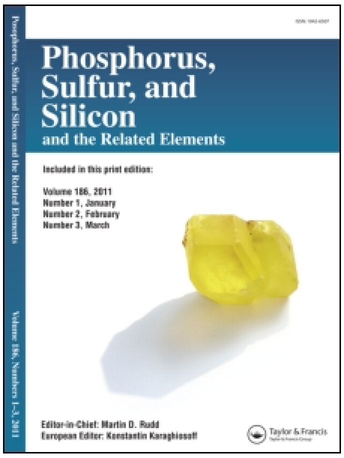

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CYCLIC POLYCHALCOGENIDE COMPOUNDS WITH SILICON AND GERMANIUM ATOMS

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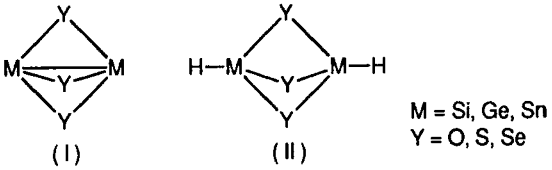
Abstract A new trithiadisilabicyclo[1.1.1]pentane **1-S3** as well as its selenium analogue **1-Se3** were prepared by dechalcogenation of the corresponding tetrachalcogena[2.1.1]hexanes. The X-ray analysis clearly prooved that the distance between the bridging silicon atoms of **1-S3** and **1-Se3** are 2.407 and 2.515 Å, respectively, values which are within the range of common Si-Si single bonds. Under appropriate conditions trihydro- and trihalosilanes react with elemental chalcogens respective chalcogen transfer reagents to give adamantane-type silachalcogenanes or bicyclopolychalcogenasilanes. E. g. treatment of *tert*-butyl-germanium trichloride with ammonium pentasulfide afforded a double decker type germathiane **7**, which thermally rearranged to the corresponding adamantane-type isomer **5**.

INTRODUCTION

Sesquichalcogenides with incorporated group 14 elements of the type $(RE)_{2n}Y_{3n}$ (E = Si, Ge, Sn; Y = O, S, Se) have attracted much attention due to the unique structural properties exhibited by this class of compounds.

Under appropriate conditions trihydro- and trihalosilanes react with elemental chalcogens respective chalcogen transfer reagents to give adamantane-type silachalcogenanes[1-4] and/or bicyclopolychalcogenasilanes[5] depending on the steric size of substituents.

Calculations predict, that the structures of [1.1.1]propellanes of the type M_2Y_3 (M=Si, Ge, Sn; Y = O, S, Se) (I) and the corresponding bicyclo[1.1.1]pentanes $H_2M_2Y_3$ (II) shoud be very similar, for especially the distance between the bridgehead



atoms should be comparable.[6-8] Interestingly, trioxadisilabicyclo[1.1.1]pentane is predicted to have an extremely short distance between the bridging silicon atoms of only 2.06 Å, which is even smaller than that of Si=Si double bonds.[7] We succeeded in the synthesis of the first example of a double decker-type sesquisulfide, namely $(^tBuGe)_4S_6$

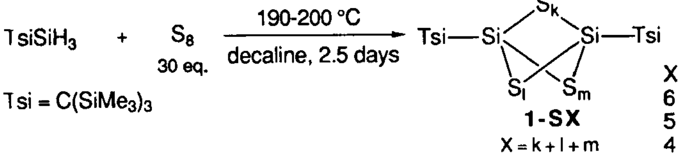
(7), and could show, that this compound thermally rearranges into an adamantane-like constitutional isomer **5**. Conversions of tetrachlorodisilanes or -digermanes with chalcogenation reagents resulted in the formation of nor- and bis-noradamantanes of the molecular formulas $(RSi)_4S_5$ (**9**), $(RSi)_4Se_5$ (**10**), $(RGe)_4S_5$ (**15**) and $(RGe)_4S_4$ (**14**).[9,10]

Herein we report two topics concerning the formation of chalcogen-group 14 element cage-molecules: (a) the synthesis and structural features of trithia- and triselena-disilabicyclo[1.1.1]pentanes[11,12], and (b) the preparation and rearrangements of double decker and adamantane type sila- and germapolychalcogenides[10].

REACTION OF TRISYLSILANE WITH SULFUR AND SELENIUM

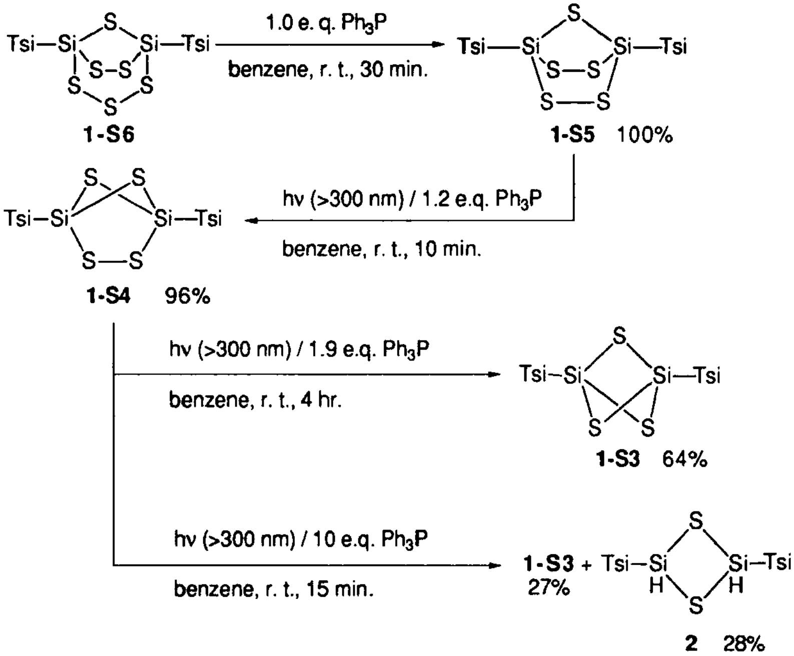
A decaline solution of trisylsilane (tris(trimethylsilyl)methylsilane = $TsiSiH_3$) and 30 equivalents of elemental sulfur was heated to 190 °C for 2.5 days to yield after chromatographic separation disilabicyclo[l.m.n]polysulfides with l+m+n = 4, 5, 6 (Scheme 1). Desulfurization reactions of disilabicyclo[l.m.n]polysulfides are summarized in Scheme 2. When reacted with PPh_3, **1-S6** was quantitatively converted into **1-S5**. Irradiation (hν ≥ 300 nm) of **1-S5** in the presence of triphenylphosphine yielded **1-S4**, which was further desulfurized upon prolonged photolysis to 2,4,5-trithia-1,3-disilabicyclo[1.1.1]pentane (**1-S3**) in 64% yield. The structure of **1-S3** was determined by single crystal X-ray diffraction analysis. Interestingly the bridgehead Si--Si distance of 2.407 Å is within the range of usual Si—Si single bonds (2.227—2.697 Å)[13]. When the photolysis of **1-S4** was performed in the presence of a 10-fold excess of PPh_3 disilthiane **2** was formed besides **1-S3** in respective 28% and 27% yields, while **1S-3** did not further react under identical conditions. Thus, most likely the initial step of the photochemical desulfurization of **1-S5** and **1-S4** is cleavage of a S-S bond. Trapping of the resulting thiyl biradical by one or two molecules of PPh_3 would then lead to the formation of **1-S3** and **2**.

Scheme 1

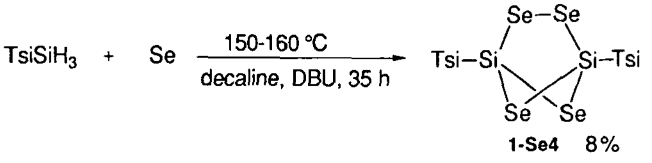


X	Isolated Yield	[k. l. m]
6:	12%	[3.2.1]
5:	12%	[2.2.1]
4:	22%	[2.1.1]

Scheme 2



In similar manner, 1,4-bis[tris(trimethylsilyl)methyl]-2,3,5,6-tetraselena-1,4-disilabicyclo[2.1.1]hexane (**1-Se4**) was obtained from the reaction of $TsiSiH_3$ with selenium and DBU (1,8-diazabicyclo[5.4.0]-7-undecene) in decaline at 200-210 °C (eq. 1).[12] The structure of **1-Se4** was unequivocally determined by single crystal X-ray diffraction analysis (Figure 1). The tetraselenadisilabicyclo[2.1.1]hexane framework and the SiMe group exhibited inversional disorder with regard to the center of symmetry, which locates the middle Se atoms of the Si-Se-Si bridges. The Si-Se-Si angle of 74.8° is very sharp, compared with a normal Si-Se-Si angle (ca. 96 °)[14] , and has almost the same value as the Si-O-Si angle of 2,4,5-trioxa-1,3-disilabicyclo[1.1.1]pentane (74.7°)[7]. After irradiation with a low pressure Hg lamp for 18h, **1-Se4** was converted to **1-Se3** (eq. 2), whose structure was confirmed by X-ray crystal analysis. The bridgehead Si---Si distance of 2.515 Å is similar to that of the sulfur analogue **1-S3** and thus is within the range of Si-Si single bonds (Figure 2), while the Si-Se bonds (2.323 Å) are slightly lengthened compared to usual Si-Se bonds (2.27 Å). The most interesting feature is the sharp Si-Se-Si angle (65.43-65.70 °), which can be regarded as an angle of a three-membered-ring compound; a normal Si-Se-Si angle is ca. 95 °. The ^{77}Se NMR of **1-Se3** exhibits one singlet at +830 ppm with an extreme downfield shift relative to normal silaselenanes (-199 to -610 ppm). The ^{29}Si-^{77}Se coupling constant of **1-Se3** (J =



(1)

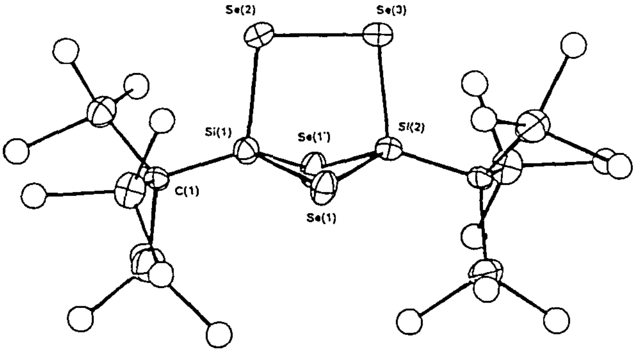
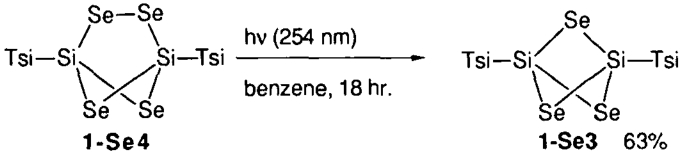


Figure 1. X-ray structure of **1-Se4**. Selected bond lengths (Å) and angles (deg): Si(1)-Se(1), 2.252; Si(2)-Se(1), 2.234; Si(1)-Se(3), 2.325; Si(1)-Se(1'), 2.331; Si(2)-Se(1'), 2.312; Si(2)-Se(2), 2.294; Se(2)-Se(3), 2.353; Si(1)-C(1), 1.855; Si(1)-Si(2), 2.820; Si(1)-Se(1)-Si(2), 77.9; Si(1)-Se(1')-Si(2), 74.8; Se(1)-Si(1)-Se(1'), 95.9; Se(1)-Si(1)-Se(3), 100.9; Si(1)-Se(3)-Se(2), 95.7; Si(2)-Se(2)-Se(3), 95.9; Se(1)-Si(2)-Se(2), 100.9.



(2)

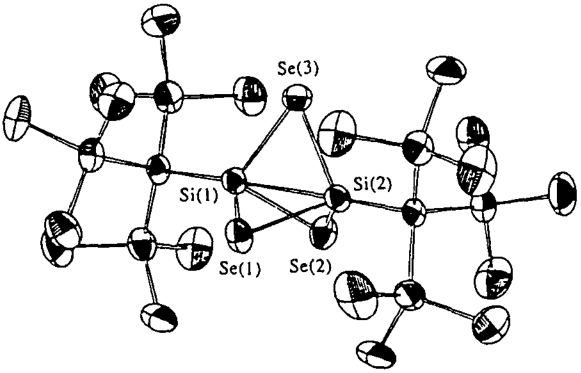
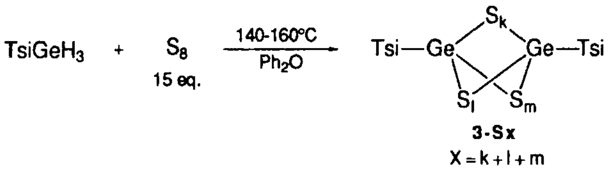


Figure 2. X-ray structure of **1-Se3**. Selected bond lengths (Å) and angles (deg): Si(1)-Se(1), 2.319; Si(1)-Se(2), 2.323; Si(1)-Se(3), 2.326; Si(2)-Se(1), 2.316; Si(2)-Se(2), 2.325; Si(2)-Se(3), 2.327; Si(1)-Si(2), 2.515; Si(1)-C(1), 1.848; Si(2)-C(2), 1.867; Si(1)-Se(1)-Si(2), 65.70; Si(1)-Se(2)-Si(2), 65.51; Si(1)-Se(3)-Si(2), 65.43; Se(1)-Si(1)-Se(2), 93.61; Se(1)-Si(1)-Si(2), 57.09

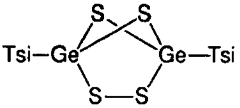
48.5 Hz) is smaller than that of disilaselenirane (J = 78 Hz)[15], which indicates that the s character of the Si-Se bond in **1-Se3** is rather small.

REACTION OF TRISYLGERMANE WITH SULFUR

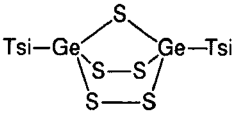
Treatment of $TsiGeH_3$ with a 50-fold excess of elemental sulfur in Ph_2O at 140-160 °C for 2 days provided tetrathiadigermabicyclo[2.1.1]hexane (**3-S4**), pentathiadigermabicyclo[2.2.1]heptane (**3-S5**), hexathiadigermabicyclo[3.2.1]octane (**3-S6**, Figure 3) and heptathiadigermabicyclo[3.3.1]nonane (**3-S7**) in 6%, 6%, 26% and 9% yields, respectively,[16] whose structures were confirmed by X-ray analysis. Compounds **3-S7** and **3-S6** were converted into **3-S6** respective **3-S5** by reaction with equimolar amounts of PPh_3. Irradiation (hν = 300 nm) of **3-S5** in the presence of excess PPh_3 for 1.5 h gave **3-S4** in 60% yield.



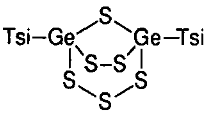
X	Isolated Yield	[k. l. m]
7:	9%	[3.3.1]
6:	26%	[3.2.1]
5:	6%	[2.2.1]
4:	6%	[2.1.1]



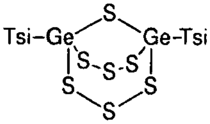
3-S4



3-S5



3-S6



3-S7

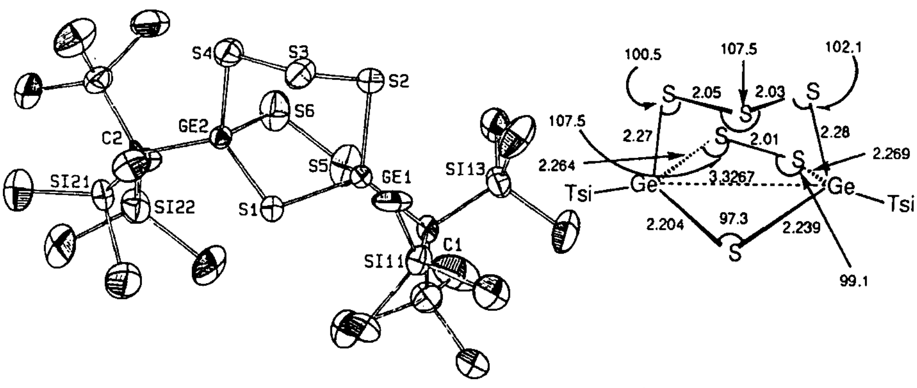
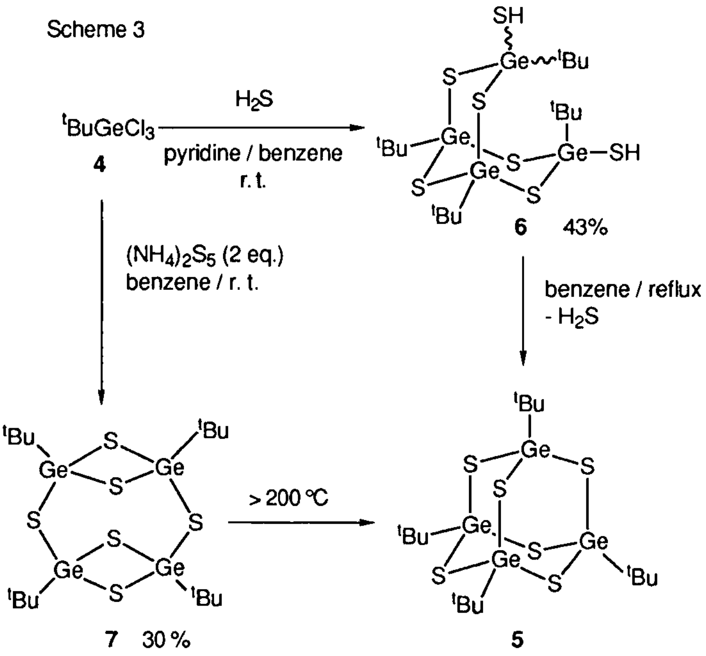


Figure 3. X-ray structure of **3-Se6**. Selected bond lengths (Å) and angles (deg).

ADAMANTANE AND DOUBLE DECKER-TYPE SESQUICHALCOGENIDES

Treatment of *tert*-butyltrichlorogermane (**4**) with H_2S/pyridine in refluxing benzene yielded adamantane-type sesquisulfide **5** of the stoichiometry $(^tBuGe)_4S_6$ in 67% yield. When this reaction was carried out at room temperature, two diastereomeric bis(germanethiols) (**6**) were formed in 43% yield (Scheme 3). The latter thermally released H_2S to afford **5**.

Scheme 3



On the other hand, when ammonium pentasulfide was applied as sulfur source, sesquisulfide **7** was obtained in 30% yield (Scheme 3). Unfortunately ^1H and ^{13}C NMR data **7** and **5** did not permit to distinguish between the double decker- and adamantane-type structures. However, this was possible by Raman spectroscopy. Thus in the range of the Ge-S framework vibrations (200-650 cm^{-1}), the Raman spectra of **7** exhibits six bands, whereas that of **5** only gives two bands as shown in Figure 4. This observation does not only allow to differentiate the two isomers but also reveals, that the molecular symmetry of **7** (D_{2h}) is lower than that of **5** (Td). Futhermore the rearrangement of **7** to **5** was followed by Raman spectroscopy, i. e. the five bands of **7** vanished and simultaneously the strong band of **5** appeared. The double decker-structure of **7** was confirmed by X-ray structure analysis (Figure 5). The molecules crystallographically possess three orthogonal 2-fold axes. The Ge atoms and S atoms

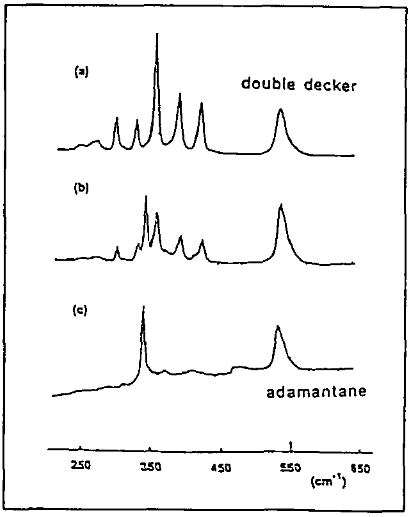


Figure 4. Raman spectral changes associated with heating of double decker (a) at room temperature, (b) at ca 200 °C, and (c) at ca 300 °C.

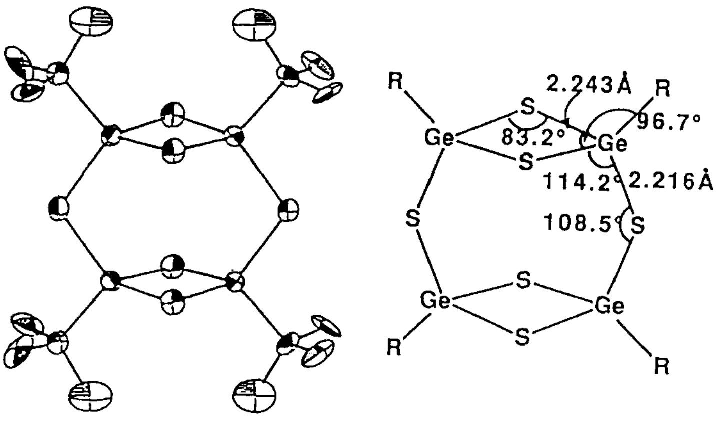


Figure 5. ORTEP drawing and bond distance / angle diagram of 7.

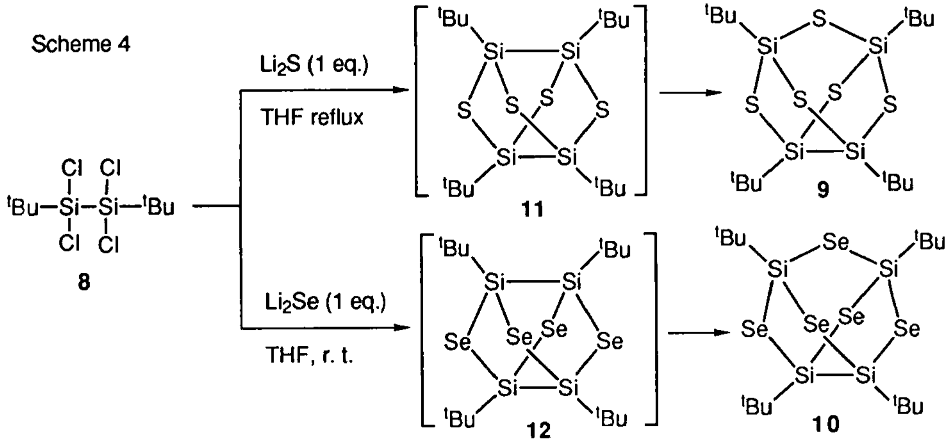
form two four-membered and two eight-membered rings which are mutually perpendicular; the four-membered rings are almost planar.

This unique formation of the double decker structure is highly depending on the proper choice of the substituents. When the reaction was performed with $MesGeCl_3$ (Mes =2,4,6-trimethylphenyl) instead of *tert*-butyltrichlorogermane (**4**), only the adamantane-like sesquisulfide was obtained.

NOR- AND BIS-NOR-ADAMANTANE-TYPE CHALCOGENIDES

After a solution of di-*tert*-butyltetrachlorodisilane **8** in THF was refluxed together with one equivalent of lithium sulfide or stirred with lithium selenide at room temperature the tetra(*tert*-butylsilicon)penta-chalcogenides **9** respective **10** were formed (Scheme 4).

Scheme 4



Each pentachalcogenide exhibited the resonances of one *tert*-butyl group in the ^1H and ^{13}C-NMR spectra. The nor-adamantane structures of **9** and **10** were determined by X-ray crystal analysis (Figure 6).

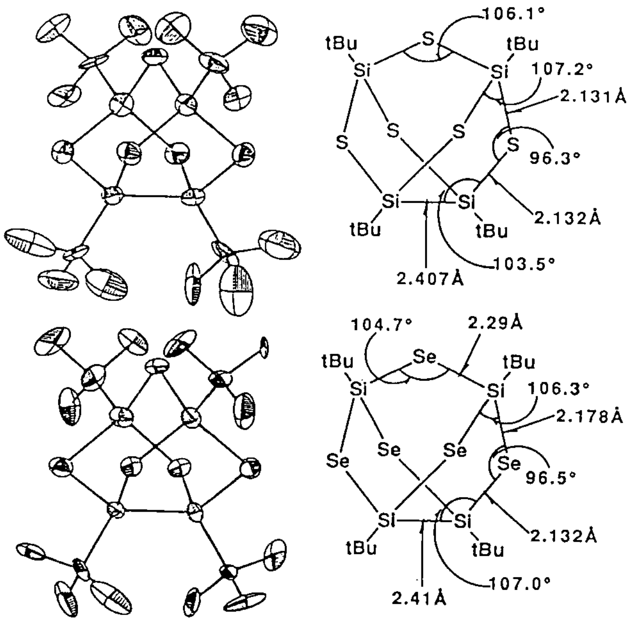
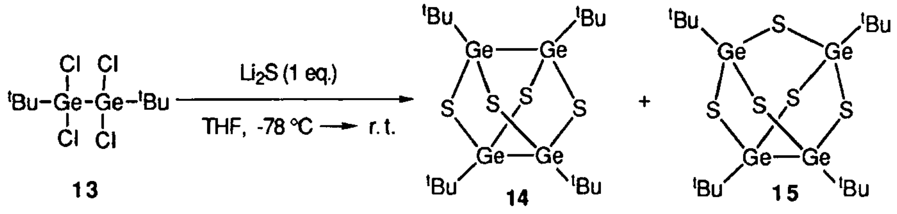


Figure 6. ORTEP drawings and bond distance / angle diagrams of **9** and **10**.

Most likely, the bis-nor-adamantane derivatives **11** and **12** are initially formed. Insertion of a sulfur respective selenium atom into one of the two strained Si-Si bonds would them lead to the observed products.

On the other hand, when di-*tert*-butyltetrachlorodigermane was converted with lithium sulfide at -78 °C the corresponding bis-nor-adamantane **14** was formed besides pentasulfide **15**, whose structures were assigned by X-ray analysis (Scheme 5 and Figure 7). Presumably due to the long Ge-Ge bond distance **14** is less strained than the silicon analogues **11** and **12**, and thus sulfur insertion is less favoured.

Scheme 5



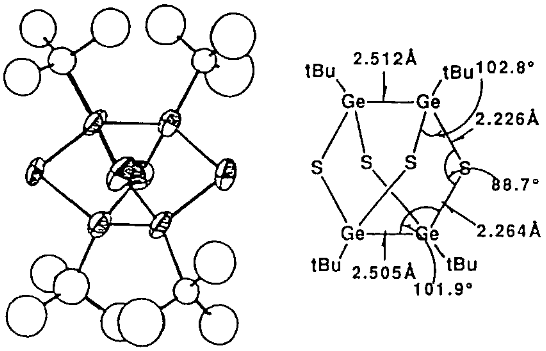


Figure 7. ORTEP drawing and bond distance / angle diagram of 14.

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