

Organosilicon chalcogenides with trisilane units – bicyclo[3.3.1]nonanes, bicyclo[3.2.2]nonanes and spiro[4.4]nonanes

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Abstract

Treatment of 1,2,3-trichloropentamethyltrisilane (**1**) with H₂S/NEt₃ results in the formation of a mixture of two isomers of (Me₅Si₃)₂S₃ with a bicyclo[3.3.1]nonane (**2a**) and a bicyclo[3.2.2]nonane (**2b**) skeleton, while the reaction of **1** with Li₂Se yields one product only, (Me₅Si₃)₂Se₃ (**3a**), with a bicyclo[3.3.1]nonane structure. Besides ¹H, ¹³C, ²⁹Si and ⁷⁷Se NMR spectroscopy **3a** has also been characterized by a crystal structure analysis.

Compounds Si(SiMe₂EMR₂E)₂ (**5a–h**; MR₂: SiMe₂ (**5a, c, d**), SiPh₂ (**5b**), GeMe₂ (**5e, f**), SnMe₂ (**5g, h**); E = S (**5a, b, e, g**), Se (**5c, f, h**), Te (**5d**)) with a spiro[4.4]nonane skeleton have been obtained in mixture with varying amounts of the corresponding six-membered rings (R₂ME)₃ by reactions of mixtures of 1,2,2,3-tetrachlorotetramethyltrisilane (**4**) and diorganodichlorosilanes, Me₂GeCl₂ or Me₂SnCl₂, with H₂S/NEt₃, Li₂Se or Li₂Te and have been characterized in situ by multinuclear NMR spectroscopy (¹H, ¹³C, ²⁹Si, ¹¹⁹Sn, ⁷⁷Se, ¹²⁵Te) and GC-MS.

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1. Introduction

Reactions of organochlorosilanes with either H₂E/amine (E = S, Se) or alkaline metal chalcogenides (M₂E, E = S, Se, Te) are the most important routes to organosilicon chalcogenides.

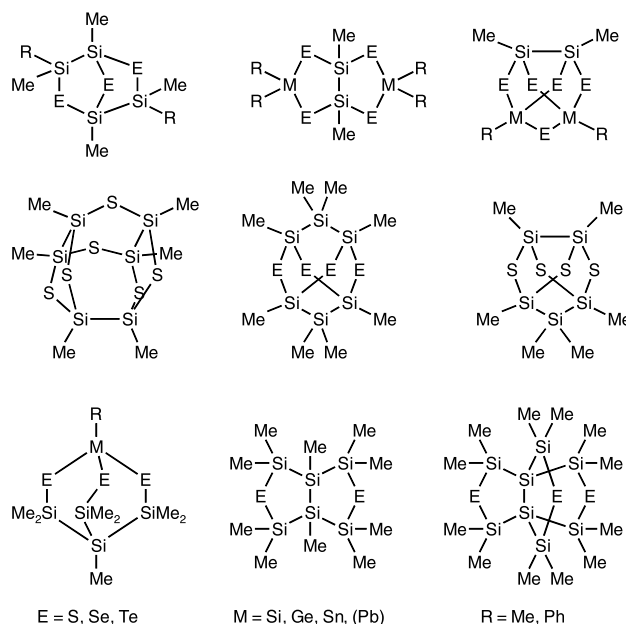
Depending on the number of chloro substituents of the starting organosilane R_{4-x}SiCl_x and the steric demand of the organic substituents R acyclic disilchalcogenides R₃SiESiR₃ [1,2], four or six-membered ring chalcogenides (R₂SiE)_{2,3} [3–6] or silsesquichalcogenides (RSiE_{1.5})₄ with adamantane [7,8] or double-decker like structures [9] have been obtained.

Other approaches to compounds with Si–E bonds employ the reaction of Si–H bonds with sulfur or selenium at elevated temperatures [10–13], insertion of elemental chalcogens into Si–Si bonds of cyclosilanes [14–18] or addition of chalcogens to disilenes [19,20], tetrasilabutadienes [21] or silylenes [22–25].

Our recent studies on organosilicon chalcogenides were focussed on cyclic and polycyclic compounds with oligosilane units. Starting from methylchlorooligosilanes reactions with either H₂S/NEt₃ or Li₂E (E = S, Se, Te) led to the characterization of a variety of new cyclic and polycyclic organosilicon chalcogenides with disilane [26–31], trisilane [32–34] (and related disilylmethane [28,34]), isotetrasilane [35] (and related trisilylmethane [36]), branched hexasilane [29] as well as octasilane [37] units, see Scheme 1.

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Scheme 1. Polycyclic organosilicon chalcogenides with oligosilane units (Si₂–Si₈).

The structures of the compounds formed as well as DFT calculations on model systems suggest that five-membered rings (Si₃E₂ or Si₄E) are the most stable ring size. If the formation of five-membered rings is not possible, six-membered rings are formed, whereas the formation of four-membered rings is favored by more bulky substituents. Besides information from crystal structure analyses the formation of different ring sizes can also be deduced from the ²⁹Si NMR chemical shifts [38].

Due to the manifold possible substitution patterns chloro functionalized trisilanes offer the possibility to synthesize a large variety of new cyclic and polycyclic organosilicon chalcogenides.

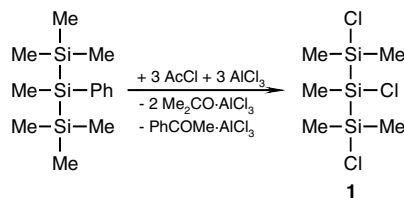
So far we have investigated the nature of reaction products of methylchlorotrisilanes with either terminal chloro substituents (ClMe₂Si–SiMe₂–SiMe₂Cl [34], Cl₂MeSi–SiMe₂–SiMeCl₂ [33]) or chloro substituents at the central silicon atom (Me₃Si–SiClMe–SiMe₃ [39], Me₃Si–SiCl₂–SiMe₃ [32]) with H₂S/NEt₃ or Li₂E.

The aim of this work is to expand these investigations to trisilanes with chloro substituents at both, terminal and central silicon atoms, namely reactions of ClMe₂Si–SiClMe–SiMe₂Cl and ClMe₂Si–SiCl₂–SiMe₂Cl with either H₂S/NEt₃ or Li₂E (E = S, Se, Te).

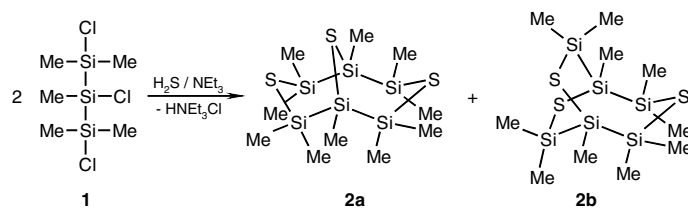
2. Results and discussion

2.1. 3,7,9-Trichalcogenahexasilabicyclo[3.3.1]nonanes and 3,6,8-trichalcogenahexasilabicyclo[3.2.2]nonanes

ClMe₂Si–SiClMe–SiMe₂Cl (**1**) was prepared starting from 2-phenylheptamethyltrisilane by reaction with three equivalents of acetyl chloride and aluminum chloride.

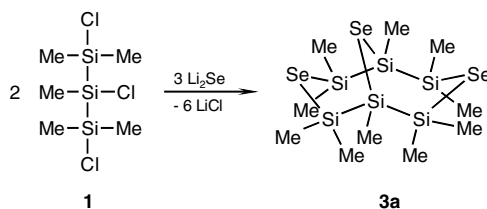


The reaction of **1** with H₂S/NEt₃ may lead to two isomeric products showing either a bicyclo[3.3.1]nonane skeleton (**2a**) or a bicyclo[3.2.2]nonane skeleton (**2b**) with two trisilane units.



GC/MS as well as NMR analyses of the obtained reaction products show that both isomers are formed. Assignment of the NMR signals is possible on the basis that in **2a** the four SiMe_2 units are equivalent resulting in one ^{29}Si NMR signal while two signals due to SiMe_2 units are observed for the isomer **2b**. Based on this assignment **2a** is the major reaction product besides some 35% of **2b**, see Fig. 1.

However, if **1** is reacted with Li_2Se in THF the bicyclo[3.3.1]nonane **3a** is formed exclusively.



The NMR data of **2a–b** and **3a** are given in Table 1. **2a** and **3a** are built of two fused six-membered rings. Previous investigations on other cyclic and polycyclic organosilicon chalcogenides have shown that the formation of five-membered rings is always accompanied by significant low field shifts of δ_{Si} while (smaller) high field shifts are observed in six-membered rings in comparison with acyclic silanes which have the same first coordination sphere at silicon. In our case a comparison of the ^{29}Si NMR chemical shifts of **2a** and **3a** with those of the acyclic chalcogenobutyl substituted trisilanes $\text{BuSMe}_2\text{Si}^{\text{B}}-\text{Si}^{\text{A}}\text{MeSBu}-\text{Si}^{\text{B}}\text{Me}_2\text{SBu}$ (δ_{Si} A: -24.63 ppm, B: 1.31 ppm [40]) and $\text{BuSeMe}_2\text{Si}^{\text{B}}-\text{Si}^{\text{A}}\text{MeSeBu}-\text{Si}^{\text{B}}\text{Me}_2\text{SeBu}$ (δ_{Si} A: -32.7 ppm, B: -4.5 ppm [41]) reveals that all ^{29}Si NMR signals are shifted to higher field by several ppm in accordance with the formation of six-membered rings.

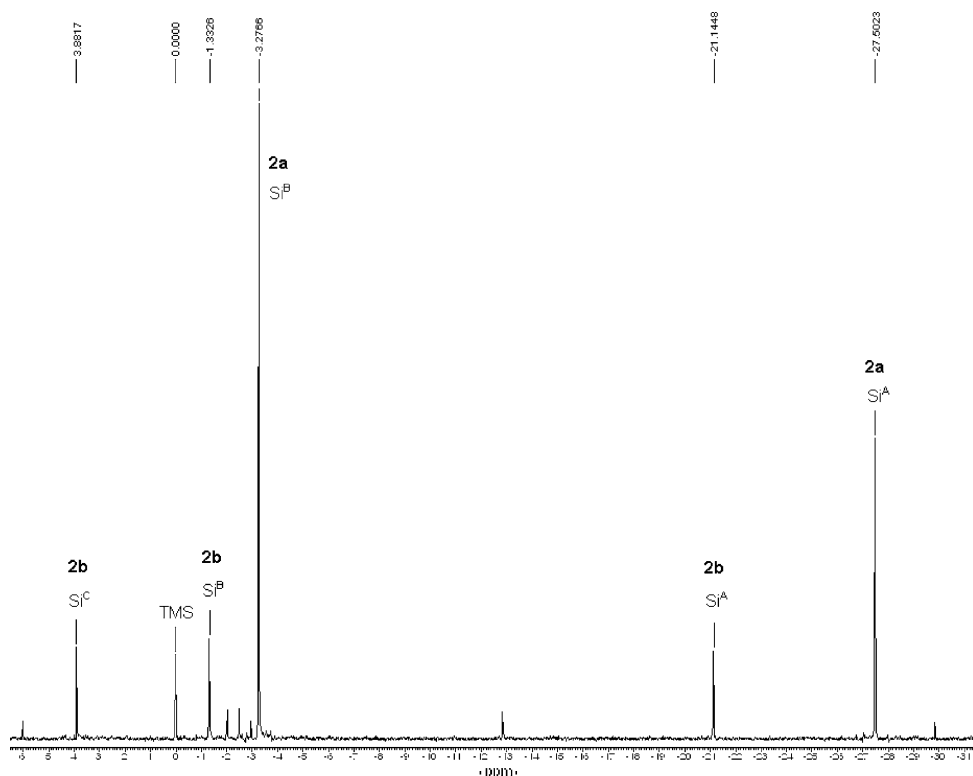
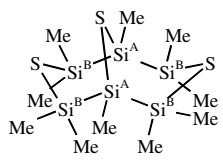
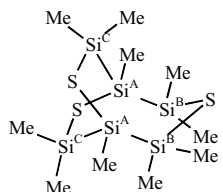
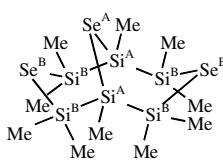


Fig. 1. ^{29}Si NMR spectrum of a product mixture of **2a** and **2b** obtained by reaction of **1** with $\text{H}_2\text{S}/\text{NEt}_3$.

Table 1
 ^1H , ^{13}C , ^{29}Si and ^{77}Se NMR data of **2a**, **2b** and **3a**

Compound	δ_{Se}	$^1J_{\text{SiSe}}$	δ_{Si}	$^1J_{\text{SiSi}}$	δ_{C}	δ_{H}
2a 			A: -27.50 B: -3.27	78.0	-2.01 2.39/2.87 $^1J_{\text{SiC}}$: 46.1	0.415 0.466/0.580
2b 			A: -21.14 B: 3.88 C: -1.33	76.0 ^a 2J : 12.2	-1.35 1.78/2.12 3.20/3.37	0.47 0.485/0.488 0.523/0.545
3a 	A: -494 B: -310	103.1 113.3	A: -37.20 B: -10.31	74.6	-2.83 2.16/2.54	0.487 0.569/0.704

^a Assignment of ^1H , ^{13}C and ^{29}Si NMR signals to $\text{Si}^{\text{B}}\text{Me}_2$ or $\text{Si}^{\text{C}}\text{Me}_2$ is uncertain.

On the other hand **2b** contains one six-membered ring and one seven-membered ring. This results in non-uniform changes of the ^{29}Si NMR signals in comparison with the acyclic compound $\text{BuSMe}_2\text{Si}-\text{SiMeSBu}-\text{SiMe}_2\text{SBu}$. Most likely the ^{29}Si NMR signal at -1.33 ppm corresponds to the SiMe_2 units within the six-membered ring.

Besides NMR **3a** could also be characterized by a crystal structure analysis. The result is shown in Fig. 2.

Important bond lengths and angles of **3a** are given in Table 2. All bond lengths are in the typical ranges for single bonds. As observed in other organosilicon selenides the bond angles at the selenium atoms are smaller than the tetrahedral angle reflecting the high p character of the bond orbitals at selenium.

It is interesting to note that in the molecular structure of **3a** one of the two six-membered rings adopts a chair conformation while the other one is in a boat conformation. This is also evident from the sequence of dihedral angles in both six-membered rings, see Table 3. While a chair conformation calls for the sequence $+\varphi, -\varphi, +\varphi, -\varphi, +\varphi, -\varphi$, the sequence $+\varphi, -\varphi, 0, +\varphi, -\varphi, 0$ corresponds to an ideal boat conformation. However, in solution a fast equilibrium of the conformations of the two six-membered rings occurs resulting in one ^{29}Si and one ^{77}Se NMR signal for both $\text{Me}_2\text{Si}-\text{Se}-\text{SiMe}_2$ units.

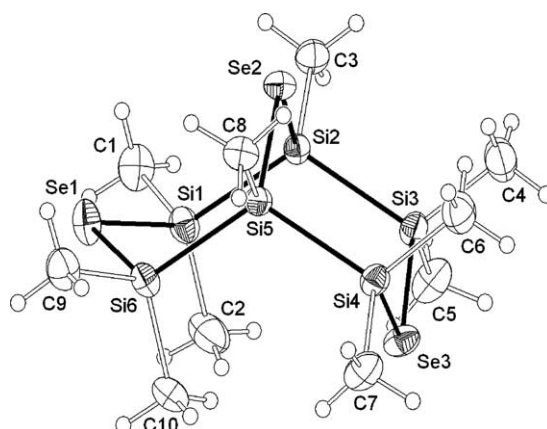


Fig. 2. Molecular structure of **3a**. Thermal ellipsoids are shown at the 30% probability level.

Table 2
Distances and angles in (Me₅Si₃)₂Se₃ (**3a**)

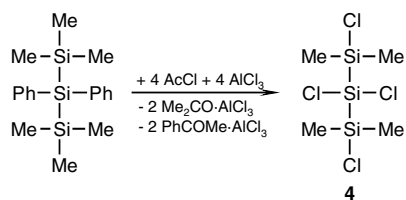
Atoms	Bond lengths (Å)	Atoms	Bond angles (°)
Si1–Si2	2.355(2)	Si1–Si2–Si3	114.03(9)
Si2–Si3	2.336(2)	Si4–Si5–Si6	113.95(8)
Si4–Si5	2.335(2)	Si1–Se1–Si6	104.44(7)
Si5–Si6	2.363(2)	Si2–Se2–Si5	101.76(6)
Si1–Se1	2.276(2)	Si3–Se3–Si4	104.77(6)
Si2–Se2	2.299(2)	Se1–Si1–Si2	111.32(8)
Si3–Se3	2.292(2)	Se2–Si2–Si1	112.56(7)
Si4–Se3	2.295(2)	Se2–Si2–Si3	109.22(7)
Si5–Se2	2.299(1)	Se3–Si3–Si2	110.43(7)
Si6–Se1	2.293(2)	Se3–Si4–Si5	110.49(7)
Si1–C1	1.894(7)	Se2–Si5–Si4	108.32(7)
Si1–C2	1.842(8)	Se2–Si5–Si6	112.42(7)
Si2–C3	1.878(6)	Se1–Si6–Si5	111.08(7)
Si3–C4	1.868(7)		
Si3–C5	1.866(7)		
Si4–C6	1.867(7)		
Si4–C7	1.863(6)		
Si5–C8	1.883(6)		
Si6–C9	1.887(7)		
Si6–C10	1.861(7)		

Table 3
Torsion angles in the six-membered rings of (Me₅Si₃)₂Se₃ (**3a**)

Atoms	Torsion angle (°)
Si2–Si1–Se1–Si6	–58.41(7)
Si1–Se1–Si6–Si5	59.34(8)
Se1–Si6–Si5–Se2	0.83(7)
Si6–Si5–Se2–Si2	–59.85(7)
Si5–Se2–Si2–Si1	61.07(7)
Se2–Si2–Si1–Se1	–2.50(8)
Si2–Si3–Se3–Si4	–58.89(7)
Si3–Se3–Si4–Si5	59.88(7)
Se3–Si4–Si5–Se2	–67.85(7)
Si4–Si5–Se2–Si2	66.97(7)
Si5–Se2–Si2–Si3	–66.64(7)
Se2–Si2–Si3–Se3	66.44(7)

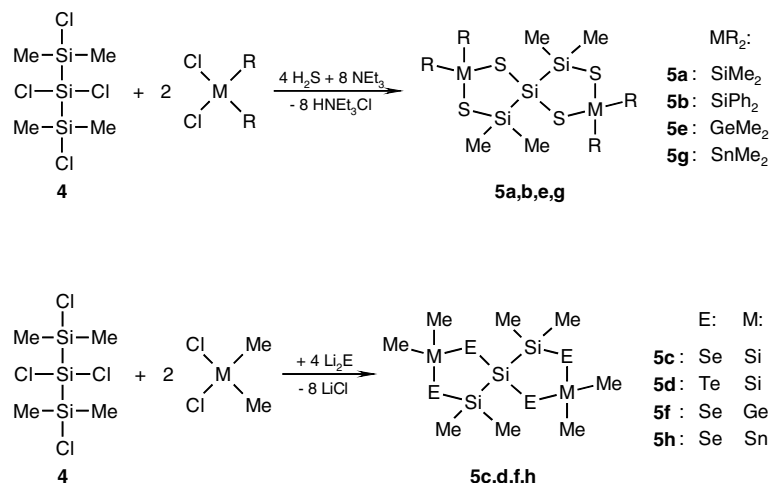
2.2. 1,3,6,8-Tetrachalcogenaspiro[4.4]nonanes

In analogy to **1** ClMe₂Si–SiCl₂–SiMe₂Cl (**4**) was accessible by treatment of Me₃Si–SiPh₂–SiMe₃ with four equivalents of acetyl chloride and aluminum chloride.



Reaction of **4** with H₂S/NEt₃ or Li₂E, respectively, did not yield any products soluble in organic solvents like hexane or toluene.

It is known from our previous studies, that such systems always prefer the formation of products with five-membered rings. Therefore, we reacted **4** mixed with two equivalents of a diorganodichlorosilane, -germane or -stannane (Me₂SiCl₂, Ph₂SiCl₂, Me₂GeCl₂, Me₂SnCl₂) with H₂S/NEt₃ or Li₂E. These reactions led to the formation of 1,3,6,8-tetrachalcogenaspiro[4.4]nonanes (**5a–h**).



In addition to compounds **5a–h** the six-membered ring compounds (R₂ME)₃ [38] are always formed as by-products in 20–50% amount, see Fig. 3.

When the ratio **4**:Me₂SiCl₂ is changed to 1:1 for the preparation of **5a**, the amount of the by-product (Me₂SiS)₃ is reduced to 10%, but its formation is not suppressed completely. However, compounds **5a–h** have been identified unambiguously by NMR spectroscopy and in some cases by their mass spectra.

The connectivities like Si–Se–Sn can also be derived unambiguously by the observation of satellites in the NMR spectra due to ¹J_{SiSe}, ¹J_{SnSe} or ²J_{SiSn} as shown in Fig. 4 as one example.

Due to their molecular symmetry, all compounds **5a–h** exist as a mixture of two enantiomers and additionally the organyl substituents at Si^B and Si^C (or Ge, Sn) are diastereotopic giving raise to two different ¹H and ¹³C NMR signals.

The NMR data of all prepared products with a spiro[4.4]nonane skeleton (**5a–h**) are summarized in Table 4.

As ¹H NMR signals of Si^BMe₂ and Si^CMe₂ of **5a** are very close to each other the relative assignment of the ¹H and ¹³C NMR signals was supported by a ¹H–¹³C heterocorrelated 2D NMR experiment, see Fig. 5. That means that the data given for **5a** in Table 4 in the same line belong to the same CH₃ group.

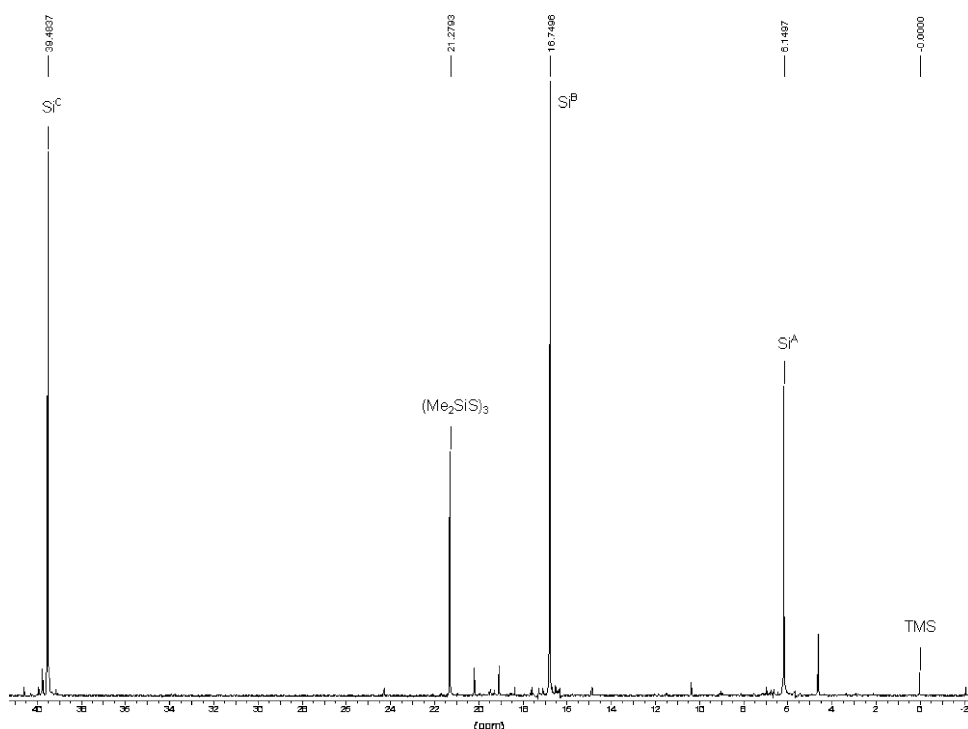


Fig. 3. ²⁹Si NMR spectrum of **5a** which contains some 20 mol% (Me₂SiS)₃.

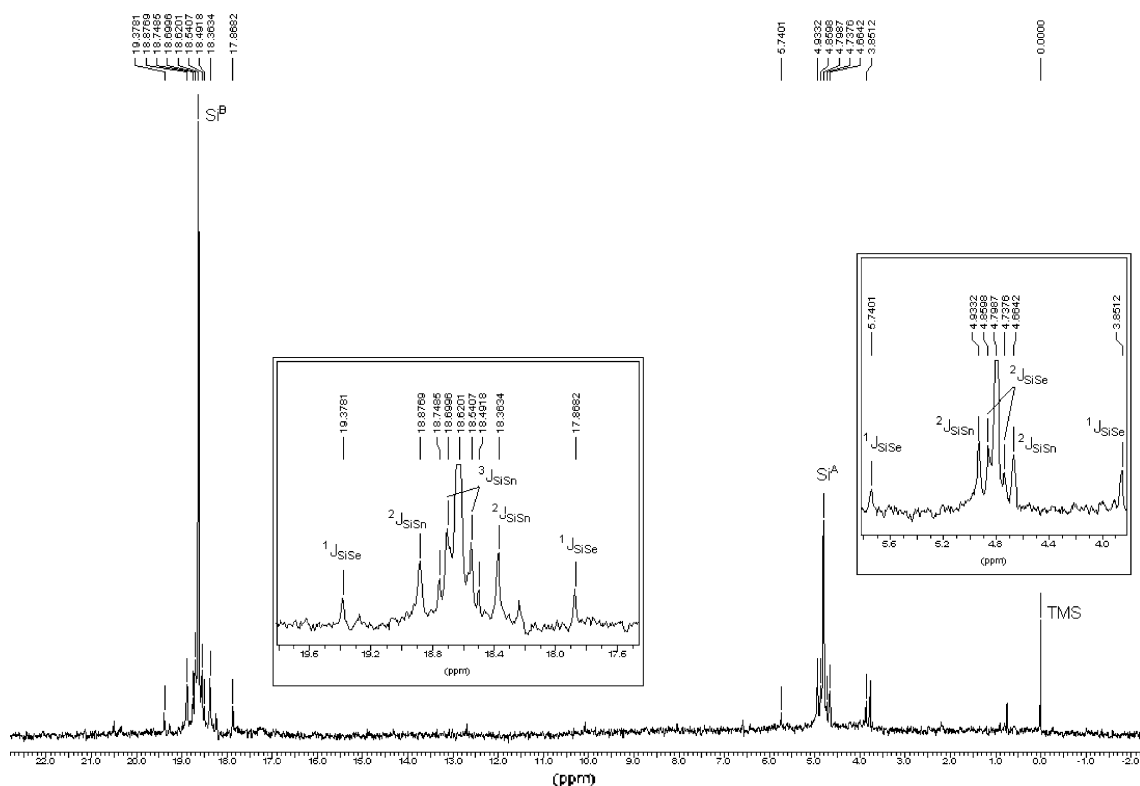


Fig. 4. ^{29}Si NMR spectrum of **5h** showing satellite signals due to couplings with ^{77}Se and ^{119}Sn .

In accordance with the formation of five-membered rings in **5a–h** the ^{29}Si NMR signals are shifted significantly to lower field. This is evident from a comparison of $\delta_{\text{Si}^{\text{A}}}$ in the spiro[4.4]nonanes with the values of chalcogenobutyl substituted trisilanes $(\text{Me}_3\text{Si}^{\text{B}})_2\text{Si}^{\text{A}}(\text{EBu})_2$ (E = S, $\delta_{\text{Si}^{\text{A}}}$: -6.4 ppm [40]; E = Se, $\delta_{\text{Si}^{\text{A}}}$: -18.8 ppm [41]) having the same first coordination sphere at Si^{A} or for $\delta_{\text{Si}^{\text{B}}}$ in comparison with $\delta_{\text{Si}^{\text{B}}}$ in the trisilanes $(\text{BuEMe}_2\text{Si}^{\text{B}})_2\text{Si}^{\text{A}}\text{Me}_2$ [40,41] and $(\text{BuEMe}_2\text{Si}^{\text{B}})_2\text{Si}^{\text{A}}\text{MeEBu}$ (see above). For E = Te no comparison can be made because acyclic tellurosubstituted trisilanes are unknown so far.

For Si^{C} a comparison with the ^{29}Si NMR chemical shifts of the chalcogenobutyl substituted monosilanes $\text{Me}_2\text{Si}(\text{SBu})_2$ (δ_{Si} : 24.8 ppm [40]), $\text{Ph}_2\text{Si}(\text{SBu})_2$ (δ_{Si} : 11.9 ppm [40]), $\text{Me}_2\text{Si}(\text{SeBu})_2$ (δ_{Si} : 18.1 ppm [41]) and $\text{Me}_2\text{Si}(\text{TeBu})_2$ (δ_{Si} : -24.6 ppm [42]) also reveals low field shifts due to the incorporation into five-membered rings. These low field shifts even exceed by some 5 ppm those of monosilanyl units in the simple five-membered rings $\text{R}_2\text{Si}(\text{E})_2\text{Si}_2\text{Me}_4$ [38].

A similar observation can be made for δ_{Sn} of the tin containing compounds **5g** and **5h** by comparison with δ_{Sn} of the chalcogenomethyl substituted stannanes $\text{Me}_2\text{Sn}(\text{EMe})_2$ (E = S, δ_{Sn} : 144 ppm [43]; E = Se, δ_{Sn} : 57 ppm [44]).

3. Experimental

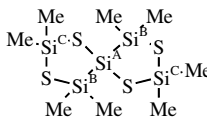
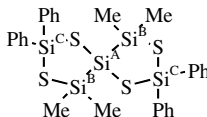
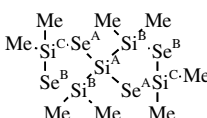
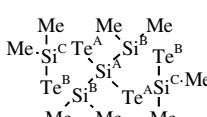
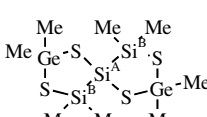
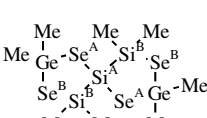
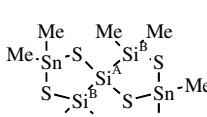
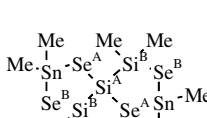
3.1. NMR and GC/MS measurements

All NMR spectra were recorded on a Bruker DPX 400 in CDCl_3 solution and TMS as internal standard for ^1H , ^{13}C and ^{29}Si . In order to achieve a sufficient signal to noise ratio for obtaining $^1J_{\text{Si}^{\text{C}}}$, $^1J_{\text{Si}^{\text{Si}}}$, $^1J_{\text{Si}^{\text{Se}}}$ or $^1J_{\text{Si}^{\text{Te}}}$ satellites ^{29}Si INEPT spectra were also recorded. ^{119}Sn , ^{77}Se and ^{125}Te NMR spectra were obtained using an IGATED pulse program.

External Me_4Sn , Ph_2Se_2 (δ_{Se} : 460 ppm [45]) and Ph_2Te_2 (δ_{Te} : 422 ppm [46]) in CDCl_3 were used as standards for ^{119}Sn , ^{77}Se and ^{125}Te .

Mass spectra were measured on a Hewlett–Packard 5890 (GC)/5971 (MS, ionization energy: 70 eV, column: 30 m \times 0.25 mm \times 0.25 μm , phenylmethylpolysiloxane, column temperature: 80 $^\circ\text{C}$ (3 min)/20 K/min/200 $^\circ\text{C}$, flow: He 0.5 ml/min).

Table 4
¹H, ¹³C, ²⁹Si, ¹¹⁹Sn, ⁷⁷Se and ¹²⁵Te NMR data of the spiro[4.4]nonanes (**5a–h**)

Compound	δ_E/δ_{Sn}	δ_{Si}	$^1J_{SiE}$	$^1J_{SiSi}$	δ_C	$^1J_{SiC}$	δ_H
5a 		A: 6.15 B: 16.75 C: 39.48		78.2	2.21 2.48 7.20 8.93	50.6 47.6 57.5 59.1	0.660 0.549 0.679 0.695
5b 		A: 6.98 B: 16.54 C: 20.73			1.94/2.08 a		0.474/0.416 a
5c 	Se ^A : -267 Se ^B : -280	A: 6.82 B: 18.14 C: 30.49	145.8 113.2 $^1J_{SiSe^A}$: 129.2 $^1J_{SiSe^B}$: 129.9	70.0	1.96/2.45 8.87/10.04		0.772/0.651 0.880
5d 	Te ^A : -719 Te ^B : -731	A: -38.51 B: 9.01 C: -15.71	346.0 396.0 $^2J_{SiTe^A}$: 30.6 321.2		1.71/3.55 10.86/11.42		0.919/0.830 1.427/1.431
5e 		A: 8.61 B: 18.52		77.8	2.07/2.65 9.72/11.38	49.5 47.5	0.646/0.503 0.964/0.980
5f 	Se ^A : -255 Se ^B : -269	A: 8.75 B: 20.10	118.6	72.4	2.06/2.42 9.27/12.30		0.761/0.615 0.957/0.974
5g 	Sn: 205.5	A: 7.35 B: 17.79	$^2J_{SiSn}$: 22.3 $^2J_{SiSn}$: 46.5 $^3J_{SiSn}$: 10.9	78.0	2.32/3.31 3.34/4.91	b c	0.613/0.443 0.823/0.867
5h 	Se ^A : -388 Se ^B : -406 Sn: 122.0	A: 4.80 B: 18.62	150.2 120.0 $^2J_{SiSe^B}$: 9.7 d		2.64/2.73 3.57/4.58		0.732/0.580 0.99

^a Ph: ¹³C: *i*: 135.45/135.75, *o*: 134.53/135.01, *m*: 127.75/127.87, *p*: 130.41/130.44; ¹H: *m* + *p*: 7.35, *o*: 7.67/7.74.

^b $^1J_{SnC}$: 381.1.

^c $^1J_{SnC}$: 401.8.

^d $^1J_{SnSe^A}$: 1156.8, $^1J_{SnSe^B}$: 1181.3, $^2J_{SnSi^A}$: 21.3, $^2J_{SnSi^B}$: 41.6, $^3J_{SnSi^B}$: 12.9.

3.2. Crystal structure analysis

The X-ray structure analysis measurement of **3a** was performed on a Rigaku AFC7 with Mercury CCD at ambient temperature. Crystal data: size: 0.18 × 0.17 × 0.07 mm, formula weight: 555.76 g/mol, space group: *P*2₁/*c* (monoclinic), unit cell: *a* = 16.026(2) Å, *b* = 12.130(2) Å, *c* = 12.669(2) Å, β = 93.144(7)°, volume: 2459.1(6) Å³ (*Z* = 4), density (calc.): 1.501 g cm⁻³, linear absorption coefficient: 4.770 mm⁻¹ (Mo K α).

For data collection, unit cell refinement and data reduction of **3a** the program package CRYSTAL CLEAR [47] was used. The structure was solved using direct methods (SHELXS-97 [48]), refined using least-squares-methods (SHELXL-97 [48]) and drawn using DIAMOND [49]. The ellipsoids of nonhydrogen atoms are shown at the 30% probability level. All hydrogen atoms were localized from Fourier difference maps.

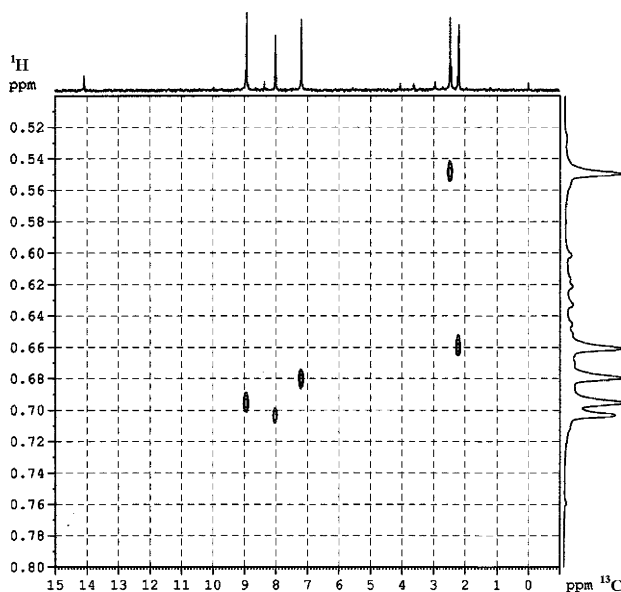


Fig. 5. ^1H - ^{13}C heterocorrelated 2D NMR spectrum of **5a** containing some 20 mol% $(\text{Me}_2\text{SiS})_3$ (δ_{C} : 8.0 ppm, δ_{H} : 0.705 ppm).

Absorption correction: multi-scan, measured reflections: 18068, independent reflections: 5887, observed reflections: 4403 ($I > 2\sigma_I$), θ range: 2.11° – 28.00° , completeness (θ_{max}): 99.1%, R_{int} : 0.0410, index ranges: $-19 \leq h \leq 21$, $-15 \leq k \leq 15$, $-15 \leq l \leq 16$, number of parameters: 182, final R_1 : 0.0680 ($I > 2\sigma_I$), R_1 : 0.0963 (all data), wR_2 : 0.1529 ($I > 2\sigma_I$), wR_2 : 0.1642 (all data), goodness of fit: 1.124, maximum/minimum residual electron density: $+1.275/-1.167 \text{ e}/\text{\AA}^3$.

3.3. Starting materials

Sulfur, selenium, tellurium, 1.0 M Li[BET₃H] in THF (Super Hydride[®]), Me_2SiCl_2 , Ph_2SiCl_2 , MeCOCl , AlCl_3 , H_2S and NEt_3 were commercially available. $(\text{Me}_3\text{Si})_2\text{-SiPhMe}$ and $(\text{Me}_3\text{Si})_2\text{-SiPh}_2$ were prepared as described in [50,51]. 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 $\text{ClMe}_2\text{Si-SiClMe-SiMe}_2\text{Cl}$ (**1**) and $\text{ClMe}_2\text{Si-SiCl}_2\text{-SiMe}_2\text{Cl}$ (**4**)

$(\text{Me}_3\text{Si})_2\text{SiPhMe}$ (8.0 g, 30 mmol) was dissolved in *n*-hexane (30 ml) and aluminum chloride (16 g, 120 mmol) was added. Acetyl chloride (8.5 ml, 120 mmol) was added slowly at 0°C to the stirred reaction mixture. After stirring overnight at room temperature the upper phase was separated. After removal of the solvent in vacuo the product was distilled to yield 4.8 g (18 mmol, 60%) pure **1**, b.p. 75°C at 0.7 kPa.

1 GC/MS (*m/e*, relative intensity): 264/266 (M^+ , 1), 249/251 ($\text{M}^+ - \text{Me}$, 1), 229 ($\text{M}^+ - \text{Cl}$, 5), 171 ($\text{Me}_3\text{Si}_2\text{Cl}_2$, 3), 151 ($\text{Me}_4\text{Si}_2\text{Cl}$, 18), 136 ($\text{Me}_3\text{Si}_2\text{Cl}$, 49), 93 (Me_2SiCl , 36), 73 (Me_3Si , 100); NMR (ppm, Hz) ^{29}Si : 19.83 (SiMe_2), -0.58 (SiMe), $^1J_{\text{SiSi}}$: 89.3; ^{13}C : 1.88/2.55 (SiMe_2), -2.22 (SiMe); ^1H : 0.645/0.652 (SiMe_2), 0.714 (SiMe).

In a similar reaction treatment of $(\text{Me}_3\text{Si})_2\text{SiPh}_2$ (8.5 g, 26 mmol) with aluminum chloride (17.4 g, 130 mmol) and acetyl chloride (9.3 ml, 130 mmol) yielded 5.9 g (21 mmol, 79%) pure **4**, b.p. 80°C at 0.9 kPa. NMR (ppm, Hz) ^{29}Si : 17.68 (SiMe_2Cl), 13.40 (SiCl_2), $^1J_{\text{SiSi}}$: 98.6; ^{13}C : 1.30, $^1J_{\text{SiC}}$: 52.2; ^1H : 0.71.

3.5. Reaction of **1** with $\text{H}_2\text{S}/\text{NEt}_3$, formation of **2a** and **2b**

1 (0.27 g, 1.0 mmol) was dissolved in *n*-hexane (30 ml) and H_2S was bubbled through the solution while NEt_3 (0.48 ml, 3.5 mmol) was added slowly by a syringe. After stirring for 1 h the reaction mixture was filtered from precipitated ammonium salts and the solvent was removed in vacuo. The crystalline residue (0.2 g) consisted of 65% **2a** besides 35% **2b** based on the NMR spectra of the product.

2a/2b GC/MS: 414 (M^+ , 28), 399 ($\text{M}^+ - \text{Me}$, 11), 355 ($\text{Me}_7\text{Si}_5\text{S}_3\text{CH}_2$, 6), 341 ($\text{Me}_7\text{Si}_5\text{S}_3$, 9), 309 ($\text{Me}_7\text{Si}_5\text{S}_2$, 8), 281 ($\text{Me}_7\text{Si}_4\text{S}_2$, 5), 249 ($\text{Me}_7\text{Si}_4\text{S}$, 38), 234 ($\text{Me}_6\text{Si}_4\text{S}$, 50), 191 ($\text{Me}_5\text{Si}_3\text{S}$, 21), 131 (Me_5Si_2 , 32), 116 (Me_4Si_2 , 22), 73 (Me_3Si , 100) [two GC peaks with identical MS], *Anal.* Calc. for $\text{C}_{10}\text{H}_{30}\text{S}_3\text{Si}_6$ (415.06): C, 28.94; H, 7.29. Found: C, 27.83; H, 6.93%.

3.6. Reaction of **1** with Li_2Se , formation of **3a**

Selenium powder (120 mg, 1.5 mmol) was added to 3 ml of a 1.0 M $\text{Li}[\text{BEt}_3\text{H}]$ solution in THF to form a white suspension of Li_2Se in THF.

1 (0.27 g, 1.0 mmol), diluted with THF (1 ml) was slowly added to the Li_2Se suspension at 0 °C. After stirring for 30 min the solvent was removed in vacuo and the residue dissolved in *n*-hexane (10 ml). After filtration from precipitated LiCl and removal of the solvent colorless crystalline **3a** (0.3 g, 54%) was obtained. Single crystals were grown from saturated hexane solutions.

Anal. Calc. for $\text{C}_{10}\text{H}_{30}\text{Se}_3\text{Si}_6$ (555.76): C, 21.61; H, 5.44. Found: C, 20.91; H, 5.87%.

3.7. Preparation of 1,3,6,8-tetrachalcogenaspiro[4.4]nonanes (**5a–h**)

In case of the sulfur compounds (**5a**, **5b**, **5e**, **5g**) **4** (0.285 g, 1.0 mmol) and 2.0 mmol of the appropriate diorganodichloro compound (Me_2SiCl_2 , Ph_2SiCl_2 , Me_2GeCl_2 or Me_2SnCl_2) were dissolved in 20 ml *n*-hexane (or 15 ml toluene in case of Me_2SnCl_2).

H_2S was bubbled through the stirred solution while NEt_3 (1.1 ml, 8 mmol) was slowly added. After filtration from precipitated triethylammonium chloride the solvent was removed in vacuo to yield **5a**, **5b**, **5e** or **5g**, respectively, besides 20–30% of the corresponding six-membered ring compounds $(\text{R}_2\text{ME})_3$ as colorless oils.

If the starting molar ratio **4**: Me_2SiCl_2 is changed to 1:1, the resulting liquid product consisted of 90% **5a** besides 10% $(\text{Me}_2\text{Si})_3$ as checked by NMR spectroscopy.

5a GC/MS: 388 (M^+ , 14), 373 ($\text{M}^+ - \text{Me}$, 1), 283 ($\text{Me}_5\text{Si}_4\text{S}_3$, 2), 223 ($\text{Me}_5\text{Si}_3\text{S}_2$, 5), 208 ($\text{Me}_4\text{Si}_3\text{S}_2$, 62), 193 ($\text{Me}_3\text{Si}_3\text{S}_2$, 11), 165 ($\text{Me}_3\text{Si}_2\text{S}_2$, 21), 148 ($\text{Me}_4\text{Si}_2\text{S}$, 18), 133 ($\text{Me}_3\text{Si}_2\text{S}$, 21), 116 (Me_4Si_2 , 5), 73 (Me_3Si , 100).

5e GC/MS: 478 ($\text{Me}_8\text{Si}_2^{72}\text{Ge}^{74}\text{GeS}_4$ (M^+), 1), 463 ($\text{M}^+ - \text{Me}$, 1), 373 ($\text{Me}_5\text{Si}_2^{72}\text{Ge}^{74}\text{GeS}_3$, 0.5), 359 ($\text{Me}_4\text{Si}_2^{72}\text{Ge}^{74}\text{GeS}_3\text{H}$, 1), 313 ($\text{Me}_5\text{Si}^{72}\text{Ge}^{74}\text{GeS}_2$, 2), 283 ($\text{Me}_3\text{Si}^{72}\text{Ge}^{74}\text{GeS}_2$, 1), 269 ($\text{Me}_2\text{Si}^{72}\text{Ge}^{74}\text{GeS}_2\text{H}$, 2), 255 ($\text{Me}_5\text{Si}_3\text{S}_3$, 6), 206 ($\text{Me}_4^{72}\text{Ge}^{74}\text{Ge}$, 21), 165 ($\text{Me}_3\text{Si}_2\text{S}_2$, 20), 119 ($\text{Me}_3^{74}\text{Ge}$, 21), 73 (Me_3Si , 100). [Isotopic patterns are in accordance with the numbers of Ge atoms.]

5g GC/MS: 555 ($\text{Me}_8\text{Si}_2^{120}\text{Sn}^{118}\text{Sn}$ ($\text{M}^+ - \text{Me}$), 20), 407 ($\text{Me}_5\text{Si}_3^{120}\text{SnS}_4$, 10), 317 ($\text{Me}_3\text{Si}_2^{120}\text{SnS}_3$, 8), 257 ($\text{Me}_3\text{Si}^{120}\text{SnS}_2$, 11), 227 ($\text{MeSi}^{120}\text{SnS}_2$, 18), 165 ($\text{Me}_3\text{Si}_2\text{S}_2 + \text{Me}_3^{120}\text{Sn}$, 45), 73 (Me_3Si , 100). [Isotopic patterns are in accordance with the numbers of Sn atoms.]

In case of the selenium and tellurium compounds (**5c**, **5d**, **5f**, **5h**) **4** (0.285 g, 1.0 mmol) and 2.0 mmol of the appropriate dimethyldichloro compound (Me_2SiCl_2 , Me_2GeCl_2 or Me_2SnCl_2) were dissolved in THF (1 ml) and added at 0 °C (or –30 °C in case of the tellurium compound **5d**) to a Li_2Se (or Li_2Te) suspension (4.0 mmol) prepared freshly from selenium (or tellurium) powder (4.0 mmol) and 8 ml 1.0 M $\text{Li}[\text{BEt}_3\text{H}]$ as described in Section 3.6.

Work-up as described for **3a** yielded colorless to yellow (**5d**) oils containing the expected spiro[4.4]nonanes **5c**, **5d**, **5f** or **5h** admixed with 30–50% of the corresponding six-membered ring compounds $(\text{Me}_2\text{ME})_3$ as derived from the NMR spectra.

4. Supplementary material

Crystallographic data (excluding structure factors) for **3a** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 221784. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223336033 or deposit@ccdc.cam.ac.uk).

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References

- [1] N.W. Mitzel, A. Schier, H. Beruda, H. Schmidbaur, *Chem. Ber.* 125 (1992) 1053.
- [2] J.H. So, P. Boudjouk, H.H. Hong, W.P. Weber, *Inorg. Synth.* 29 (1992) 30.
- [3] M.M. Millard, L.J. Pazdernik, W.F. Haddon, R.F. Lundin, *J. Organomet. Chem.* 52 (1973) 283.

- [4] L. Pazdernik, F. Brisse, R. Rivest, *Acta Crystallogr., Sect. B* 33 (1977) 1780.
- [5] P. Boudjouk, S.R. Bahr, D.P. Thompson, *Organometallics* 10 (1991) 778.
- [6] S.R. Bahr, P. Boudjouk, G.J. McCarthy, *Chem. Mater.* 4 (1992) 383.
- [7] S.R. Bahr, P. Boudjouk, *Inorg. Chem.* 31 (1992) 712.
- [8] J.C.J. Bart, J.J. Daly, *J. Chem. Soc., Dalton Trans.* (1975) 2063.
- [9] M. Unno, Y. Kawai, H. Shioyama, H. Matsumoto, *Organometallics* 16 (1997) 4428.
- [10] H.-G. Horn, M. Probst, *Monatsh. Chem.* 126 (1995) 1169.
- [11] F. Feher, R. Luepschen, *Z. Naturforsch. B* 26 (1971) 1191.
- [12] H. Yoshida, Y. Kabe, W. Ando, *Organometallics* 10 (1991) 27.
- [13] N. Choi, K. Asano, N. Sato, W. Ando, *J. Organomet. Chem.* 516 (1996) 155.
- [14] M. Weidenbruch, A. Schäfer, *J. Organomet. Chem.* 269 (1984) 231.
- [15] M. Weidenbruch, A. Grybat, W. Saak, E.-M. Peters, K. Peters, *Monatsh. Chem.* 130 (1999) 157.
- [16] E. Hengge, H.G. Schuster, *J. Organomet. Chem.* 231 (1982) C17.
- [17] C.W. Carlson, R. West, *Organometallics* 2 (1983) 1798.
- [18] M. Wojnowska, W. Wojnowski, R. West, *J. Organomet. Chem.* 199 (1980) C1.
- [19] R. West, D.J. De Young, K.J. Haller, *J. Am. Chem. Soc.* 107 (1985) 4942.
- [20] R.P.K. Tan, G.R. Gillette, D.R. Powell, R. West, *Organometallics* 10 (1991) 546.
- [21] A. Grybat, S. Boomgaarden, W. Saak, H. Marsmann, M. Weidenbruch, *Angew. Chem.* 111 (1999) 2161.
- [22] P. Jutzi, A. Möhrke, A. Müller, H. Bögge, *Angew. Chem.* 101 (1989) 1527.
- [23] B. Gehrhus, P.B. Hitchcock, M.F. Lappert, J. Heinicke, R. Boese, D. Bläser, *J. Organomet. Chem.* 521 (1996) 211.
- [24] M. Haaf, A. Schmiedel, T.A. Schmedake, D.R. Powell, A.J. Millevolte, M. Denk, R. West, *J. Am. Chem. Soc.* 120 (1998) 12714.
- [25] M. Weidenbruch, L. Kirmaier, E. Kroke, W. Saak, *Z. Anorg. Allg. Chem.* 623 (1997) 1277.
- [26] U. Herzog, U. Böhme, G. Roewer, G. Rheinwald, H. Lang, *J. Organomet. Chem.* 602 (2000) 193.
- [27] U. Herzog, U. Böhme, G. Rheinwald, *J. Organomet. Chem.* 627 (2001) 144.
- [28] U. Herzog, G. Rheinwald, *J. Organomet. Chem.* 628 (2001) 133.
- [29] U. Herzog, U. Böhme, E. Brendler, G. Rheinwald, *J. Organomet. Chem.* 630 (2001) 139.
- [30] U. Herzog, G. Rheinwald, *J. Organomet. Chem.* 648 (2002) 220.
- [31] U. Herzog, H. Borrmann, *J. Organomet. Chem.* 675 (2003) 42.
- [32] U. Herzog, H. Borrmann, *Inorg. Chem. Commun.* 6 (2003) 718.
- [33] U. Herzog, H. Borrmann, *J. Organomet. Chem.* 681 (2003) 5.
- [34] U. Herzog, U. Böhme, *Silicon Chem.* (2003) (submitted).
- [35] U. Herzog, G. Rheinwald, *Organometallics* 20 (2001) 5369.
- [36] U. Herzog, G. Rheinwald, H. Borrmann, *J. Organomet. Chem.* 660 (2002) 27.
- [37] U. Herzog, G. Rheinwald, *Eur. J. Inorg. Chem.* (2001) 3107.
- [38] U. Herzog, G. Rheinwald, *J. Organomet. Chem.* 627 (2001) 23.
- [39] H. Lange, U. Herzog, *J. Organomet. Chem.* 660 (2002) 36.
- [40] U. Herzog, G. Roewer, *Main Group Metal Chem.* 22 (1999) 19.
- [41] U. Herzog, *J. Prakt. Chem.* 342 (2000) 379.
- [42] U. Herzog, *Main Group Metal Chem.* 24 (2001) 31.
- [43] J.D. Kennedy, W. McFarlane, *J. Chem. Soc., Perkin Trans 2* (1974) 146.
- [44] J.D. Kennedy, W. McFarlane, *J. Chem. Soc., Dalton Trans.* (1973) 2134.
- [45] M. Lardon, *J. Am. Chem. Soc.* 92 (1970) 5063.
- [46] H.C.E. McFarlane, W. McFarlane, *J. Chem. Soc., Dalton Trans.* (1973) 2416.
- [47] Rigaku Corp., 2000.
- [48] G.M. Sheldrick, *SHELX-97* [Includes *SHELXS-97*, *SHELXL-97*, *CIFTAB*], *SHELX-97: Programs for Crystal Structure Analysis (Release 97-2)*, University of Göttingen, Germany, 1997.
- [49] M. Berndt, K. Brandenburg, H. Putz, *DIAMOND 2.1: Crystal Impact GbR*, www.crystalimpact.de, Bonn, Germany, 1999.
- [50] U. Herzog, G. Roewer, *J. Organomet. Chem.* 527 (1997) 117.
- [51] U. Herzog, G. Roewer, *J. Organomet. Chem.* 544 (1997) 217.