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Novel Chalcogenides of Silicon with Bicyclo[2.2.2]octane Skeletons, $MeSi(SiMe_2E)_3MR$ (E = S, Se, Te; M = Si, Ge, Sn; R = Me, Ph)

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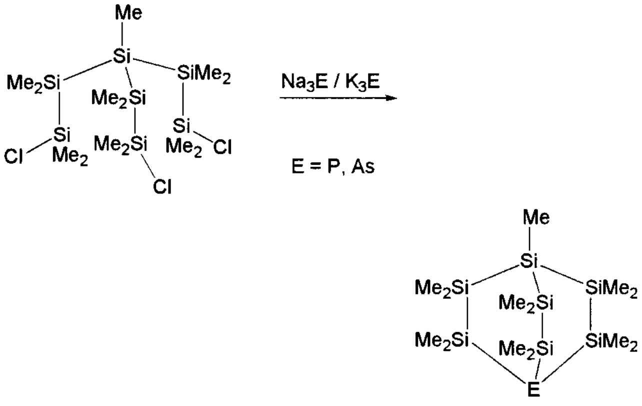
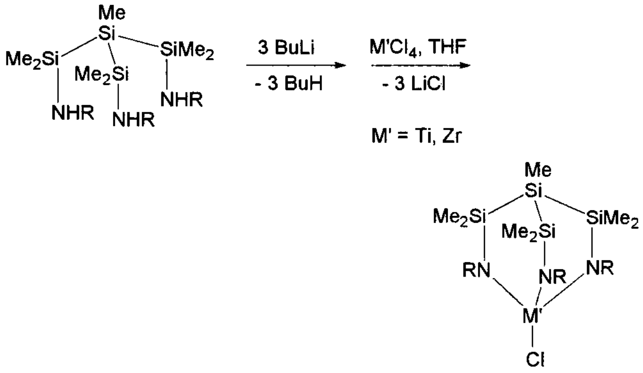
The reactions of 1:1 mixtures of the isotetrasilane $MeSi(SiMe_2Cl)_3$ and organo group 14 trichlorides $RMCl_3$ (R = Me, Ph; M = Si, Ge, Sn) with Li_2E (E = S, Se, Te) in THF yielded the new bicyclo[2.2.2]octanes $MeSi(SiMe_2E)_3MR$ (**2**−**4**). The products were identified by multinuclear NMR spectroscopy. Trends of the NMR data are discussed. The molecular structures of $MeSi(SiMe_2S)_3GeMe$ (**2c**), $MeSi(SiMe_2Se)_3SiMe$ (**3a**), $MeSi(SiMe_2Se)_3GeMe$ (**3c**), and $MeSi(SiMe_2Se)_3SnMe$ (**3e**) are reported.

Introduction

Bicyclo[2.2.2]octanes are an interesting class of ring systems because of their high symmetry. Several groups have already reported on bicyclo[2.2.2]octanes containing silicon and other heteroelements. Bicyclo[2.2.2]-octanes containing a branched heptasilane unit and a group 15 element have been described by Hassler et al.[1] They were obtained by reaction of the corresponding trichloroheptasilane and an alkaline metal phosphide or arsenide:



Gade et al. have used the branched tetrasilane $MeSi(SiMe_2Cl)_3$ (**1**) to build up tripodal amino ligands for group 4, 14, and 15 metals. With **1** as the starting material, the reaction with a primary amine yielded the triamines $MeSi(SiMe_2NHR)_3$. Subsquent lithiation[2] and reaction with halides of group 4,[3] 14,[4,5] or 15[6] elements resulted in heterobicyclo[2.2.2]octanes which are useful starting materials for heterobimetallic compounds with unsupported M−M′ bonds:[7,8]



These results led us to investigate whether it would be possible to build up related bicyclo[2.2.2]octanes with chalcogen atoms in place of the NR or $SiMe_2$ units. In the course of our previous investigations on silicon chalcogenides derived from oligosilanes, we have shown that cyclic and polycyclic compounds containing five- and six-membered rings are preferred. Usually no acyclic products are formed when chlorine-substituted oligosilanes are treated with either H_2S/NEt_3[9] or Li_2E (E = S, Se, Te).[10−12]

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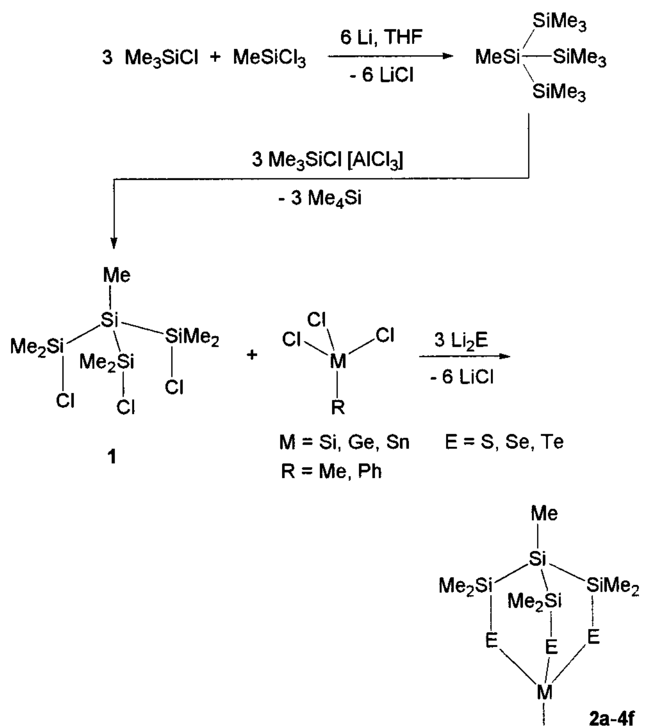
Table 1. ^{29}Si, ^{119}Sn, ^{77}Se, and ^{125}Te NMR Data (δ in ppm and J in Hz) of the Bicyclo[2.2.2]octanes $RM(ESi^BMe_2)_3Si^AMe$ (2−4)

compd	E	M	R	δ_E	δ_M	$^1J_{ME}$	δ_{Si^A}	δ_{Si^B}	$^1J_{SiSi}$	$^1J_{Si^BE}$	$^3J_{MSi^A}$
2a	S	Si	Me		Si: 11.4		−89.6	−0.8	65.8		17.3
2b	S	Si	Ph		Si: 2.9		−88.4	−0.5	65.8		14.9
2c	S	Ge	Me				−92.8	0.9	66.1		
2d	S	Ge	Ph				−91.2	1.1	65.6		
2e	S	Sn	Me		Sn: 66.3		−86.8	3.3[a]	65.8		133.6
2f	S	Sn	Ph		Sn: 3.4		−85.6	3.5[b]	65.8		129.5
3a	Se	Si	Me	Se: −101	Si: −20.0	155.0	−94.4	−5.5	65.6	99.5	17.2
3b	Se	Si	Ph	Se: −107	Si: −24.8	157.3	−93.0	−5.3	65.1	99.7	16.3
3c	Se	Ge	Me	Se: −29			−98.5	−4.6	65.7	103.1	
3d	Se	Ge	Ph	Se: −41			−96.6	−4.6	65.1	103.0	
3e	Se	Sn	Me	Se: −188	Sn: −150.9	1362	−91.4	−3.6[c]	65.1	104.4	142.4
3f	Se	Sn	Ph	Se: −198	Sn: −200.0	1387	−89.8	−3.6[d]	65.1	103.8	138.3
4a	Te	Si	Me	Te: −287	Si: −146.5	378.4	−108.0	−27.0[e]	63.1	262.4	
4b	Te	Si	Ph	Te: −305			−105.7	−26.8			
4d	Te	Ge	Ph	Te: −119			−111.3	−27.4			
4f	Te	Sn	Ph	Te: −501	Sn: −725		−103.1	−28.9[f]	62.4	267.8	132.2

[a] $^2J_{SiSn}$ = 24.4 Hz. [b] $^2J_{SiSn}$ = 23.7 Hz. [c] $^2J_{SiSn}$ = 27.8 Hz. [d] $^2J_{SiSn}$: 27.1 Hz. [e] $^2J_{SiTe}$ = 10.9 Hz. [f] $^2J_{SiSn}$ = 26.2 Hz and $^2J_{SiTe}$ = 13.0 Hz.

Scheme 1



Results and Discussion

$MeSi(SiMe_2Cl)_3$ (**1**) is a frequently used methylchlorooligosilane which can be obtained easily in two steps from Me_3SiCl and $MeSiCl_3$ and by subsequent chlorination of the formed isotetrasilane $MeSi(SiMe_3)_3$[13] (see Scheme 1).

In contrast to the formation of the N-containing bicyclo[2.2.2]octanes discussed above, it is not necessary to build up the bicyclic skeleton step by step: i.e., first introduction of the three amino groups and then lithiation and subsequent closure of the ring system by reaction with a metal halide. The direct reaction of 1:1 molar mixtures of **1** and a group 14 trichloride ($RMCl_3$, M = Si, Ge, Sn) with 3 equiv of Li_2E (E = S, Se, Te) prepared in situ from elemental E and 2 equiv of Li[BEt_3H] in THF results in clean formation of the desired bicyclo[2.2.2]octanes (Scheme 1).

Only in the case of the tellurium compounds are the yields rather low and large amounts (up to 50%) of byproducts are observed by NMR spectroscopy. However, in these cases the formation of bicyclo[2.2.2]octanes at all is remarkable. These are the first organo group 14 tellurides with an $RM(Te)_3$ coordination. While organotrichlorides of silicon, germanium, and tin form sesquichalcogenides with adamantane structures ($R_4M_4E_6$) on treatment with either M_2S or M_2Se, no related sesquitellurides have been reported so far and also our attempts to obtain organosilicon tellurides with $RSi(Te)_3$ units failed.[12] The only exception may be the tellurogermanate $(Et_4N)_4Ge_4Te_{10}$ with the adamantane-like anion $Ge_4Te_{10}^{4-}$, prepared by extraction of an alloy of the composition $K_4Ge_4Te_{10}$ with ethylenediamine and addition of Et_4NBr.[14] However, this anion bears no organic substituents and has been prepared under quite different reaction conditions.

The NMR data of all prepared bicyclo[2.2.2]octanes are summarized in Table 1. A comparison of the ^{29}Si NMR chemical shifts of the isotetrasilane units of the bicyclo[2.2.2]octanes with the compounds $MeSi^A(Si^BMe_2SBu)_3$ (δ_A, −79.4 ppm; δ_B, 4.8 ppm)[15] and $MeSi^A(Si^BMe_2SeBu)_3$ (δ_A, −77.3 ppm; δ_B, −1.1 ppm)[16] is remarkable, because there are the same substitution patterns at the silicon atoms but in acyclic compounds. While the ^{29}Si NMR chemical shifts of the $SiMe_2$ are close to the values found in the bicyclo[2.2.2]octanes **2a**−**f** and **3a**−**f**, large differences occur for the central SiMe units. Previous investigations have shown that the incorporation of the silicon atoms into a six-membered ring results in a high-field shift of the ^{29}Si NMR signals.[10] Concerning the central SiMe units, these silicon atoms can be regarded as being incorporated into three six-membered rings, which results in the strong high-field shift of these signals in all synthesized bicyclo[2.2.2]octanes. Unfortunately, no related acyclic telluro-substituted isotetrasilanes are known. Our attempts to react methylchlorooligosilanes such as **1** with BuTeLi resulted in excessive Si−Si bond cleavage.[17] Similar observations can be made by comparing the ^{29}Si NMR

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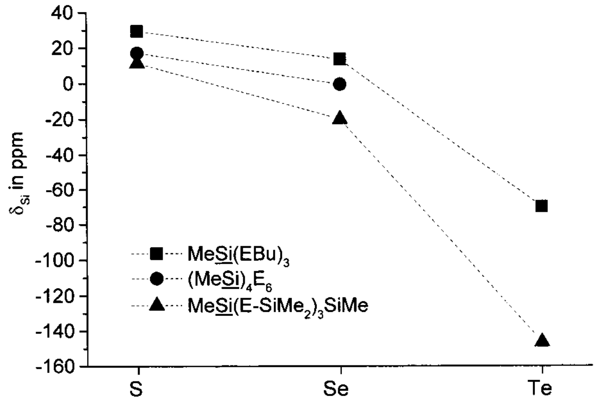

Figure 1. Effect of ring systems on the ^{29}Si NMR chemical shift in Me*Si*E$_3$ units for E = S, Se, Te.

chemical shifts of the RSiE$_3$ unit of **2a**−**4a** and **2b**−**4b** with those of the related silanes MeSi(SBu)$_3$ (29.5 ppm), PhSi(SBu)$_3$ (22.7 ppm),[15] MeSi(SeBu)$_3$ (13.5 ppm), PhSi(SeBu)$_3$ (11.3 ppm),[16] and MeSi(TeBu)$_3$ (−70.0 ppm).[17] Here again the incorporation of the RSi(E)$_3$ unit into the bicyclo[2.2.2] skeleton causes a strong high-field shift for the same R and E (see also Figure 1). Additionally the ^{29}Si NMR chemical shifts of the related silsesquichalcogenides with adamantane-like structures are presented in Figure 1; data are taken from ref 12. A similar conclusion can also be drawn for M = Sn when comparing the ^{119}Sn chemical shifts of **2e** and **3e** with those of MeSn(SMe)$_3$ (167 ppm)[18] and MeSn(SeMe)$_3$ (15 ppm).[19]

While the $^1J_{SiSi}$, $^1J_{SiSe}$, $^1J_{SiTe}$, $^1J_{SnSe}$, and $^1J_{SiC}$ values observed in the bicyclo[2.2.2]octanes are in the expected range for those coupling constants, the ^3J constants between the bridgehead atoms are remarkably large. $^3J_{SiSi}$ coupling constants of 15−17 Hz are observed in **2a**,**b** and **3a**,**b**, which are much larger than $^nJ_{SiSi}$ ($n > 1$) in open-chain[20,21] or simple cyclic[22−24] oligosilanes.

$^3J_{SnSi}$ coupling constants observed in **2e**,**f** and **4e**,**f** (M = Sn) are by a factor of 8−9 larger than $^3J_{SiSi}$ in related bicyclo[2.2.2]octanes with M = Si. This is approximately the same ratio as between the observed $^1J_{SiASe}$ (**3a**,**b**) and $^1J_{SnSe}$ (**3e**,**f**) coupling constants. It had been stated previously that the incorporation of silicon into strained polycyclic ring systems results in remarkably large $^nJ_{SiSi}$ ($n > 1$) coupling constants.[25] In the case of the bicyclo[2.2.2]octanes only coupling constants between the bridgehead positions seem to be affected, which can be seen in the observation of $^3J_{MSiA}$ and even a $^4J_{SnC}$ value in **2f** and **3f** while $^2J_{SiSi}$ values are not observed, and the measured $^2J_{SnSi}$ values are much smaller than $^3J_{SnSi}$ values of the same compounds.

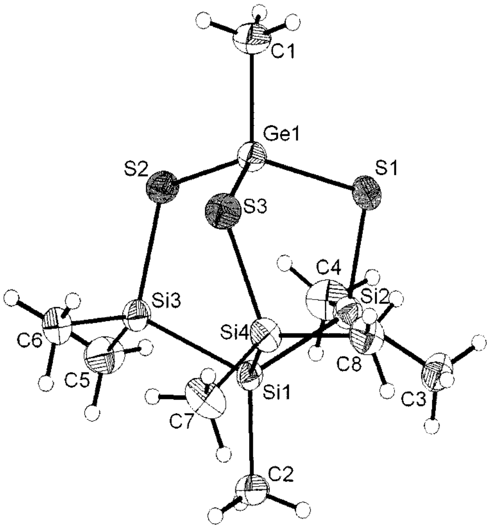

Figure 2. Molecular structure of **2c**.

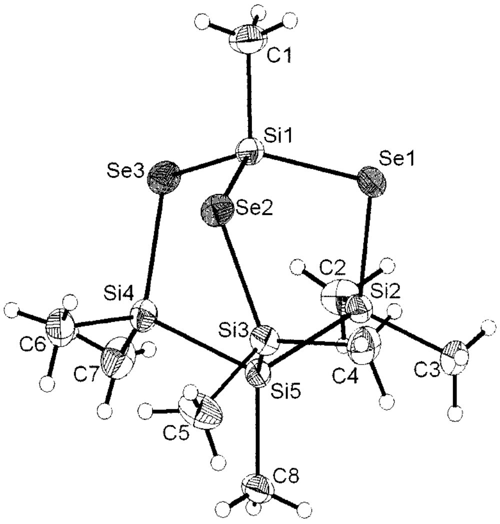

Figure 3. Molecular structure of **3a**.

The molecular structures of **2c** and **3a**,**c**,**e** have been determined by X-ray analyses, and Figures 2 and 3 show the molecular structures of **2c** and **3a**, respectively (the atom numbering of **3c**,**e** is analogous to that of **2c**). Bond lengths and angles are summarized in Tables 2−5. All four compounds crystallize in the same space group with similar cell constants (see Table 6).

All bond lengths are in the expected range. The already described tendency that Si−E bond lengths decrease with the number of sulfur substituents at silicon can be observed again in **3a**. While within the SiSe$_3$ unit the Si(1)−Se bonds are on average 2.276 Å, the Si−Se bonds toward the isotetrasilane unit are on average 2.309 Å. The Ge−S as well as Sn−Se bond lengths of **2c** and **3e** are close to the values found in the corresponding adamantanes (MeGe)$_4$S$_6$ (average Ge−S 2.218 Å[26]) and (MeSn)$_4$Se$_6$ (average Sn−Se 2.528 Å[27]). The angles at the chalcogen atoms are within 103.1−104.7° for E = S (**2c**) and 100.6−103.3° (**3a**), 99.8−102.9° (**3c**), and 98.2−102.6° (**3e**) for E = Se; in

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Table 2. Selected Bond Distances (Å) and Angles (deg) of 2c

Bond Distances			
Ge(1)−S(1)	2.2277(6)	Ge(1)−C(1)	1.930(2)
Ge(1)−S(2)	2.2288(6)	Si(1)−C(2)	1.892(2)
Ge(1)−S(3)	2.2285(6)	Si(2)−C(3)	1.878(2)
Si(2)−S(1)	2.1685(7)	Si(2)−C(4)	1.867(2)
Si(3)−S(2)	2.1751(7)	Si(3)−C(5)	1.874(2)
Si(4)−S(3)	2.1690(7)	Si(3)−C(6)	1.873(2)
Si(1)−Si(2)	2.3284(7)	Si(4)−C(7)	1.876(2)
Si(1)−Si(3)	2.3311(7)	Si(4)−C(8)	1.871(2)
Si(1)−Si(4)	2.3395(7)		
Bond Angles			
S(1)−Ge(1)-S(2)	111.77(2)	S(1)−Si(2)−Si(1)	108.36(3)
S(1)−Ge(1)−S(3)	112.46(2)	S(2)−Si(3)−Si(1)	106.28(3)
S(2)−Ge(1)−S(3)	110.03(2)	S(3)−Si(4)−Si(1)	107.21(3)
Ge(1)−S(1)−Si(2)	103.11(2)	Si(2)−Si(1)−Si(3)	107.05(3)
Ge(1)−S(2)−Si(3)	104.72(2)	Si(2)−Si(1)−Si(4)	104.99(2)
Ge(1)−S(3)−Si(4)	103.14(3)	Si(3)−Si(1)−Si(4)	106.11(3)
Torsion Angles			
Ge(1)−S(1)−Si(2)−Si(1)	31.43(3)		
Ge(1)−S(2)−Si(3)−Si(1)	32.24(3)		
Ge(1)−S(3)−Si(4)−Si(1)	34.16(3)		

Table 3. Selected Bond Distances (Å) and Angles (deg) of 3a

Bond Distances			
Si(1)−Se(1)	2.2722(7)	Si(1)−C(1)	1.852(3)
Si(1)−Se(2)	2.2794(7)	Si(2)−C(2)	1.866(3)
Si(1)−Se(3)	2.2770(7)	Si(2)−C(3)	1.875(3)
Si(2)−Se(1)	2.3054(7)	Si(3)−C(4)	1.865(3)
Si(3)−Se(2)	2.3011(7)	Si(3)−C(5)	1.871(3)
Si(4)−Se(3)	2.2996(7)	Si(4)−C(6)	1.874(3)
Si(2)−Si(5)	2.3271(9)	Si(4)−C(7)	1.873(3)
Si(3)−Si(5)	2.3232(10)	Si(5)−C(8)	1.888(3)
Si(4)−Si(5)	2.3345(8)		
Bond Angles			
Se(1)−Si(1)−Se(2)	112.89(3)	Se(1)−Si(2)−Si(5)	106.23(3)
Se(1)−Si(1)−Se(3)	111.00(3)	Se(2)−Si(3)−Si(5)	108.63(3)
Se(2)−Si(1)−Se(3)	113.46(3)	Se(3)−Si(4)−Si(5)	108.22(3)
Si(1)−Se(1)−Si(2)	103.30(3)	Si(2)−Si(5)−Si(3)	108.09(4)
Si(1)−Se(2)−Si(3)	100.96(2)	Si(2)−Si(5)−Si(4)	107.28(3)
Si(1)−Se(3)−Si(4)	100.63(2)	Si(3)−Si(5)−Si(4)	106.19(3)
Torsion Angles			
Si(1)−Se(1)−Si(2)−Si(5)	30.71(3)		
Si(1)−Se(2)−Si(3)−Si(5)	30.92(4)		
Si(1)−Se(3)−Si(4)−Si(5)	32.86(4)		

Table 4. Selected Bond Distances (Å) and Angles (deg) of 3c

Bond Distances			
Ge(1)−Se(1)	2.3546(5)	Ge(1)−C(1)	1.935(3)
Ge(1)−Se(2)	2.3540(5)	Si(1)−C(2)	1.890(3)
Ge(1)−Se(3)	2.3524(5)	Si(2)−C(3)	1.878(3)
Si(2)−Se(1)	2.2991(8)	Si(2)−C(4)	1.873(3)
Si(3)−Se(2)	2.3021(8)	Si(3)−C(5)	1.870(3)
Si(4)−Se(3)	2.3052(8)	Si(3)−C(6)	1.863(3)
Si(1)−Si(2)	2.3398(9)	Si(4)−C(7)	1.868(2)
Si(1)−Si(3)	2.3268(10)	Si(4)−C(8)	1.866(3)
Si(1)−Si(4)	2.3310(9)		
Bond Angles			
Se(1)−Ge(1)−Se(2)	113.27(1)	Se(1)−Si(2)−Si(1)	109.11(3)
Se(1)−Ge(1)−Se(3)	109.96(2)	Se(2)−Si(3)−Si(1)	109.17(3)
Se(2)−Ge(1)−Se(3)	112.45(2)	Se(3)−Si(4)−Si(1)	106.79(3)
Ge(1)−Se(1)−Si(2)	99.82(2)	Si(2)−Si(1)−Si(3)	107.28(3)
Ge(1)−Se(2)−Si(3)	100.40(2)	Si(2)−Si(1)−Si(4)	107.77(3)
Ge(1)−Se(3)−Si(4)	102.91(2)	Si(3)−Si(1)−Si(4)	108.71(4)
Torsion Angles			
Ge(1)−Se(1)−Si(2)−Si(1)	32.58(3)		
Ge(1)−Se(2)−Si(3)−Si(1)	30.87(3)		
Ge(1)−Se(3)−Si(4)−Si(1)	29.89(3)		

Table 5. Selected Bond Distances (Å) and Angles (deg) of 3e

Bond Distances			
Sn(1)−Se(1)	2.5269(6)	Sn(1)−C(1)	2.128(4)
Sn(1)−Se(2)	2.5296(5)	Si(1)−C(2)	1.890(4)
Sn(1)−Se(3)	2.5230(5)	Si(2)−C(3)	1.863(5)
Si(2)−Se(1)	2.3055(11)	Si(2)−C(4)	1.871(6)
Si(3)−Se(2)	2.3055(12)	Si(3)−C(5)	1.864(5)
Si(4)−Se(3)	2.3041(12)	Si(3)−C(6)	1.869(5)
Si(1)−Si(2)	2.3386(15)	Si(4)−C(7)	1.873(5)
Si(1)−Si(3)	2.3403(14)	Si(4)−C(8)	1.881(4)
Si(1)−Si(4)	2.3429(17)		
Bond Angles			
Se(1)−Sn(1)−Se(2)	111.63(2)	Se(1)−Si(2)−Si(1)	108.27(5)
Se(1)−Sn(1)−Se(3)	107.14(2)	Se(2)−Si(3)−Si(1)	110.60(5)
Se(2)−Sn(1)−Se(3)	112.40(2)	Se(3)−Si(4)−Si(1)	111.61(5)
Sn(1)−Se(1)−Si(2)	102.63(3)	Si(2)−Si(1)−Si(3)	110.00(5)
Sn(1)−Se(2)−Si(3)	99.40(3)	Si(2)−Si(1)−Si(4)	108.62(6)
Sn(1)−Se(3)−Si(4)	98.20(3)	Si(3)−Si(1)−Si(4)	109.34(6)
Torsion Angles			
Sn(1)−Se(1)−Si(2)−Si(1)	27.21(6)		
Sn(1)−Se(2)−Si(3)−Si(1)	30.68(5)		
Sn(1)−Se(3)−Si(4)−Si(1)	31.77(5)		

all cases these are smaller than the tetrahedral angle. This is in agreement with molecular structures of other cyclic and polycyclic group 14 chalcogenanes.[9−11] It is remarkable that in **2c** and **3a**,**c** as well as **3e** two of the angles M−E−Si are very similar while the third one is on average 3° larger. In all four compounds characterized by X-ray structure analyses the ME_3 cap is twisted on average by 20° with respect to the $SiSi_3$ unit. This results also in the observed dihedral angles M−E−Si−Si of approximately 30°.

Experimental Section

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. To get a sufficient signal-to-noise-ratio of ^{29}Si NMR spectra for resolving $^1J_{SiC}$, $^1J_{SiSi}$, $^nJ_{SiSe}$, $^nJ_{SiSn}$, or $^nJ_{SiTe}$ satellites, ^{29}Si INEPT spectra were also recorded. ^{77}Se, ^{119}Sn, and ^{125}Te spectra were measured using an IGATED pulse program. External Me_4Sn, Ph_2Se_2 (δ_{Se} 460 ppm), and Ph_2Te_2 (δ_{Te} 422 ppm) in $CDCl_3$ were used as standards for ^{119}Sn, ^{77}Se, and ^{125}Te.

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, flow He 0.5 mL/min). The molecule peaks as well as all identified fragments showed the expected patterns due to the content of elements with several isotopes, namely Ge, Sn, and Se.

2. Crystal Structure Analysis. X-ray structure analysis measurements were performed on a Bruker SMART CCD area detector at 173 K, using Mo Kα radiation ($\lambda = 0.710\,73$ Å, graphite monochromator). Crystal data of **2c** and **3a**,**c**,**e** as well as data collection and refinement details are given in Table 6. The unit cells were determined with the program SMART.[28] For data integration and refinement of the unit cells the program SAINT[28] was used. The space groups were determined using the program XPREP.[28] All data were corrected for absorption using SADABS.[29] The structures were solved using direct methods (SHELX-97[30]), refined using full-matrix least-squares methods on F^2 (SHELX-97), and drawn using

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(28) Bruker AXS Inc., Madison, WI, 1998.

(29) Sheldrick, G. M. Sadabs V2.01, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen, Göttingen, Germany, 2000.

(30) Sheldrick, G. M. Shelx97: Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen, Göttingen, Germany, 1997.

Table 6. Crystal Data of 2c and 3a,c,e as Well as Data Collection and Refinement Details

	2c	**3a**	**3c**	**3e**
empirical formula	$C_8H_{24}GeS_3Si_4$	$C_8H_{24}Se_3Si_5$	$C_8H_{24}GeSe_3Si_4$	$C_8H_{24}Se_3Si_4Sn$
cryst shape	plate	block	block	rod
cryst color	colorless	colorless	colorless	colorless
cryst size	0.70 × 0.50 × 0.12	0.60 × 0.42 × 0.35	0.60 × 0.50 × 0.40	0.80 × 0.30 × 0.20
fw	401.43	497.590	542.11	588.20
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
unit cell dimens				
a (Å)	10.2181(15)	10.2283(6)	10.238(2)	10.3290(14)
b (Å)	11.6391(18)	11.6430(7)	11.668(2)	11.7081(16)
c (Å)	16.638(3)	16.8521(9)	16.914(2)	17.066(2)
β (deg)	93.396(3)	93.386(2)	93.775(3)	95.253(2)
V (Å^3); Z	1975.3(5); 4	2003.4(13); 4	2016.1(6); 4	2055.2(5); 4
calcd density (g/cm^3)	1.350	1.650	1.786	1.901
linear abs coeff (mm^{-1})	2.090	5.788	7.154	6.771
scan method	ω scans	ω scans	ω scans	ω scans
abs cor	none	empirical	empirical	empirical
max/min transmissn	0.7875/0.3224	0.2365/0.1288	0.1620/0.0993	0.3445/0.0743
no. of measd rflns	15886	8657	16133	8972
no. of indep rflns	5666	4530	5779	4446
no. of obsd rflns	4398	3801	4516	3222
R(int)	0.0298	0.0201	0.0330	0.0319
θ range for collecn (deg)	2.00−30.82	1.99−29.44	1.99−30.88	1.98−29.41
index ranges	$-14 \leq h \leq 14$	$-11 \leq h \leq 13$	$-13 \leq h \leq 12$	$-13 \leq h \leq 9$
	$-14 \leq k \leq 16$	$-10 \leq k \leq 15$	$-16 \leq k \leq 9$	$-10 \leq k \leq 15$
	$-23 \leq l \leq 18$	$-22 \leq l \leq 12$	$-23 \leq l \leq 23$	$-19 \leq l \leq 21$
completeness to θ_{max} (%)	91.3	81.6	90.9	78.3
final R1/wR2 ^{a} ($I > 2\sigma(I)$)	0.0274/0.0649	0.0257/0.0638	0.0269/0.0577	0.0296/0.0566
final R1/wR2 ^{a} (all data)	0.0435/0.0707	0.0332/0.0661	0.0430/0.0620	0.0536/0.0629
weighting scheme factors (a/b)^a	0.0338/0.3826	0.0410/0	0.0281 /0	0.0277/0
goodness of fit (S)^b on F^2	1.008	0.997	1.027	0.955
no. of used rflns/params	5666/153	4530/235	5779/153	4446/241
H locating and refining	geom/constr	difmap/refall	geom/constr	difmap/refall
max/min e density (e/Å^3)	0.577/−0.363	0.380/−0.542	0.423/−0.794	0.512/−0.710

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^2)]^{1/2})$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, 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.

DIAMOND.[31] The ellipsoids of the non-hydrogen atoms are at the 50% probability level.

3. Starting Materials. S, Se, Te, 1 M Li[BEt$_3$H] in THF (Super Hydride), $RSiCl_3$, $RGeCl_3$, and $RSnCl_3$ (R = Me, Ph) were commercially available. THF was distilled from sodium potassium alloy prior to use. The other solvents were dried over KOH or sodium wire. All reactions were carried out under argon by applying standard Schlenk techniques. MeSi(SiClMe$_2$)$_3$ was prepared as described previously.[32]

4. Preparation of the Bicyclo[2.2.2]octanes MeSi(SiMe$_2$S)$_3$MR (2a−f: M = Si, Ge, Sn; R = Me, Ph). In a typical reaction 96 mg (3.0 mmol) of sulfur was dissolved in a mixture of 6.0 mL of a 1 M solution of Li[BEt$_3$H] and an additional 3 mL of THF to form a Li_2S solution. A mixture of 0.33 g (1.0 mmol) of **1** and 1.0 mmol of the appropriate $RMCl_3$ (M = Si, Ge, Sn; R = Me, Ph) dissolved in 1 mL of THF was added slowly to the stirred Li_2S solution in THF at 0 °C. After the mixture was stirred for 20 min, the solvent was replaced by 10 mL of hexane. The product was filtered from precipitated lithium chloride, and the solvent was removed in vacuo, yielding the bicyclo[2.2.2]octanes **2a**−**f** as crystalline residues in 50−70% yield, with the exception of **2a**, which remained a colorless oil. In the case of the preparation of **2b**,**d** larger amounts of byproducts were observed by NMR spectroscopy in the crude products. For further purification the products were recrystallized from hexane.

2a: GC/MS (m/e, relative intensity) 356 (M$^+$, 31), 341 (M − Me, 20), 297 ($Me_5Si_4S_3CH_2$, 12), 283 ($Me_5Si_4S_3$, 11), 251 ($Me_5Si_4S_2$, 3), 223 ($Me_5Si_3S_2$, 5), 191 (Me_5Si_3S, 14), 176 (Me_4Si_3S, 14), 131 (Me_5Si_2, 17), 116 (Me_4Si_2, 16), 73 (Me_3Si, 100).

2b: Anal. Calcd for $C_{13}H_{26}S_3Si_5$ (418.98): C, 37.27; H, 6.25. Found: C, 37.54; H, 6.18.

2c: GC/MS (m/e, relative intensity) 402 (M$^+$, 5), 387 (M − Me, 20), 313 ($Me_7Si_4S_3$, 10), 281 ($Me_7Si_4S_2$, 45), 223 ($Me_5Si_3S_2$, 13), 191 (Me_5Si_3S, 23), 163 (Me_5Si_2S, 11), 131 (Me_5Si_2, 30), 116 (Me_4Si_2, 14), 73 (Me_3Si, 100); mp 182 °C. Anal. Calcd for $C_8H_{24}GeS_3Si_4$ (401.43): C, 23.94; H, 6.03. Found: C, 23.82; H, 6.51.

2d: GC/MS (m/e, relative intensity) 464 (M$^+$, 11), 449 (M − Me, 1), 387 (M − Ph, 2), 329 ($Me_5Si_3S_3Ge$, 9), 313 ($Me_7Si_4S_3$, 15), 281 ($Me_7Si_4S_2$, 15), 223 ($Me_5Si_3S_2$, 41), 209 (22), 178 (Me_3Si_2Ph, 14), 163 (Me_2Si_2Ph, 32), 135 (Me_2SiPh, 100), 73 (Me_3Si, 78).

2e: GC/MS (m/e, relative intensity) 433 (M − Me, 24), 375 ($Me_5Si_3S_3Sn$, 2), 343 ($Me_5Si_3S_2Sn$, 10), 313 ($Me_7Si_4S_3$, 18), 281 ($Me_7Si_4S_2$, 11), 223 ($Me_5Si_3S_2$, 4), 191 (Me_5Si_3S, 37), 163 (Me_5Si_2S, 6), 131 (Me_5Si_2, 29), 73 (Me_3Si, 100). Anal. Calcd for $C_8H_{24}S_3Si_4Sn$ (447.53): C, 21.47; H, 5.41. Found: C, 21.10; H, 5.73.

2f: GC/MS (m/e, relative intensity) 510 (M$^+$, 3), 495 (M − Me, 0.5), 433 (M − Ph, 40), 375 ($Me_5Si_3S_3Sn$, 35), 343 ($Me_5Si_3S_2Sn$, 11), 313 ($Me_7Si_4S_3$, 19), 281 ($Me_7Si_4S_2$, 19), 223 ($Me_5Si_3S_2$, 23), 191 (Me_5Si_3S, 44), 153 (22), 135 (Me_2SiPh, 75), 131 (Me_5Si_2, 27), 73 (Me_3Si, 100).

5. Preparation of the Bicyclo[2.2.2]octanes MeSi(SiMe$_2$Se)$_3$MR (3a−f: M = Si, Ge, Sn; R = Me, Ph). A 0.24 g quantity (3.0 mmol) of selenium powder was added to a mixture of 6.0 mL of a 1 M solution of Li[BEt$_3$H] and 3 mL of THF to form a white Li_2Se suspension. As described above, a mixture of 0.33 g (1.0 mmol) of **1** and 1.0 mmol of the appropriate $RMCl_3$ (M = Si, Ge, Sn; R = Me, Ph) dissolved in 1 mL of THF was added slowly to the stirred Li_2Se suspension at 0 °C. Workup as described in part 4 yielded the bicyclo[2.2.2]octanes **3a**−**f** in 50−70% yield as crystalline residues which could be recrystallized from hexane for further purifica-

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(31) Berndt, M.; Brandenburg, K.; Putz H. Diamond 2.1; Crystal Impact GbR, www.crystalimpact.de, Bonn, Germany, 1999.

(32) Herzog, U.; Schulze, N.; Trommer, K.; Roewer, G. *J. Organomet. Chem.* **1997**, *547*, 133.

tion, but in most cases no byproducts could be identified by NMR spectroscopy.

3a: GC/MS (*m*/*e*, relative intensity) 498 (M^+ ($Me_8Si_5{}^{78}Se^{80}Se_2$), 6), 483 (M − Me, 4), 439 ($Me_5Si_4{}^{78}Se^{80}Se_2CH_2$, 2), 425 ($Me_5Si_4{}^{78}Se^{80}Se_2$, 1), 377 ($Me_7Si_4{}^{80}Se_2$, 1), 347 ($Me_5Si_4{}^{80}Se_2$, 3), 319 ($Me_5Si_3{}^{80}Se_2$, 2), 239 ($Me_5Si_3{}^{80}Se$, 11), 224 ($Me_4Si_3{}^{80}Se$, 7), 195 ($Me_3Si_2{}^{80}SeCH_2$, 4), 131 ($Me_5Si_2$, 19), 116 ($Me_4Si_2$, 14), 73 ($Me_3Si$, 100); mp 202 °C. Anal. Calcd for $C_8H_{24}Se_3Si_5$ (497.59): C, 19.31; H, 4.86. Found: C, 18.95; H, 4.70.

3b: GC/MS (*m*/*e*, relative intensity) 560 (M^+ ($Me_7Si_5{}^{78}Se^{80}Se_2Ph$), 18), 545 (M − Me, 4), 501 ($Me_4Si_4{}^{78}Se^{80}Se_2CH_2Ph$, 2), 487 ($Me_4Si_4{}^{78}Se^{80}Se_2Ph$, 4), 423 (2), 365 (4), 319 ($Me_5Si_3{}^{80}Se_2$, 5), 301 (10), 286 (18), 257 (12), 224 ($Me_4Si_3{}^{80}Se$, 8), 193 (Me_4Si_2Ph, 15), 178 (Me_3Si_2Ph, 20), 135 (Me_2SiPh, 100), 131 (Me_4Si_2, 14), 105 (SiPh, 12), 73 (Me_3Si, 56).

3c: GC/MS (*m*/*e*, relative intensity) 544 (M^+ ($Me_8Si_4{}^{78}Se^{80}Se_2{}^{74}Ge$), 2), 529 (M − Me, 6), 377 ($Me_7Si_4{}^{80}Se_2$, 13), 319 ($Me_5Si_3{}^{80}Se_2$, 3), 239 ($Me_5Si_3{}^{80}Se$, 17), 211 ($Me_5Si_2{}^{80}Se$, 5), 195 ($Me_3Si_2{}^{80}SeCH_2$, 4), 131 (Me_5Si_2, 22), 116 (Me_4Si_2, 8), 73 (Me_3Si, 100). Anal. Calcd for $C_8H_{24}GeSe_3Si_4$ (542.11): C, 17.72; H, 4.46. Found: C, 17.33; H, 4.45.

3d: GC/MS (*m*/*e*, relative intensity) 606 (M^+ ($Me_7PhSi_4{}^{78}Se^{80}Se_2{}^{74}Ge$), 5), 471 ($Me_5Si_3{}^{78}Se^{80}Se_2{}^{74}Ge$, 9), 467 (9), 377 ($Me_7Si_4{}^{80}Se_2$, 8), 330 (11), 317 (17), 281 ($Me_7Si_4C_5H_4$, 12), 207 ($Me_4Si_2C_7H_7$, 35), 178 (Me_3PhSi_2, 14), 135 (Me_2PhSi, 82), 73 (Me_3Si, 100).

3e: decomposes at 160 °C (turns black).

6. Preparation of the Bicyclo[2.2.2]octanes MeSi(SiMe$_2$Te)$_3$MR (4a−f: M = Si, Ge, Sn; R = Me, Ph). A 0.38 g quantity (3.0 mmol) of tellurium powder was added to a mixture of 6.0 mL of a 1 M solution of Li[BEt$_3$H] and 3 mL of THF. The reaction mixture turned dark purple and became light red after 1 h, after all tellurium had been consumed. A mixture of 0.33 g (1.0 mmol) of **1** and 1.0 mmol of the appropriate $RMCl_3$ (M = Si, Ge, Sn; R = Me, Ph) dissolved in 1 mL of THF was added slowly to the stirred Li_2Te suspension at −30 °C. Workup as described in part 4 yielded yellow oily residues containing the desired bicyclo[2.2.2]octanes **4a**,**b**,**d**,**f**, in addition to further unidentified byproducts as determined by NMR spectroscopy. Because of the high reactivity toward moisture and oxygen and the low thermal stability of **4a**−**f**, no further purification was attempted. On contact with oxygen **4a**−**f** decompose almost immediately with formation of a black precipitate of elemental tellurium.

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Supporting Information Available: A table giving ^{1}H and ^{13}C NMR data of **2**−**4**, tables of X-ray crystal data for **2c** and **3a**,**c**,**e**, and figures showing trends of ^{29}Si, ^{77}Se ,and ^{125}Te NMR chemical shifts and NMR spectra of the tellurium compounds **4a**−**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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