Synthesis and Reactivity of Novel Bis(stannyl)silanes

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Dedicated to Prof. Dr. H. Oehme on the occasion of his 60th birthday

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Bis(stannyl)silanes of types $R_3Sn-SiR'_2-SnR_3$ and $R_2(H)Sn-SiR'_2-Sn(H)R_2$ with R' being methyl, phenyl, *iso*-propyl or *tert*-butyl have been synthesized by treatment of difunctionalized diorganosilanes with alkali stannides (R = Me, 'Bu; R' = Me, 'Pr; **1** - **6**, **8**) or with triphenyl-tin chloride and magnesium (R = Ph; R' = Me, Ph, 'Pr; **7**, **9**). Me₃Sn-Si'Bu₂-SnMe₃ **4**, was halogenated using SnCl₄, to yield the bis(chlorostannyl)silane **11**.

The reaction of bis(stannyl)diorganosilanes $R_3SnSiR'_2SnR_3$ with catalytic amounts of Pd(PPh₃)₄ resulted in unexpected rearrangements under formation of the silyldistannanes $R_3SnSnR_2SiR'R_2$. These compounds undergo addition reactions with alkynes. All compounds have been identified by NMR, IR, MS and elemental analysis. Compounds **5**, **6** and **7** have also been characterized by X-ray crystallography.

1. Introduction

Stannylsilanes are well known and frequently used reagents in organic synthesis [1]. The focus of our interest is the investigation of tin-silicon systems as precursors for polymeric species. The development of these systems mandates a detailed investigation of the reactivity of the precursor molecules. This includes the exploration of reactions of stannylsilanes treated with alkynes in the presence of Pd catalysts [2 - 5].

Recently, we described the synthesis of α, ω -bis-(chloro- and bromostannyl)oligodimethylsilanes of type A [6]. The preparation of these compounds is only possible if the steric demand of the substituents at the tin atoms is large (*e. g. tert*-butyl); utilization of smaller groups results in cleavage of Si-Sn bonds.

 $R_{2}Sn(X)-(SiMe_{2})_{n}-Sn(X)R_{2} (A)$ $R = {}^{t}Bu; X = Cl, Br; n = 2 - 6$ $R_{2}Sn(Z)-SiR'_{2}-Sn(Z)R_{2} (B, C)$ $B: R = Z = Me, Ph; R' = {}^{t}Bu, {}^{i}Pr, Me$ $C: R = {}^{t}Bu, Z = H, R' = Me, {}^{i}Pr$

Compounds of type **A** are expected to be particulary suitable as precursors for cyclic stannylsilanes with di- or tristannyl moieties and ring sizes of four, five and six atoms [7]. To investigate the reactivity of differently substituted bis(stannyl)diorganosilanes, compounds of the types **B** and **C** have been synthesized. The distinction between type **B** and **C** derivatives is based on the steric demand of ligands connected to the tin atoms: compounds of type **B** carry small substituents, while type **C** derivatives feature *tert*.butyl ligation in addition to a hydride function.

Our investigations have also focused on the reactivity of bis(stannyl)silanes towards alkynes in the presence of transition metal compounds. Surprisingly, we encountered rearrangements of type **B** stannylsilanes in the presence of palladium complexes, followed by alkyne insertion reactions. Bis(stannyl)silanes of type **C** do not undergo these rearrangements due to the sterically demanding substituents at the tin atoms.

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Table I. Yields and starting materials (X-SiR'₂-X; MSn- R_2Z) for the syntheses of the bis(triorganostannyl)silanes 1 - 9.

No.	R	Ζ	R'	Х	Μ	Yield
1 [6]	Me	Me	Me	Cl	Na	80%
2 [6]	^t Bu	Н	Me	Cl	Li	89%
3	Me	Me	ⁱ Pr	F	Na	74%
4	Me	Me	^t Bu	OTf	Li	88%
	Me	Me	^t Bu	Cl	K	65%
5	^t Bu	H	ⁱ Pr	Cl	Li	97%
6 [6]	Ph	Ph	Me	Cl	Li	60%
7	Ph	Ph	ⁱ Pr	Cl	Mg	95%
8	Ph	Ph	^t Bu	OTf	Na	80%
9	Ph	Ph	Ph/Me	F	Mg	75%

2. Results and Discussion

2.1. Syntheses

All compounds were synthesized according to reaction routes developed for the synthesis of bis(stannyl)dimethylsilanes [6]. However, metathesis reactions with difluorosilanes are slow, especially in conjunction with sterically demanding substituents such as *tert*-butyl or *iso*-propyl. Introduction of chloro- or triflate-substituted silanes, rather than the fluoro derivatives, facilitates the reaction.

Bis(stannyl)silanes $R_3Sn-SiR'_2-SnR_3$ were obtained in high yields by treatment of difunctionalized diorganosilanes with alkali tri- or diorganylstannides (1 - 6, 8, eq. (1)) or, alternatively, by reaction with triphenylchlorostannane in the presence of magnesium (7, 9, eq. (2)).

 $\begin{array}{l} R'_{2}SiX_{2} + 2\ MSnR_{2}Z\ \overline{} R_{2}Sn(Z) - R'_{2}Si - Sn(Z)R_{2}(1)\\ X = F, Cl, CF_{3}SO_{3}; M = Li, Na, K\\ 1: R = Z = R' = Me\\ 2: R = 'Bu, Z = H, R' = Me\\ 3: R = Z = Me, R' = 'Pr\\ 4: R = Z = Me, R' = 'Pr\\ 4: R = Z = Me, R' = 'Bu\\ 5: R = 'Bu, Z = H, R' = 'Pr\\ 6: R = Z = Ph, R' = Me\\ 8: R = Z = Ph, R' = Me\\ 8: R = Z = Ph, R' = 'Bu\\ R'_{2}SiX_{2} + 2\ Ph_{3}SnCl \xrightarrow{+2Mg}{-2Mg(X)Cl} Ph_{3}Sn-R'_{2}Si-SnPh_{3} \ (2)\\ X = F, Cl\\ 7: R' = 'Pr; 9: R' = Ph/Me \end{array}$

In contrast to the reactions illustrated in eq. (1), treatment of di-*tert*-butyldichlorosilane with two equivalents of lithium di-*tert*-butylhydridostannide did not result in the desired product **10** probably

owing to the steric shielding at both the silicon and the tin atom by the *tert*-butyl groups. Only unchanged starting materials were isolated:

$${}^{\prime}Bu_{2}SiCl_{2} + 2 LiSn^{\prime}(H)Bu_{2}$$

$$\xrightarrow{} H'Bu_{2}Sn-{}^{\prime}Bu_{2}Si-Sn^{\prime}Bu_{2}H (10)$$
(3)

2.2. Reactivity

In contrast to derivatives of the type Me₃Sn-(SiMe₂)_n-SnMe₃ ($n \ge 1$) and the stannylsilanes **3**, **7** and **9**, compound **4** can be halogenated at the tin centers without cleavage of the Si-Sn bond. A classic redistribution reaction involving treatment with SnCl₄ yields the dihalogenated compound (eq. (4)). The steric shielding effected by the *tert*-butyl groups in **4**, as compared to methyl, *iso*-propyl or phenyl substituents in **3**, **7** and **9**, is responsible for the selectivity of this reaction route.

$$\begin{array}{l} \text{Me}_{3}\text{Sn}^{-1}\text{Bu}_{2}\text{Si}\text{-Sn}\text{Me}_{3} \ (4) \\ \xrightarrow{2/3 \text{ Sn}\text{Cl}_{4}}{-2/3 \text{ Me}_{3}\text{Sn}\text{Cl}} & \text{Me}_{2}\text{Sn}(\text{Cl})\text{-}^{\prime}\text{Bu}_{2}\text{Si}\text{-Sn}(\text{Cl})\text{Me}_{2} \ (11) \end{array}$$

Reactions leading to derivatives with four or more chlorine atoms at the Si-Sn skeleton are still under investigation and will be discussed in a subsequent publication.

As recently observed [6], halogenation of α,ω bis(di-*tert*-butylhydridostannyl)dimethylsilanes with more than one silicon atom separating the tin centers, to yield type **A** compounds, can be easily achieved by employing haloforms. Unlike these derivatives, the comparable monosilyl hydrides **2** and **5** [6] cannot be transformed into the halides.

H-'Bu₂Sn-R₂Si-Sn-'Bu₂H (5)

$$\xrightarrow{+2 \text{ CHX}_3}$$
 X-'Bu₂Sn-R₂Si-Sn-'Bu₂X (2: R = Me; 5: R = ^{*i*}Pr)

Instead, treatment of **2** and **5** with CHX₃ (X = Cl, Br), SnCl₄ or PCl₅ results in Si-Sn bond cleavage under formation of oligomeric stannanes and halosilanes. With milder halogenation agents such as Me_nSiCl_{4-n} / amine no reactions are observed.

In order to examine the reactivity of 1 - 9 towards transition metal complexes, we treated 1, 3 and 7 with tetrakis(triphenylphosphine) palladium (eq. (6)). Surprisingly, a novel and unexpected rearrangement of the *Sn-Si-Sn* fragment under formation of distannylsilanes 12 - 14 with a *Sn-Sn-Si* atom sequence was observed.



(6)

Scheme 1. Rearrangement of 1 and reaction with alkynes in the presence of Pd(PPh₃)₄.

 $R_{3}Sn-SiR'_{2}-SnR_{3} \xrightarrow{+Pd(PPh_{3})_{4}} R_{3}Sn-SnR_{2}-SiR'_{2}R$ 12: R = Me, R'= Me $13: R = Me, R'= {}^{i}Pr$ $14: R = Ph, R'= {}^{i}Pr$

This rearrangement is only observed if small substituents are present at the silicon center. Bis-(stannyl)silanes carrying the sterically more demanding *tert*-butyl groups (*e. g.* compound **4**) do not undergo the rearrangement. The application of heat (up to 100 °C) did not give better results; only Si-Sn bond cleavage was observed. Reacting the hydrido substituted derivatives **2** and **5** with Pd(PPh₃)₄ also resulted in tin-silicon bond cleavage.

The rearrangement product **12** (eq. (6)) reacts in the presence of catalytic amounts of Pd(PPh₃) with one equivalent of an alkyne in a regioselective *cis*addition to the β -distannylvinylsilanes **15** and **16** (Scheme 1). We were unable to find any indication for an insertion reaction of a second equivalent of alkyne into the Sn-Sn bonds of **15** or **16**. Alteration of the reaction conditions and stoichiometric ratio of the starting materials did not change this result.

Products 15 and 16 are also available by treating 1 with alkynes in the presence of tetrakis(triphenylphosphine) palladium in a one-pot reaction. It is believed that 12 is the intermediate in this rearrangement reaction.

In order to compare the thermodynamic stabilities of compounds **1** and **12**, we performed semiempirical geometry optimizations using PM3 \cdot [10] methods. For **1** we calculated -164.098 kJ/mol as heat of formation; for **12**, a value of -226.945 kJ/mol was obtained. Density functional calculations using the ADF program^[11] afforded -16177.585 kJ/mol for **1** and -16247.128 kcal/mol for **12** as total bonding energies after a geometry optimization [12], confirming that **12** is more stable than **1**, a fact

Table II. ¹¹⁹Sn and ²⁹Si NMR data of compounds **1** - **9** and **11**; chemical shifts [ppm] and coupling constants [Hz].

No.	R	Ζ	R'	$\delta^{119} \mathrm{Sn}$	$^{2}J_{\mathrm{Sn-Sn}}$	δ^{29} Si	${}^{1}J_{\mathrm{Si-Sn}}$
1 ^a	Me	Me	Ме	-98.4	703	-38.3	508/486
2^{a}	^t Bu	Η	Me	-111.3 ^b	_	-34.9	347/331
3	Me	Me	ⁱ Pr	-108.3	655	-1.4	447/426
4	Me	Me	'Bu	-110.2	609	10.9	445/425
5	^t Bu	Н	^{<i>i</i>} Pr	-104.4°	190	11.7	256/245
6 ^a	Ph	Ph	Me	-155.5	712	-31.9	521/497
7	Ph	Ph	ⁱ Pr	-157.0	661	7.8	437/417
8	Ph	Ph	^t Bu	-160.0	615	12.8	437/417
9	Ph	Ph	Me/Ph	-1627.0	570	-31.4	n.d.
11	Me	Cl	^t Bu	119.5	900	32.4	443/422
^a See lit [6]: ^b $L_{a} = 1280 \text{ Hz}$: ^c $L_{a} = 1257 \text{ Hz}$							

⁴ See lit. [6]; ^{b 1} $J_{Sn-H} = 1280 \text{ Hz}$; ^{c 1} $J_{Sn-H} = 1257 \text{ Hz}$.

arising from the formation of the Sn-Sn-bond. This thermodynamic statement is also verified by experiments conducted according to eq. (6).

2.3. Characterization

¹¹⁹Sn and ²⁹Si NMR data of **1** - **9**,**11** and **12** - **16** are summarized in Tables II and III. Remarkably, the distannyl derivatives **12** - **16** do not show simple AX-spin systems for the ${}^{1}J_{119}Sn-119}Sn$ coupling satellites (Table III); the distannyl derivatives **12** - **14** exhibit AM type spin systems, and for the β -distannyl-vinylsilanes **15** and **16** AB type satellites have been found.

X-ray-quality crystals of compound **5** were obtained by crystallization from a saturated *n*-hexane solution, compounds **6** and **7** were crystallized from diethylether. Compounds **5** - **7** exhibit almost perfect tetrahedral geometry about the silicon and tin centers. Small deviations from tetrahedral geometry are induced by sterical effects. Si-Sn, Si-C and Sn-C distances are within the usual range.

	-		o110 - 0	a110 - b	1 -	.20	1 -	2 -	2 -
No.	R	R'	δ^{119} Sn ^a	δ^{119} Sn ⁶	J_{Sn-Sn}	δ^{29} Si	$J_{\mathrm{Si-Sn}}$	$^{2}J_{\mathrm{Si-Sn}}$	J_{Si-Sn}
12	Me	Me	-111.7	-263.6	2825/2700	-8.1	527/503	84	_
13 ^a	Me	^{<i>i</i>} Pr	-110.8	-274.6	2935/2805	14.4	485/463	69	_
14	Ph	ⁱ Pr	-147.7	-241.2	2645/2527	16.3	484/463	70/67	_
15	Me	Me	-98.4	-140.5	4235/4050	11.7	_	_	32
16	Me	Me	-97.3	-150.4	4770/4560	32.4	_	-	34

Table III. ¹¹⁹Sn and ²⁹Si NMR data of compounds 11 - 15; chemical shifts [ppm] and coupling constants [Hz].

^a Only determined by ²⁹Si- and ¹¹⁹Sn NMR spectroscopy.

Table IV. Selected interatomic bond distances (Å) and angles (deg) for **5**, **6** and **7**.

	5	6	7
Si(1)-Sn(1)	2.6061(16)	2.5713(4)	2.5935(9)
Si(1)-Sn(2)	2.6094(15)		2.5946(9)
Si(1)-C(19)	1.915(5)	1.875(2)	1.898(4)
Si(1)-C(20)	1.907(6)	1.875(3)	1.899(4)
Sn(1)-H(1)	1.79(4)		
Sn(2)-H(2)	1.78(4)		
Sn(1)-Si(1)-Sn(2)	111.29(5)	116.49(3)	109.11(3)
C(19)-Si(1)-Sn(1)	106.17(15)	107.28(9)	106.96(13)
C(20)-Si(1)-Sn(1)	106.34(15)	108.33(9)	107.19(13)
C(19)-Si(1)-Sn(2)	112.96(17)		111.59(12)
C(20)-Si(1)-Sn(2)	113.42(17)		112.35(13)
C(19)-Si(1)-C(20)	106.7(2)	109.0(2)	109.4(2)
C(1)-Sn(1)-C(7)	108.4(2)	105.41(7)	102.92(13)
C(1)-Sn(1)-C(13)		106.50(7)	104.48(13)
C(13)-Sn(1)-C(7)		110.04(7)	107.71(13)
C(25)-Sn(1)-C(31)	110.69(15)		103.6(2)
C(25)-Sn(1)-C(37)			106.0(2)
C(31)-Sn(1)-C(37)			106.48(14)
C(1)-Sn(1)-H(1)	89.8(18)		
C(7)-Sn(1)-H(1)	101.1(18)		
Si(1)-Sn(1)-H(1)	108.8(18)		
C-Sn-Si	112.55(17)	106.51(5)	110.76(9)
	116.44(17)	112.93(5)	113.84(9)
	116.86(17)	115.19(5)	113.07(11)
	116.90(11)		111.11(10)
	117.20(17)		113.87(9)
	117.53(10)		118.00(9)

3. Experimental

General

All reactions were carried out under an atmosphere of inert gas (N₂ or argon) using modified Schlenk techniques. All solvents used were dried by standard methods and freshly distilled prior to use. The bis(stannyl)dimethylsilanes **1**, **2** and **6** and the alkali stannides were prepared according to published procedures [6, 8, 9]. All other reagents were obtained commercially. ¹H, ¹³C, ²⁹Si and ¹¹⁹Sn NMR spectra were recorded using a Bruker DPX 400 spectrometer (solvents CDCl₃ or C₆D₆, internal



Fig. 1. X-ray structure of **5**. Thermal ellipsoids denote 50% of probability displacement (ORTEP3).

reference Me_4Si or Me_4Sn) or a Bruker DRX 300 spectrometer (solvents hexane or thf with D_2O capillary). Mass spectral analyses were recorded using a MAT 8200. Elemental analyses were performed on a LECO-CHNS-932 analyzer.

3.1. Syntheses of bis(stannyl)silanes

General procedure for compounds 3, 4, 6 and 8

In a 100 ml Schlenk tube the adequate amount of hexaorganodistannane was dissolved in thf. Sodium and naphthalene were added. The resulting reaction mixture was stirred at r. t. for 14 h. After filtration to remove excess sodium, the resulting solution of sodium triorganostannide was added slowly to a cooled solution ($-40 \,^{\circ}$ C) of difunctionalized diorganosilane dissolved in thf. The mixture was stirred for 3 h at $-40 \,^{\circ}$ C and then slowly warmed to r. t. After evaporation of the volatiles in vacuum the residue was extracted twice with 80 ml of an ether/hexane mixture (80:20). The extracts were filtered (G3) to remove the sodium salts. The solvents were removed in vacuum and the crude product purified by distillation or crystallization.

Bis(trimethylstannyl)diisopropylsilane 3

 Me_6Sn_2 (6.6 g, 20 mmol) in 80 ml of thf, sodium (1 g, 40 mmol), naphthalene (0.1 g, 4 mmol) and diflu-



Fig. 2. X-ray structure of **6**. Thermal ellipsoids denote 50% of probability displacement (ORTEP3).

orodi*iso*propylsilane (3.0 g, 20 mmol) in 20 ml of thf. – Yield: 6.5 g (74%) of **3** as a colorless liquid, b. p. 66 – 70 °C (0.005 mm Hg). – ¹H NMR (400.13 MHz, C₆D₆) δ 0.14 (s, 18 H, Sn(CH₃)₃, ²J_{Sn-H} = 46 Hz), 1.06 (d, 12 H, CH₃, ¹J_{H-H} = 7 Hz), 1.43 (m, 2 H, CH, ¹J_{H-H} = 7 Hz). – ¹³C {¹H} NMR (100.63 MHz, C₆D₆) δ –9.1 (Sn(CH₃)₃, ¹J_{Sn-C} = 245/234 Hz), 14.4 (SiCH, ²J_{Sn-C} = 40 Hz), 21.6 (SiCH(CH₃)₂, ¹J_{Sn-C} = 245 Hz). MS *m*/z (%): 442 [M⁺ / 3%], 427 [M⁺-Me / 6], 279 [M⁺-SnMe₃ / 34], 237 [M⁺-SnMe₃-^{*i*}Pr / 9], 163 [Me₃Sn⁺ / 19], 129 [Si^{*i*}Pr₂Me / 95]. Elemental analysis for C₁₂H₃₂SiSn₂ (441.89 g/mol)

Calcd C 32.6 H 7.3%, Found C 33.7 H 7.7%.

Bis(trimethylstannyl)di-tert-butylsilane 4

Procedure a: Hexamethyldistannane (3 g, 9.2 mmol), sodium (0.43 g, 18.7 mmol), naphthalene (0.1 g, 4 mmol) and di-*tert*-butylsilylbis(trifluoromethanesulfonate) (3.0 g, 9.2 mmol) in 20 ml thf. Yield: 3.8 g (88%) of **4** as a colorless solid.

Fig. 3. X-ray structure of **7**. Thermal ellipsoids denote 50% of probability displacement (ORTEP3).

Procedure b: Hexamethyldistannane (2.5 g, 7.6 mmol), sodium (0.35 g, 15.2 mmol), naphthalene (0.1 g, 4 mmol) and di-*tert*-butyldichlorosilane (1.6 g, 7.6 mmol) in 10 ml thf). Yield: 2.3 g (65%) of **4** as a colorless solid, m. p.: 78 - 80 °C. – ¹H NMR (400.13 MHz, C₆D₆) δ 0.18 (s, 18 H, Sn(CH₃)₃, ²J_{Sn-H} = 48 Hz), 1.61 (s, 18 H, C(CH₃)₃). – MS *m*/*z* (%): 470 [M⁺ / 10%], 455 [M⁺-Me / 5], 317 [M⁺-SnMe₃ / 20], 163 [Me₃Sn⁺ / 25], 142 [Si'Bu₂ / 100].

Elemental analysis for $C_{14}H_{36}SiSn_2$ (469.95 g/mol) Calcd C 35.8 H 7.7%, Found C 36.2 H 7.4%.

Bis(triphenylstannyl)di-tert-butylsilane 8

Hexaphenyldistannane (7.15g, 10.2 mmol), sodium (0.47 g, 20.4 mmol), naphthalene (0.1 g, 4 mmol) and di-*tert*-butylsilylbis(trifluoromethanesulfonate) (4.49 g, 3.3 ml, 10.2 mmol) in 20 ml thf. Yield: 3.8 g (88%) of **8** as a colorless solid. – ¹H NMR (400.13 MHz, C₆D₆) δ 7.10 - 7.8 (m, 30 H, Ph), 1.71 (s, 18 H, C(CH₃)₃). – MS

m/*z* (%): 842 [M⁺ / 5%], 785 [M⁺-'Bu / 5], 765 [M⁺-Ph / 3], 434 [Si'BuSnPh₃ / 25], 349 [Ph₃Sn / 100], 142 [Si'Bu₂ / 10], 85 [Si'Bu / 40].

Elemental analysis for $C_{44}H_{48}SiSn_2$ (832.29 g/mol) Calcd C 62.7 H 5.7%, Found C 61.9 H 5.6%.

Bis(di-tert-butylstannyl)diisopropylsilane 5

A solution of *n*-butyllithium (6.3 ml, 10 mmol, 1.6 M in hexane) was added dropwise to a cooled (-70 °C) solution of di-iso-propylamine (1.0 g, 10 mmol) in a mixture of 15 ml hexane and 15 ml thf. The mixture was stirred for 20 min at 0 °C. The resulting lithium diisopropylamide (LDA) solution was added dropwise to a cooled (-65 °C) solution of di-tert-butyltindihydride (2.4 g, 10 mmol) in 50 ml of hexane and 50 ml of thf. The reaction mixture was slowly warmed to -50 °C and di-iso-propyldichlorosilane (0.93 g, 5 mmol) was added. After warming the reaction mixture to -30 °C, 25 ml of petrol ether (30 - 60 °C) was added and stirred for one hour at -10 °C. The mixture was hydrolyzed by addition of 20 ml of water. The organic layer was separated and dried using calcium chloride. After removal of the drying agent the solvents were evaporated, yielding 2.8 g (97%) of 5 as a colorless crystalline product, m. p. 76 °C. – ¹H NMR (400.13 MHz, C_6D_6) δ 1.28 (d, 12 H, CH(CH₃)₂, ${}^{3}J_{H-H} = 7$ Hz), 1.50 (s, 36 H, C(CH₃)₃, ${}^{3}J({}^{1}H^{-119}Sn) =$ 63 Hz), 1.72 (septett, 2 H, $CH(CH_3)_2$, ${}^3J_{H-H} = 7$ Hz), 5.3 (s, 2H, Sn*H*, ${}^{1}J_{Sn-H} = 1257$ Hz, ${}^{1}J_{Sn-H} = 1201$ Hz). $-{}^{13}C$ {¹H} NMR (100.63 MHz, C₆D₆) δ 16.3 (SiCH, ${}^{2}J_{\text{Sn}-\text{C}} = 19 \text{ Hz}$, 23.2 (SiCH(CH₃)₂, ${}^{3}J_{\text{Sn}-\text{C}} = 16 \text{ Hz}$), 30.3 $(SnC(CH_3)_3, {}^{1}J_{Sn-C} = 308 \text{ Hz}, {}^{1}J({}^{13}C-{}^{117}Sn) = 294 \text{ Hz}),$ 34.7 (SnC(CH₃)₃). - MS m/z (%): 582 [M⁺/3], 525 [M⁺-^{*t*}Bu / 21], 467 [M⁺-2^{*t*}Bu / 11], 353 [H₂^{*t*}Bu₂Sn₂⁺ / 74], 297 $[H_3^{t}BuSn_2^{+} / 80], 177 [H_2^{t}BuSn^{+} / 29], 57 [^{t}Bu^{+} / 100],$ 43 [^{*i*}Pr⁺ / 55]. – IR (nujol) ν (Sn-H) = 1771 cm⁻¹.

Elemental analysis for $C_{22}H_{52}SiSn_2$ (582.16 g/mol) Calcd C 45.4 H 9.0%, Found C 43.8 H 9.0%.

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Bis(triphenylstannyl)diisopropylsilane 7

In a 100 ml Schlenk tube dichlorodi*iso*propylsilane (0.5 g, 2.5 mmol) and triphenyltin chloride (1.9 g, 5 mmol) were dissolved in 80 ml of thf. Magnesium turnings (0.9 g, 37 mmol) were added. The reaction mixture was stirred at r. t. for approx. 120 h. After evaporation of the thf, the oily residue was extracted twice with 80 ml of a ether/hexane mixture (80:20). The extracts were filtered (G3) to remove magnesium salts. The crude product was obtained after evaporation of the solvents in vacuum. Purification was by recrystalisation from ether yielding 2.0 g (95%) of 7 as a colorless solid, m. p. 145 °C. – ¹H NMR

(400.13 MHz, CDCl₃) δ 1.18 (d, 12 H, CH(CH₃)₂), 1.43 (m, 2 H, CH(CH₃)₂), 7.20 (m, 18 H, *m*-Ph, *p*-Ph), 7.62 (d, 12 H, *o*-Ph, ³J_{Sn-H} = 43 Hz). – ¹³C {¹H} NMR (100.63 MHz, C₆D₆) δ 15.4 (SiCH, ²J_{Sn-C} = 24 Hz), 22.0 (SiCH(CH₃)₂, ³J_{Sn-C} = 20 Hz), 128.3 (*p*-Ph), 128.4 (*m*-Ph, ³J_{Sn-C} = 44 Hz), 137.6 (*o*-Ph, ²J_{Sn-C} = 37 Hz) 140.0 (*i*-Ph, ¹J_{Sn-C} = 389/371 Hz). – MS *m*/*z* (%): 736 [M⁺-Ph / 2], 465 [M⁺-SnPh₃ / 21], 388 [M⁺-SnPh₃-Ph / 47], 345 [M⁺-SnPh₃-Ph -^{*i*}Pr / 11], 197 [PhSn⁺ / 39], 149 [Si^{*i*}PrPh⁺ / 100], 121 [SiPhMe⁺ / 73].

 $\begin{array}{l} \mbox{Elemental analysis for $C_{42}H_{44}SiSn_2$ (814.32)} \\ \mbox{Calcd} C 62.0 H 5.5\%, \\ \mbox{Found} C 61.8 H 5.5\%. \\ \end{array}$

Bis(triphenylstannyl)phenylmethylsilane 9

Compound **9** was prepared according to the procedure of derivative **7**. Starting materials: triphenylchlorostannane (7.15 g, 18.6 mmol), Mg turnings (2.0 g, 83 mmol) and phenyl(methyl)difluorosilane (1.47 g, 9.3 mmol) in 40 ml of thf. – Yield: 6.7 g (88%) of **7** as a colorless solid, m. p. 166 - 167 °C. – ¹H NMR (400.13 MHz, C₆D₆) δ 7.12 - 7.75 (m, 35 H, Ph), 0.71 (s, 3 H, SiCH₃, ³J_{Sn-H}= 46 Hz).– MS *m*/*z* (%): 820 [M⁺ / 2%], 743 [M⁺-Ph / 5], 471 [M⁺-SnPh₃ / 60], 349 [Ph₃Sn / 100].

Elemental analysis for $C_{43}H_{38}SiSn_2$ (820.28 g/mol) Calcd C 63.0 H 4.7%, Found C 62.2 H 4.9%.

3.2. Reactions with tin(IV)chloride

Bis(chlorodimethylstannyl)di-tert-butylsilane 11

A solution of 1.4 g (3 mmol) **4** and 0.52 g (0.23 ml, 2 mmol) SnCl₄ in a mixture of 5 ml of thf and 5 ml of toluene were stirred overnight at r. t.. The solvent was removed *in vacuo*. Crystallisation from diethylether yielded 1.3 g (2.5 mmol / 85%) of **11** as a colorless solid. – MS m/z (%): 510 [M⁺ / 2%], 492 [M⁺-Me / 5]; 475 [M⁺-Cl / 2], 440 [M⁺-2Cl / 10], 347 [M⁺-SnMe₃ / 60]; 148 [Me₂Sn / 100].

Elemental analysis for $C_{12}H_{30}Cl_2SiSn_2$ (510.78) Calcd C 28.2 H 5.9%, Found C 28.8 H 6.1%.

3.3 General procedure for a rearrangement of bis(tri $organostannyl)silanes with <math>Pd(PPh_3)_4$

A solution of 2.5 mmol of a stannylsilane and 0.05 mmol of tetrakis(triphenylphosphine) palladium in 20 - 25 ml of toluene was stirred for 15 h at 60 °C. The solvent was removed under reduced pressure and 25 ml of diethylether was added. The solution was filtered (G3) and the solvent was removed *in vacuo*. The remaining residue was purified by destillation or crystallisation.

Octamethyl-1-sila-2,3-distannapropane 12

0.8 g (2.1 mmol) of **1** and 0.2 g (0.17 mmol) of Pd(PPh₃)₄ were dissolved in 5 ml of toluene. Adsorptive filtration of the crude product using n-hexane as mobile phase yielded 0.65 g (1.7 mmol / 81%) of **11** as a colorless highly viscous oil. $-C_8H_{24}SiSn_2$, 345.7 g/mol. $-{}^1HNMR$ (400.13 MHz, CDCl₃) δ : 0.171 (s, 6 H, Sn(CH₃)₂, ${}^2J_{Sn-H}$ = 25 Hz), 0.170 (s, 9H, Sn(CH₃)₃, ${}^2J_{Sn-H}$ = 26 Hz), 0.23 (s, 9 H, Si(CH₃)₃, ${}^3J_{Sn-H}$ = 24 Hz); ${}^{13}C$ { 1H } NMR (100.63 MHz, CDCl₃) δ : -5.4 (s, ${}^1J_{Sn-C}$ = 184/176 Hz, Sn(CH₃)₂), -9.4 (s, ${}^1J_{Sn-C}$ = 230/220 Hz, Sn(CH₃)₃), 1.5 (s, ${}^1J_{Sn-C}$ = 55/44 Hz, Si(CH₃)₃). -MS m/z (%):384 [M⁺, 5%], 369 [M⁺-Me], 311 [M⁺-SiMe₃ / 7], 223 [M⁺ -SnMe₃ / 20], 73 [SiMe₃ / 100].

l,1-Diisopropylhexamethyl-1-sila-2,3-distannapropane **13**

1.25 g (2.8 mmol) of **3** and 0.2 g (0.17 mmol) of Pd(PPh₃)₄ were dissolved in 5 ml of toluene. Adsorptive filtration of the crude product using *n*-hexane as mobile phase yielded 1.1 g (1.68 mmol) of a colorless highly viscous oil. The composition of the reaction mixture was determined by ²⁹Si and ¹¹⁹Sn NMR spectroscopy. The product mixture contains 80 - 85% of **13** and between 15 and 20% of starting material **3** which we were unable to separate.

1,1-diisopropylhexaphenyl-1-sila-2,3-distannapropane 14

1.2 g (1.47 mmol) of 7 and 0.15 g (0.13 mmol) of Pd(PPh₃)₄ were dissolved in 5 ml of toluene. Adsorptive filtration of the crude product using n-hexane as mobile phase yielded 1.05 g (1.3 mmol) of a colorless highly viscous oil. Crystallization from diethylether / hexane gave 0.8 g (0.98 mmol / 88%) of 14 as a colorless solid. – ¹³C {¹H} NMR (100.63 MHz, CDCl₃) δ : 14.2 (²*J*_C-*Sn* = 48 Hz, SiCH(CH₃)₂), 19.5 (³*J*_C-*Sn* = 18 Hz, SiCH(CH₃)₂), Ph₃Sn: 127.9 (*p*-Ph), 128.3 (*m*-Ph, ³*J*_{Sn-C} = 42 Hz), 137.5 (*o*-Ph, ²*J*_{Sn-C} = 38 Hz, ³*J*_{Sn-C} = 14 Hz), 140.3 (*i*-Ph, ¹*J*_{Sn-C} = 390/373 Hz, ²*J*_{Sn-C} = 43 Hz), Ph₂Sn: 127.8 (*p*-Ph), 128.45 (*m*-Ph, ³*J*_{Sn-C} = 42 Hz), 138.4 (*o*-Ph, ²*J*_{Sn-C} = 43 Hz, ³*J*_{Sn-C} = 15 Hz) 139.2 (*i*-Ph, ¹*J*_{Sn-C} = n.f. ²*J*_{SnSn-C} = 23 Hz), SiPh: 127.2 (*p*-Ph), 129.1 (*m*-Ph), 135.8 (*o*-Ph, ³*J*_{Sn-C} = 18 Hz), n.f. (*i*-Ph).

3.4. Reaction of 1 with alkynes

2.5 mmol of 1, 7.5 mmol of alkyne (15: phenylacetylene, 16: methylpropargylether) and 0.05 mmol of tetrakis(triphenylphosphine) palladium in a solution of 20-25 ml of toluene were stirred for 15 h at 60 °C. The resulting products were purified by filtration over dry silica gel, followed by removal of the solvent *in vacuo*. Yields: **15**: 1.17 g (57%), **16**: 0.33 g (30%).

Spectroscopic data

15: ¹H NMR (400.13 MHz, CDCl₃) δ: 0.18 (s, 9 H, Si(CH₃)₃), 0.185 (s, 9H, ²J_{Sn-H} = 49/47 Hz Sn(CH₃)₃), 0.27 (s, 6 H, ²J_{Sn-H} = 47/45 Hz, Sn(CH₃)₂), 6.55 (s, 1 H, ³J_{Sn-H} = 175/167 Hz, Me₂SnC=CH), 6.98 (m, 2 H, *Ph*), 7.14 (m, 1 H, Ph), 7.26 (m, 2 H, *Ph*); ¹³C {¹H} NMR (100.63 MHz, CDCl₃) δ: -9.4 (s, ¹J_{Sn-C} = 250/238 Hz, Sn(CH₃)₃), -6.5 (s, ¹J_{Sn-C} = 238/227 Hz, (CH₃)₂), 0.4 (s, S(CH₃)₃), 125.7 (s, Ph), 125.9 (s, *Ph*), 128.0 (s, Ph), 147.5 (s, ²J_{Sn-C} = 62 Hz, C=CSiMe₃), 151.7 (s, ²J_{Sn-C} = 52 Hz, i-C, *Ph*), 165.6 (s, ¹J_{Sn-C} = 340/326 Hz, Me₂SnC=C). - MS *m*/z (%): 486 [M⁺ / 5%], 471 [M⁺-Me / 59], 325 [M⁺-SnMe₃ / 79], 175 [M⁺-SnMe₂SnMe₃ / 44], 73 [SiMe₃ / 100]

16: ¹H NMR (400.13 MHz, CDCl₃) δ : 0.10 (s, 9 H, Si(CH₃)₃), 0.21 (s, 9 H, ²J_{Sn-H} = 49/47 Hz Sn(CH₃)₃), 0.31 (s, 6 H, ²J_{Sn-H} = 47/45 Hz, Sn(CH₃)₂), 3.27 (s, 3 H, CH₂OMe), 4.00 (s, 2H, ³J_{Sn-H} = 18 Hz, CH₂OMe), 6.56 (s, 1 H, ³J_{Sn-H} = 178/170 Hz, Me₂SnC=CH). - ¹³C {¹H} NMR (100.63 MHz, CDCl₃) δ : -9.4 (s, ¹J_{Sn-C} = 248/236 Hz, Sn(CH₃)₃), -8.0 (s, ¹J_{Sn-C} = 239/228 Hz, Sn(CH₃)₂), 0.2 (s, Si(CH₃)₃), 57.5 (s, CH₂OMe), 84.8 (s, ²J_{Sn-C} = 57 Hz, CH₂OMe), 143.5 (s, ²J_{Sn-C} = 55 Hz, C=CSiMe₃), 162.2 (s, ¹J_{Sn-C} = 340/325 Hz Me₂SnC=C). - GC-MS *m*/*z* (%): 441 [M⁺-Me / 100], 293 [M⁺-SnMe₃ / 97].

Crystallographic analysis: Crystals of 5 and 6 were removed from the Schlenk flask under a stream of N2 and immediately covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon). A suitable crystal was selected under the microscope, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream of the diffractometer [16]. The data sets for compounds 5 and 6 were collected using a Siemens SMART system at 86 K (custom built low-temperature device, Prof. H. Hope), complete with 3-circle goniometer and CCD detector operating at -54 °C. The data collections nominally covered a hemisphere of reciprocal space utilizing a combination of three sets of exposures, each with a different F angle, and each exposure covering 0.3° in ω . Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections; no decay was observed. An absorption correction was applied utilizing the program SADABS [17].

A crystal of 7 was sealed in a Lindemann-glass capillary. Data for compound 7 were acquired using a Nonius Kappa CCD at 291 K. The data collection covered almost the whole sphere of reciprocal space with 360 frames via ω -rotation ($\Delta/\omega = 1^\circ$) at two times 10 s for 7 per frame.

	5	6	7
Formula	$C_{22}H_{52}SiSn_2$	$C_{38}H_{36}SiSn_2$	$C_{42}H_{44}SiSn_2$
Fw	582.11	758.14	814.24
Space group	I2/a	C2/c	$P2_1$
a [Å]	18.9508(3)	18.4027(4)	9.276(1)
<i>b</i> [Å]	10.8160(1)	8.0742(2)	17.236(1)
<i>c</i> [Å]	28.5569(3)	24.0194(5)	12.727(1)
β [deg]	100.998(1)	108.115(1)	109.796(1)
$V [Å^3]$	5745.86(12)	3392.07(13)	1914.6(3)
Z	8	4	2
$d_{calc.} [g/cm^3]$	1.346	1.485	1.412
Lin. abs. coeff. $[mm^{-1}]$	1.784	1.532	1.362
T [K]	86	86	293(1)
2θ Range, [deg.]	2.9 - 50	3.6 - 56.7	5.2 - 56.5
Indep. refl.	5021	4126	8621
No. parameter	231	186	411
R1, wR2 (all data)	0.0644, 0.1054	0.0264, 0.0543	0.0458, 0.1025
R1, wR2 (> 2s)	0.0446, 0.0977	0.0217, 0.0515	0.0274, 0.0492

Table V. Summary of data collection, structure solution and refinement of compounds 5, 6 and 7.

 $R1 = ||F_{o}| - |F_{c}|| / |F_{o}|; wR2 = \Sigma \{(F_{o})^{2} - (F_{c})^{2}\}^{2} / w\{(F_{o})^{2}\}^{2}.$

In all cases graphite monochromated MoK α radiation $(\lambda = 0.71073 \text{ Å})$ was employed. The crystal structures of the compounds were solved by Direct Methods, as included in the SHELX program package [18] (5, 6) and SHELXS97 [19] (7). Missing atoms were located in subsequent difference Fourier maps and included in the refinement. The structures of all compounds were refined by full-matrix least-squares refinement on F² (SHELX-93 [20] (5, 6) and SHELX97 [21] (7)). Hydrogen atoms at the tin atoms in 5 and 6 were located in a difference map and included in the refinement using distance restraints and Uiso at 1.2 Ueq of the carrier tin atom. All other hydrogen atoms were placed geometrically and refined using a riding model, including free rotation about C-C bonds for methyl groups with Uiso constrained at 1.2 for non-methyl groups, 1.5 for methyl groups times U_{eq} of the carrier C atom for 5, 6 and a common U_{iso} for aryl (0.095(3) $Å^2$), alkyl (0.099(5) $Å^2$) for 7. Scattering factors were those provided with the SHELX program system. All non-hydrogen atoms were refined anisotropically. Disorder was handled by including split positions for the affected groups and included in the refinement of

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the respective occupancies. A set of restraints was applied to aid in modeling the disorder [18]. Further details about the refinements and how disorder was handled are outlined in the Supporting Information. Details of the data collections and refinements are given in Table V, selected bond lengths and angles are given in Table IV. Full details for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 132 617 for compound **5**, CCDC No. 132 618 for compound **6**, CCDC No. 133 131 for compound **7** and are also available in CIF format from the authors.

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