sup>a)</sup> two diastereomers, <sup>b)</sup> diastereotopic SeBu groups

**Table 5**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chem. shifts (in ppm) in disilanes  $\text{Si}_2\text{Me}_{6-x-y}\text{Cl}_x(\text{SeBu})_y$   
SeBu:  $\text{Se-C}^1\text{H}_2\text{-C}^2\text{H}_2\text{-C}^3\text{H}_2\text{-C}^4\text{H}_3$ 

compound	$\delta_{\text{C}}^{\text{Si}^{\text{A}}\text{Me}}$	$\delta_{\text{C}}^{\text{Si}^{\text{B}}\text{Me}}$	SeBu: $\text{C}^1\text{-C}^4$	$\delta_{\text{H}}^{\text{Si}^{\text{A}}\text{Me}}$	$\delta_{\text{H}}^{\text{Si}^{\text{B}}\text{Me}}$	SeBu $\text{C}^1\text{-C}^4$
$\text{Si}^{\text{A}}\text{Me}_3\text{-Si}^{\text{B}}\text{Me}_2\text{Cl}$	-3.0	2.0	-	0.16	0.47	-
$\text{Si}^{\text{A}}\text{Me}_3\text{-Si}^{\text{B}}\text{Me}_2\text{SeBu}$	-2.15	-1.1	17.9, 35.3, 22.95, 13.55	0.14	0.43	2.48, 1.64, 1.41, 0.90
$\text{SiMe}_2\text{Cl-SiMe}_2\text{Cl}$	1.5	-	-	0.56	-	-
$\text{Si}^{\text{A}}\text{Me}_2\text{Cl-Si}^{\text{B}}\text{Me}_2\text{SeBu}$	1.2	-1.8	18.6, 35.1, 22.8, 13.5	0.54	0.52	2.53, 1.65, 1.41, 0.91
$\text{SiMe}_2(\text{SeBu})\text{-SiMe}_2(\text{SeBu})$	-0.8	-	18.55, 35.15, 22.9, 13.5	0.51	-	2.53, 1.65, 1.41, 0.91
$\text{Si}^{\text{A}}\text{Me}_2\text{Cl-Si}^{\text{B}}\text{MeCl}_2$	0.8	5.8	-	0.66	0.93	-
$\text{Si}^{\text{A}}\text{Me}_2\text{Cl-Si}^{\text{B}}\text{Me}(\text{SeBu})_2$	2.6	-0.2	21.5, 34.6, 22.9, 13.5	0.60	0.84	2.65, 1.69, 1.41, 0.92
$\text{Si}^{\text{A}}\text{Me}_2(\text{SeBu})\text{-Si}^{\text{B}}\text{Me}(\text{SeBu})_2$	-0.1	0.7	A: 19.2, 35.1, 22.9, 13.5 B: 21.6, 34.6, 22.9, 13.5	0.57	0.82	2.59 (A) / 2.65 (B), 1.69, 1.42, 0.92
$\text{SiMeCl}_2\text{-SiMeCl}_2$	5.1	-	-	0.98	-	-
$\text{Si}^{\text{A}}\text{MeCl}_2\text{-Si}^{\text{B}}\text{MeCl}(\text{SeBu})$	6.1	2.8	<sup>b)</sup>	-	<sup>c)</sup>	-
$\text{SiMeCl}(\text{SeBu})\text{-SiMeCl}(\text{SeBu})$	3.7/ 3.8 <sup>a)</sup>	-	<sup>b)</sup>	-	<sup>c)</sup>	-
$\text{Si}^{\text{A}}\text{MeCl}_2\text{-Si}^{\text{B}}\text{Me}(\text{SeBu})_2$	6.8	-0.25	<sup>b)</sup>	-	<sup>c)</sup>	-
$\text{Si}^{\text{A}}\text{MeCl}(\text{SeBu})\text{-Si}^{\text{B}}\text{Me}(\text{SeBu})_2$	4.5	0.6	<sup>b)</sup>	-	<sup>c)</sup>	-
$\text{SiMe}(\text{SeBu})_2\text{-SiMe}(\text{SeBu})_2$	1.2	-	22.0, 34.4, 22.9, 13.55	0.87	-	2.69, 1.69, 1.42, 0.92

<sup>a)</sup> two diastereomers, <sup>b)</sup>  $\text{C}^1$ : 21.4 (in  $\text{SiClMeSeBu}$ ) or 21.9 (in  $\text{SiMe}(\text{SeBu})_2$ ),  $\text{C}^2$ : 34.4,  $\text{C}^3$ : 22.6–22.8,  $\text{C}^4$ : 13.5; <sup>c)</sup>  $\text{SiMe} + \text{C}^4$ : 0.90–0.96,  $\text{C}^1$ : 2.78 (in  $\text{SiClMeSeBu}$ ) or 2.70 (in  $\text{SiMe}(\text{SeBu})_2$ ),  $\text{C}^2$ : 1.70,  $\text{C}^3$ : 1.43

**Table 6** multiple linear regression results of  $^{77}\text{Se}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR parameters in disilanes  $\text{Si}_2\text{Me}_{6-x-y}\text{Cl}_x(\text{SeBu})_y$ 

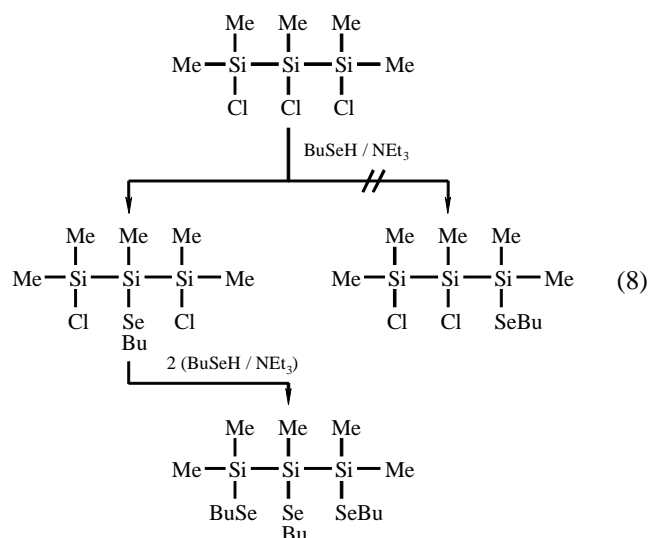
parameter	A0 (ppm)	A1 (ppm)	A2 (ppm)	A3 (ppm)	A4 (ppm)	r	sd (ppm)
$\delta_{\text{H}}^{\text{Si-CH}_3}$	0.081	0.371	0.095	0.334	0.073	0.998	0.021
$\delta_{\text{C}}^{\text{Si-CH}_3}$	-2.71	4.36	-0.33	1.56	0.47	0.995	0.31
$\delta_{\text{Se}}$	-143.9	81.8	-4.4	13.5	5.9	0.9987	2.18
$^1J_{\text{SiSe}}$	90.3 Hz	42.9 Hz	3.14 Hz	28.7 Hz	3.0 Hz	0.9997	0.56
$^2J_{\text{SiSe}}$	13.15 Hz	2.20 Hz	-2.42 Hz	0.13 Hz	1.16 Hz	0.980	0.56

parameter =  $A0 + A1 * X_{\text{Cl1}} + A2 * X_{\text{Cl2}} + A3 * X_{\text{Se1}} + A4 * X_{\text{Se2}}$

$X_{\text{Cl1}}$  = number of chlorine substituents at  $\text{Si}^1$ ,  $X_{\text{Cl2}}$  = number of chlorine substituents at  $\text{Si}^2$

$X_{\text{Se1}}$  = number of selenobutyl substituents at  $\text{Si}^1$ ,  $X_{\text{Se2}}$  = number of selenobutyl substituents at  $\text{Si}^2$

trichloropentamethyltrisilane yields with one equivalent BuSeH/NEt<sub>3</sub> exclusively substitution at the middle silicon atom under formation of (SiClMe<sub>2</sub>)<sub>2</sub>SiMe(SeBu). Further treatment with 2 HSeBu/NEt<sub>3</sub> or reaction with 3 equivalents BuSeLi results in the formation of (SiMe<sub>2</sub>(SeBu))<sub>2</sub>SiMe(SeBu):



The chlorine substituents in (Me<sub>3</sub>Si)<sub>2</sub>SiCl<sub>2</sub> react only very slowly with HSeBu/NEt<sub>3</sub> (mainly starting materials after 2 days reaction at room temperature in *n*-hexane) but addition of BuSeLi to (Me<sub>3</sub>Si)<sub>2</sub>SiCl<sub>2</sub> yielded the expected substitution products (Me<sub>3</sub>Si)<sub>2</sub>SiCl(SeBu) and (Me<sub>3</sub>Si)<sub>2</sub>Si(SeBu)<sub>2</sub>, which contain the new silyl groups (R<sub>3</sub>Si)<sub>2</sub>SiCl(SeR) and (R<sub>3</sub>Si)<sub>2</sub>Si(SeR)<sub>2</sub>.

Addition of one or two equivalents HSeBu/NEt<sub>3</sub> to solutions of tris-(chlorodimethylsilyl)methylsilane resulted in the formation of the partially substituted isotetrasilanes MeSi(SiMe<sub>2</sub>Cl)<sub>2</sub>(SiMe<sub>2</sub>SeBu) and MeSi(SiMe<sub>2</sub>Cl)(SiMe<sub>2</sub>SeBu)<sub>2</sub>, respectively. Both compounds were present in a maximum amount of approximately 52%. The completely substituted product SiMe(SiMe<sub>2</sub>SeBu)<sub>3</sub> was obtained by reaction of SiMe(SiClMe<sub>2</sub>)<sub>3</sub> with three equivalents BuSeLi.

An isotetrasilane bearing six selenobutyl substituents, MeSi(SiMe(SeBu))<sub>3</sub>, was prepared by addition of 6 equivalents BuSeLi to a solution of MeSi(SiCl<sub>2</sub>Me)<sub>3</sub>.

The NMR data of all prepared selenobutyl substituted tri- and isotetrasilanes are summarized in tables 7 and 8 (data of the starting methylchlorotrisilanes and isotetrasilanes see in [1]).

<sup>1</sup>H and <sup>13</sup>C NMR shifts are close to values of the same silyl group in selenobutyl substituted disilanes. <sup>77</sup>Se

**Table 7** <sup>29</sup>Si and <sup>77</sup>SeNMR chem. shifts (in ppm) and coupling constants (in Hz) of seleno-butyl substituted tri- and isotetrasilanes

compound		$\delta_{\text{Si}}$	$^1J_{\text{SiSi}}$	$^1J_{\text{SiCl}}$	$\delta_{\text{Se}}$	$J_{\text{SiSe}}$
Si <sup>A</sup> ClMe <sub>2</sub> -Si <sup>B</sup> Me <sub>2</sub> -Si <sup>C</sup> Me <sub>2</sub> SeBu	A	26.3		53.0		
	B	-43.2				<sup>2</sup> J: 15.1
	C	-3.8			-121	<sup>1</sup> J: 121.5
(Si <sup>A</sup> Me <sub>2</sub> SeBu) <sub>2</sub> Si <sup>B</sup> Me <sub>2</sub>	A	-2.9				<sup>2</sup> J: 14.6
	B	-43.2			-119	<sup>1</sup> J: 122.0
(Si <sup>A</sup> ClMe <sub>2</sub> ) <sub>2</sub> Si <sup>B</sup> MeSeBu	A	22.5	81.6	48.6		<sup>2</sup> J: 11.7
	B	-35.6		39.4	-176	<sup>1</sup> J: 129.3
(Si <sup>A</sup> Me <sub>2</sub> (SeBu)) <sub>2</sub> Si <sup>B</sup> MeSeBu	A	-4.5	70.5	44.7	-111	<sup>1</sup> J: 125.4 <sup>2</sup> J: 9.7
	B	-32.7			-158	<sup>1</sup> J: 128.3 <sup>2</sup> J: 15.5
(Si <sup>A</sup> Me <sub>3</sub> ) <sub>2</sub> Si <sup>B</sup> Cl(SeBu)	A	-11.4			-80	
	B	11.2				<sup>1</sup> J: 163.3
(Si <sup>A</sup> Me <sub>3</sub> ) <sub>2</sub> Si <sup>B</sup> (SeBu) <sub>2</sub>	A	-11.4	64.2	44.7	-145	
	B	-18.8				<sup>1</sup> J: 152.1
MeSi <sup>A</sup> (Si <sup>B</sup> Me <sub>3</sub> ) <sub>2</sub> (Si <sup>C</sup> Me <sub>2</sub> SeBu)	A	-84.1			-99	<sup>2</sup> J: 15.1
	B	-12.2				
	C	-0.1				<sup>1</sup> J: 125.4
MeSi <sup>A</sup> (Si <sup>B</sup> Me <sub>3</sub> )(Si <sup>C</sup> Me <sub>2</sub> SeBu) <sub>2</sub>	A	-80.5			-100	<sup>2</sup> J: 16.5
	B	-11.9				
MeSi <sup>A</sup> (Si <sup>B</sup> ClMe <sub>2</sub> ) <sub>2</sub> (Si <sup>C</sup> Me <sub>2</sub> SeBu)	A	-76.6			-104	<sup>1</sup> J: 125.4 <sup>2</sup> J: 18.0
	B	28.1				<sup>3</sup> J: 15
	C	-3.1				<sup>1</sup> J: 124.4
MeSi <sup>A</sup> (Si <sup>B</sup> ClMe <sub>2</sub> )(Si <sup>C</sup> Me <sub>2</sub> SeBu) <sub>2</sub>	A	-77.0			-102	<sup>2</sup> J: 17.0
	B	29.1				<sup>3</sup> J: 17.0
	C	-2.1				<sup>1</sup> J: 124.4
MeSi <sup>A</sup> (Si <sup>B</sup> Me <sub>2</sub> SeBu) <sub>3</sub>	A	-77.3			-100	<sup>2</sup> J: 17.0
	B	-1.1				<sup>1</sup> J: 125.4
MeSi <sup>A</sup> (Si <sup>B</sup> Me(SeBu)) <sub>2</sub>	A	-66.1			-87	<sup>2</sup> J: 12.6
	B	3.83		45.7		<sup>1</sup> J: 154.5

**Table 8**  $^{13}\text{C}$  and  $^1\text{H}$  NMR chem. shifts (in ppm) of selenobutyl substituted tri- and *iso*-tetrasilanes

compound		$\delta_{\text{C}}/\text{SiMe}$	$\delta_{\text{H}}/\text{SiMe}$	$\delta_{\text{C}}/\text{SeBu}$	$\delta_{\text{H}}/\text{SeBu}$
$\text{Si}^{\text{A}}\text{ClMe}_2\text{-Si}^{\text{B}}\text{Me}_2\text{-Si}^{\text{C}}\text{Me}_2\text{SeBu}$	A	3.2	0.54	18.6, 35.2,	2.52, 1.65,
	B	-6.8	0.26	22.9, 13.5	1.41, 0.91
	C	-0.1	0.52		
$(\text{Si}^{\text{A}}\text{Me}_2\text{SeBu})_2\text{Si}^{\text{B}}\text{Me}_2$	A	0.1	0.51	18.5, 35.2,	2.52, 1.65,
	B	-5.9	0.25	22.9, 13.5	1.41, 0.91
$(\text{Si}^{\text{A}}\text{ClMe}_2)_2\text{Si}^{\text{B}}\text{MeSeBu}$	A	1.85/2.22 <sup>a)</sup>	0.63	19.8, 35.1,	2.64, 1.66,
	B	-2.25	0.66	22.8, 13.5	1.41, 0.91
$(\text{Si}^{\text{A}}\text{Me}_2(\text{SeBu}))_2\text{Si}^{\text{B}}\text{MeSeBu}$	A	0.51/0.69 <sup>a)</sup>	0.58	19.1 (A)/	2.56 (A)/
	B	-4.5	0.61	19.8 (B), 35.1, 22.9, 13.6	2.62, 1.65, 1.41, 0.91
$(\text{Si}^{\text{A}}\text{Me}_3)_2\text{Si}^{\text{B}}\text{Cl}(\text{SeBu})$	A	-0.1	0.25	24.0, 33.9, 22.8, 13.5	2.66, 1.66, 1.42, 0.91
$(\text{Si}^{\text{A}}\text{Me}_3)_2\text{Si}^{\text{B}}(\text{SeBu})_2$	A	-0.1	0.25	22.8, 34.7, 23.0, 13.6	2.63, 1.66, 1.42, 0.91
$\text{MeSi}^{\text{A}}(\text{Si}^{\text{B}}\text{Me}_3)_2(\text{Si}^{\text{C}}\text{Me}_2\text{SeBu})$	A	-12.7		18.8, 35.2,	2.55, 1.65,
	B	0.4	0.18	23.0, 13.6	1.41, 0.91
	C	1.7	0.52		
$\text{MeSi}^{\text{A}}(\text{Si}^{\text{B}}\text{Me}_3)(\text{Si}^{\text{C}}\text{Me}_2\text{SeBu})_2$	A	-11.75		18.8, 35.2,	2.55, 1.65,
	B	0.45	0.23	23.0, 13.6	1.41, 0.91
	C	1.75/1.80 <sup>a)</sup>	0.56		
$\text{MeSi}^{\text{A}}(\text{Si}^{\text{B}}\text{ClMe}_2)_2(\text{Si}^{\text{C}}\text{Me}_2\text{SeBu})$	A	-12.5	0.34	19.2, 35.1,	2.55, 1.65,
	B	4.9	0.64	23.0, 13.6	1.41, 0.91
	C	1.3	0.62		
$\text{MeSi}^{\text{A}}(\text{Si}^{\text{B}}\text{ClMe}_2)(\text{Si}^{\text{C}}\text{Me}_2\text{SeBu})_2$	A	-11.6	0.32	19.2, 35.1,	2.55, 1.65,
	B	5.2	0.64	23.0, 13.6	1.41, 0.91
	C	1.54/1.60 <sup>a)</sup>	0.62		
$\text{MeSi}^{\text{A}}(\text{Si}^{\text{B}}\text{Me}_2\text{SeBu})_3$	A	-10.8	0.30	19.2, 35.1,	2.55, 1.65,
	B	1.9	0.61	23.0, 13.6	1.41, 0.91
$\text{MeSi}^{\text{A}}(\text{Si}^{\text{B}}\text{Me}(\text{SeBu}))_2_3$	A	-7.4	0.46	22.6, 34.5,	2.68, 1.68,
	B	3.3	1.01	23.0, 13.6	1.43, 0.92

<sup>a)</sup> diastereotopic methyl groups

NMR chemical shifts in the terminal silyl groups  $\text{SiMe}_2(\text{SeBu})$  and  $\text{SiMe}(\text{SeBu})_2$  are shifted to lower field if the size of the oligosilane is increased from di- to tetrasilane. On the other hand selenobutyl substituents at the linear silyl units  $(\text{R}_3\text{Si})_2\text{SiMe}(\text{SeBu})$  and  $(\text{R}_3\text{Si})_2\text{Si}(\text{SeBu})_2$  have  $^{77}\text{Se}$  chemical shifts at very high field.

As already observed in disilanes the  $^{29}\text{Si}$  chemical shifts of SeBu-substituted silyl groups in tri- and isotetrasilanes are shifted 5–8 ppm per SeBu substituent to higher field compared with the analogously thiobutyl substituted tri- and isotetrasilanes in [1].

Since each isotetrasilane of the type  $\text{MeSi}(\text{SiMeY}_2)_3$ ,  $\text{Y} = \text{Me}, \text{Cl}, \text{SeBu}$ , contains one *tert*-SiMe group, correlations of the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR chemical shifts of this group might be most useful for assignments and determinations of composition mixtures. The regression results are listed in table 9. The effects of chlorine and selenobutyl substituents towards  $\delta_{\text{H}}$  are almost identical with the values found in disilanes for substituents at

$\text{Si}^2$ . Whereas  $\delta_{\text{C}}$  of the *tert*-SiMe group is five times more sensitive to the number SeBu than the number of chlorine substituents, the effects of SeBu and Cl towards  $\delta_{\text{Si}}$  are of similar size.

## Experimental

All NMR spectra were recorded on a Bruker DPX 400 in  $\text{CDCl}_3$  solution and TMS as internal standard for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$ .  $^{77}\text{Se}$  NMR measurements are calibrated with  $\text{Ph}_2\text{Se}_2$  ( $\delta_{\text{Se}} = +460$  ppm) as external standard. In order to get a sufficient signal/noise ratio of  $^{29}\text{Si}$  NMR spectra for obtaining  $^1J_{\text{SiC}}$ ,  $^1J_{\text{SiSi}}$ ,  $^1J_{\text{SiSe}}$  and  $^2J_{\text{SiSe}}$  satellites also  $^{29}\text{Si}$  INEPT spectra were recorded.

MS spectra were recorded on a Hewlett Packard 5971 (ionization energy: 70 eV, column: 30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ , phenylmethylpolysiloxane, column temperature: 80  $^\circ\text{C}$  (3 min)/20 K/min, flow: He 0.5 ml/min).

**Table 9** multiple linear regression results of the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR shift of *tert*-SiMe groups in isotetrasilanes  $\text{MeSi}(\text{SiMeY}_2)_3$ ,  $\text{Y} = \text{Me}, \text{Cl}, \text{SeBu}$ 

parameter	A0 (ppm)	A1 (ppm)	A2 (ppm)	r	sd (ppm)
$\delta_{\text{H}}^{\text{tert}}\text{Si-CH}_3$	0.073	0.091	0.068	0.993	0.02
$\delta_{\text{C}}^{\text{tert}}\text{Si-CH}_3$	-13.82	0.21	1.05	0.997	0.16
$\delta_{\text{Si}}^{\text{tert}}\text{Si-CH}_3$	-87.92	4.02	3.61	0.999	0.29

$\delta = A0 + A1 * X_{\text{Cl}} + A2 * X_{\text{Se}}$   $X_{\text{Cl}}$  = total number of chlorine substituents/molecule  
 $X_{\text{Se}}$  = total number of selenobutyl substituents/molecule



### Starting Materials

Elemental selenium, triethylamine, 1.6M BuLi solution in *n*-hexane and all monosilanes  $\text{Me}_x\text{Ph}_y\text{SiCl}_z$  were commercially available. The used oligosilanes  $\text{Si}_2\text{Me}_5\text{Cl}$  and  $\text{SiClMe}_2\text{-SiClMe}_2$  [12],  $\text{SiCl}_2\text{Me-SiClMe}_2$  [13],  $\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$  [14],  $\text{SiClMe}_2\text{-SiMe}_2\text{-SiClMe}_2$  [12],  $\text{SiClMe}_2\text{-SiClMe-SiClMe}_2$  [10],  $\text{SiMe}_3\text{-SiCl}_2\text{-SiMe}_3$  [15],  $\text{SiMe(SiClMe}_2)_3$ ,  $\text{Me}_3\text{Si-SiMe(SiClMe}_2)_2$  and  $\text{MeSi(SiCl}_2\text{Me)}_3$  [10] were prepared as described previously.

### Preparation of a BuSeLi Solution and Reaction with Chlorosilanes (General Procedure)

10 ml of a 1.6M BuLi solution in *n*-hexane were added to a suspension of 1.3 g (16.5 mmole) selenium powder in 30 ml dried THF under stirring and cooling in an ice bath. During the addition of BuLi the selenium powder dissolves and the solution becomes dark orange. The colour disappears almost if all BuLi is added. The formed 0.4M BuSeLi solution was used immediately.

The chlorosilane (approximately 1–2 mmole) was dissolved in 20 ml dried *n*-hexane and the calculated amount of 0.4M BuSeLi solution was added by a syringe under stirring. After stirring over night the reaction mixture was filtered from precipitated LiCl and the solvents were removed *in vacuo* yielding the selenobutyl substituted silanes as light yellow coloured oils.

In some cases also mass spectra of the formed selenobutyl substituted silanes could be obtained:

$\text{Me}_3\text{SiSeBu}$ , MS (*m/e*, rel. Int.): 210 ( $\text{M}^+$ , 8), 195 ( $\text{Me}_2\text{SiSeBu}$ , 5), 139 ( $\text{Me}_2\text{SiSeH}$ , 12), 123 ( $\text{MeSiSe}$ , 5), 73 ( $\text{Me}_3\text{Si}$ , 100)

$\text{Me}_2\text{SiCl(SeBu)}$ , MS: 230 ( $\text{M}^+$ , 18), 174 ( $\text{Me}_2\text{SiClSeH}$ , 29), 159 ( $\text{MeSiClSeH}$ , 9), 123 ( $\text{MeSiSe}$ , 4), 93 ( $\text{Me}_2\text{SiCl}$ , 100), 57 ( $\text{Bu}$ , 24)

$\text{MeSiCl}_2\text{(SeBu)}$ , MS: 250 ( $\text{M}^+$ , 8), 194 ( $\text{MeSiCl}_2\text{SeH}$ , 13), 138 ( $\text{BuSeH}$ , 12), 113 ( $\text{MeSiCl}_2$ , 22), 57 ( $\text{Bu}$ , 100)

$\text{Me}_2\text{PhSi(SeBu)}$ , MS: 272 ( $\text{M}^+$ , 8), 257 ( $\text{MePhSiSeBu}$ , 1), 135 ( $\text{Me}_2\text{PhSi}$ , 100), 105 ( $\text{PhSi}$ , 6)

$\text{MePh}_2\text{Si(SeBu)}$ , MS: 334 ( $\text{M}^+$ , 10), 197 ( $\text{MePh}_2\text{Si}$ , 100), 105 ( $\text{PhSi}$ , 9)

$\text{Ph}_2\text{SiCl(SeBu)}$ , MS: 354 ( $\text{M}^+$ , 18), 217 ( $\text{Ph}_2\text{SiCl}$ , 100), 181 (12)

Compounds bearing more than one SeBu substituent yielded only one GC peak of the decomposition product  $\text{Bu}_2\text{Se}_2$ :  $\text{Bu}_2\text{Se}_2$ , MS: 274 ( $\text{M}^+$ , 32), 218 ( $\text{BuSe}_2\text{H}$ , 32), 162 ( $\text{Se}_2\text{H}_2$ , 13), 135 (9), 57 ( $\text{Bu}$ , 100)

If the BuSeLi solution is prepared at room temperature and is added to a solution of  $\text{Me}_3\text{SiCl}$  in *n*-hexane, the product consists mainly of an equimolar mixture of  $\text{Bu}_2\text{Se}$  and  $(\text{Me}_3\text{Si})_2\text{Se}$  besides 20 mole-%  $\text{Me}_3\text{SiSeBu}$ .

$\text{Bu}_2\text{Se}$ :  $\delta_{\text{Se}}$ : +158 ppm,  $\delta_{\text{C}}/\text{ppm}$ : 23.4, 32.8, 23.0, 13.6,  $\delta_{\text{H}}/\text{ppm}$ : 2.53, 1.63, 1.41, 0.91

MS: 194 ( $\text{M}^+$ , 21), 165 ( $\text{BuSe(CH}_2)_2$ , 4), 138 ( $\text{BuSeH}$ , 40), 109 (16), 57 ( $\text{Bu}$ , 100)

$(\text{Me}_3\text{Si})_2\text{Se}$ :  $\delta_{\text{Se}}$ : -337 ppm,  $\delta_{\text{Si}}$ : 11.8 ppm,  $^1J_{\text{SiSe}}$ : 107 Hz,  $\delta_{\text{C}}$ : 4.5 ppm,  $^1J_{\text{SiC}}$ : 52.7 Hz,  $\delta_{\text{H}}$ : 0.45 ppm, MS: 226 ( $\text{M}^+$ , 6), 211 ( $\text{Me}_5\text{Si}_2\text{Se}$ , 14), 73 ( $\text{Me}_3\text{Si}$ , 100)

### Preparation of BuSeH

3.8 g (35 mmol)  $\text{Me}_3\text{SiCl}$  were added to 80 ml of a 0.4M BuSeLi solution (32 mmol). The reaction mixture was stirred over night, the solvents were removed in *vacuo* and the residue was dissolved in 5 ml *n*-hexane. After filtration from precipitated LiCl and removal of the solvent *in vacuo* 1.12 g (35 mmol) methanol were added and after stirring for 10 min the product was fractionated from  $\text{MeOSiMe}_3$  *in vacuo* yielding 2.9 g (66%) BuSeH as a colourless liquid.

BuSeH:  $\delta_{\text{Se}}$ : -16 ppm,  $\delta_{\text{C}}/\text{ppm}$ : 17.4 ( $\text{SeCH}_2$ ), 36.1, 22.7, 13.4 ( $\text{CH}_3$ ),  $\delta_{\text{H}}/\text{ppm}$ : -0.82 ( $\text{SeH}$ ,  $^1J_{\text{SeH}}$ : 43.3 Hz,  $^3J_{\text{HH}}$ : 6.7 Hz), 2.47 ( $\text{SeCH}_2$ ), 1.57, 1.29, 0.80 ( $\text{CH}_3$ )

BuSeH has already been prepared by reduction of  $\text{Bu}_2\text{Se}_2$  with  $\text{H}_3\text{PO}_2$  (*Kp.* 113 °C, *d.* 1.22 g/cm<sup>3</sup>,  $\delta_{\text{H}}$  ( $\text{SeH}$ ): -0.58 ppm,  $^1J_{\text{SeH}}$ : 42.0 Hz,  $^3J_{\text{HH}}$ : 6.7 Hz) [16].

### Reaction of BuSeH with Chlorosilanes (General Procedure)

Between 1 and 2 mmole of the chlorosubstituted silane or oligosilane (depending on the molar mass and the number of chlorine substituents to be substituted) were dissolved in 20 ml dried *n*-hexane and first the calculated amount of butylselenol and second under intensive stirring the equimolar amount of triethylamine was added at room temperature. The course of the reaction can be followed visually by the gradual precipitation of the by-product triethylammonium chloride. In general it can be said that the reactivity increases with the number of chlorine substituents and decreases with the number of phenyl substituents

After stirring over night the reaction mixture was filtered from the precipitated ammonium salt. The solvent was removed *in vacuo* yielding the selenobutyl derivative as a light yellow oil.

### References

- [1] U. Herzog, G. Roewer, *Main Group Metal Chemistry* **1999**, 22, 579
- [2] M. R. Detty, M. D. Seidler, *J. Org. Chem.* **1981**, 46, 1283
- [3] K. A. Hooton, A. L. Allred, *Inorg. Chem.* **1965**, 4, 671
- [4] J. W. Anderson, G. K. Barker, J. E. Drake, M. Rodger, *J. Chem. Soc., Dalton Trans.* **1973**, 1716
- [5] a) M. R. Detty, *Tetrahedron Lett.* **1978**, 5087; b) D. Liotta, P. B. Paty, J. Johnston, G. Zima, *Tetrahedron Lett.* **1978**, 5091
- [6] N. Miyoshi, H. Ishii, K. Kondo, S. Murai, N. Sonoda, *Synthesis* **1979**, 300
- [7] P. Boudjouk, S. R. Bahr, D. P. Thompson, *Organometallics* **1991**, 10, 778
- [8] F. Uhlig, B. Stadelmann, A. Zechmann, P. Lassacher, H. Stüger, E. Hengge, *Phosphorus, Sulfur, and Silicon*, **1994**, 90, 29
- [9] E. A. Williams in S. Patai, Z. Rappoport (Eds.), „The Chemistry of Organic Silicon Compounds“ Ch. 8, **1989**, 511
- [10] U. Herzog, E. Brendler, G. Roewer, *J. Organomet. Chem.* **1996**, 511, 85
- [11] U. Herzog, K. Trommer, G. Roewer, *J. Organomet. Chem.* **1998**, 552, 99
- [12] H. Sakurai, K. Tominaga, T. Watanabe, M. Kumada, *Tetrahedron* **1966**, 45, 5493
- [13] H. Sakurai, T. Watanabe, M. Kumada, *J. Organomet. Chem.* **1967**, 7, P15

- [14] R. Lehnert, M. Höppner, H. Kelling, *Z. anorg. allg. Chem.* **1990**, *591*, 209  
[15] U. Herzog, G. Roewer, *J. Organomet. Chem.* **1997**, *544*, 217  
[16] M. Schmidt, D. Block, *Chem. Ber.* **1970**, *103*, 3348

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