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Bicyclo[2.2.2]octanes $HC(SiMe_2E)_3MR$ ($E = S, Se; M = Si, Ge, Sn; R = Me, Ph, Vi$)

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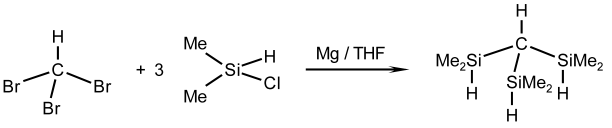
Abstract

The reactions of 1:1 mixtures of the trisilylmethane $HC(SiMe_2Cl)_3$ (**1b**) and organo Group 14 trichlorides ($RMCl_3$, R = Me, Ph, vinyl (Vi); M = Si, Ge, Sn) with Li_2E (E = S, Se) in THF yielded the new bicyclo[2.2.2]octanes $HC(SiMe_2E)_3MR$ (**2a**–**6b**). The products were identified by GC–MS and multinuclear NMR spectroscopy. Trends of the NMR data are discussed. The molecular structures of $HC(SiMe_2S)_3SiMe$ (**2a**), $HC(SiMe_2S)_3SiPh$ (**3a**), $HC(SiMe_2Se)_3SiVi$ (**4b**) and $HC(SiMe_2Se)_3GeMe$ (**5b**) are reported.

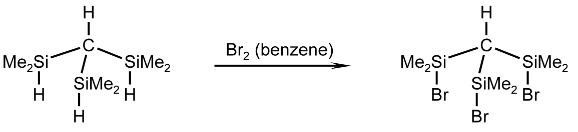
1. Introduction

Tris(bromodimethylsilyl)methane (**1a**) has been shown to be a valuable starting material to build up hetero-bicyclo[2.2.2]octane systems containing a tripodal amino ligand.

Compound **1a** has been prepared in two steps from bromoform [1]:



(1)



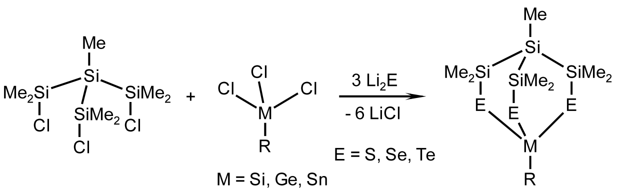
(2)

1a

Subsequent reaction with primary amines leads to the tripodal amines $HC[SiMe_2NHR]_3$ (R = *t*-Bu, Ph, *p*-Tol, *p*-F–C_6H_4, etc.) [2–4]. After lithiation with BuLi, these amines are able to coordinate to early transition metals (Y [5], Ti [6,7], Zr [4,5,8,9], Hf [8], Nb [7]) as well as Groups 13 (Tl [10,11]), 14 (Sn, Pb [12,13]) and 15 (Sb, Bi [14]) metals, see Scheme 1.

The as formed complexes are interesting building blocks in the generation of heterobimetallics [13] or can serve as neutral molecular catalysts in olefin polymerization [9].

In a previous paper [15], we could show that related bicyclo[2.2.2]octanes containing an isotetrasilane unit and chalcogens instead of the nitrogen atoms are formed in a very smooth reaction from $MeSi(SiMe_2Cl)_3$, $RMCl_3$ (R = Me, Ph; M = Si, Ge, Sn) and a suspension of Li_2E (E = S, Se, Te) in THF:



(3)

In this paper, we report the synthesis and characterization of a series of related trisilylmethane-derived chalcogenides of Group 14 elements.

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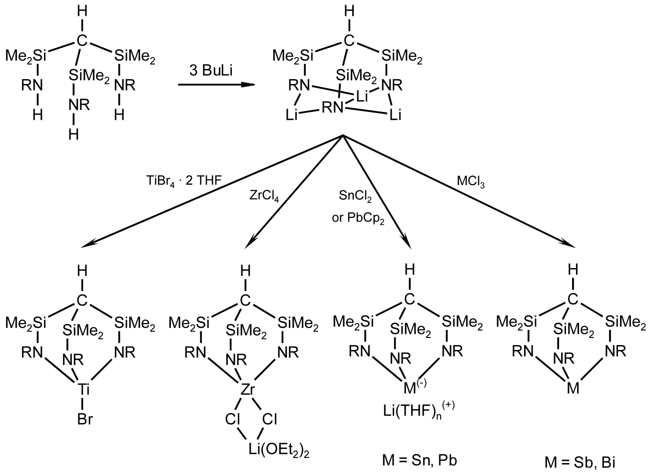
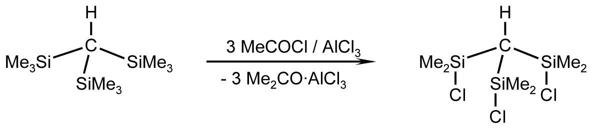


Scheme 1.

2. Results and discussion

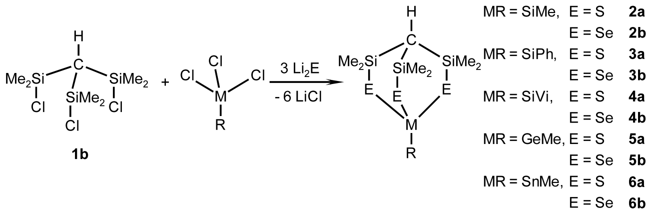
Tris(chlorodimethylsilyl)methane (**1b**) has been obtained by chlorination of $HC(SiMe_3)_3$ with acetyl chloride and aluminum chloride, a reaction which has been applied previously by our group to synthesize a variety of chlorosubstituted oligosilanes [16,17] and disilylmethanes [18]:



1b

(4)

Reactions of 1:1 molar mixtures of **1b** and organo Group 14 trichlorides with three equivalents of freshly prepared Li_2E furnished in clean reactions the new hetero-bicyclo[2.2.2]octanes containing a trisilylmethane unit and a RME_3 cap:



(5)

The NMR data of all prepared bicyclo[2.2.2]octanes are summarized in Table 1. It is interesting to compare the ^{29}Si-NMR chemical shifts of the RM units in the bicyclo[2.2.2]octanes **2a**–**3b** with those of the related acyclic compounds $RSi(EBu)_3$ ($E = S$ [19], $E = Se$ [20]) as well as the bicyclo[2.2.2]octanes $RSi(ESiMe_2)_3SiMe$ [15] and the adamantane-like silsesquichalcogenanes $(RSi)_4E_6$ [18,21].

As can be seen from Fig. 1, in all cases, the incorporation of the $RSiE_3$ unit into a polycyclic system of six-membered rings leads to a high field shift of the silicon NMR resonances but to a very different extend. In general, the high field shift in the bicyclo[2.2.2]octanes $RSi(ESiMe_2)_3CH$ reaches two thirds of the effect in the related bicyclo[2.2.2]octanes $RSi(ESiMe_2)_3SiMe$. Similar effects can be observed by comparing the ^{119}Sn-NMR chemical shifts of the tin containing bicyclo[2.2.2]octanes **6a**–**b** with those of the acyclic compounds $MeSn(SMe)_3$ (+167 ppm) [22] and $MeSn(SeMe)_3$ (+15 ppm) [23] as well as the related bicyclo[2.2.2]octanes $MeSn(ESiMe_2)_3SiMe$ ($E = S$: +66 ppm, $E = Se$: −151 ppm) [15].

On the other hand, there is no high field shift due to the incorporation into a bicyclo[2.2.2]octane skeleton for the silicon atoms of the $SiMe_2$ units. The sulfur compounds **2a**–**6a** show a ^{29}Si-NMR signal for the $SiMe_2$ units of 12.7–15.1 ppm whereas, the acyclic compound $HC(SiMe_2{-}SBu)_3$ with the same first coordination sphere at silicon reveals a ^{29}Si-NMR chemical shift of 13.99 ppm.

Despite the same first coordination sphere, there are significant differences in the ^{77}Se-NMR chemical shifts between **2b**–**6b** and the corresponding bicyclo[2.2.2]octanes $RM(SeSiMe_2)_3SiMe$ [15]. In all cases, the compounds $RM(SeSiMe_2)_3$*SiMe* show ^{77}Se-NMR resonances at 80–100 ppm lower field than $RM(SeSiMe_2)_3$*CH* for the same unit RM. Furthermore, the ^{13}C-NMR chemical shifts of the bridgehead CH unit should be mentioned. The observed resonances for **2a**–**6b** are in most cases even at higher field than for the permethylated trisilylmethane (3.94 ppm) and resemble the high field ^{29}Si-NMR resonances of the bridgehead SiMe units in the corresponding bicyclo[2.2.2]octanes $RM(ESiMe_2)_3SiMe$.

The molecular structures of of **2a**, **3a**, **4b** and **5b** have been determined, see Figs. 2–6. Compound **4b** crystallizes with two crystallographically independent molecules in the asymmetric unit, the trisilylmethane unit of one of them (molecule B) is disordered (see Fig. 5). Bond lengths and angles of **2a**, **3a**, **4b** and **5b** are summarized in Tables 2–5.

All bond lengths are in the expected range. The previously described tendency that Si–S bond lengths are decreasing with the number of sulfur substituents at silicon can be observed again in **2a** and **3a**. While within the SiS_3 units the Si(1)–S bonds are in average 2.13 Å, the Si–S bonds towards the trisilylmethane units (Si(2)–S(1), Si(3)–S(2), Si(4)–S(3)) are in average 2.17 Å. The same holds for the Si–Se bond lengths in **4b** (2.25–2.27 Å at Si(1), 2.30–2.32 Å at Si(2)–Si(4)). The angles at the chalcogen atoms are with 99.4–99.9 (**2a**) and 98.9–99.4 (**3a**) for $E = S$ and 95.7–97.4 (**4b**), 96.3–96.9° (**5b**) for $E = Se$ in all cases smaller than the tetrahedral angle. This is in agreement with molecular structures of other

Table 1
^1H-, ^{13}C-, ^{29}Si-, ^{119}Sn- and ^{77}Se-NMR data of the bicyclo[2.2.2]octanes $HC(SiMe_2E)_3MR$ (M = Si, Ge, Sn; R = Me, Ph, Vi; E = S, Se) (chemical shifts in ppm, coupling constants in Hz)

	M	R	E	δ_{Se}	δ_M	$^1J_{MSe}$	δ_{Si}	$^1J_{SiSe}$	$\delta_{C(R)}$	$\delta_{C(SiMe_2)}$	$^1J_{SiC}$	$\delta_{C(CH)}$	$\delta_{H(R)}$	$\delta_{H(SiMe_2)}$	$\delta_{H(CH)}$
2a	Si	Me	S	–	19.37	–	12.70	–	8.71	6.93	57.0	1.32	0.91	0.56	0.06
2b	Si	Me	Se	−180	−5.72	149.5	11.76	98.7	9.93 $^1J_{SiC}$: 57.0	7.23	55.2	1.96	1.23	0.66	−0.05
3a	Si	Ph	S	–	11.28	–	12.98	–	*i*: 135.88 *o*: 133.41 *m*: 128.00 *p*: 130.80	7.04	56.4	5.83	*o*+*p*: 7.39 *m*: 7.83	0.60	0.14
3b	Si	Ph	Se	−187	−10.80		11.91	99.1		7.29	53.5			0.69	
4a	Si	Vi	S	–	7.89	–	12.82	–	CH: 135.32 CH_2: 135.46	7.00	56.0	5.86	[a]	0.57	0.13
4b	Si	Vi	Se	−193	−15.25	149.7	11.79	98.8	CH: 135.23 CH_2: 135.29	7.27	53.8	2.52	[b]	0.67	0.02
5a	Ge	Me	S	–	–	–	13.89	–	11.37	7.52	55.9	1.45	1.24	0.56	0.05
5b	Ge	Me	Se	−130	–	–	12.44	103.5	12.28	7.72	53.5	2.61	1.51	0.66	−0.06
6a	Sn	Me	S	–	105	–	15.09	–	9.32	8.45	55.2	3.57	1.14	0.57	0.10
6b	Sn	Me	Se	−283	−68	1320	12.75	106.4	7.73	8.71		1.87	1.29	0.67	

[a] Vinyl, CH: 6.32 ($^1J_{CH}$: 145.4), CH_2: ($^1J_{CH}$: 146.6) 6.10 ($^3J_{HH}$: 19, $^2J_{HH}$: 2)/6.15 ($^3J_{HH}$: 15).

[b] Vinyl, CH: 6.44, CH_2: 6.07 ($^3J_{HH}$: 19, $^2J_{HH}$: 2)/6.08 ($^3J_{HH}$: 12).

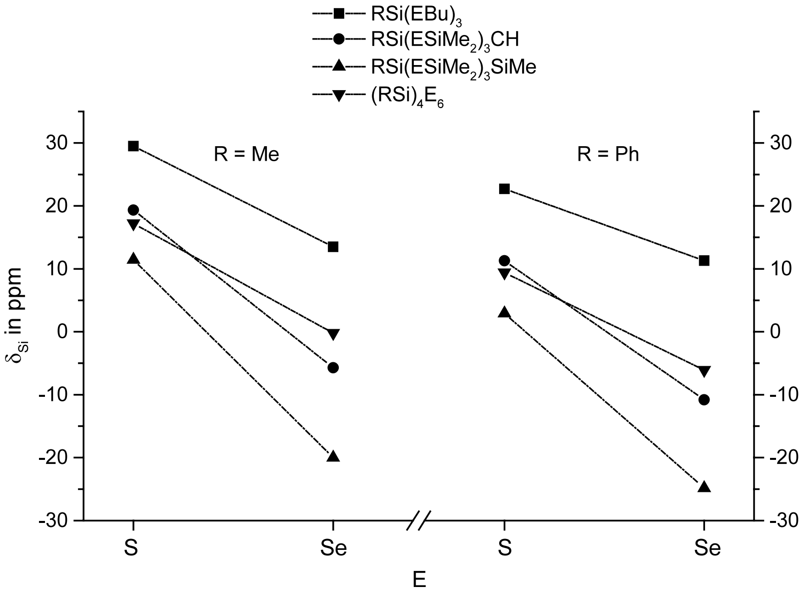


Fig. 1. ^{29}Si-NMR chemical shift of RSiE$_3$ units in acyclic RSi(EBu)$_3$ [19,20], bicyclic RSi(ESiMe$_2$)$_3$CH (this work), RSi(ESiMe$_2$)$_3$SiMe [15] and tricyclic adamantane-like (RSi)$_4$E$_6$ [18,21].

cyclic and polycyclic Group 14 chalcogenanes [24–26]. In all four compounds characterized by X-ray structure analysis, the ME$_3$ cap is twisted by 18–19° with respect to the HCSi$_3$ unit. This results also in the observed dihedral angles M–E–Si–C of ca. 26–29°. This twist gives raise to chirality of the molecules.

Compound **2a** crystallizes in the non-centrosymmetric space group $P2_1$ and contains only one of the two enantiomers of the bicyclo[2.2.2]octane cage. As can be seen from Fig. 7, the molecules are oriented along the crystallographic b-axis.

3. Experimental

3.1. NMR and GC–MS measurements

All NMR spectra were recorded on a Bruker DPX 400 in CDCl$_3$ solution and Me$_4$Si as internal standard for ^{1}H, ^{13}C and ^{29}Si. In order to get a sufficient signal to noise ratio of ^{29}Si-NMR spectra for obtaining $^1J_{SiC}$, $^1J_{SiSi}$, $^1J_{SiSe}$ or $^2J_{SiSn}$ satellites also ^{29}Si INEPT spectra were recorded. ^{77}Se and ^{119}Sn spectra were recorded using an IGATED pulse program.

External Me$_4$Sn and Ph$_2$Se$_2$ (δ_{Se}: 460 ppm) in CDCl$_3$ were used as standards for ^{119}Sn and ^{77}Se.

Mass spectra were measured on a Hewlett-Packard 5971 (ionization energy: 70 eV, column: 30 m × 0.25 mm × 0.25 µm, phenylmethylpolysiloxane, column temperature: 80 °C (3 min)/20 K/min/200 °C, flow: He 0.5 ml min^{-1}).

3.2. Crystal structure analysis

X-ray structure analysis measurements of **2a**, **3a** and **4b** were performed on a BRUKER SMART CCD, while a RIGAKU AFC7 with Mercury CCD was used for **5b**. Crystal data of **2a**, **3a**, **4b** and **5b** as well as data collection and refinement details are given in Table 6.

The unit cells of **2a**, **3a** and **4b** were determined with the program SMART [27]. For data integration and refinement of the unit cells, the program SAINT [27] was used. The space groups were determined using the programs XPREP [27]. All data were corrected for absorption using SADABS [28]. For the data collection, unit cell refinement and data reduction of **5b** the program package Crystal Clear (Rigaku Corp. (2000)) was used. The structures were solved using direct methods (SIR-97 [29]), refined using least-squares meth-

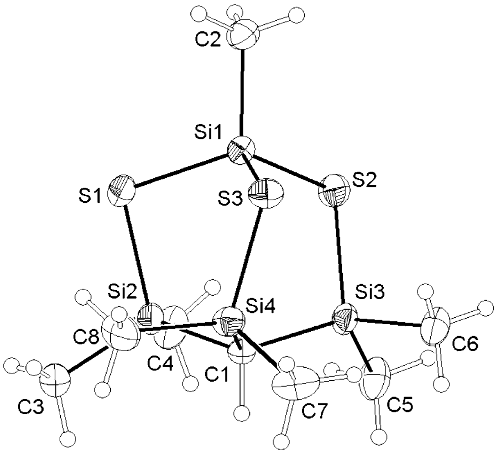


Fig. 2. ORTEP plot of the molecular structure of **2a**.

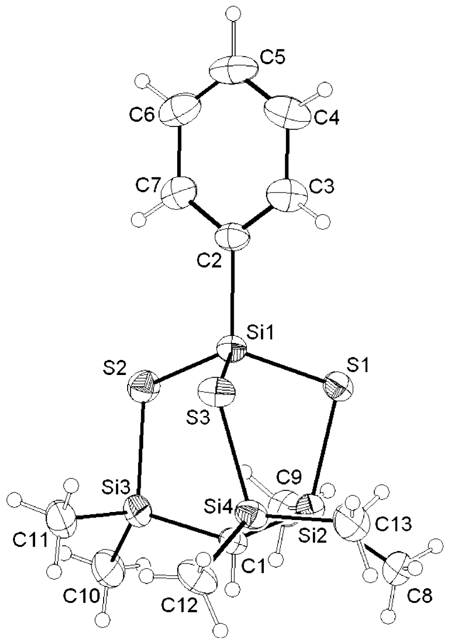


Fig. 3. ORTEP plot of the molecular structure of **3a**.

ods (SHELXL-97 [30]) and drawn using DIAMOND [31]. The ellipsoides at the non-hydrogen atoms are shown at the 50% probability level for **2a** and **3a** and 30% for **4b** and **5b**.

3.3. Starting materials

S, Se, 1 M Li[BEt$_3$H] in THF (Super Hydride), MeSiCl$_3$, PhSiCl$_3$, ViSiCl$_3$, MeGeCl$_3$ and MeSnCl$_3$, were commercially available. HC(SiMe$_3$)$_3$ was prepared as described in Ref. [32]. THF was distilled from sodium potassium alloy prior to use. The other solvents were dried over KOH or Na wire. All reactions were carried out under Ar applying standard Schlenk techniques.

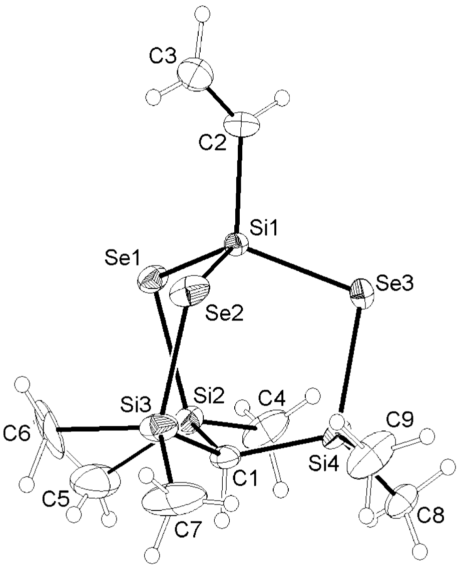


Fig. 4. ORTEP plot of the molecular structure of molecule A of **4b**. Thermal ellipsoids are shown at the 30% probability level.

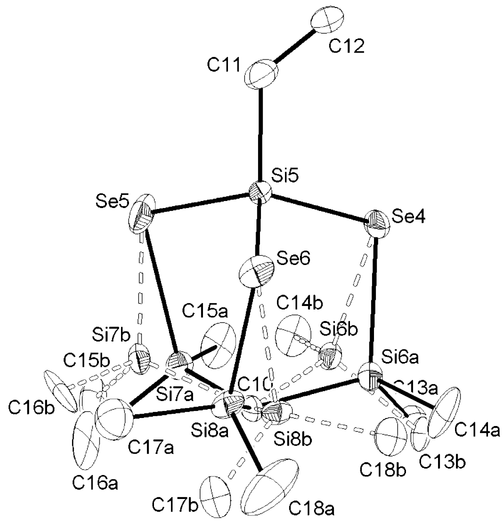


Fig. 5. ORTEP plot of the molecular structure of molecule B of **4b**. Thermal ellipsoids are shown at the 30% probability level, hydrogen atoms are omitted for clarity.

3.4. Preparation of tris(chlorodimethylsilylmethane), HC(SiMe$_2$Cl)$_3$ (1b)

HC(SiMe$_3$)$_3$ (7.7 g, 33 mmol) was dissolved in 10 ml hexane and AlCl$_3$ (14.0 g, 105 mmol) was added. Acetyl chloride (8.25 g, 105 mmol) was slowly added to the stirred mixture at 0 °C. After stirring over night at room temperature (r.t.), the upper layer of hexane and **1b** was separated and the solvent removed in vacuo to yield 7.9 g (82%) pure **1b** as oily residue.

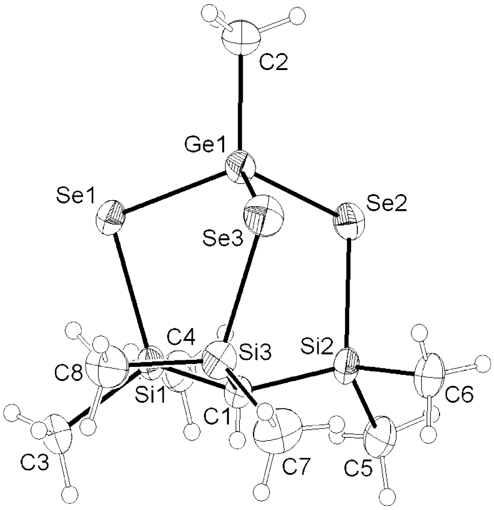


Fig. 6. ORTEP plot of the molecular structure of **5b**. Thermal ellipsoids are shown at the 30% probability level.

Table 2
Selected bond distances (Å) and angles (°) of **2a**

Atoms	Distances	Atoms	Angles
Si(1)–S(1)	2.133(2)	S(1)–Si(1)–S(2)	110.41(8)
Si(1)–S(2)	2.129(2)	S(1)–Si(1)–S(3)	110.57(8)
Si(1)–S(3)	2.138(2)	S(2)–Si(1)–S(3)	111.14(7)
Si(2)–S(1)	2.172(2)	Si(1)–S(1)–Si(2)	99.41(6)
Si(3)–S(2)	2.165(2)	Si(1)–S(2)–Si(3)	99.90(7)
Si(4)–S(3)	2.168(2)	Si(1)–S(3)–Si(4)	99.68(8)
Si(2)–C(1)	1.898(4)	S(1)–Si(2)–C(1)	107.8(2)
Si(3)–C(1)	1.891(5)	S(2)–Si(3)–C(1)	107.6(2)
Si(4)–C(1)	1.885(5)	S(3)–Si(4)–C(1)	107.9(2)
Si(1)–C(2)	1.860(6)	Si(2)–C(1)–Si(3)	112.5(2)
Si(2)–C(3)	1.861(6)	Si(2)–C(1)–Si(4)	113.3(2)
Si(2)–C(4)	1.855(5)	Si(3)–C(1)–Si(4)	113.1(3)
Si(3)–C(5)	1.852(6)		
Si(3)–C(6)	1.868(5)	Si(1)–S(1)–Si(2)–C(1)	27.6(2)
Si(4)–C(7)	1.862(5)	Si(1)–S(2)–Si(3)–C(1)	27.5(2)
Si(4)–C(8)	1.864(5)	Si(1)–S(3)–Si(4)–C(1)	26.7(2)

$HC(SiMe_3)_3$, NMR (ppm, Hz): ^1H: 0.105 ($SiMe_3$), −0.782 (HC); ^{13}C: 3.27 ($SiMe_3$) $^1J_{SiC}$: 51.0, 3.94 (HC) $^1J_{SiC}$: 37.6; ^{29}Si: −0.42.

Compound **1b**, NMR (ppm, Hz): ^1H: 0.664 ($SiMe_2$), 0.713 (HC); ^{13}C: 6.14 ($SiMe_2$) $^1J_{SiC}$: 60.2, 15.69 (HC) $^1J_{SiC}$: 39.5; ^{29}Si: 26.38.

$HC(SiMe_3)_3$, GC–MS (*m*/*e*, relative intensity): 217 (M–Me, 100), 129 ($HCSi_2Me_4$, 22), 73 ($SiMe_3$, 28).

Compound **1b**, GC–MS: 279 (M–Me, 100), 257 (M–Cl, 8), 169 ($HCSi_2Me_2Cl_2$, 26), 149 ($HCSi_2Me_3Cl$, 34), 93 ($SiMe_2Cl$, 21).

If the chlorination reaction is incomplete, besides **1b** also the doubly chlorinated trisilylmethane $Me_3SiCH(SiMe_2Cl)_2$ can be detected as by-product.

$Me_3Si^ACH(Si^BMe_2Cl)_2$, NMR (ppm, Hz): ^1H: 0.241 (Si^AMe_3), 0.503 (HC), 0.578 (Si^BMe_2); ^{13}C: 2.74 (Si^AMe_3) $^1J_{SiC}$: 52.5, 11.98 (HC), 6.35/6.41 (Si^BMe_2, diastereotopic Me-groups) $^1J_{SiC}$: 58.8; ^{29}Si: A: −0.45, B: 27.49.

Table 3
Selected bond distances (Å) and angles (°) of **3a**

Atoms	Distances	Atoms	Angles
Si(1)–S(1)	2.1358(8)	S(1)–Si(1)–S(2)	111.44(3)
Si(1)–S(2)	2.1263(8)	S(1)–Si(1)–S(3)	109.49(3)
Si(1)–S(3)	2.1372(8)	S(2)–Si(1)–S(3)	111.57(3)
Si(2)–S(1)	2.1765(8)	Si(1)–S(1)–Si(2)	98.93(3)
Si(3)–S(2)	2.1737(8)	Si(1)–S(2)–Si(3)	99.20(3)
Si(4)–S(3)	2.1717(8)	Si(1)–S(3)–Si(4)	99.36(3)
Si(2)–C(1)	1.886(2)	S(1)–Si(2)–C(1)	107.10(7)
Si(3)–C(1)	1.882(2)	S(2)–Si(3)–C(1)	107.41(7)
Si(4)–C(1)	1.884(2)	S(3)–Si(4)–C(1)	107.35(7)
Si(1)–C(2)	1.867(2)	Si(2)–C(1)–Si(3)	113.02(10)
Si(2)–C(8)	1.864(2)	Si(2)–C(1)–Si(4)	113.01(10)
Si(2)–C(9)	1.856(2)	Si(3)–C(1)–Si(4)	113.64(11)
Si(3)–C(10)	1.859(2)		
Si(3)–C(11)	1.867(3)	Si(1)–S(1)–Si(2)–C(1)	29.07(7)
Si(4)–C(12)	1.862(2)	Si(1)–S(2)–Si(3)–C(1)	27.91(8)
Si(4)–C(13)	1.863(3)	Si(1)–S(3)–Si(4)–C(1)	27.30(7)

Table 4
Selected bond distances (Å) and angles (°) of molecule A of **4b**

Atoms	Distances	Atoms	Angles
Si(1)–Se(1)	2.274(5)	Se(1)–Si(1)–Se(2)	111.9(2)
Si(1)–Se(2)	2.253(5)	Se(1)–Si(1)–Se(3)	110.4(2)
Si(1)–Se(3)	2.265(5)	Se(2)–Si(1)–Se(3)	111.4(2)
Si(2)–Se(1)	2.298(5)	Si(1)–Se(1)–Si(2)	97.4(2)
Si(3)–Se(2)	2.316(7)	Si(1)–Se(2)–Si(3)	95.7(2)
Si(4)–Se(3)	2.303(6)	Si(1)–Se(3)–Si(4)	96.9(2)
Si(2)–C(1)	1.880(19)	Se(1)–Si(2)–C(1)	108.3(5)
Si(3)–C(1)	1.890(17)	Se(2)–Si(3)–C(1)	109.9(6)
Si(4)–C(1)	1.905(18)	Se(3)–Si(4)–C(1)	108.7(6)
Si(1)–C(2)	1.868(17)	Si(2)–C(1)–Si(3)	115.0(9)
Si(2)–C(4)	1.89(2)	Si(2)–C(1)–Si(4)	113.6(9)
Si(2)–C(5)	1.91(3)	Si(3)–C(1)–Si(4)	113.8(10)
Si(3)–C(6)	1.86(3)	Si(1)–C(2)–C(3)	126.0(16)
Si(3)–C(7)	1.85(3)		
Si(4)–C(8)	1.862(17)	Si(1)–Se(1)–Si(2)–C(1)	26.8(6)
Si(4)–C(9)	1.88(2)	Si(1)–Se(2)–Si(3)–C(1)	26.6(7)
C(2)–C(3)	1.29(3)	Si(1)–S(3)–Si(4)–C(1)	26.3(6)

3.5. *Preparation of the bicyclo[2.2.2]octanes $HC(SiMe_2S)_3MR$ (MR = SiMe, SiPh, SiVi, GeMe, SnMe, **2a**–**6a**)*

Compound **1b** (0.29 g, 1.0 mmol) and organotrichloride $RMCl_3$ (1.0 mmol) (MR = SiMe, SiPh, SiVi, GeMe, SnMe) were mixed in 1 ml hexane. This mixture was quickly added to a stirred solution of 3.0 mmol Li_2S in THF, prepared from 0.096 g (3.0 mmol) sulfur and 6.0 ml of a 1 M solution of $LiBEt_3H$ in THF as described previously [15]. After stirring for 20 min, the solvent was replaced by 10 ml hexane and filtered. Removal of the

Table 5
Selected bond distances (Å) and angles (°) of **5b**

Atoms	Distances	Atoms	Angles
Ge(1)–Se(1)	2.3426(6)	Se(1)–Ge(1)–Se(2)	110.88(3)
Ge(1)–Se(2)	2.3490(6)	Se(1)–Ge(1)–Se(3)	110.49(2)
Ge(1)–Se(3)	2.3450(7)	Se(2)–Ge(1)–Se(3)	108.18(2)
Si(1)–Se(1)	2.3030(11)	Ge(1)–Se(1)–Si(1)	96.29(3)
Si(2)–Se(2)	2.2970(11)	Ge(1)–Se(2)–Si(2)	96.87(3)
Si(3)–Se(3)	2.3047(13)	Ge(1)–Se(3)–Si(3)	95.71(4)
Si(1)–C(1)	1.892(4)	Se(1)–Si(1)–C(1)	108.85(14)
Si(2)–C(1)	1.887(4)	Se(2)–Si(2)–C(1)	109.08(13)
Si(3)–C(1)	1.882(4)	Se(3)–Si(3)–C(1)	109.41(13)
Ge(1)–C(2)	1.935(4)	Si(1)–C(1)–Si(2)	114.6(2)
Si(1)–C(3)	1.864(4)	Si(1)–C(1)–Si(3)	115.0(2)
Si(1)–C(4)	1.857(5)	Si(2)–C(1)–Si(3)	114.8(2)
Si(2)–C(5)	1.859(5)		
Si(2)–C(6)	1.858(5)	Ge(1)–Se(1)–Si(1)–C(1)	28.8(2)
Si(3)–C(7)	1.872(5)	Ge(1)–Se(2)–Si(2)–C(1)	26.3(2)
Si(3)–C(8)	1.860(4)	Ge(1)–Se(3)–Si(3)–C(1)	29.2(2)

Table 6
Crystal data of **2a**, **3a**, **4b**, and **5b** as well as data collection and refinement details

	2a	**3a**	**4b**	**5b**
Empirical formula	$C_8H_{22}S_3Si_4$	$C_{13}H_{24}S_3Si_4$	$C_9H_{22}Se_3Si_4$	$C_8H_{22}GeSe_3Si_3$
Formula weight	326.80	388.86	479.51	512.01
Temperature (K)	173(2)	173(2)	173(2)	295(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Crystal shape	Block	Broken triangular plate	Rod	Block
Crystal color	Colorless	Colorless	Colorless	Colorless
Space group	$P2_1$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
Unit cell dimensions				
a (Å)	8.843(1)	8.719(1)	9.631(10)	9.7295(8)
b (Å)	10.274(1)	22.136(3)	13.908(12)	10.3208(5)
c (Å)	9.389(1)	11.034(1)	14.986(10)	18.3213(16)
α (°)			105.81(2)	
β (°)	97.792(3)	107.124(3)	91.40(1)	98.897(4)
γ (°)			105.20(2)	
V (Å^3)	845.14(15)	2035.0(5)	1854(3)	1817.6(2)
Z	2	4	4	4
D_{calc} (g cm^{-3})	1.284	1.269	1.718	1.871
Linear absorption coefficient (mm^{-1})	0.696	0.590	6.190	7.866
Crystal size (mm)	0.30 × 0.10 × 0.06	0.48 × 0.25 × 0.10	0.40 × 0.20 × 0.20	0.30 × 0.25 × 0.10
Scan method	ω scans	ω scans	ω scans	ϕ scans
Absorption correction	Empirical	Empirical	Empirical	Numerical
Theta range for collection (°)	2.19–30.85	1.84–30.91	1.42–30.60	2.25–28.0
Index ranges	$-10 \le h \le 12$, $-9 \le k \le 14$, $-7 \le l \le 13$	$-12 \le h \le 12$, $-30 \le k \le 31$, $-15 \le l \le 13$	$-13 \le h \le 13$, $-19 \le k \le 14$, $-21 \le l \le 21$	$-12 \le h \le 10$, $-13 \le k \le 13$, $-24 \le l \le 19$
Measured reflections	4230	16 856	15 074	20 268
Observed reflections	2541	3815	4671	3062
Independent reflections	3367 [$R_{int} = 0.0312$]	5886 [$R_{int} = 0.0437$]	10 121 [$R_{int} = 0.0620$]	4237 [$R_{int} = 0.0387$]
Max/min transmission	0.9594/0.8183	0.9434/0.7650	0.3707/0.1909	0.6933/0.3106
Completeness to θ_{max} (%)	80.5	91.4	88.7	96.6
Number of parameters	143	277	379	147
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0470$, $wR^2 = 0.1031$ [a]	$R_1 = 0.0380$, $wR^2 = 0.0789$ [a]	$R_1 = 0.1092$, $wR^2 = 0.3397$ [a]	$R_1 = 0.0392$, $wR^2 = 0.0905$ [a]
R indices (all data)	$R_1 = 0.0728$, $wR^2 = 0.1139$ [a]	$R_1 = 0.0804$, $wR^2 = 0.0917$ [a]	$R_1 = 0.1970$, $wR^2 = 0.3722$ [a]	$R_1 = 0.0637$, $wR^2 = 0.0972$ [a]
Goodness-of-fit (S) [b] on F^2	0.986	0.993	1.063	0.984
w-parameters (a/b)	0.0607/0	0.042/0	0.163/32.633	0.0586/0
H-locating and refining	Geom./constr.	Difmap/refall	Geom./constr.	Difmap/refall
Max/min e-density (e Å^{-3})	0.499/−0.475	0.383/−0.324	2.255/−1.173	0.857/−0.554

[a] $R_1 = \Sigma (||F_o| - |F_c||)/\Sigma |F_o|$, $wR^2 = [\Sigma (w(F_o^2 - F_c^2)^2)/\Sigma (wF_o^2)]^{1/2})$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

[b] $S = [\Sigma\, w(F_o^2 - F_c^2)^2]/(n - p)^{1/2}$; n, used reflections, p, used parameters.

solvent from the filtrate yielded **2a**–**6a** as colorless crystals in 50–70% yield.

Compound **2a**: m.p. 163 °C, **3a**: m.p. 149 °C, **4a**: m.p. 116 °C.

Compound **2a**, GC–MS: 326 ([M]$^+$, 26), 311 (M−Me, 100), 221 ($HCSi_3Me_4S_2$, 22), 131 (Si_2Me_5, 20), 73 ($SiMe_3$, 82), elemental analysis: $C_8H_{22}S_3Si_4$ ($M = 326.80$ g mol^{-1}, calc./exp.): C, 29.40/28.95; H, 6.79/6.53%.

Compound **3a**, GC–MS: 388 ([M]$^+$, 32), 373 (M−Me, 100), 283 ($HCSi_3Me_3S_2Ph$, 18), 221 ($HCSi_3Me_4S_2$, 7), 135 ($SiMe_2Ph$, 56), 73 ($SiMe_3$, 22), elemental analysis: $C_{13}H_{24}S_3Si_4$ (M = 388.87 g mol^{-1}, calc./exp.): C, 40.15/39.51; H, 6.22/6.33%.

Compound **4a**, GC–MS: 338 ([M]$^+$, 24), 323 (M−Me, 100), 233 ($HCSi_3Me_3S_2Vi$, 19), 221 ($HCSi_3Me_4S_2$, 10), 131 (Si_2Me_5, 15), 85 ($SiMe_2Vi$, 35), 73 ($SiMe_3$, 33), elemental analysis: $C_9H_{22}S_3Si_4$ (M = 338.81 g mol^{-1}, calc./exp.): C, 31.91/32.14; H, 6.55/6.91%.

Compound **5a**, GC–MS: 372 ([M]$^+$, 22), 357 (M−Me, 100), 267 ($HCSi_2Me_4S_2Ge$, 8), 221 ($HCSi_3Me_4S_2$, 15), 129 ($HCSi_2Me_4$, 23), 119 ($GeMe_3$, 42), 73 ($SiMe_3$, 56), elemental analysis: $C_8H_{22}GeS_3Si_3$ (M = 371.30 g mol^{-1}, calc./exp.): C, 25.88/25.92; H, 5.97/6.44%.

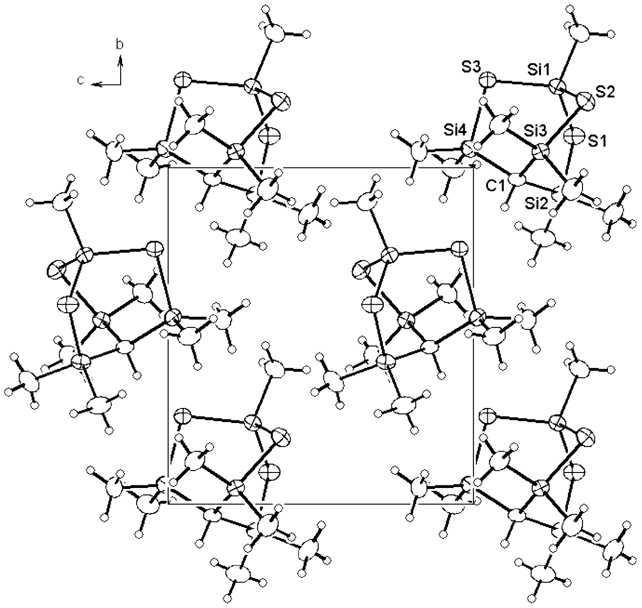


Fig. 7. The crystal structre of **2a**, view down the crystallographic *a*-axis. The molecules are oriented in a way that the S_3SiMe units point in the direction of the *b*-axis. In accordance with the non-centrosymmetric space groups all molecules show the same chirality.

Compound **6a**, GC–MS: 418 ($[M]^+$, 16), 403 (M–Me, 100), 375 ($HCSi_2Me_6S_3Sn$, 2), 313 ($HCSi_2Me_4S_2Sn$, 3), 283 ($HCSi_2Me_2S_2Sn$, 2), 251 ($HCSi_3Me_6S_2$, 6), 221 ($HCSi_3Me_4S_2$, 20), 161 ($HCSi_2Me_4S$, 62), 131 (Si_2Me_5, 21), 73 ($SiMe_3$, 38), elemental analysis: $C_8H_{22}S_3Si_3Sn$ ($M = 417.40$ g mol^{-1}, calc./exp.): C, 23.02/22.41; H, 5.31/5.87%.

3.6. Preparation of the bicyclo[2.2.2]octanes $HC(SiMe_2Se)_3MR$ (MR = SiMe, SiPh, SiVi, GeMe, SnMe, **2b**–**6b**)

Applying essentially the same procedure as described above, a mixture of 0.29 g (1.0 mmol) **1b** and 1.0 mmol of an organotrichloride $RMCl_3$ (MR = SiMe, SiPh, SiVi, GeMe, SnMe) in 1 ml hexane was added to a stirred suspension of 3.0 mmol Li_2Se in THF, freshly prepared from 0.24 g (3.0 mmol) Se powder and 6.0 ml of a 1 M solution of $LiBEt_3H$ in THF. **2b**–**6b** were obtained as colorless crystalline solids from hexane solutions in 45–65% yield.

Compound **2b**, GC–MS: 468 ($[M]^+$, 49), 453 (M–Me, 52), 317 ($HCSi_3Me_4Se_2$, 25), 207 (5), 193 (8), 129 ($HCSi_2Me_4$, 27), 73 ($SiMe_3$, 100), elemental analysis: $C_8H_{22}Se_3Si_4$ ($M = 467.50$ g mol^{-1}, calc./exp.): C, 20.55/21.12; H, 5.31/5.29%.

Compound **3b**, GC–MS: 530 ($[M]^+$, 49), 515 (M–Me, 36), 379 ($HCSi_3Me_3Se_2Ph$, 17), 317 ($HCSi_3Me_4Se_2$, 10), 207 (24), 135 ($SiMe_2Ph$, 100), 129 ($HCSi_2Me_4$, 37), 73 ($SiMe_3$, 66), elemental analysis: $C_{13}H_{24}Se_3Si_4$ ($M = 529.57$ g mol^{-1}, calc./exp.): C: 29.48/28.97; H, 4.57/5.04%.

Compound **4b**, GC–MS: 480 ($[M]^+$, 79), 465 (M–Me, 65), 329 ($HCSi_3Me_3Se_2Vi$,16), 317 ($HCSi_3Me_4Se_2$, 15), 267 ($HCSi_3Me_6Se$, 9), 179 ($HCSi_2Me_2Se$, 27), 129 ($HCSi_2Me_4$, 47), 85 ($SiMe_2Vi$, 100), 73 ($SiMe_3$, 97), elemental analysis: $C_9H_{22}Se_3Si_4$ ($M = 479.51$ g mol^{-1}, calc./exp.): C: 22.54/22.44; H, 4.62/4.28%.

Compound **5b**, GC–MS: 512 ($[M]^+$, 46), 497 (M–Me, 50), 361 ($HCSi_2Me_4Se_2Ge$, 7), 347 ($HCSi_3Me_6Se_2$, 26), 317 ($HCSi_3Me_4Se_2$, 12), 267 ($HCSi_3Me_6Se$, 15), 209 ($HCSi_2Me_4Se$, 33), 179 ($HCSi_2Me_2Se$, 19), 129 ($HCSi_2Me_4$, 60), 73 (Me_3Si, 100), elemental analysis: $C_8H_{22}GeSe_3Si_3$ ($M = 512.00$ g mol^{-1}, calc./exp.): C, 18.76/19.53; H: 4.33/5.06%.

Compound **5b**, elemental analysis: $C_8H_{22}Se_3Si_3Sn$ ($M = 558.10$ g mol^{-1}, calc./exp.): C, 17.22/17.99; H, 3.97/4.43%.

3.7. Preparation of tris(thiobutyldimethylsilyl)methane, $HC(SiMe_2{-}SBu)_3$

In analogy to the preparation of other thiobutyl substituted silanes published in Ref. [19], 0.29 g (1.0 mmol) **1b** and 0.27 g (3.0 mmol) 1-butanethiol were dissolved in 15 ml hexane and 0.42 ml (3.0 mmol) NEt_3 were slowly added by a syringe. After stirring for 1 week at r.t., the mixture was filtered and the solvent removed in vacuo yielding $HC(SiMe_2{-}SBu)_3$ as a colorless oily residue in almost quantitative yield. The product was characterized by ^1H-, ^{13}C- and ^{29}Si-NMR:

^1H-NMR (ppm): 0.52 ($SiMe_2$), 2.50 ($S{-}CH_2$), 1.58 ($S{-}CH_2{-}CH_2$), 1.41 ($S{-}CH_2{-}CH_2{-}CH_2$), 0.91 ($S{-}CH_3$); ^{13}C: 4.24 ($SiMe_2$), 27.05 ($S{-}CH_2$), 34.93 ($S{-}CH_2{-}CH_2$), 21.94 ($S{-}CH_2{-}CH_2{-}CH_2$), 13.63 ($S{-}CH_3$); ^{29}Si: 13.99 ($^1J_{SiC}$: 55.2 Hz).

If the reaction is stopped after 2 days, the product is essentially a mixture of the partially substituted products $HC(SiMe_2Cl)_2(SiMe_2SBu)$ and $HC(SiMe_2Cl)(SiMe_2SBu)_2$.

$HC(SiMe_2Cl)_2(SiMe_2SBu)$: ^1H-NMR (ppm): 0.652 ($SiMe_2Cl$), 0.542 ($SiMe_2SBu$); ^{13}C: 6.62/6.54 ($SiMe_2Cl$, diastereotopic Me-groups), 3.48 ($SiMe_2SBu$); ^{29}Si: 26.95 ($SiMe_2Cl$), 12.70 ($SiMe_2SBu$).

$HC(SiMe_2Cl)(SiMe_2SBu)_2$: ^1H-NMR (ppm): 0.642 ($SiMe_2Cl$), 0.531 ($SiMe_2SBu$); ^{13}C: 6.95 ($SiMe_2Cl$), 3.90/3.88 ($SiMe_2SBu$); ^{29}Si: 27.66 ($SiMe_2Cl$), 13.34 ($SiMe_2SBu$).

The ^1H- and ^{13}C-NMR chemical shifts of the thiobutyl units are identical with those of $HC(SiMe_2{-}SBu)_3$.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 179838–179840, 186693 for compounds **2a**, **3a**, **4b** and **5b**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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