Syntheses and Reactivity of Stannyloligosilanes. III [1]

Lithiated Stannasilanes – Building Blocks for Monocyclic Si–Sn Rings

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Abstract. Dilithiated di(stannyl)oligosilanes ($^tBu_2Sn(Li)$–$(SiMe_2)_n$–$Sn(Li)^tBu_2$; **4**, n = 2; **5**, n = 3) were synthesized by the reaction of lithium diisopropylamide (LDA) with the α,ω-hydrido tin substituted oligosilanes ($^tBu_2Sn(H)$–$(SiMe_2)_n$–$Sn(H)^tBu_2$; **1**, n = 2; **2**, n = 3). Surprisingly, the reaction of **1** and **3** ($^tBu_2Sn(H)$–$(SiMe_2)_4$–$Sn(H)^tBu_2$) with LDA resulted not in the formation of the lithiated compound, but what one can find is the formation of the 5,5-ditert.butyl-octamethyl-1,2,3,4-tetrasila-5-stannacyclopentane (**8**) (n = 4) in addition to the expected product **4** (n = 4) and the 3,3,6,6-tetratert.butyl-octamethyl-1,2,4,5-tetrasila-3,6-distannacyclohexane (**7**) (n = 3).

Reactions of **4** and **5** with dimethyl and diphenyldichlorosilanes yielding monocyclic Si–Sn derivatives (**9**–**11**) are also discussed. The solid-state structures of **7** and **11** were determined by X-ray crystallography.

Keywords: Tin; Stannasilanes; *monocyclic* Silicon-Tin rings; NMR spectroscopy; Crystal structure

Synthese und Reaktivität von Stannyloligosilanen. III. Lithiierte Stannasilane – Bausteine für monocyclische Si–Sn-Ringe

Inhaltsübersicht. Zweifach lithiierte Di(stannyl)oligosilane ($^tBu_2Sn(Li)$–$(SiMe_2)_n$–$Sn(Li)^tBu_2$; **4**, n = 2; **5**, n = 3) werden durch die Reaktion von Lithiumdiisopropylamid (LDA) mit den α,ω-Hydridozinn-substitutierten Oligosilanen ($^tBu_2Sn(H)$–$(SiMe_2)_n$–$Sn(H)^tBu_2$; **1**, n = 2; **2**, n = 3) erhalten. Überraschenderweise ergibt die Umsetzung von **1** und **3** (n = 4) mit LDA nicht nur die erwarteten lithiierten Verbindungen **4** und **6**. Statt dessen findet man die Bildung eines 5,5-Ditert.butyl-octamethyl-1,2,3,4-tetrasila-5-stannacyclopentanes (**8**) (n = 4) und, bei Verwendung von **1** als Ausgangsstoff, eines 3,3,6,6-Tetratert.butyl-octamethyl-1,2,4,5-tetrasila-3,6-distannacyclohexanes (**7**) als Konkurrenzprodukt zu **4**. Umsetzung von **4** und **5** mit Dimethyl- oder Diphenyldichlorosilan ergeben die monocyclischen Si–Sn-Derivate **9**–**11**. Die Molekülstrukturen von **7** und **11** werden ebenfalls diskutiert.

1 Introduction

Chain type α,ω-functionalized oligosilanes are possible precursors for the synthesis of polymeric materials as well as the formation of cyclic derivatives. The development of silicon polymers containing other group 14 elements, requires a detailed investigation of the synthesis and reactivity of precursor molecules. Our special interest is focused on cyclic Si–Sn containing compounds due to their possible applications in ring opening polymerisations.

Recently we described the exploration of synthetic avenues, structural features, and the reactivity of linear ($^tBu_2Sn(Z)$–$(SiMe_2)_n$–$Sn(Z)^tBu_2$; Z = H, Cl, Br, n = 2–6) [2] and branched ($MeSi[SiMe_2$–$Sn(Z)R_2]_3$; Z = H, Me, Ph, Cl, Br, R = Me, ^tBu, Ph) [1] stannyloligosilanes. Initial studies concerned with the chemistry of branched stannylsilanes with lithium diisopropylamide yielding cyclic derivatives were discussed as well [1]. The utilization of linear halogen substituted stannyloligosilanes as building blocks for the preparation of monocyclic Si–Sn derivatives with ring sizes ranging from four to six were also reported [3]. As a continuation of this work, we are now describing the reactions of linear stannyloligosilanes with lithium diisopropylamide (LDA) and subsequent of reactions of the resulting dilithio derivatives with diorganodichlorosilanes.

2 Results and Discussion

The reaction of 1,1,5,5-tetratert.butyl-hexamethyl-1,5-distanna-2,3,4-trisilapentane (**2**) with two equivalents

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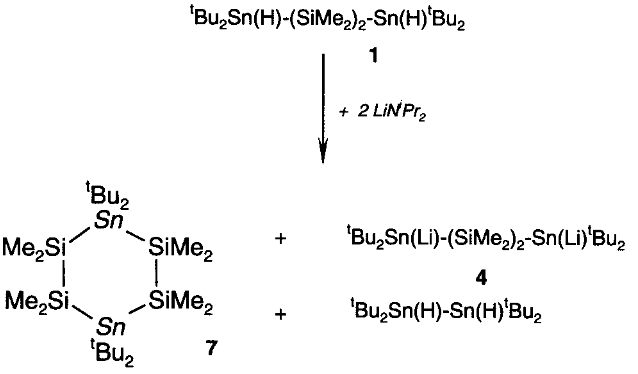
of LDA served well in the preparation of the expected dilithio derivative **5** (eq. (1)).

$$^{t}Bu_2Sn(H)–(SiMe_3)_2–Sn(H)^{t}Bu_2 \xrightarrow[-2\,HN^{i}Pr_2]{+2\,LDA} \underset{\mathbf{5}}{^{t}Bu_2Sn(Li)–(SiMe_2)_3–Sn(Li)^{t}Bu_2} \qquad (1)$$

Compound **2** can be converted quantitatively into derivative **5** by maintaining a temperature range between –30 °C and 0 °C.

Surprisingly, one can not apply this reaction to stannasilanes containing disila (**1**) or tetrasila (**3**) moieties instead of the trisilane unit. The reaction of the disilane derivative **1** resulted in a mixture of the expected dilithio compound **4**, the tetratert.butyldihydridodistannane, and a silicon and tin containing ring. The latter one was identified as the 3,3,6,6-tetratert.butyl-1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrasila-3,6-distannacyclohexane (**7**) (Scheme 1).

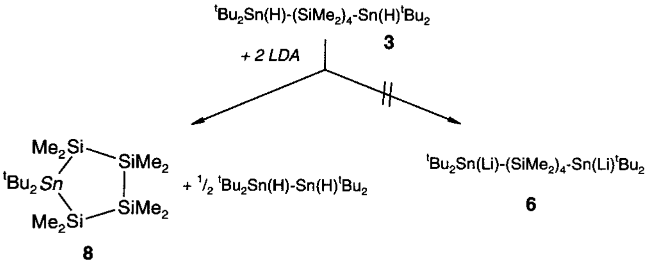


Scheme 1 Reaction of **1** with two equiv. of LDA.

The ratio of the products **4** and **7** can be varied by changing the reaction conditions; lower temperatures yield higher amounts of **4**, whereas higher temperatures affords higher yields of compound **7**, but the concurrent formation of derivative **4** is still observed.

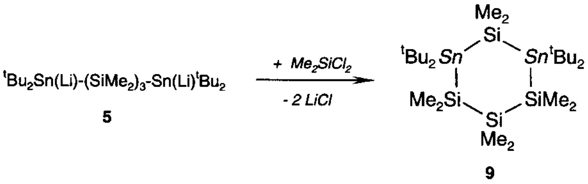
The reaction of the tetrasilane derivative **3** with two equiv. of LDA results not in the formation of the expected dilithio compound **6**, instead the five membered Si–Sn ring **8** under formation of the byproduct tetratert.butyldihydridodistannane is observed. In contrast to the reaction of **1** the composition of the product mixture did not depend on the reaction temperature.

Although we have only little experimental evidence to postulate a reaction mechanism, we propose that the formation of the dilithio substituted Si–Sn derivatives is the kinetically controlled step while the formation of the five and the six membered rings **7** and **8** is the thermodynamically controlled part of the reaction. In the cases of using the disilane **1** or the tetrasilane **3** as starting materials the formation of the thermodynamically favored five (**7**) and six membered (**8**) rings is the rate determining step of the reaction. Rearrangement and ring closure reactions of branched stannasilanes have been observed recently when reacting MeSi[SiMe$_2$–Sn(H)^{t}Bu$_2$]$_3$ with three equiv. of LDA [1].



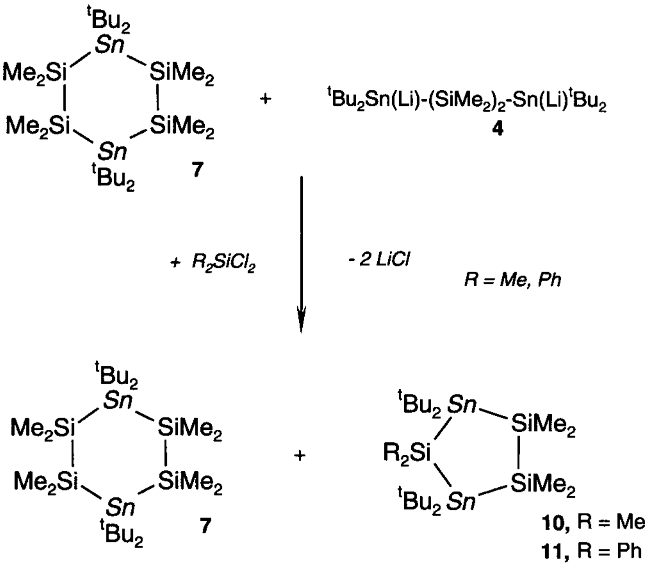
Scheme 2 Reaction of **3** with LDA.

Novel monocyclic Si–Sn derivatives were obtained by reacting **5** or mixtures of **4** and **7** with diorganodichlorosilanes. The reaction of **5** with one equiv. of dimethyldichlorosilane afforded the six membered ring **9** (Eq. (2)).



(2)

Treatment of the mixture of **4** and **7** with dimethyl- or diphenyldichlorosilane gave **7** together with the five membered rings **10** or **11** (Scheme 3).



Scheme 3 Treatment of a mixture of **4** and **7** with diorganodichlorosilanes.

Fortunately, the two reaction products may be separated using column chromatography (using silica gel) and fractional crystallization from n-hexane. The X-

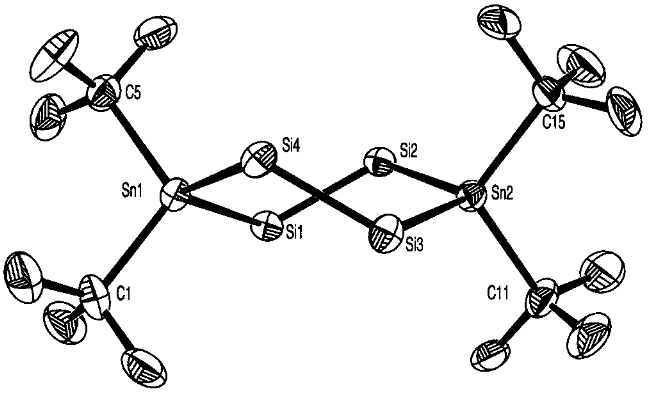


Fig. 1 View of a molecule of **7** showing 30% probability displacement ellipsoids (ORTEP3). Hydorgen atoms and carbon atoms bonded to silicon have been removed for clarity.

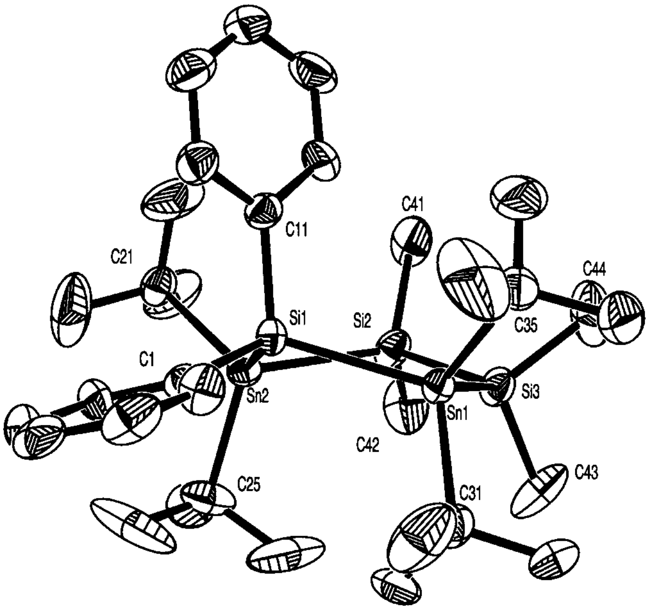


Fig. 2 View of a molecule of **11** showing 30% probability displacement ellipsoids (ORTEP3). Hydorgen atoms have been removed for clarity.

ray structures of **7** and **11** are shown in figure 1 and 2. Unit cell data, refinement details, and selected interatomic parameters are summarized in tables 1 and 2. X-ray quality crystals of **7** and **11** were obtained from saturated n-hexane solutions. Compounds **7** and **11** exhibit almost perfect tetrahedral environment at the tin and silicon atoms. Small deviations from the tetrahedral structure are induced by sterical effects. Si–Sn, Si–C, and Sn–C distances are within the usual range. Remarkable is the ring conformation of compound **7** (Figure 1), exhibiting a twisted conformation caused by the larger steric demands of the tert.butyl groups, a more rare example for the conformation of six membered oligosilanes [4].

Table 1 Crystal data and structure refinement for **7** and **11**

	7	**11**
Formula	$C_{24}H_{60}Si_4Sn_2$	$C_{32}H_{58}Si_3Sn_2$
fw, g/Mol	698.46	764.43
cryst syst	monoclinic	monoclinic
cryst size, mm	0.20 × 0.18 × 0.18 mm	0.25 × 0.15 × 0.13
space group	*P*2(1)/*n*	*P*2(1)/*n*
a, Å	9.505(2)	10.553(2)
b, Å	21.947(4)	18.521(4)
c, Å	17.404(3)	19.966(4)
β°	96.69(3)	101.13(3)
V, Å^3	3605.9(12)	3829.0(13)
Z	4	4
ρ_{calcd}, Mg/m^3	1.287	1.326
μ, mm^{-1}	1.528	1.416
F(000)	1440	1568
θ range, deg	3.00 to 25.99	3.00 to 25.49
index ranges	$0 \leq h \leq 11$	$0 \leq h \leq 12$
	$0 \leq k \leq 27$	$0 \leq k \leq 22$
	$-21 \leq l \leq 21$	$-24 \leq l \leq 23$
no. of reflections collected	7502	7505
no. of indep reflns/R_{int}	7066/0.0636	7102/0.0546
no. of refined params	292	352
GooF (F^2)	0.971	1.012
*R*1 (*F*) ($I > 2\sigma(I)$)	0.0743	0.0626
*wR*2 (F^2) (all Data)	0.1593	0.1686
Largest diff. Peak/hole, e/Å^3	0.772/–0.580	0.994/–1.121

$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \text{sqrt}\Sigma w\{(F_o)^2 - (F_c)^2\}/\Sigma w\{(F_o)^2\}^2$.

Table 2 Selected Bond Lengths/Å and Angles/° for **7** and **11**

7		**11**	
Sn(1)–Si(4)	2.595(3)	Sn(1)–Si(3)	2.597(3)
Sn(1)–Si(1)	2.597(3)	Sn(1)–Si(1)	2.623(2)
Si(1)–Si(2)	2.341(4)	Sn(2)–Si(1)	2.616(2)
Sn(2)–Si(2)	2.586(3)	Sn(2)–Si(2)	2.623(3)
Sn(2)–Si(3)	2.594(3)	Si(3)–Si(2)	2.339(4)
Si(3)–Si(4)	2.334(4)		
C(5)–Sn(1)–C(1)	108.9(4)	C(35)–Sn(1)–C(31)	107.5(4)
C(5)–Sn(1)–Si(4)	108.9(3)	C(35)–Sn(1)–Si(3)	111.4(3)
C(1)–Sn(1)–Si(4)	109.8(3)	C(31)–Sn(1)–Si(3)	109.8(3)
C(5)–Sn(1)–Si(1)	109.8(4)	C(35)–Sn(1)–Si(1)	112.1(3)
C(1)–Sn(1)–Si(1)	109.5(3)	C(31)–Sn(1)–Si(1)	113.4(3)
Si(4)–Sn(1)–Si(1)	110.36(9)	Si(3)–Sn(1)–Si(1)	102.69(8)
C(15)–Sn(2)–C(11)	110.6(5)	C(21)–Sn(2)–C(25)	109.0(4)
C(15)–Sn(2)–Si(2)	108.7(3)	C(21)–Sn(2)–Si(1)	114.2(3)
C(11)–Sn(2)–Si(2)	109.6(3)	C(25)–Sn(2)–Si(1)	115.4(3)
C(15)–Sn(2)–Si(3)	110.1(3)	C(21)–Sn(2)–Si(2)	110.5(3)
C(11)–Sn(2)–Si(3)	108.2(3)	C(25)–Sn(2)–Si(2)	107.4(4)
Si(2)–Sn(2)–Si(3)	109.53(9)	Si(1)–Sn(2)–Si(2)	99.82(8)

3 Experimental Part

3.1 General Methods

All reactions were carried out under an atmosphere of inert gas (N_2 or Ar) using Schlenk techniques. All solvents were dried by standard methods and freshly distilled prior to use. The compounds **1**–**3** [2] and lithium diisopropylamide [5] were prepared according to published procedures. All other chemicals used as starting materials were obtained commercially. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DPX 400 spectrometer (solvents $CDCl_3$ or C_6D_6, internal reference Me_4Si). ^{29}Si and ^{119}Sn NMR spectra were recorded using a Bruker DPX 400 spectrometer (solvents $CDCl_3$ or C_6D_6, internal reference Me_4Si or Me_4Sn, respectively) or a Bruker DRX 300 spectrometer (solvents hexane or THF with D_2O-capillary, internal reference Me_4Si or Me_4Sn, respectively). If not otherwise stated, the NMR experiments were carried out ^{1}H decoupled. MS analyses were recorded using a MAT 8200. Elemental analyses were performed on a LECO-CHNS-932 analyzer.

3.2 General Procedure for the formation of 4 and 5

A solution of LDA (5.4 mmol in 15 mL of n-hexane and 15 mL of THF) was added dropwise to a cooled solution (0 °C) of **1**, **2** or **3** (2.7 mmol) in 100 mL of a 1 : 1 mixture of THF and n-hexane. The reaction mixture was stirred at this temperature for 1 h. The solution was examined by ^{29}Si and ^{119}Sn NMR spectroscopy.

Attempts towards the formation of 1,4-Dilithio-1,1,4,4-tetratert.butyl-tetramethyl-1,4-distanna-2,3-disilabutane (4)

Starting materials: 8.0 mmol (3.5 g) of **1** in 100 mL of THF/hexane (1 : 1), 16.0 mmol LDA in 60 mL of THF/hexane (1 : 1). **7** occurs as a byproduct of the synthesis of **4**.

NMR investigation of the reaction solution: **4**: ^{29}Si NMR (59.63 MHz, D_2O-cap.): δ –28.4 [^{1}J($^{119/117}$Sn–^{29}Si): not detected], ^{119}Sn (111.92 MHz, D_2O-cap.): δ –94.8. **7**; ^{29}Si NMR (59.63 MHz, D_2O-cap.): $\delta = -33.6$ [^{1}J($^{119/117}$Sn–^{29}Si): 272/260 Hz, ^{2}J($^{119/117}$Sn–^{29}Si): 80 Hz]. ^{119}Sn NMR (111.92 MHz, D_2O-cap.): $\delta = -164.2$ [^{1}J($^{119/117}$Sn–^{29}Si): 274 Hz].

^{t}Bu$_2$Sn(H)–Sn(H)^{t}Bu$_2$: ^{119}Sn NMR (111.92 MHz, D_2O-cap.): $\delta = -83.7$ [^{1}J(^{119}Sn–^{117}Sn): 1260 Hz].

1,5-Dilithio-1,1,5,5-tetratert.butyl-hexamethyl-1,5-distanna-2,3,4-trisilapentane (5)

Starting materials: 2.4 mmol (1.52 g) of **2** in 100 mL of THF/hexane (1 : 1), 5.4 mmol LDA in 30 mL of THF/hexane (1 : 1).

^{29}Si NMR (59.63 MHz, D_2O-cap.): $\delta = -29.6$ [^{1}J($^{119/117}$Sn–^{29}Si): not detected], $\delta = -37.0$ [^{2}J($^{119/117}$Sn–^{29}Si): not detected]. ^{119}Sn (111.92 MHz, D_2O-cap.): $\delta = -104.7$.

3.3 Attempts towards the formation of 6 – Synthesis of 8

Starting materials: 2.0 mmol (1.38 g) of **3** in 100 mL of THF/hexane (1 : 1), 4.0 mmol LDA in 30 mL of THF/hexane (1 : 1). **8** was recrystallized from n-hexane. Yield: 0.50 g (54%).
EA: $C_{16}H_{42}Si_4Sn$, 465.5 g/mol, found (calc.): C 39.7 (41.28), H 8.8 (9.09)%.

Mp.: 74–76 °C. ^{1}H NMR (400.15 MHz, $CDCl_3$): $\delta = 0.17$ [12 H, Sn–Si–Si*Me*$_2$], 0.39 [12 H, Sn–Si*Me*$_2$, ^{3}J($^{119/117}$Sn–^{1}H): 24 Hz], 1.29 [36 H, Sn–C–*Me*$_3$, ^{3}J($^{119/117}$Sn–^{1}H): 58/56 Hz]. ^{13}C NMR (100.63 MHz, $CDCl_3$): $\delta = -3.99$ [Sn–Si–Si*Me*$_2$], 0.00 [Sn–Si*Me*$_2$], 32.04 [Sn–*C*–Me$_3$], 36.7 [Sn–C–*Me*$_3$]. ^{29}Si NMR (59.63 MHz, D_2O-cap.): $\delta = -38.0$ [$^{2/3}$J($^{119/117}$Sn–^{29}Si): 73 Hz], –36.8 [^{1}J($^{119/117}$Sn–^{29}Si): 276/261 Hz]. ^{119}Sn NMR (111.92 MHz, D_2O-cap.): $\delta = -151.0$ [^{1}J($^{119/117}$Sn–^{29}Si): 273 Hz]. MS (M/z): 465 [M^{+}, 20%], 408 [M^{+} – tert.butyl, 90%], 351 [M^{+} – 2 × tert.butyl, 30%], 278 [$SnSi_3Me_5$, 92%].

3.4 General Procedure for the formation of 9–11

A freshly prepared solution of **4** or **5** in 20 mL of THF were cooled to the temperature given below. The specified amount of R_2SiCl_2 was solved in thf and added dropwise to the cooled reaction mixture which was then allowed to reach room temperature and stirred overnight. The solvents were evaporated in vacuo and the solid residue was treated with n-hexane. After filtration (G4) the solvent was removed in vacuo.

4,4,6,6-tetratert-butyl-1,1,2,2,3,3,5,5-octamethyl-1,2,3,5-tetrasila-4,6-distannacyclohexane (9)

Starting materials: 2.4 mmol of **5**, 0.31 g (2.4 mmol) Me_2SiCl_2. Reaction temperature 0 °C. The resulting oil was purified by column chromatography (silica gel/n-hexane). Recrystallization from n-hexane/diethylether (1 : 1) gave 1.2 g (71%) of **9**.
EA: $C_{24}H_{60}Si_4Sn_2$, 698.49 g/mol, found (calc.): C 41.8 (41.27), H 8.8 (8.66)%.

Mp.: 168 °C. ^{29}Si NMR (59.63 MHz, D_2O-cap.): $\delta = -38.2$ [^{2}J($^{119/117}$Sn–^{29}Si): 72 Hz], –37.0 [^{1}J($^{119/117}$Sn–^{29}Si): 273/261 Hz, ^{3}J($^{119/117}$Sn–^{29}Si): 95 Hz], –30,7 [^{1}J($^{119/117}$Sn–^{29}Si): 229/218 Hz]. ^{119}Sn NMR (111.92 MHz, D_2O-cap.): $\delta = -156.2$ [^{2}J(^{119}Sn–^{117}Sn): 291 Hz, ^{1}J($^{119/117}$Sn–^{29}Si): 228 Hz].

3,3,5,5-tetratert-butyl-1,1,2,2,4,4-hexamethyl-1,2,4-trisila-3,5-distannacyclopentane (10)

Starting materials: 8 mmol of a mixture of **4** and **7**, 1.03 g (8 mmol) Me_2SiCl_2. Reaction temperature 0 °C. The resulting oil was purified by column chromatography (silica gel/n-hexane) to give 3.07 g of a mixture of **7** and **10**. The residue was dissolved in 20 ml of n-hexane, stored at –35 °C to give 1.18 g (23%) of **7**. After removel of three quarter of the solvent in vacuo the solution was stored again at –35 °C to give 1.38 g (25%) of **10**. Mp.: 150 °C (dec.).

EA: $C_{22}H_{54}Si_3Sn_2$, 640.34 g/mol, found (calc.): C 41,1 (41,3), H 9,0 (8,5)%.

^{1}H NMR (400.15 MHz, $CDCl_3$): $\delta = 0.36$ [12 H, 2 × SiMe$_2$], 0.39 [6 H, SiMe$_2$], 1.26 [36 H, Sn–C–Me$_3$, ^{3}J($^{119/117}$Sn–^{1}H): 43 Hz]. ^{29}Si NMR (59.63 MHz, D_2O-cap.): $\delta = -32.3$ [^{1}J($^{119/117}$Sn–^{29}Si): 294/281 Hz, ^{2}J($^{119/117}$Sn–^{29}Si): 90 Hz], –31.1 [^{1}J($^{119/117}$Sn–^{29}Si): 228/212 Hz]. ^{119}Sn NMR (111.92 MHz, D_2O-cap.): $\delta = -147.6$ [^{2}J(^{119}Sn–^{117}Sn): 365]. MS (M/z): 640 [M^{+}, 100%], 583 [M^{+} – tert.butyl, 20%], 527 [M^{+} – 2 × tert.butyl, 20%], 469 [M^{+} – 3 × tert.butyl, 40%].

3,3,5,5-tetratert-butyl-1,1,2,2-tetramethyl-4,4-diphenyl-1,2,4-trisila-3,5-distannacyclopentane (11)

5,6 mmol of a mixture of **4** and **7**, 1.42 g (5.6 mmol) Ph_2SiCl_2. Reaction temperature –65 °C. The resulting oil was purified by column chromatography (silica gel/n-hexane) to give 2.28 g of a mixture of **7** and **11** (75% **11**; 25% **7**; determined by NMR spectroscopy). The residue was dissolved in 20 ml of n-hexane, and stored at –35 °C to give 0.85 g (22%) of **7**. After removel of three quarter of the solvent in vacuo the solution was stored again at –35 °C to give 0.85 g (20%) of **11**. Mp.: 160 °C. EA: $C_{32}H_{58}Si_3Sn_2$, 764.49 g/mol, found (calc.): C 50,5 (50,28), H 8,1 (7,65)%.

^{1}H NMR (400.15 MHz, $CDCl_3$): $\delta = 0.53$ [12 H, 2 × SiMe$_2$, ^{3}J($^{119/117}$Sn–^{1}H): 23 Hz], 1.18 [36 H, Sn–C–Me$_3$, ^{3}J($^{119/117}$Sn–^{1}H): 60 Hz], 7.24 ppm [Si–Ph], 7.56 [Si–Ph]. ^{13}C NMR (100.63 MHz, $CDCl_3$): $\delta = -1.8$ [2 × SiMe$_2$], 32.3 [Sn–*C*–Me$_3$, ^{1}J(^{119}Sn–^{13}C): 244 Hz], 34.2 [Sn–C–*Me*$_3$], 127.6, 128.3, 137.5, 138.2 [12 C, Si–Ph]. ^{29}Si NMR (59.63 MHz, D_2O-cap.): $\delta = -31.5$ [^{1}J($^{119/117}$Sn–^{29}Si): 274/265 Hz, ^{2}J($^{119/117}$Sn–^{29}Si): 67 Hz], –11.2 [^{1}J($^{119/117}$Sn–^{29}Si): 190 Hz]. ^{119}Sn NMR (111.92 MHz, D_2O-cap.): $\delta = -152.3$ [^{2}J(^{119}Sn–^{117}Sn): 310 Hz]. MS (M/z): 765 [M^{+}, 2%], 707 [M^{+} – tert.-butyl, 75%], 649 [M^{+} – 2 × tert.butyl, 10%], 591 [M^{+} – 3 × tert.butyl, 15%], 534 [M^{+} – 4 × tert.butyl, 17%], 478 [M^{+} – 4 × tert.butyl – SiMe$_2$, 10%], 457 [M^{+} – 4 × tert.butyl – Ph, 10%], 400 [M^{+} – 4 × tert.butyl – SiMe$_2$ – Ph, 30%].

3,3,6,6-tetratert-butyl-1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrasila-3,6-distannacyclohexane (7)

7: Mp.: 214 °C.

EA: $C_{24}H_{60}Si_4Sn_2$, 698.49 g/mol, found (calc.): C 41.6 (41.27), H 9.0 (8.66)%.

^{1}H NMR (400.15 MHz): $\delta = 0.37$ [24 H, Sn–Si*Me*$_2$, ^{3}J($^{119/117}$Sn–^{1}H): 56 Hz], 1.28 [36 H, Sn–C–*Me*$_3$, ^{3}J($^{119/117}$Sn–^{1}H): 24 Hz]. ^{29}Si NMR (59.63 MHz): $\delta = -33.6$ [^{1}J($^{119/117}$Sn–^{29}Si): 272/260 Hz, ^{2}J($^{119/117}$Sn–^{29}Si): 80 Hz]. ^{119}Sn NMR (111.92 MHz): $\delta = -164.2$ [^{1}J($^{119/117}$Sn–^{29}Si): 274 Hz].

Crystallography of 7 and 11. The crystals were mounted on the diffractometer in a sealed Lindemann capillary. The data were collected on a Nonius MACH3 diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 291 K. Three standard reflections were recorded every 60 minutes and an anisotropic intensity loss up to 5.6% for compound **7** and 4.5% for compound **11** was detected during X-ray exposure. The structure was solved by Direct Methods (SHELXS97) [6]. Missing atoms were located in subsequent Difference Fourier Cycles and refined by full-matrix least-squares of F^2 (SHELXL97) [7]. All hydrogen atoms were placed geometrically and refined using a riding model with a common isotropic temperature factor (**7**: $C{-}H_{prim.}$ 0.96 Å, U_{iso} 0.111(6) Å^2; **11**: $C{-}H_{prim.}$ 0.96 Å, U_{iso} 0.173(9) Å^2; $C{-}H_{Aryl}$ 0.93 Å, U_{iso} 0.097(12) Å^2. Atomic scattering factors for neutral atoms and real imaginary dispersion terms were taken from International tables for X-ray Crystallography [8].

4 Supplementary material

Full details for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 149463 for compound **7**, CCDC No. 149464 for compound **11**. Copies of data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk), and are also available in CIF format from the authors.

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