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1,3-Dichloro-1,1,2,2,3,3-hexa-*tert*-butyltristannane: Thermolysis involving trapping of stannylene, $^{t}Bu_2Sn$: and reactivity with various nucleophiles

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ABSTRACT

The bifunctional 1,3-dichloro-tristannane $Cl^{t}Bu_2Sn\text{-}Sn^{t}Bu_2\text{-}Sn^{t}Bu_2Cl$, **1**, has been investigated with respect to thermolysis and nucleophilic substitution. Thermolysis of **1** leads to slow elimination of the stannylene which may be trapped by elemental sulphur, PhSSPh and 2,3-dimethylbutadiene. Reactions of **1** with the silyllithium reagent $PhMe_2SiLi$, lead to new group 14 catenanes $PhMe_2Si\text{-}Sn^{t}Bu_2\text{-}{}^{t}Bu_2Sn\text{-}Sn^{t}Bu_2\text{-}Cl$, **9,** and $PhMe_2Si\text{-}Sn^{t}Bu_2\text{-}{}^{t}Bu_2Sn\text{-}Sn^{t}Bu_2\text{-}Sn^{t}Bu_2\text{-}SiPhMe_2$, **10**. Both **9** and **10** have been characterized by single crystal X-ray diffraction. Overall the new chemistry illustrates the significance of $^{t}Bu_2Sn$: during such reactions, either loss or addition!

1. Introduction

The chemistry of oligo- and polystannanes has received attention in the last few decades [1], primarily associated with the interesting property of σ–σ* delocalization which undergoes progressive red shifts of the UV absorption with the increase in chain length. This is similar to the polysilane/germane families and has the potential to impart interesting electronic and optical properties [2]. Relatively few publications dealing with the reactivity studies of the oligostannanes have appeared due to the limited synthetic methodologies and inherent lability of the weak Sn-Sn bond [3], and oligostannenes, acyclic as well as cyclic, tend to readily eliminate stannylenes [4,5]. Recently, we reported the one-step high yield synthesis of 1,3-dichloro-1,1,2,2,3,3-hexa-^{t}butyltristannane, **1**, and illustrated its ready photochemical transformation to 1,2-dichloro-1,1,2,2-tetra-^{t}butyldistannane, **2**, and finally $^{t}Bu_2SnCl_2$, **3**, Eq. (1) [6].

$$\mathrm{Cl-{}^{t}Bu_2Sn-Sn^{t}Bu_2-Sn^{t}Bu_2-Cl}\ (\mathbf{1}) \xrightarrow[-{}^{t}\mathrm{Bu_2Sn}]{h\nu} \mathrm{Cl-{}^{t}Bu_2Sn-Sn^{t}Bu_2-Cl}\ (\mathbf{2}) \xrightarrow[-{}^{t}\mathrm{Bu_2Sn}]{h\nu} {}^{t}\mathrm{Bu_2SnCl_2}\ (\mathbf{3}) \tag{1}$$

The tristannane, **1** is an interesting bifunctional organotin compound and we now report our studies on this material involving both silyl-substitution chemistry and $^{t}Bu_2Sn$: trapping experiments.

2. Results and discussion

2.1. Attempted $^{t}Bu_2Sn$: Trapping

From the above chemical results and our previous studies it is clear that **1** is photochemically and thermally labile, and indeed during apparently simple reactions the loss of $^{t}Bu_2Sn$ seems facile, but preliminary attempts to trap the stannylene upon photochemical elimination were unsuccessful. We have now performed a controlled thermolysis in a sealed Pyrex NMR tube in C_6D_6 at 110 °C. Periodic monitoring of the reaction by ^{119}Sn NMR exhibited that **1** is completely transformed into 1,2-dicholoro-1,1,2,2-tetra-^{t}-butyldistannane, **2**, with the black deposits of elemental tin after 2 d. A typical NMR monitoring sequence is provided in the supporting material. We attempted to trap the supposedly eliminated di-^{t}butyl stannylene, $^{t}Bu_2Sn$: using MeI and benzil, both reported systems to trap stannylenes [7,8], but, our attempts were unsuccessful. However, we were able to trap $^{t}Bu_2Sn$: with

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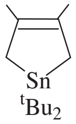
2,3-dimethylbutadiene in low yields of ~20% from such thermolyses along with distannane **2**, Eq. (2). The ^{119}Sn NMR of the reaction mixture displayed a resonance at 43.5 ppm indicating the formation of 1,1-di-^{t}butyl-3,4-dimethyl-1-stannacyclopent-3-ene, **4**, a value in agreement with a literature ^{119}Sn NMR value for the independently synthesized material [5].

$$\text{Cl-}^t\text{Bu}_2\text{Sn-Sn}^t\text{Bu}_2\text{-Sn}^t\text{Bu}_2\text{-Cl}\ (\mathbf{1}) \xrightarrow{hv} \text{Cl-}^t\text{Bu}_2\text{Sn-Sn}^t\text{Bu}_2\text{-Cl}\ (\mathbf{2}) + {}^t\text{Bu}_2\text{Sn} \qquad (2)$$

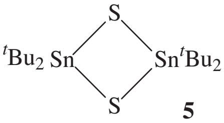
$${}^t\text{Bu}_2\text{Sn} + \text{CH}_2\text{=CMeCMe=CH}_2 \rightleftharpoons$$



4

The low thermal stability of the adduct **4** is responsible for the low yields and indeed this type of material has been used for the thermal generation of stannylenes! [5] Other recognized stannylene trapping agents utilize the strong Sn-S bond as a driving force for the reaction [9]. Thus, we have used both S, and PhSSPh, in attempted trapping experiments. The reaction of **1** with elemental sulfur at 60 °C in C_6D_6 after 20 h predominantly produced the dithiadistannetane, **5**, a previously reported material displaying a ^{119}Sn resonance at 123.9 ppm [10], along with trace amounts of **2**. Further heating for another 4 h exhibited another small intensity ^{119}Sn signal at 106.3 ppm reflecting the formation of tetra-^{t}butyldistannathiane, Cl-^{t}Bu$_2$Sn-S-SnBu$^t{}_2$–Cl, **6**, Eq. (3). These results are in accord with chemistry reported by Beckmann *et al* who showed that the dithiadistannetane, **5**, reacts with di-^{t}butyltin dichloride to form an equilibrium mixture of **5** and **6** [10b].

$$\mathbf{1} \xrightarrow[60^\circ\text{C}]{\text{S}}$$



5

$$+ \text{Cl-}^t\text{Bu}_2\text{Sn-Sn}^t\text{Bu}_2\text{-Cl} + \text{Cl-}^t\text{Bu}_2\text{Sn-S-Sn}^t\text{Bu}_2\text{-Cl}\ (\mathbf{6}) \qquad (3)$$

^{119}Sn 124 ppm ^{119}Sn110 ppm ^{119}Sn 106 ppm

Neumann and Gaspar groups have reported the utility of PhSSPh as a stannylene trap [4,5,7]. The reaction of tristannane **1** with PhSSPh initially formed S-S stannylene inserted product ^{t}Bu$_2$Sn(SPh)$_2$, **7**, exhibiting a ^{119}Sn resonance at 54.4 ppm. However, in our chemistry a further reaction between this product and ^{t}Bu$_2$SnCl$_2$ resulted in the formation of ^{t}Bu$_2$Sn(Cl)SPh, **8**, which displays a ^{119}Sn NMR resonance at 68.7 ppm, Eq. (4). Such disproportionation is typical of organotin chemistry.

$$\mathbf{1} \xrightarrow{\text{Ph}_2\text{S}_2, 60^\circ\text{C}} \underset{^{119}\text{Sn}:54\text{ppm}}{{}^t\text{Bu}_2\text{Sn(SPh)}_2}\ (\mathbf{7}) + \underset{^{119}\text{Sn}:69\text{ppm}}{{}^t\text{Bu}_2\text{SnCl(SPh)}_2}\ (\mathbf{8}) \qquad (4)$$

We performed an independent reaction between **7** and **3** to verify this disproportionation reaction.

*2.2. Reaction of **1** with nucleophiles*

The presence of the reactive Sn-Cl bonds in **1** suggested the possibility of substitution chemistry at the terminal tin atoms. Given our interest in the group 14 catorcane system [11], we initially attempted to form new materials containing Si-Sn bonds *via* salt-elimination chemistry involving silyl-lithium reagents. The results of the reaction of **1** with PhMe$_2$SiLi in non-polar hexane as solvent are illustrated in Eqs. (5a,b).

$$\mathbf{1} \xrightarrow{\text{PhMe}_2\text{SiLi}(1:1)} \text{PhMe}_2\text{Si}-{}^t\text{Bu}_2\text{Sn}-\text{Sn}^t\text{Bu}_2-\text{Sn}^t\text{Bu}_2\text{Cl}\ (\mathbf{9}) \qquad (5a)$$

$$\mathbf{1} \xrightarrow{\text{PhMe}_2\text{SiLi}(1:2)} \text{PhMe}_2\text{Si}-{}^t\text{Bu}_2\text{Sn}-\text{Sn}^t\text{Bu}_2-\text{Sn}^t\text{Bu}_2-\text{Sn}^t\text{Bu}_2-\text{SiPhMe}_2\ (\mathbf{10}) \qquad (5b)$$

The reaction with a 1:1 molar ratio at low temperature, produced a white solid, PhMe$_2$Si-^{t}Bu$_2$Sn-SnBu$^t{}_2$-SnBu$^t{}_2$-Cl, **9** in low yield (~2%) along with several intractable tin products. The reproducibility of this reaction was variable. The ^{119}Sn NMR of the product **9** exhibited signals at 99.1 ppm (**Sn**-Cl), 5.9 ppm (**Sn**-Si) and −74.8 ppm (Sn-**Sn**-Sn). We managed to grow the crystals of **9** in hexanes and the structure is displayed in Fig. 1.

The Sn-Sn bond distances of 2.8586(6) and 2.8784 (5) Å are comparable to those for Cl-^{t}Bu$_2$Sn-SnBu$^t{}_2$-SnBu$^t{}_2$-Cl of 2.8681(6) Å [6]. The Sn-Sn bond at the silyl end is significantly longer than that at the chlorine end due to the extra steric feature introduced by the silyl group. The single Sn-Si bond distance of 2.6326(13) Å is significantly longer than that of 2.5791(9) Å for H-^{t}Bu$_2$Sn-SiMe$_2$-SiMe$_2$-SnBu$^t{}_2$-H [12]. The Si-Sn-Sn and Sn-Sn-Sn bond angles are

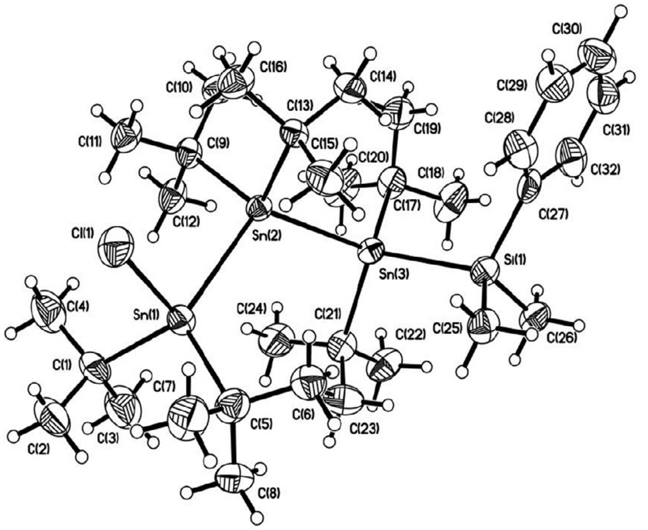


Fig. 1. Crystal structure of **9**: Sn1-Sn2 = 2.8784(5)Å; Sn2-Sn3 = 2.8586(6)Å; Sn1-Cl = 2.4110(13)Å; Si-Sn3 = 2.6326(13)Å, (CCD # 1531616).

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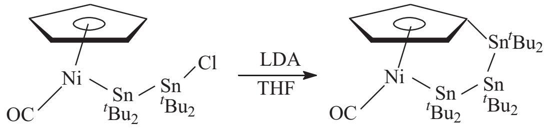
119.49(3) and 115.34(2)° respectively. The torsion angle for the backbone chain Si-(Sn)3 is −83.39(3)° in comparison the torsion angle for the Cl-(Sn)3 chain is 157.91(3)° [6].

When the reaction of tristannane **1** with PhMe$_2$SiLi in hexane involved a 1:2 ratio at low temperature, with the goal of obtaining the bis-silyl derivative, again the reaction led to a complex mixture, which after repeated recrystallization produced a light yellow solid, PhMe$_2$Si-^{t}Bu$_2$Sn-SnBu$^t{}_2$-SnBu$^t{}_2$-SnBu$^t{}_2$-SiMe$_2$Ph, **10**, also in very low yield along with several intractable tin products. The ^{119}Sn NMR of the crude disila-tetrastannane **10** exhibited signals at 4.3 and −76.1 ppm. The structure of **10** is confirmed by the X-ray crystallography and shows the chain comprising four tin atoms presumably due to insertion of ^{t}Bu$_2$Sn: stannylene across the Sn-Sn bond at some stage during the reaction process, which was unexpected, Fig. 2.

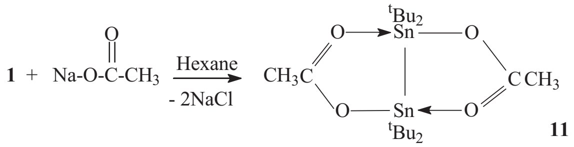
However, a similar insertion of stannylene into the Sn-Sn bond was reported by Braunschweig during the synthesis of the half-sandwich complex of nickel distannane as shown in Eq. (6) [14].



(6)

The Sn-Sn bond distances are 2.9560(8) to 3.0027(11) Å, significantly longer than the Sn-Sn bond distances for **9** due the steric demands of the extra *tert*-butyl groups**.** The structure has a center of inversion along the central Sn-Sn bond and this can be compared with the related structures X-^{t}Bu$_2$Sn-SnBu$^t{}_2$-SnBu$^t{}_2$-SnBu$^t{}_2$-X, X = Br, I [15]. The backbone comprising the Si-Sn-Sn-Sn-Sn-Si chain adopts all *transoid* conformation in contrast to the structure for **9**. The other oligo-stannanes Ph$_3$Sn-(Sn^{t}Bu$_2$)$_n$-SnPh$_3$, (n = 2,3,4) also adopts the *transoid* arrangement of tin atoms [13].

The reaction of tristannane **1** with the MeMgBr and reducing agents like LiAlH$_4$ and even with the mild reducing agent diisobutyl aluminum hydride under varying reaction conditions involving temperature (−78 °C to RT), always led the formation of unidentified tin products. No methyl-substituted or the reduced product was isolated from these reactions. However, the reaction of tristannane **1** with sodium acetate in hexane in 1:2 stoichiometry at room temperature successfully produced *bis*-(di-^{t}butyltin dicarboxylate), [^{t}Bu$_2$Sn(O$_2$CCH$_3$)]$_2$, **11**, in high yield, Eq. (7). The tristannane **1** underwent the “loss” of ^{t}Bu$_2$Sn: even at room temperature to produce the distannane carboxylate **11**. Attempts to trap stannylene with 2,3-dimethyl-1,3-butadiene in this reaction were unsuccessful. Compound **11** was also obtained from the independent reaction of distannane **2** with sodium acetate.



(7)

^{119}Sn: **-160.5 ppm**

Compound **11** was characterized by NMR spectroscopy and single –crystal X-ray crystallography. ^{119}Sn NMR displays a single resonance at −160.5 ppm indicating that two tin atoms are essentially in identical environment. The observed chemical shift is consistent with those reported for other diorganotin carboxylates indicating

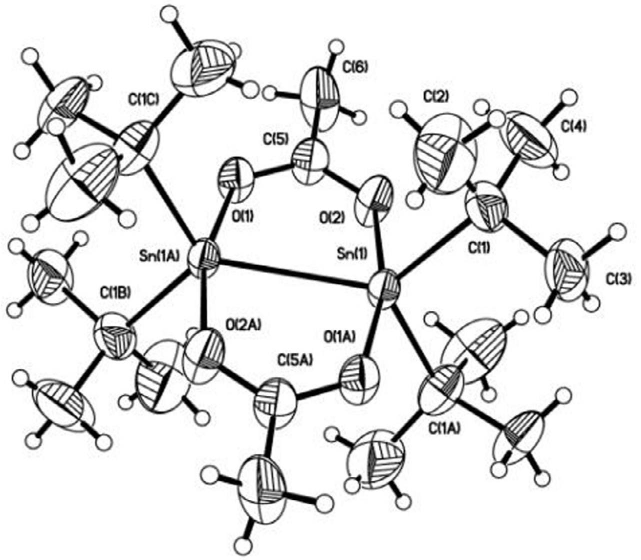


Fig. 3. Crystal structure of **11** at 35% of probability level. Sn1-Sn1A = 2.7402(3)Å; Sn1-O1 = 2.290(3)Å; Sn1-O2 = 2.313(3)Å; O(1)-Sn(1)-O(2) = 164.5(5)°; O(1)-Sn(1)-Sn(1A) = 84.30(6)°, (CCD # 1531618).

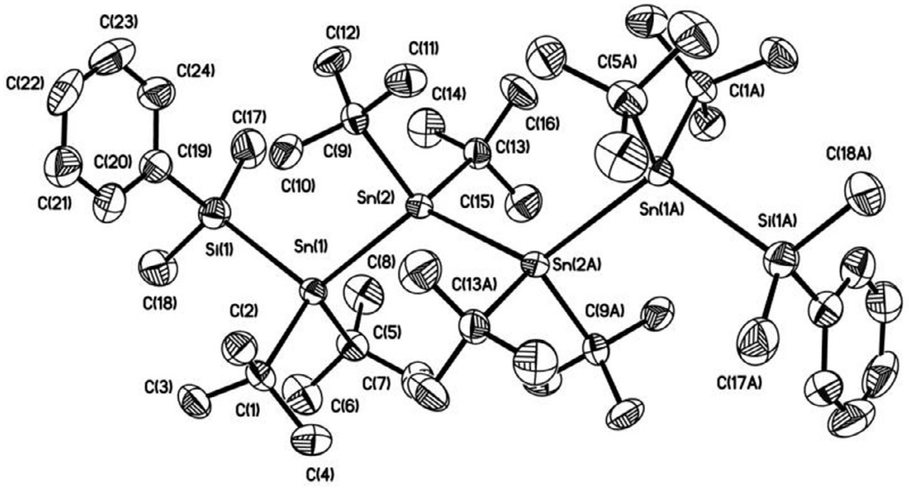


Fig. 2. Crystal structure of **10**. Si1-Sn1 = 2.662(3)Å; Sn1-Sn2 = 2.9560(8)Å; Sn2-Sn2A = 3.0027(11)Å, (CCD # 1531617).

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the five-coordinated tin atoms [16]. The magnitude of ^1J (^{117}Sn-^{117}Sn) coupling constant of 7835 Hz for **11** is significantly lower than 14980 Hz observed for $Me_4Sn_2(OAc)_2$ [17]; its IR spectrum displayed a strong band at 1550 cm^{-1} attributed to υ (CO) suggesting that the carboxylate ligand is bridging the two tin atoms, and its ^{13}C NMR spectrum displays a resonance at 183.5 ppm due to the carbonyl resonance of acetate group. The molecular structure of the tin carboxylate is shown in Fig. 3 with important bond lengths (Å) and angles (°).

The two tin atoms are unsymmetrically bridged by the acetate group with two unequal Sn-O bond distances of 2.290(3) Å and 2.313(3) Å forming an 8-membered ring. The Sn-Sn bond distance of 2.7402(3) Å is significantly longer than the Sn-Sn distance of 2.691(1) Å in $Ph_4Sn_2(OAc)_2$ [15], reflecting the steric bulk of the *t*-butyl groups. The geometry around both the tin atoms is trigonal bipyramidal, the basal plane defined by two ^{t}butyl group and other tin atom and two oxygen atoms of the acetate groups occupying the axial positions.

3. Conclusions

Thermolysis of the title compound **1** results in the slow elimination of $^tBu_2Sn$: which may be efficiently trapped by a variety of materials. This is in contrast to the photochemical treatment of **1**, where the loss of $^tBu_2Sn$: is more rapid, but not readily trapped. The title compound has the potential to be a useful precursor reagent for extension of group 14 catenanes, and when successful the resulting products, $PhMe_2Si$-$^tBu_2Sn$-$^tBu_2Sn$-$^tBu_2SnCl$, **9**, and $PhMe_2Si$-$^tBu_2Sn$-$^tBu_2Sn$-$^tBu_2Sn$-$SiPhMe_2$, **10**, appear to be thermodynamically and kinetically stable. However, during the reactions to form such interesting materials much alternative chemistry occurs involving Sn-Sn bond cleavage and $^tBu_2Sn$: elimination.

4. Experimental section

All manipulations were carried out under Argon atmosphere using Schlenk or vacuum line techniques. THF was distilled under nitrogen from benzophenone ketyl prior to use. Other solvents, hexanes, benzene and toluene were dried over sodium metal and distilled before use. Tristannane **1** and distannane **2** were synthesized by the reported methods [6,12c]. NMR spectra were recorded on 300 MHz Bruker spectrometer in C_6D_6. All reactions mixtures were freeze-pumpthaw degassed before flame sealing of the NMR tube.

4.1. Thermolysis of 1

In a typical experiment, a Pyrex NMR tube was charged with 0.15 g, 0.19 mmol of **1** in 0.5 mL of C_6D_6. The tube was sealed under vacuum and heated in an oven at 110 °C. The progress of the reaction was monitored by ^{119}Sn and ^{13}C NMR spectroscopy. After 2 d of thermal reaction the color of the solution became light brown with little black deposits of elemental tin and the ^{119}Sn NMR showed the disappearance of resonances at 114.5 and −0.8 ppm due to tristannane **1** and appearance of a single new resonance at 110.5 ppm indicating the complete conversion of **1** to distannane **2**.

4.2. Thermolysis of 1 in the presence of 2, 3-dimethyl-1,3-butadiene

Pyrex NMR tube was charged with 0.15 g, 0.19 mmol of **1** and 0.016 g (0.19 mmol) of 2,3-dimethyl-1,3-butadiene in 0.4 mL of C_6D_6. The tube was sealed under vacuum and heated in an oven at 110 °C. The progress of the reaction was monitored by ^{119}Sn and ^{13}C NMR spectroscopy. After 3 d of thermal reaction the color of the solution became dark red with the formation of a tin mirror. The ^{119}Sn NMR displaced a new resonance at 43.5 ppm due the formation of the stannylene trapped adduct 1,1-di-^{t}butyl-3,4-dimethyl-1-stannacyclopent-3-ene, **4** [5], in 20% yield along with the appearance of a resonance at 110.5 ppm due to distannane **2**.

In a separate reaction, the stannylene trapped adduct **4** was not formed from the photolysis experiment of **1** with 2, 3-dimethyl-1,3-butadiene.

4.3. Thermolysis of 1 in the presence of benzil

A Pyrex NMR tube was charged with 0.15 g, 0.19 mmol of **1**, and 0.08 g (0.38 mmol) of benzil in 0.4 mL of toluene. The tube was sealed under vacuum and heated in an oven at 100 °C. The progress of the reaction was monitored by ^{119}Sn. After 2 d the color of the solution became light yellow and the tristannane of **1** was completely converted into distannane **2**. No stannylene trapped benzil adduct was observed in NMR spectroscopy.

4.4. Thermolysis of 1 in the presence of sulfur

A Pyrex NMR tube was charged with 0.10 g, 0.13 mmol of **1** and 0.012 g (0.38 mmol) of sulfur in 0.4 mL of C_6D_6. The tube was sealed under vacuum and heated in an oil bath at 60 °C. The progress of the reaction was monitored by ^{119}Sn and ^{13}C NMR spectroscopy. After 20 h of the thermal reaction, dithiastannetane **5** showing a ^{119}Sn resonance at 123.9 ppm was formed in 90% yield, along with trace amounts of tristannane **1** and distannane **2** remaining in the reaction mixture. Further heating for 4 h produced a small intensity ^{119}Sn signal at 106.3 ppm which is due to tetra-^{t}butyldistannathiane, **6**, Cl-$^tBu_2Sn$-S-$SnBu^t{}_2$–Cl [10b], produced in trace amounts due to the insertion of S atom in the Sn-Sn bond of **2.**

4.5. Thermolysis of 1 in the presence of diphenyl disulfide

A Pyrex NMR tube was charged with 0.14 g, 0.18 mmol of **1** and 0.039 g (0.18 mmol) of Ph_2S_2 in 0.4 mL of C_6D_6. The tube was sealed under vacuum and heated in an oil bath at 60 °C. The progress of the reaction was monitored by ^{119}Sn and ^{13}C NMR spectroscopy. After 10 h of thermolysis we initially observed the formation of S-S inserted product $^tBu_2Sn(SPh)_2$, **7**, displaying a ^{119}Sn resonance at 54.4 ppm [5]. After further heating for 10 h, the starting material **1** was completely consumed, and a ^{119}Sn NMR resonance appeared at 68.7 ppm showing the formation of ^{t}-$Bu_2Sn(Cl)SPh$, **8**.

4.6. Thermal reaction of $^tBu_2Sn(SPh)_2$ with $^tBu_2SnCl_2$

A Pyrex NMR tube was charged with 0.34 g, 0.75 mmol of $^tBu_2$-$Sn(SPh)_2$ and 0.23 g (0.75 mmol) of $^tBu_2SnCl_2$ in 0.4 mL of C_6D_6. The tube was sealed under vacuum and heated in an oil bath at 60 °C. After 4 h of thermolysis, the ^{119}Sn NMR of the reaction showed only one resonance 68.7 ppm due to the formation of $^tBu_2SnCl$ (SPh), **8**.

4.7. Reaction of 1 with $PhMe_2SiLi$

A flame dried 250 mL three-necked flask equipped with dropping funnel and a condenser was charged with 0.1.4 g (1.8 mmol) of tristannane **1** in 60 mL of hexanes and maintained at −25 °C. To this was added slowly a brown solution of $PhMe_2SiLi$ (prepared from 0.25 g, 0.92 mmol of $PhMe_2SiSiMe_2Ph$ and four-fold excess Li in 25 mL of THF) *via* a dropping funnel. The addition of $PhMe_2SiLi$ was conducted over a period of 30 min. The temperature of the reaction mixture was raised slowly to room temperature and the solvents evaporated under vacuum. To the residue was added 50 mL of hexane, stirred and filtered on celite. The solution was concentrated and left in the refrigerator. Repeated recrystallizations resulted in white crystals of the silyl substituted tristannane **9** in low 2% yield. ^{1}H NMR: δ 0.68 ($SiMe_2$) 1.40, 1.46, 1.54 (^{t}Bu), 7.15 (Ph). ^{13}C NMR: δ 2.67 (SiMe), 32.1, 34.2, 35.2 (^{t}Bu), 32.3, 34.2, 39.1 ($C(CH_3)_3$), 129.1, 133.5, 134.9, 141.0 (Ph). ^{119}Sn NMR: 99.1, 5.9, −74.8. ^{29} Si NMR: −10.2 ppm.

We carried the reaction of tristannane **1** with $PhMe_2SiLi$ in hexane changing the stoichiometry of the reactants from 1:1 to 1:2 ratio at low temperature, after work-up, the reaction led to a complex mixture, which after repeated recrystallization produced a light yellow solid, $PhMe_2Si$-$^{t}Bu_2Sn$-$SnBu^{t}_2$-$SnBu^{t}_2$-$SnBu^{t}_2$-$SiMe_2Ph$, **10** also in very low yield, less than 1%.

4.8. Reaction of 1 with sodium acetate

A 50 mL flame- dried Schlenk flask was charged with 0.21 g (0.26 mmol) of sodium acetate in 10 mL of hexanes. Tristannane **1**, 0.1 g (0.30 mmol) in 10 mL hexanes was slowly added into the flask maintained at −25 °C. The reaction mixture was slowly stirred at low temperature for 30 min and then the mixture was brought to room temperature and further stirred for 2 h. Salts were filtered off and the solution was concentrated and left in the refrigerator. White crystals of *bis*-(di-^{t}butyltin dicarboxylate), $[^{t}Bu_2Sn(O_2CCH_3)]_2$ **11** were obtained in 65% yield. ^{1}H NMR: δ 1.51 (s, $^{3}J_{^{119}Sn-^{1}H}$ = 82 Hz, $^{3}J_{^{117}Sn-^{1}H}$ = 78 Hz 36H, ^{t}Bu), 1.87 (s, $^{4}J_{^{119}Sn-^{1}H}$ = 40 Hz, 6H, CH_3). ^{13}C NMR: δ 24.1 (Me), 31.7 (^{t}Bu), 36.6 ($C(CH_3)_3$), 183.7 (CO). ^{119}Sn NMR: −160.5 (^{1}J (^{117}Sn-^{117}Sn)=7835 Hz). Anal. Calcd. for $C_{20}H_{42}O_4Sn_2$: C, 41.14; H, 7.25. Found: C, 40.95; H, 7.00.

4.9. Reaction of 1 with sodium acetate in the presence of 2,3-dimethyl-1,3-butadiene

A Pyrex NMR tube was charged with 0.10 g, 0.13 mmol of **1** and 0.021 g (0.26 mmol) of sodium acetate and 0.013 g of 2,3-dimethyl-1,3-butadiene in 0.4 mL of C_6D_6. The NMR tube was flame sealed under vacuum. The reaction mixture in the tube was sonicated for 3 h. The ^{119}Sn NMR of the solution showed only the formation of *bis*-(di-^{t}butyltin dicarboxylate), $[^{t}Bu_2Sn(O_2CCH_3)]_2$, **11**. No other resonance associated with the adduct 1,1-di-^{t}butyl-3,4-dimethyl-1-stannacyclopent-3-ene, **4** was observed indicating stannylenes were not trapped.

Acknowledgements

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Appendix A. Supplementary data

The cif files for **9** (CCD # 1531616), **10** (CCD # 1531617), and **11** (CCD # 1531618); ^{119}Sn NMR monitoring of the thermal decomposition of **1**. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2017.03.045.

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