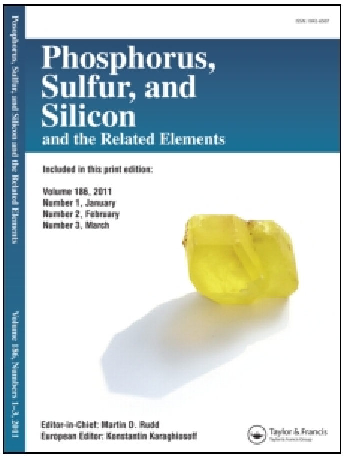

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Small Rings with and Without Tin-Tin Bonds

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SMALL RINGS WITH AND WITHOUT TIN-TIN BONDS

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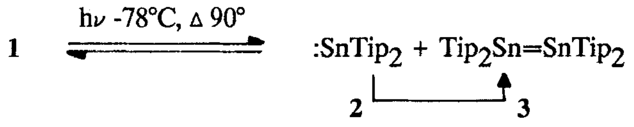
Abstract Thermolysis of hexakis(2,4,6-triisopropylphenyl)cyclotristannane **1** generates tetrakis(2,4,6-triisopropylphenyl)distannene **3** which can be trapped by various reagents. Addition of phenylacetylene to **3** yields a 1,2-distannacyclobutene derivative. Reaction of **3** with tellurium and selenium leads to tellura- and selenadistanniranes, **7**, **9**, with an excess of these chalcogens the 1,3-dichalcogenadistannetanes, **8**, **10**, are formed. With elemental sulfur the 1,3-dithiadistannetane **12** along with the 1,2-dithiadistannetane **13** is formed. Thiadistannirane **11**, which is not accessible by this route, is, however, smoothly obtained by reaction of **3** with methylthiirane.

Hexakis(2,4,6-triisopropylphenyl)cyclotristannane **1**, first synthesized by Masamune and Sita[1] by a multiple step procedure, can easily be prepared by treating tin(II) chloride with arylmagnesium bromide[2]:

Tip = 2,4,6-triisopropylphenyl

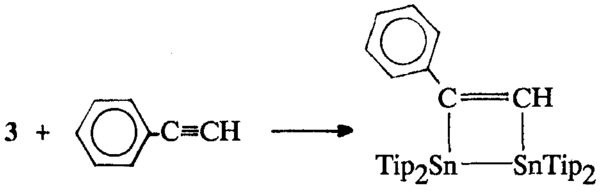
1

Compound **1**, which is stable in solution at 0°C and below, can be converted into tetrakis(2,4,6-triisopropylphenyl)distannene **3** either photochemically or by thermolysis:



The equilibration between **1** and **3** has been followed by ^{1}H NMR and UV-VIS spectroscopy. **3** was further characterized by its ^{119}Sn NMR spectrum[1]. At elevated temperatures three signals are detected in the ^{119}Sn NMR spectra which can be attributed to **1** (-368 ppm), **2** (1420 ppm) and **3** (410 ppm)[3].

Molecules **2** and **3** can both be trapped by several addition reactions. For example, **2** reacts with 2,3-dimethylbutadiene at room temperature and at 80°C giving the stannacyclopentene derivative[1,4]. On the other hand, treatment of **1** at 80°C with phenylacetylene yields the distannacyclobutene derivative **4**, presumably formed by a [2+2]-cycloaddition reaction with the acetylene:

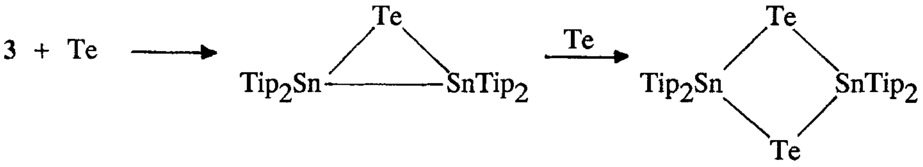


4

Physical propterties ($\delta(^{119}Sn)$: -47 ppm, -117 ppm, $^{1}J(^{119}Sn^{117}Sn)$ = 4269 Hz, $^{1}J(^{119}Sn^{119}Sn)$ = 4462 Hz) of the air and moisture stable compound **4** are fully consistent with a distannacyclobutene framework. The X-ray structure determination reveals a planar four-membered ring, with slightly elongated tin-tin and carbon-carbon bonds within the ring.

Recently, Veith, Krebs et al.[5] and Sita[6] showed that the formation of distannacyclobutenes does not necessarily require the presence of a distannene but can also be explained by a twofold addition of stannylenes to the CC triple bond. On the other hand, molecules with multiple bonds between heavy main group elements have proven to be excellent building blocks for otherwise not accessible compounds. For example, disilenes and digermenes react with chalcogens to give three membered rings, like thia-[7], selena- and telluradisiliranes[8], and thia-[9], selena-[9,10] and telluradigermiranes[11], respectively.

Treatment of **3** with tellurium in toluene at 80 - 90°C yields the telluradistannirane **7**. With an excess of tellurium or by reaction of **7** with further tellurium the 1,2-ditelluradistannetane **8** is obtained[2]:



7 **8**

The structures of **7** and **8** have been elucidated by a complete NMR study (see table 1). The X-ray structure analysis of **7** shows a nearly equilateral triangle with slightly elongated tin-tin and tin-tellurium bond lengths.

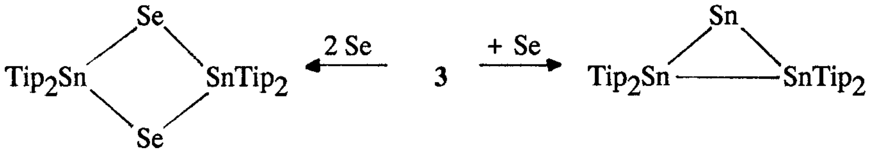
Table 1

NMR-data of reaction products of **3** with chalcogens (X)

Compound	δ(Sn)[a]	δ(X)[b]	^{1}J(SnSn)[c]	^{2}J(SnSn)[c]	^{1}J(SnX)[c]
7	-594	-903	3382		844/806
8	-752	171		417	1975/1894
9	-393	-378	4873		432/413
10	-253	84		318	868/831
11	-309		5745		
12	-47			174	
13	122		4666		

a) 93.23 MHz, in ppm, versus Me$_4$Sn; b) for X = ^{125}Te: 78.87 MHz, versus Me$_2$Te, for X = ^{77}Se: 47.67 MHz, versus Me$_2$Se, in ppm; c) ^{119}Sn^{117}Sn-, $^{119/117}$Sn^{125}Te-, $^{119/117}$Sn^{77}Se couplings in Hz

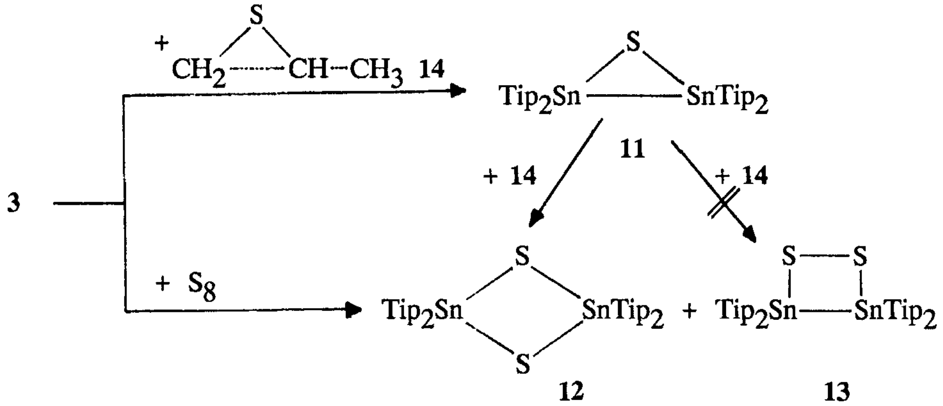
The reaction of **3** with selenium is very similar to that of tellurium, but due to the higher reactivity of selenium only mixtures of the selenadistannirane **9** and the 1,3-diselenadistannetane **10** are formed, which can be seperated by fractional crystallization (for NMR data see table 1)[12]:



10 **9**

The reaction of elemental sulfur with **3** proceeds differently, since two isomeric dithiadistannetanes are formed. One of them is the already known 1,3-dithiadistannetane **12**[13]. The other isomer was identified as the 1,2-dithiadistannetane **13**. The formation of this four-membered ring is surprising, because the analogous ring systems with heavy main group 4 elements were previously unknown. Thiadistannirane **11** is easily accessible by treatment of **3** with methylthiirane **14**. With an excess of **14** exclusively **12** is formed[12].

11, **12** and **13** are characterized by their NMR data (table 1) and, in the case of **13**, by an X-ray structure determination[12]. **12** and **13** are rather stable in solution and cannot be converted into one another by heating for several days.



These findings make it plausible that in the formation of **11** and **13** probably the tin-tin double bond is involved. Addition of a S_2 fragment to **3** leads to **13** whereas **12** is formed by insertion of sulfur into the tin-tin bond of **11** during the heterogeneous reaction at the sulfur surface.

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