The First Stable 1,2-Thiastannete and 1,2-Selenastannete: their Syntheses and Crystal Structures

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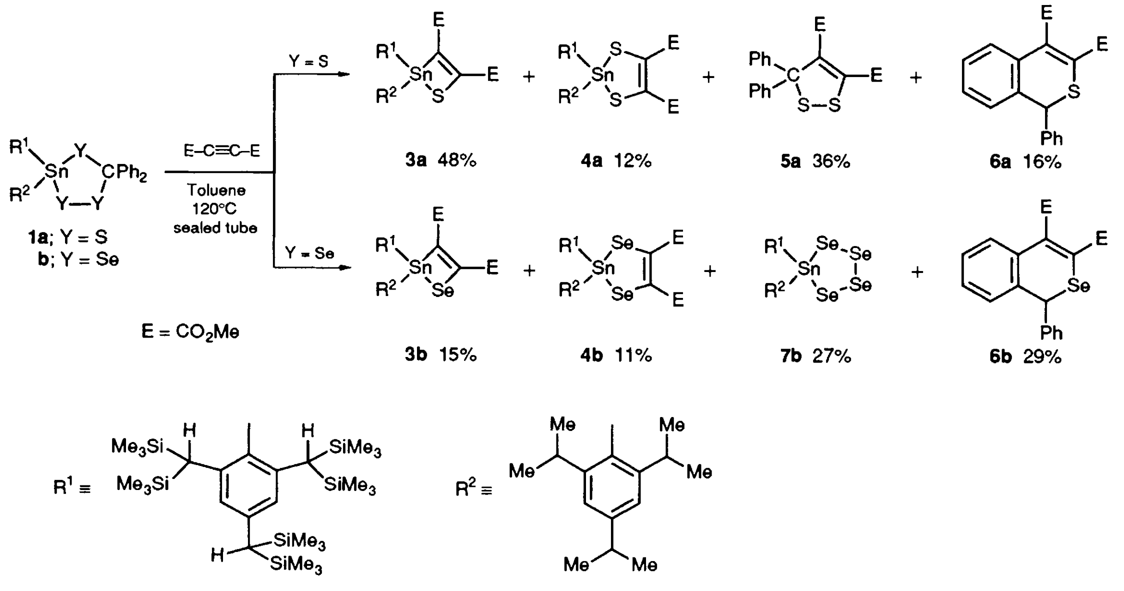
Thermal decomposition of overcrowded 1,2,4,3-trichalcogenastannolanes **1** resulted in the formation of the first stable 1,2-chalcogenastannete derivatives **3** *via* [2 + 2]cycloaddition of intermediary stannanethione and stannanselone **2**; the molecular structures of **3** were determined by X-ray crystallographic analysis.

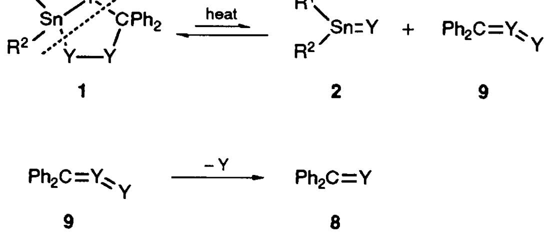
Recently, a variety of strained rings and double-bond systems containing group 14 metals (Si, Ge and Sn) have been synthesized by kinetic stabilization using bulky substituents.[1]

We previously succeeded in the synthesis of novel 1,2,3,4,5-tetrachalcogenametallolanes $R^1(Ar)MY_4$\{R^1 = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl\}[2] and 1,2,4,3-trichalcogenametallolanes $R^1(Ar)MY_3CPh_2$ **1**[3] [M = Si, Ge, or Sn; Ar = mesityl or 2,4,6-triisopropylphenyl (R^2); Y = S or Se], which are thought to be good precursors of group 14 metal–chalcogen double-bond compounds $R^1(Ar)M = Y$, by taking advantage of a new and effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl[4] (R^1). We present here the synthesis of the first 1,2-thia- and 1,2-selena-stannetes **3a** and **3b** *via* [2 + 2]cycloaddition of stannanethione **2a** and stannaneselone **2b** (Schemes 1 and 2).

When a toluene solution of **1a** was heated in the presence of an excess of dimethyl acetylenedicarboxylate (DMAD) (*ca.* 5 equiv.) at 120 °C for 6 h in a sealed tube, 1,2-thiastannete (**3a**, 48%) and 1,3,2-dithiastannole (**4a**, 12%) were obtained along with 1,2-dithiole (**5a**, 36%) and benzothiopyran (**6a**, 16%). Under similar reaction conditions **1b** gave the corresponding 1,2-selenastannete (**3b**, 15%), 1,3,2-diselenastannole (**4b**,



Scheme 1



Scheme 2

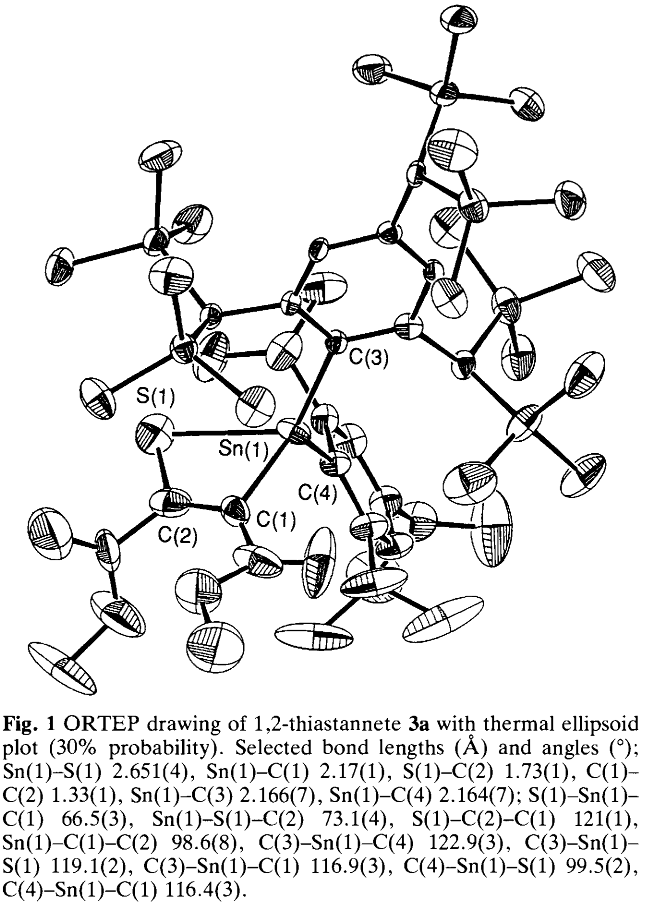


Fig. 1 ORTEP drawing of 1,2-thiastannete **3a** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (°); Sn(1)–S(1) 2.651(4), Sn(1)–C(1) 2.17(1), S(1)–C(2) 1.73(1), C(1)–C(2) 1.33(1), Sn(1)–C(3) 2.166(7), Sn(1)–C(4) 2.164(7); S(1)–Sn(1)–C(1) 66.5(3), Sn(1)–S(1)–C(2) 73.1(4), S(1)–C(2)–C(1) 121(1), Sn(1)–C(1)–C(2) 98.6(8), C(3)–Sn(1)–C(4) 122.9(3), C(3)–Sn(1)–S(1) 119.1(2), C(3)–Sn(1)–C(1) 116.9(3), C(4)–Sn(1)–S(1) 99.5(2), C(4)–Sn(1)–C(1) 116.4(3).

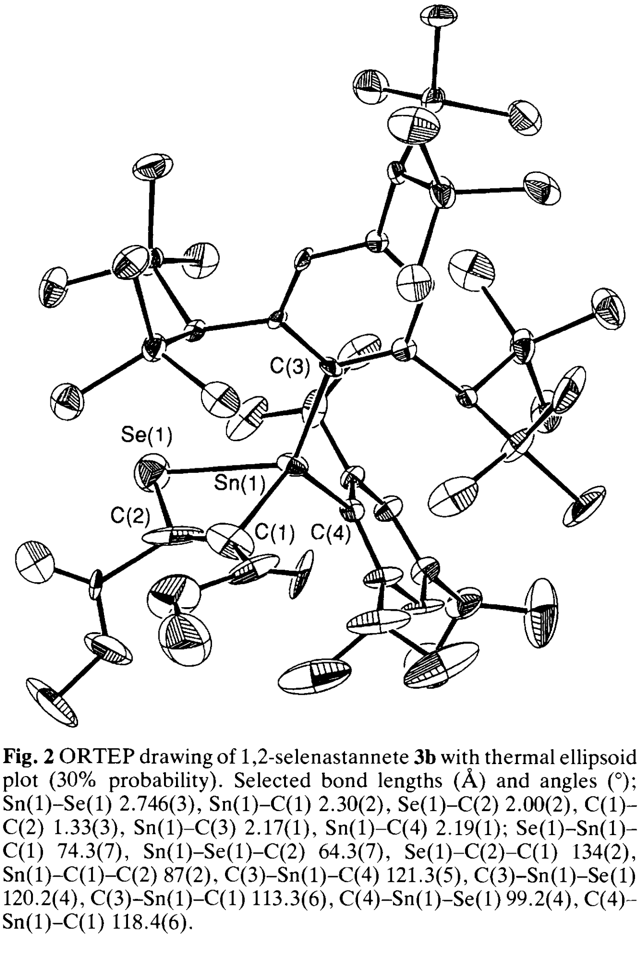


Fig. 2 ORTEP drawing of 1,2-selenastannete **3b** with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (°); Sn(1)–Se(1) 2.746(3), Sn(1)–C(1) 2.30(2), Se(1)–C(2) 2.00(2), C(1)–C(2) 1.33(3), Sn(1)–C(3) 2.17(1), Sn(1)–C(4) 2.19(1); Se(1)–Sn(1)–C(1) 74.3(7), Sn(1)–Se(1)–C(2) 64.3(7), Se(1)–C(2)–C(1) 134(2), Sn(1)–C(1)–C(2) 87(2), C(3)–Sn(1)–C(4) 121.3(5), C(3)–Sn(1)–Se(1) 120.2(4), C(3)–Sn(1)–C(1) 113.3(6), C(4)–Sn(1)–Se(1) 99.2(4), C(4)–Sn(1)–C(1) 118.4(6).

11%) and 1,2,3,4,5-tetraselenastannolane (**7b**, 27%) together with benzoselenopyran (**6b**, 29%) (Scheme 1).

Although the mechanism for the formation of all the reaction products is not clear at present, the formation of **3a** and **3b** is most reasonably explained in terms of the [2 + 2] cycloaddition reactions of intermediary stannanethione $R^1(R^2)Sn = S$ **2a** and stannaneselone $R^1(R^2)Sn = Se$ **2b** generated in the thermal retrocycloaddition of **1** (Scheme 2). Huisgen *et al.* reported a similar retrocycloaddition of 3,3,5,5-tetraphenyl-1,2,4-trithiolane, a carbon analogue of **1**, into thiobenzophenone **8a** and thioxothiobenzophenone **9a**, which were trapped by DMAD to give **6a** and **5a**, respectively.[5]

The formation of 1,2-chalcogenastannetes **3a** and **3b** is noteworthy not only as the first synthesis of this type of tin-containing small ring systems but also as the first example of [2 + 2]cycloaddition reaction of tin–chalcogen double bonds except for self-dimerization. All the products here obtained showed satisfactory spectral and analytical data, and the final molecular structures of **3a** and **3b** were unequivocally determined by X-ray crystallographic analysis as shown in Fig.1 and 2.† Both **3a** and **3b** were found to have distorted trapezoid skeletons, which showed remarkably small corner angles at the tin atoms [66.5(3)° for S(1)–Sn(1)–C(2) of **3a** and 74.3(7)° for Se(1)–Sn(1)–C(2) of **3b**] and at the sp^2 carbons α to the tin atom [98.6(8) and 87(2)° for Sn(1)–C(2)–C(1) of **3a** and **3b** respectively], reflecting the coexistence of long tin–chalcogen bonds and short carbon–carbon double bonds [Sn(1)–S(1); 2.651(4) Å, C(1)–C(2); 1.33(1) Å for **3a** and Sn(1)–Se(1); 2.746(3) Å, C(1)–C(2); 1.33(3) Å for **3b**]. Recently, Sita *et al.*[1e] and Weidenbruch *et al.*[1f] have described the X-ray structure analysis of two different types of sterically congested 1,2-distannetes, where the corner angles at sp^2 carbons were reportedly between 107.6(5) and 111.6(4)°.

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† *Crystallographic data*: compound **3a**, $C_{48}H_{88}O_4SSi_6Sn$, M = 1048.48, triclinic, space group $P\bar{1}$, a = 12.401(6), b = 22.001(7), c = 12.359(3) Å, α = 95.91(2), β = 114.94(3), γ = 79.17(4)°, V = 3002(2) Å^3, Z = 2, D_c = 1.160 g cm^{-3}, μ = 6.11 cm^{-1}. The intensity data ($2\theta < 55°$) were collected on a Rigaku AFC5R diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) and the structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 6588 observed reflections [$I > 4.00\sigma(I)$] and 541 variable parameters with $R(R_w)$ = 0.073(0.082).

Compound **3b** $C_{48}H_{88}O_4SeSi_6Sn$, M = 1095.38, triclinic, space group $P\bar{1}$, a = 12.366(2), b = 21.981(5), c = 12.368(4) Å, α = 100.76(2), β = 114.86(2), γ = 80.08(2)°, V = 2996(1) Å^3, Z = 2, D_c = 1214 g cm^{-3}, μ = 11.81 cm^{-1}. The intensity data ($2\theta < 55°$) were collected under similar conditions to **3a**, and the structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3701 observed reflections [$I > 3.50\sigma(I)$] and 541 variable parameters with $R(R_w)$ = 0.079(0.080). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Furthermore, the four-membered rings of **3a** and **3b** were not planar, and the dihedral angles between the planes S(1)–C(1)–C(2) and S(1)–C(1)–Sn(1) of **3a** and between the planes Se(1)–C(1)–C(2) and Se(1)–C(1)–Sn(1) of **3b** are 7.3 and 10.7° respectively.

The successful isolation and noticeable stability of **3a** and **3b** suggest that the combination of the bulky R^1 and R^2 groups effectively protects these highly strained molecules against their ring-opening reactions by nucleophiles.

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