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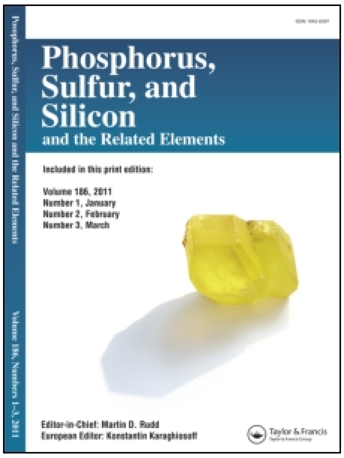

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New Cyclic and Polycyclic Ring Systems Containing Group 14 (Si, Ge, Sn) and 16 (S, Se, Te) Elements

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The reactions of Me_2MCl_2 (M = Si, Ge, Sn), $Si_2Me_4Cl_2$, $Si_2Me_3Cl_3$, $Si_2Me_2Cl_4$ and $CH_2(SiCl_2Me)_2$, and suitable mixtures thereof, with H_2S / NEt_3 and Li_2E (E = Se, Te) have been investigated and lead to a variety of new group 14 chalcogenide systems.

Keywords: silthiane; silselenane; germane; stannane; selenium; tellurium

INTRODUCTION

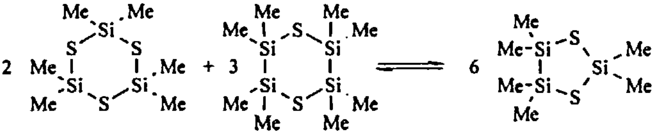
Silthianes, silselenanes and related germanium and tin compounds usually are cyclic compounds. Starting from divalent compounds (R_2MX_2) reactions with either H_2E (E = S, Se) or M_2E yield cyclic trimers $(R_2ME)_3$ [1-3] or with sterically more demanding substituents R also cyclic dimers $(R_2ME)_2$ [4,5]. No acyclic byproducts are observed in these syntheses. Trivalent group 14 derivatives produce sesquithianes or selenanes $(RM)_4E_6$ which usually adopt an adamantane structure [6-11] but in some cases also a double decker like structure has been observed [12-14]. No similar tellurane has been reported so far.

Only few papers deal with chalcogenides derived from oligosilanes [15,16] or -stannanes [17,18]. We can show, that starting from suitably functionalized oligosilanes a great variety of bi- tri- and tetracyclic ring systmes can be prepared and also other group 14 elements (C, Ge, Sn) as well as boron can be introduced into these ring systems [19,20].

RESULTS AND DISCUSSION

While the reactions of the dimethyldichloro derivatives of silicon, germanium and tin (Me_2MCl_2, **1**) with either H_2S / NEt_3 or Li_2E (E = Se, Te; prepared in situ from $LiBEt_3H$ and E) in THF result in the clean formation of the six membered ring compounds $(Me_2ME)_3$ the treatment of $ClSiMe_2SiMe_2Cl$ (**2**) with H_2S /NEt_3 or Li_2E (E = Se, Te) produces the six memberd rings $E(Si_2Me_4)_2E$.

If **1** and **2** are mixed and treated with H_2S / NEt_3 or Li_2E five membered rings are formed, see scheme 1. DFT calculations on the equlibrium according to equation (1) show, that 6 moles of the five membered ring compound are by 36.0 kJ/mol more stable than the mixture of the six membered rings:



(1)

While in $Me_4Si_2(S)_2SiMe_2$ the Si NMR signals of both silyl units are shifted by some 15 ppm downfield from the values found in the corresponding six membered rings, this down field shift increases up to 40 ppm for the Si_2Me_4 unit if E is changed via Se to Te and decreases for the monosilyl unit down to 1 ppm for E = Te.

Reactions of mixtures of **1** and $Cl_2SiMeSiMeCl_2$ (**3**) yield bicyclo[3.3.0]octanes. A carbon containing analog has been prepared by reaction of **3** with two moles cyclohexane-1,1-dithiol. While the molecular structures of the silicon and carbon containing bicyclo[3.3.0]octanes show both five membered rings adopting an envelope conformation, in $Me_2Sn(Se)_2Si_2Me_2(Se)_2SnMe_2$ the five membered rings are twisted, see figures 1 and 2. This is a result of the longer Si-Se and Se-Sn bonds in contrast to the central Si-Si bond.

If pure **3** is reacted with H_2S /NEt_3, a bis-noradamantane or a bis-nordouble decker like structure containing two disilanyl units is expected. But the strong ring strain in these molecules turns the system to form a cage compound containing three disilanyl units as shown in figure 3. DFT calculations have proven that is structure has a lower energy than the bis-noradamantane and the bis-nordouble decker like structures. The reaction of 3 with Li_2Se does not yield the selenium analog of this cage, but under cleavage of one Si-Si bond and insertion of Se a noradamantane is formed. The sulfur derivative has been prepared by treatment of 3 and two equivalents of $MeSiCl_3$ with H_2S /NEt_3 and is shown in figure 4.

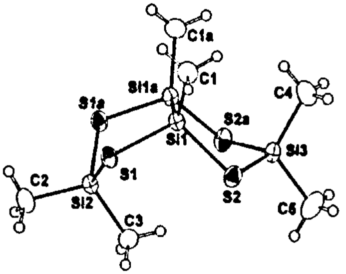


FIGURE 1
Molecular structure of
$Me_2Si(S)_2Si_2Me_2(S)_2SiMe_2$

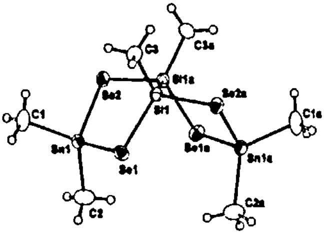


FIGURE 2
Molecular structure of
$Me_2Sn(Se)_2Si_2Me_2(Se)_2SnMe_2$

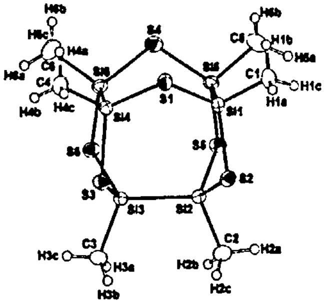


FIGURE 3
Molecular structure of
$Me_6Si_6S_6$

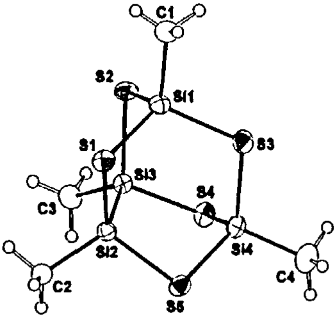
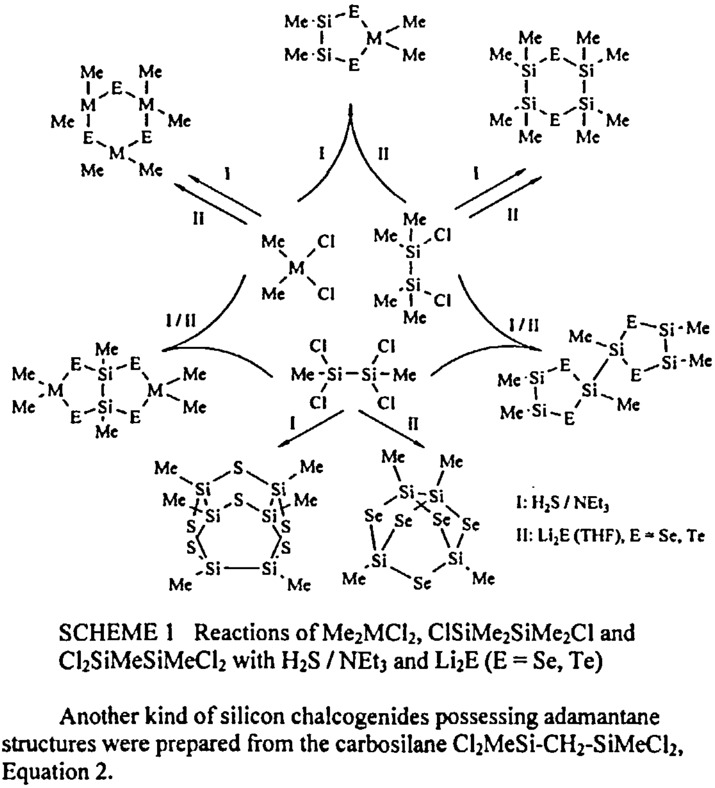
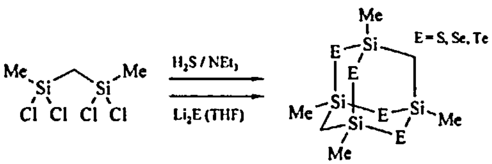


FIGURE 4
Molecular structure of
$Me_4Si_4S_5$



SCHEME 1 Reactions of Me_2MCl_2, $ClSiMe_2SiMe_2Cl$ and $Cl_2SiMeSiMeCl_2$ with H_2S / NEt_3 and Li_2E (E = Se, Te)

Another kind of silicon chalcogenides possessing adamantane structures were prepared from the carbosilane $Cl_2MeSi\text{-}CH_2\text{-}SiMeCl_2$, Equation 2.



(2)

Crystal structure analyses were carried out of all three compounds $Me_4Si_4(CH_2)_2E_4$. In all three molecules the four chalcogen atoms form an almost ideal square but due to the increasing bond lengths Si-S, Si-Se and Si-Te the adamantane cage becomes more and more distorted resulting in decreasing angles SiESi from SiSSi: 101.3 ° via SiSeSi:

98.2 ° to SiTeSi: 93.9 ° and increasing angles SiCSi at the methylene carbons (118.9 °, 122.6 °, 127.6 °). The tellurium compound, depicted in Figure 5, is the first known group 14 telluride possessing an adamantane structure.

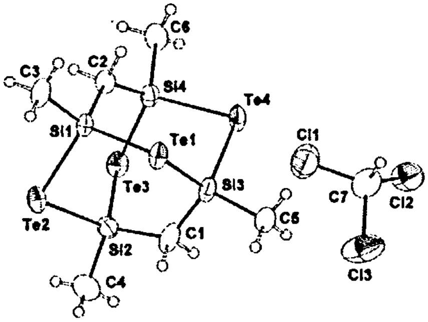
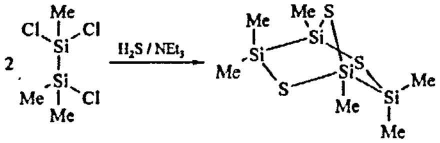
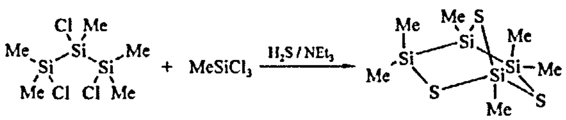


FIGURE 5 Molecular structure of $Me_4Si_4(CH_2)_2Te_4 \cdot CDCl_3$

Silthianes possessing norbornane structures are accessbile either by treatment of $Cl_2SiMeSiMe_2Cl$ or mixtures of $ClSiMe_2SiMeClSiMe_2Cl$ and $MeSiCl_3$ with H_2S / NEt_3, Equations 3 and 4.

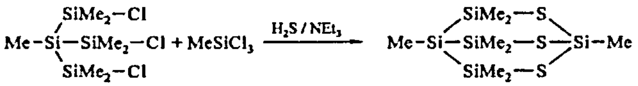


(3)



(4)

The reaction of a 1:1 mixture of $MeSi(SiMe_2Cl)_3$ and $MeSiCl_3$ yields a silthiane with a bicyclo[2,2,2]octane skeleton, Equation 5.



(5)

Attempts to prepare an isomeric compound by reaction of $ClSiMe_2SiMeClSiMe_2Cl$ in mixture with $Cl_2SiMeSiMe_2Cl$ yielded selectively a silthiane with with a bicyclo[3,2,1]octane skeleton containing one five membered ring, while the other product would contain only six membered rings.

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