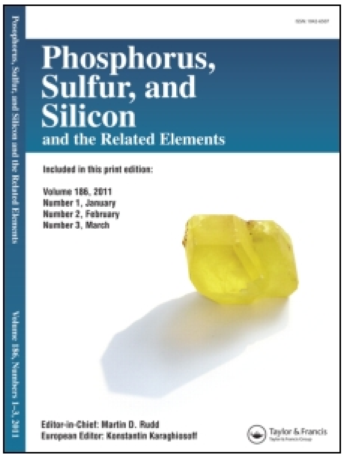

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Syntheses and Structures of Novel Molecular Organotin Chalcogenides

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Here we present the preparation of bis(trimethylsilyl)methyl-substituted tin-oxygen clusters and their precursors. Also reported are the syntheses and structures of the novel 1-chalcogena-2,4-distannacyclobutanes **14** – **16** and the unusual organotin sulphide **12**.

Keywords: tin; bulky substituents; tin-oxygen-cluster; tin-chalcogen-rings; *ab initio* calculation

INTRODUCTION

Bis(dichloroorganostannyl)alkanes $(RCl_2Sn)_2(CH_2)_n$ ($R = CH_2SiMe_3$, Me, Ph, $n = 1\text{-}3$) with sterically non-demanding substituents have been known for some time. Their reaction with sulphide, selenide or telluride provided molecular organotin chalcogenides such as $[(RXSn)_2(CH_2)_n]_2$ ($X = S$, Se, Te, $n = 1$; $X = S$, $n = 3$)[1,2]. Attempts to prepare the corresponding molecular organotin oxides (X = O) were not successful and gave polymers instead.

In order to inhibit polymerisation we have focused on the use of bulky organo substituents at tin and here we present a preliminary report at the synthesis of $\{[(Me_3Si)_2CH]Cl_2Sn\}_2X$ ($X = CMe_2$, $(CH_2)_2$, $(CH_2)_3$) (**3**, **6**, **7**) and their conversion into molecular organotin oxides **8** - **10**[3]. Also reported are the syntheses and structures of the novel 1-chalcogena-2,4-distannacyclobutanes **14** - **16** and of the unusual organotin sulphide **12**. For **14** - **16** *ab initio* and *semi empirical* calculations were carried out and the resulting data were compared with the available X-ray information[4]. Complete details of this study will form the basis of a future publication.

RESULTS AND DISCUSSION

The reaction of $(Me_2SnCl)_2CMe_2$[5] with $LiCH(SiMe_3)_2$[6] afforded $(RMe_2Sn)_2CMe_2$ (**1**, $R = CH(SiMe_3)_2$, EQUATION 1), which was converted into its tetrachloro derivative $(RCl_2Sn)_2CMe_2$ (**3**, $R = CH(SiMe_3)_2$) by stepwise reaction with Me_2SnCl_2 and $SnCl_4$ (EQUATIONS 2 - 3). The di- and trimethylene bridged ditin compounds, **6** and **7**, respectively, were prepared by reaction of $(FPh_2Sn)_2(CH_2)_n$ ($n = 2$, 3)[7] with $LiCH(SiMe_3)_2$ (EQUATION 4), followed by treatment with mercuric chloride (EQUATION 5).

Compounds **1** - **7** are colorless crystalline solids which are soluble in organic solvents. Compound **2** consists of a 1:1 mixture of diastereomers as was shown by the observation of almost equally intense two ^{119}Sn-NMR resonances. No attempt was made to separate these diastereomers.

$$(Me_2ClSn)_2CMe_2 + 2\,LiR \xrightarrow{\text{pentane}} (RMe_2Sn)_2CMe_2 + 2\,LiCl \tag{1}$$

$$\mathbf{1},\ R = CH(SiMe_3)_2$$

$$\mathbf{1} + 2\,Me_2SnCl_2 \xrightarrow[\text{110 - 120°C}]{\text{30 h}} (RMeClSn)_2CMe_2 + 2\,Me_3SnCl \tag{2}$$

$$\mathbf{2},\ R = CH(SiMe_3)_2$$

$$\mathbf{2} + SnCl_4 \xrightarrow[\text{60 - 70°C}]{\text{12 h}} (RCl_2Sn)_2CMe_2 + 2\,Me_2SnCl_2 \tag{3}$$

$$\mathbf{3},\ R = CH(SiMe_3)_2$$

$$(FPh_2Sn)_2(CH_2)_n + 2\,LiR \xrightarrow{\text{pentane}} (RPh_2Sn)_2(CH_2)_n + 2\,LiF \tag{4}$$

$$R = CH(SiMe_3)_2 \qquad \mathbf{4},\ n = 2 \quad \mathbf{5},\ n = 3$$

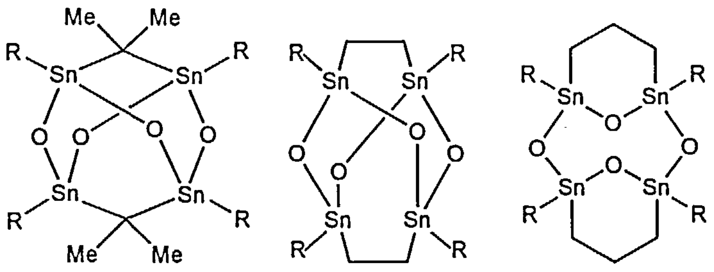
$$(FPh_2Sn)_2(CH_2)_n + 4\,HgCl_2 \xrightarrow{\text{acetone}} (RCl_2Sn)_2(CH_2)_n + 4\,PhHgCl \tag{5}$$

$$\mathbf{4},\ n = 2 \quad \mathbf{5},\ n = 3 \qquad R = CH(SiMe_3)_2 \qquad \mathbf{6},\ n = 2 \quad \mathbf{7},\ n = 3$$

Compounds **3**, **6**, and **7** are transformed in almost quantitative yields into the corresponding diorganotin oxides **8**, **9**, and **10**, respectively, by treatment with an oxygen source (CHART 1)[3].

X-Ray crystallography and ^{119}Sn solid state NMR confirmed that compounds **8** and **10** have the same structure in the solid state as they do in solution[3].

Attempts to crystallize **9** under water free conditions failed. However, reaction with air moisture provided $\{O[(RSn(CH_2)_2SnR)OH]OH\}_3.2\,H_2O$ (**9a**, $R = CH(SiMe_3)_2$) as a colorless crystalline solid. The ^{119}Sn CP MAS NMR spectrum of **9a** displayed two resonances at -163.4 and -168.5 ppm with an integral ratio of about 1 : 2 which indicates pentacoordination at tin. DTG studies of 9a revealed the loss of 5 mole equivalents of water between 95 - 155°C.



8 **9** **10**

R = $(Me_3Si)_2CH$

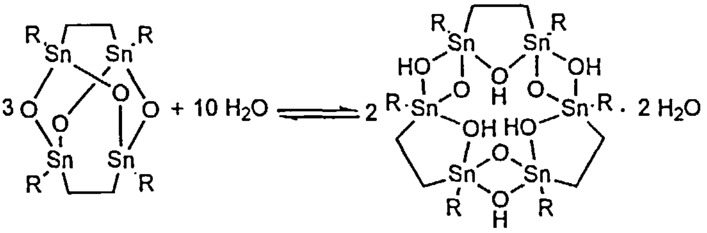
CHART 1

Dissolving single crystalline 9a in $CDCl_3$ resulted in reformation of 9 and water as was evidenced by a single ^{119}Sn NMR resonance at 24.7 ppm with $^2J(^{119}Sn\text{-}O\text{-}^{117}Sn)$ and $^3J(^{119}Sn\text{-}C\text{-}C\text{-}^{117}Sn)$ satellites of 520 and 205 Hz, respectively.

Molecular weight determination also shows that 9a easily loses water to give 9 in solution. These observations are consistent with the following equilibrium (SCHEME 1)[3].

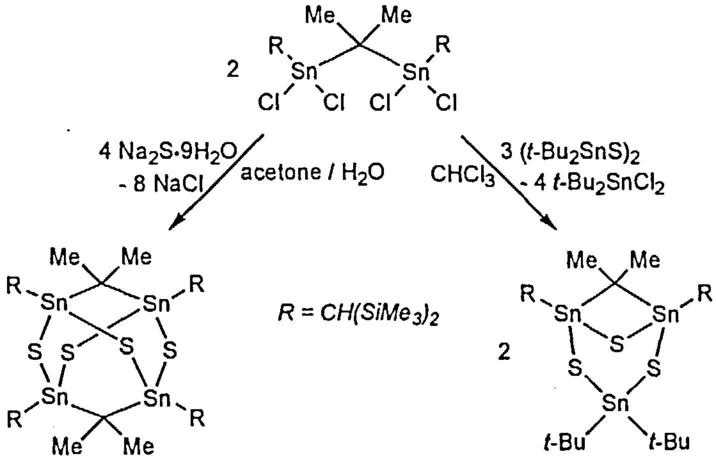
The reaction of 3 with $Na_2S.9H_2O$ yields 1,3,5,7-tetrakis-[bis(trimethylsilyl)methyl]-9,9,10,10-tetramethyl-2,4,6,8-tetrathia-1,3,5,7-tetrastannaadamantane (11) (SCHEME 2). Similar compounds have previously been prepared by treating $(RCl_2Sn)_2CH_2$ (R = Ph; CH_2SiMe_3; $FeCp(CO)_2$, $Mn(CO)_5$)[1,4] with S^{2-} sources such as $Na_2S.9H_2O$ or

(t-$Bu_2SnS)_2$. In contradiction to the behavior known from the literature the reaction of **3** with (t-$Bu_2SnS)_2$ does not afford the tetrastannaadamantane structure, but instead gives 7,7-dimethyl-5,5-di(t-butyl)-1,3-bis[bis(trimethylsilyl)methyl]-2,4,6-trithia-1,3,5-tristannabicyclo[3.1.1]heptane (**12**) (SCHEME 2).



solution, **9** $R = CH(SiMe_3)_2$ solid state, **9a**

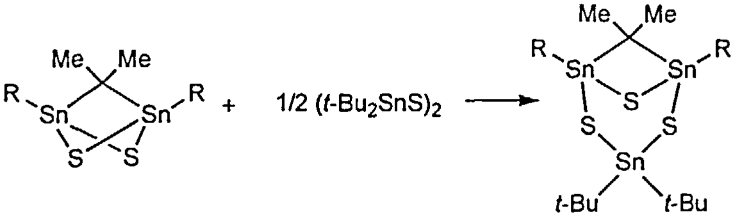
SCHEME 1 Equilibrium of 9 and **9a** in solution and in the solid state.



11 **12**

SCHEME 2 Syntheses of the novel organotin sulphides **11** and **12**.

Compound **12** can be considered formally as an adduct of $(RSnS)_2CMe_2$ with half an equivalent of $(t\text{-}Bu_2SnS)_2$ (SCHEME 3) and is the first X-ray structurally analyzed tin-sulphur compound with different organo groups bonded to tin. This class of compounds were until now only known in solution[8].



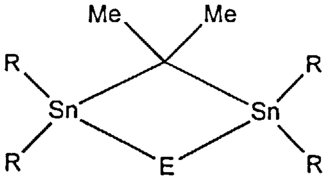
SCHEME 3 Formal reaction of $(RSnS)_2CMe_2$ with 1/2 $(t\text{-}Bu_2SnS)_2$ ($R = CH(SiMe_3)_2$).

Compound **3** reacts with $LiCH(SiMe_3)_2$ to form 2,2-bis{bis[bis-(trimethylsilyl)methyl]chlorostannyl}propane **13** in nearly quantitative yield.

$$\underset{\mathbf{3}}{(RCl_2Sn)_2CMe_2} + 2\,LiR \xrightarrow[R = CH(SiMe_3)_2]{\text{pentane, -78°C}} \underset{\mathbf{13}}{(R_2ClSn)_2CMe_2} + 2\,LiCl \qquad (6)$$

The oxygen-, sulfur-, and selenium-bridged Sn_2EC-four-membered ring systems **14** - **16** (CHART 2) were prepared by reaction of **13** with different chalcogen sources and are the first examples for Sn_2EC-four-membered ring systems. Until now only Sn_2C_2[9-12], Sn_2E_2 (E = O[13]; S[14-15]; Se[15-16]; Te[15]), Sn_2OS[16], and Sn_2CoE (E = Se; Te[17]) were known.

The identity of compounds **14** - **16** were confirmed by elemental analysis, NMR spectroscopy and, for **14** and **15**, also by X-ray analysis.



R = $CH(SiMe_3)_2$

14, E = O; **15**, E = S; **16**, E = Se

CHART 2

Ab initio and semi empirical calculations on **14** - **16** showed that with increasing size of the chalcogen the deviation from the plane of the central Sn_2EC-four-membered ring system increases.
Obviously there is not enough space for the larger sulfur or selenium atoms to remain in the plane because the ring structure is insufficiently large.

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