Monatshefte für Chemie 133, 931–943 (2002)

Monatshefte für Chemie
Chemical Monthly

Synthesis and Reactivity of Stannyloligosilanes IV [1]: From Hydrido Substituted Stannasilanes Towards Stannasiloxanes

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Summary. Hydrido substituted stannasilanes of the type $Z\text{-}SnR_2-Si(H)R'_2$ or $(R'_2Si(H))_2SnR_2$ ($Z=H$, Me, Ph; R, $R'=$ alkyl, Ph) are accessible by reaction of either alkali metal stannides ($MSn(Z)R_2$; $M=$ Li, Na) with halogen substituted silanes ($X\text{-}Si(H)R'_2$; $X=F$, Cl) or chlorostannanes (R_2SnCl_2, Ph_3SnCl) and fluorosilanes ($F-Si(H)R'_2$) in the presence of magnesium. Stannasilanes with halogen substituents at the silicon as well as the tin atom are formed by treatment of the hydrido substituted stannasilanes with $CHCl_3$ or CCl_4. The hydrido substituted stannasilanes decompose in contact with air to distannanes and siloxanes or to the linear ($^t Bu_2Sn(\text{–}O\text{–}{}^t Bu_2Si\text{–}OH)_2$) and cyclic ($(\text{–}{}^t Bu_2Sn\text{–}O\text{–}{}^i Pr_2Si\text{–}O\text{–})_2$) stannasiloxanes.

Keywords. Stannasilanes; Halogenation; Oxidation; X-Ray crystallography.

Introduction

Recently, our interest has been focused on the synthesis and the examination of compounds with tin–silicon bonds, especially in the context of open chain or cyclic precursors for polymeric materials. 1,*X*-difunctionalized stannasilanes of types **I**–**III** are possible starting materials for such Si–Sn containing polymers (**I**: $Z\text{-}SnR_2-(SiR'_2)_n-R_2Sn\text{-}Z$ ($Z=H$, Cl, Br; $R=$ Ph, ^{t}Bu; $R'=$ Me, ^{i}Pr, ^{t}Bu; $n=1$–6), **II**: $Z\text{-}SiR'_2\text{-}(SnR_2)_m-R'_2Si\text{-}Z$, **III**: $Z\text{-}(R_2Sn)_n-(SiR'_2)_m\text{-}Z$). To the best of our knowledge, only a small number of publications describe the preparation of type **I**–**III** compounds [2]. Recently, we have reported on the synthesis of type **I** stannasilanes with methyl [3] or sterically more demanding isopropyl and *tert*-butyl substituents [4] at the silicon atoms. Some earlier results with regard to silicon functionalized stannasilanes have been reported in this journal [5]. In continuation

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of this work, we here describe the synthesis of novel silicon functionalized compounds of type **II** as well as tin and silicon functionalized stannasilanes of type **III**. Furthermore, we report on the reactivity of the hydrido substituted stannasilanes towards oxygen.

Results and Discussion

Synthesis of hydrido substituted stannasilanes

The hydrido substituted stannasilanes were prepared according to synthetic pathways developed for the preparation of bis(stannyl)methylsilanes [3, 4]. Compounds **1**–**3**, **7**, and **8** were obtained by treatment of chlorosilanes with tri- or diorganylstannides (Eq. (1)).

$$R'_2\mathrm{Si(H)Cl} + M\mathrm{Sn}(Z)R_2 \xrightarrow{-M\mathrm{Cl}} \mathrm{H}-\mathrm{Si}R'_2-R_2\mathrm{Sn}\text{-}Z \tag{1}$$

	M	R'	R	Z
1 :	Li	Me	Me	Me
2 :	Na	^{i}Pr	Me	Me
3 :	Li	^{t}Bu	Me	Me
7 :	Li	^{i}Pr	^{t}Bu	H
8 :	Li	^{t}Bu	^{t}Bu	H

Compounds **4**–**6** are accessible by the reaction of mono- (Eq. (2)) and dichlorostannes (Scheme 1) with diisopropylchlorosilanes in the presence of magnesium. In contrast to the preparation of **4** which results in good yields, the preparations of **5** and **6** are accompanied by side reactions.

$$\begin{array}{c} {}^i\mathrm{Pr_2Si(H)F} + \mathrm{ClSnPh_3} + \mathrm{Mg} \xrightarrow{-\mathrm{Mg(F)Cl}} \mathrm{H}-\mathrm{Si}^i\mathrm{Pr_2}-\mathrm{SnPh_3} \\ \mathbf{4} \end{array} \tag{2}$$

$$\begin{array}{llll} R_2\mathrm{SnCl_2} + 2\mathrm{H}^i\mathrm{Pr_2SiF} \xrightarrow[-2\mathrm{Mg(F)Cl}]{+2\mathrm{Mg}} R_2\mathrm{Sn(Si}^i\mathrm{Pr_2H)_2} & + R_3\mathrm{SnSi}^i\mathrm{Pr_2H} & + (\mathrm{Si}^i\mathrm{Pr_2H})_2 & \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \mathbf{5} & \quad\mathbf{2} & & R=\mathrm{Me} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \mathbf{6} & \quad\mathbf{4} & & R=\mathrm{Ph} \end{array}$$

Scheme 1. Reactions of chlorostannanes with diisopropylfluorosilane in the presence of magnesium

The resulting crude products consist of a mixture of the desired disilylstannanes, in addition to tetraisopropyldisilane and the corresponding triorganostannasilanes. This result may be explained by an unexpected rearrangement induced by migration reactions. Methyl or phenyl group migration is frequently observed in tin chemistry [6]. We were unable to isolate pure compound **6** by distillation or recrystallization; in contrast, compounds **2** and **5** can be separated by vacuum distillation.

Halogenation of the hydrido substituted stannasilanes was carried out using known procedures [3, 4]. The Sn–H function can be chlorinated by treatment with chloroform (Eq. (3)), the Si–H function by exposure to CCl_4 (Eq. (4)).

$$\mathrm{H{-}Si}R'_2{-}{}^t\mathrm{Bu_2Sn{-}H} \xrightarrow[-\mathrm{CH_2Cl_2}]{+\mathrm{CHCl_3}} \mathrm{H{-}Si}R'_2{-}{}^t\mathrm{Bu_2Sn{-}Cl} \tag{3}$$

$$\begin{array}{ccc} \mathbf{7} & R' = {}^i\mathrm{Pr} & \mathbf{9} \\ \mathbf{8} & R' = {}^t\mathrm{Bu} & \mathbf{10} \end{array}$$

$$\mathrm{H{-}Si}R'_2{-}R_2\mathrm{Sn}\text{-}Z \xrightarrow[-\mathrm{CHCl_3}]{+\mathrm{CCl_4}} \mathrm{Cl{-}Si}R'_2{-}R_2\mathrm{Sn}\text{-}Z \tag{4}$$

$$\begin{array}{lrll} R = Z = \mathrm{Me} & \mathbf{2} & R' = {}^i\mathrm{Pr} & \mathbf{11} \\ R = Z = \mathrm{Ph} & \mathbf{4} & R' = {}^i\mathrm{Pr} & \mathbf{12} \\ R = \mathrm{Me},\ Z = {}^i\mathrm{Pr_2Si(H/Cl)} & \mathbf{5} & R' = \mathrm{Me} & \mathbf{13} \\ R = {}^t\mathrm{Bu},\ Z = \mathrm{Cl} & \mathbf{9} & R' = {}^i\mathrm{Pr} & \mathbf{14} \\ R = {}^t\mathrm{Bu},\ Z = \mathrm{Cl} & \mathbf{10} & R' = {}^t\mathrm{Bu} & \mathbf{15} \end{array}$$

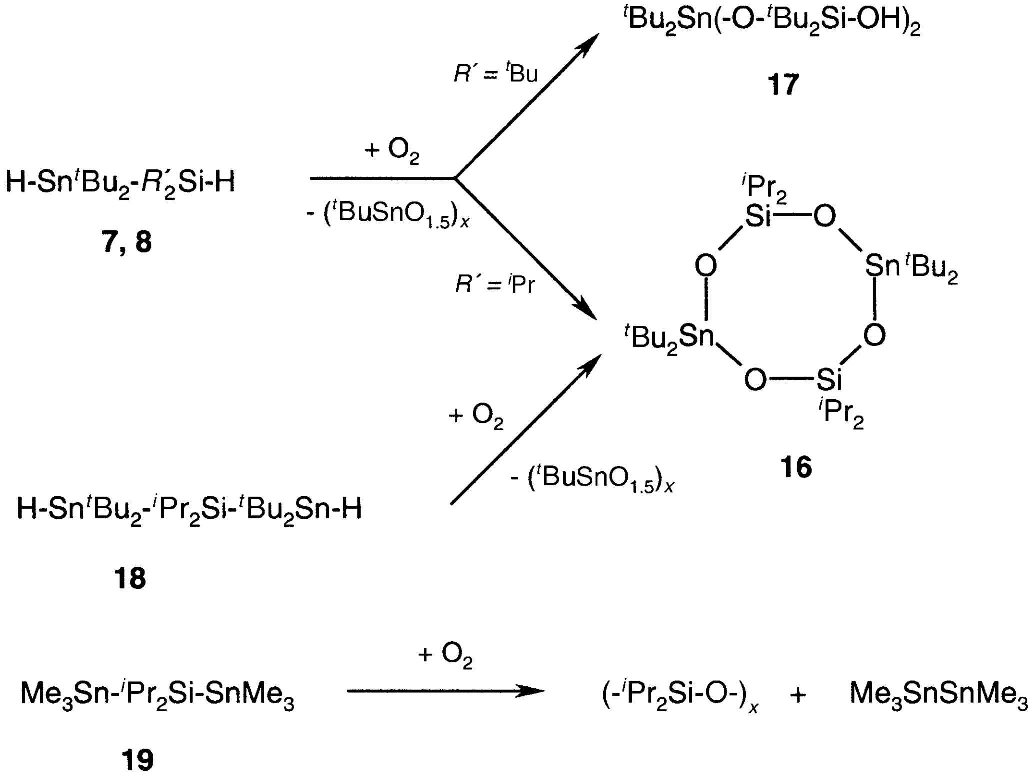
Special care and rigid control of the reaction temperature is required for the halogenation of the hydrido–tin function, since higher temperatures result in Si–Sn bond cleavage and subsequent formation of chlorosilanes and -stannanes.

Reactivity of hydrido substituted stannasilanes towards oxygen

The high reactivity of the dihydrido derivatives $\mathrm{H{-}Si}R'_2{-}{}^t\mathrm{Bu_2Sn{-}H}$ (**7**: $R' = {}^i\mathrm{Pr}$; **8**: $R' = {}^t\mathrm{Bu}$) is also recognizable in reactions towards oxygen. So far, all examined oxidation reactions of stannasilanes resulted in the formation of di- or polystannanes and siloxanes [2]. In contrast, compounds **7** and **8** gave different products. Oxidation of **7** yielded the cyclic eight-membered stannasiloxane **16**, oxidation of **8** the linear stannasiloxane **17** (Scheme 2). This divergent behaviour of **7** and **8** may be explained by the sterical demand of the substituents at the silicon atoms. The synthesis of **17** *via* an alternative pathway has recently been reported by *Jurkschat* and coworkers [7].

Surprisingly, the reaction of the bis(hydridodi-*tert*-butylstannyl)diisopropylsilane **18** [4] with oxygen also results in the formation of the eight-membered ring **16**. The expected polystannanes $({}^t\mathrm{Bu_2Sn})_x$ and oligomeric or polymeric silicones were not observed. In contrast, oxidation of $\mathrm{Me_3Sn{-}{}^iPr_2Si{-}SnMe_3}$ (**19**) results in the formation of siloxanes and hexamethyldistannane [4]. Although there is only little experimental evidence to explain these different chemical behaviour, experiments clearly show that the sterically more demanding ^{t}butyl or ^{i}propyl groups are essential on both the silicon and the tin atoms to afford Sn–O–Si derivatives. Byproducts in all three cases are identified as colorless solids with an elemental composition of $({}^t\mathrm{BuSnO_{3/2}})_n$ which are completely insoluble in common organic solvents such as *n*-alkanes, ethers, alcohols, or toluene. The solids display ^{119}Sn MAS NMR signals at -346.4 and -495.9 ppm. However, the nature of these byproducts is unknown until now.

^{119}Sn and ^{29}Si NMR data of compounds **1**–**15** are summarized in Table 1. Recent observations indicated that the ^1J(Sn–Si) coupling constants decrease if



Scheme 2. Reactions of **7** and **8** with oxygen

Table 1. ^{119}Sn and ^{29}Si NMR data of compounds **1–15** (Z'-R_2Sn–SiR'_2-Z); chemical shifts are given in ppm, coupling constants in Hz

	Z'	R	R'	Z	δ(^{119}Sn)	δ^{29}Si	^1J(Si–$^{119/117}$Sn)
1	Me	Me	Me	H	– 119.6	– 36.4	621/649
2	Me	Me	^{i}Pr	H	– 127.9	– 2.4	576/551
3	Me	Me	^{t}Bu	H	– 127.0	9.2	552/578
4	Ph	Ph	^{i}Pr	H	– 167.7	– 2.3	572/547
5	^{i}Pr$_2$Si(H)	Me	^{i}Pr	H	– 289.0	– 1.3	453/433
6[a]	^{i}Pr$_2$Si(H)	Ph	^{i}Pr	H	– 265.3	– 10.6	443/425
7	H	^{t}Bu	^{i}Pr	H	– 128.9[b]	– 0.3	406/389
8	H	^{t}Bu	^{t}Bu	H	– 113.6[c]	14.0	394/376
9	Cl	^{t}Bu	^{i}Pr	H	98.4	1.8	321/307
10	Cl	^{t}Bu	^{t}Bu	H	80.2	15.9	313/300
11	Me	Me	^{i}Pr	Cl	– 127.7	41.0	640/611
12	Ph	Ph	^{i}Pr	Cl	– 193.9	42.6	649/620
13	^{i}Pr$_2$Si(Cl)	Me	^{i}Pr	Cl	– 275.4	43.3	503/481
14	Cl	^{t}Bu	^{i}Pr	Cl	48.0	46.3	335/320
15	Cl	^{t}Bu	^{t}Bu	Cl	66.7	43.9	373/358

[a] Only determined NMR spectroscopically; [b] ^1J(Sn–H) = 1288 Hz; [c] ^1J(Sn–H) = 1260 Hz

H–Sn–Si ⇒ Cl–Sn–Si
Decreasing ^1J(Sn–Si)
7, 8 **9, 10**
Sn–Si–H ⇒ Sn–Si–Cl
Increasing ^1J(Sn–Si)
5, 9, 10 **13, 14, 15**

Scheme 3. Trends of ^1J(Sn–Si) in stannasilanes

the hydrido atom at the tin center is replaced by chlorine [3]. An identical trend is observed for the couples **7**/**9** and **8**/**10**. Due to the different bonding situation in compounds of type **B** and **C**, ^1J(Sn–Si) increases if a hydrogen atom at the silicon center is replaced by chlorine (Scheme 3, Table 1).

X-Ray quality crystals of **16** were obtained by crystallization from diethyl ether. Compound **16** crystallizes with 1.5 independent molecules in the asymmetric unit. The molecules display a slightly different geometry caused by packing effects, since the *E*-O-*E* linkages (*E* = Si, Sn) are rather flexible, and different orientation of the ^{i}propyl and ^{t}butyl substituents. One molecule, depicted in Fig. 1, possesses a center of symmetry. Unit cell data, refinement details, and selected interatomic details are summarized in Tables 2 and 3. The compound displays an eight-membered ring comprised of two silicon, two tin, and four oxygen atoms. Both tin and silicon centers are four coordinate with two *E*-C and two *E*-O contacts. The Sn–O bond lengths are between 1.949(2) and 1.958(2) Å; the Sn–C distances range from 2.161(3) to 2.175(3) Å, the Si–C contacts from 1.881(3) to 1.889(3) Å, and the Si–O contacts from 1.611(2) to 1.621(2) Å. The tin and silicon atoms display an approximate tetrahedral geometry with carbon–tin–carbon angles of 128.0(1)° and carbon–silicon–carbon angles of 116.0(1)°. Distortions from ideal geometry

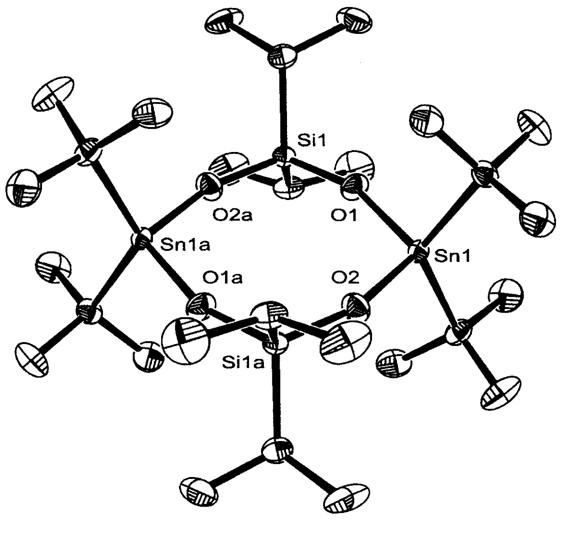


Fig. 1. Molecular structure of one molecule of **16** showing 30% probability ellipsoids (ORTEP 3)

Table 2. Crystal data and structure refinement for **16**

Formula	$C_{28}H_{64}O_2Si_2Sn_2$
Molecular weight/g · mol^{-1}	758.35
Crystal system	triclinic
Crystal size/mm	0.40 × 0.35 × 0.10
Space group	P-1
a/Å	11.1271(7)
b/Å	11.2886(7)
c/Å	24.832(1)
α/°	91.740(1)
β/°	102.556(1)
γ/°	111.450(1)
V/Å^3	2812.9(3)
Z	3
ρ_{calcd}/Mg · m^{-3}	1.343
μ/mm^{-1}	1.422
F(000)	1176
θ range/°	1.69 to 28.37
Index ranges	$-14 \leq h \leq 14$ $-13 \leq k \leq 15$ $-31 \leq l \leq 32$
No. of reflections collected	18723
No. of indep reflections/R_{int}	12894/0.0215
No. of reflections with $I > 2\sigma(I)$	11440
No. of refined parameters	488
$GooF$ (F^2)	1.078
R_1 (F) ($I > 2\sigma(I)$)	0.0327
wR_2 (F^2) (all data)	0.0824
$(\Delta/\sigma)_{\max}$	0.001
Largest diff. peak/hole/e · Å^{-3}	0.906/−1.065

are due to the different steric demands of the ligands. The Si–O–Sn, O–Si–O, and O–Sn–O bond angles range from 105.3(1) to 167.3(2)° and are similar to those known for related eight-membered stannasiloxane rings [7].

Puff and *Schuh* classified eight-membered rings comprising silicon, germanium, oxygen, and nitrogen atoms in the ring skeleton into eight conformation types [8]. Additional conformation types of stannasiloxane types have been reported recently by *Jurkschat* and coworkers [7]. According to this classification, compound **16** displays a D-type conformation with one tin atom above and one below the ring plain.

Experimental

General

All reactions were carried out under an atmosphere of inert gas (N_2 or Ar) using modified *Schlenk* techniques. All solvents used were dried by standard methods and freshly distilled prior to use. The di-*tert*-butyltindihydride was prepared according to a published procedure [9]. All other reagents were

Table 3. Selected bond length (Å) and angles (°) for the two independent molecules of **16** (**16**, **16′**)

16		**16′**	
Sn(1)–O(1)	1.954(2)	Sn(2)–O(3)	1.954(2)
Sn(1)–O(2)	1.954(2)	Sn(2)–O(6)	1.058(2)
Sn(1)–C(1)	2.161(3)	Sn(2)–C(15)	2.163(3)
Sn(1)–C(5)	2.170(3)	Sn(2)–C(19)	2.164(3)
Si(1)–O(1)	1.616(2)	Si(2)–O(3)	1.621(2)
Sia(1)–O(2)	1.611(2)	Si(2)–O(4)	1.614(2)
Si(1)–C(9)	1.881(3)	Si(2)–C(26)	1.884(3)
Si(1)–C(12)	1.881(3)	Si(2)–C(23)	1.886(3)
		Sn(3)–O(4)	1.949(2)
		Sn(3)–O(5)	1.953(2)
		Si(3)–O(5)	1.620(2)
		Si(3)–O(6)	1.618(2)
O(1)–Sn(1)–O(2)	108.5(1)	O(6)–Sn(2)–O(3)	106.7(1)
O(1)–Sn(1)–C(1)	103.7(1)	O(6)–Sn(2)–C(15)	107.5(1)
O(2)–Sn(1)–C(1)	103.3(1)	O(6)–Sn(2)–C(19)	109.2(1)
O(1)–Sn(1)–C(5)	107.1(1)	O(3)–Sn(2)–C(15)	105.0(1)
O(2)–Sn(1)–C(5)	105.3(1)	O(3)–Sn(2)–C(19)	105.4(1)
C(1)–Sn(1)–C(5)	128.0(1)	C(15)–Sn(2)–C(19)	122.0(1)
O(1)–Si(1)–O(2)	113.2(1)	O(4)–Si(2)–O(3)	113.2(1)
O(1)–Si(1)–C(9)	107.1(1)	O(4)–Si(2)–C(26)	106.2(1)
O(1)–Si(1)–C(12)	107.8(1)	O(4)–Si(2)–C(23)	107.6(1)
O(2)–Si(1)–C(9)	106.9(1)	O(3)–Si(2)–C(26)	108.8(1)
O(2)–Si(1)–C(12)	106.1(1)	O(3)–Si(2)–C(23)	108.1(1)
C(9)–Si(1)–C(12)	116.0(1)	C(26)–Si(2)–C(23)	113.1(1)
Si(1)–O(1)–Sn(1)	159.7(2)	Si(2)–O(3)–Sn(2)	149.1(1)
		Si(2)–O(4)–Sn(3)	167.3(2)
		Si(3)–O(5)–Sn(3)	152.3(2)
		Si(3)–O(6)–Sn(2)	159.7(2)

obtained commercially. ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were recorded using a Bruker DPX 400 (solvents: $CDCl_3$ or C_6D_6, internal reference: Me_4Si or Me_4Sn) or a Bruker DRX 300 spectrometer (solvents: hexane or *THF* with D_2O capillary). Mass spectra were recorded using a MAT 8200 instrument. Elemental analyses were performed on a LECO-CHNS-932 analyzer; the results agreed with the calculated values within experimental errors. No satisfactory analyses could be obtained for **1** and **10**–**15**. Crystallographic data of **16** have been deposited at the cambridge Crystallographic Data Centre, CCDC No. 171732. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (Fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk, www: http://ccdc.cam.ac.uk).

General procedure for the preparation of **1**–**3**

In a 100 cm^3 *Schlenk* tube a solution of 5 mmol freshly prepared sodium trimethylstannide was added slowly to a cooled solution (−40°C) of chlorodiisopropylsilane dissolved in 20 cm^3 of *THF*. The mixture was stirred for 3 h at −40°C and then slowly warmed to room temperature. After evaporation of the volatiles *in vacuo* the residue was extracted twice with 80 cm^3 of ether:hexane = 80:20. The extracts were filtered (G3) to remove the sodium salts. The solvents were removed *in vacuo*, and the crude product was purified by distillation.

Trimethylstannyldimethylsilan (**1**; $C_5H_{16}SiS_4$)

Starting material: 4.7 g (50 mmol) ^{t}Bu$_2$Si(H)Cl, 50 mmol Me_3SnLi; yield: 4.41 g (20 mmol, 40%); b.p.: 58–60°C/85 torr; ^{1}H NMR (400.15 MHz, C_6D_6): $\delta = 0.10$ (s, 9H, $(CH_3)_3Sn$–), 0.29 (d, 6H, –$Si(CH_3)_2$–), 4.08 (m, 1H, –$SiMe_2$–H) ppm; ^{13}C NMR (100.63 MHz, C_6D_6): $\delta = 0.03$ ppm (s, 2C, –$SiMe_2$–H, $^1J(^3C{-}^{29}Si) = 40$ Hz), -7.35 (s, 3C, Me_3Sn–, $^1J^{13}C{-}^{119/117}Sn) = 259/248$ Hz) ppm.

Trimethylstannyldiisopropylsilan (**2**; $C_9H_{24}SiSn$)

Starting material: 1.3 g (10 mmol) ^{i}Pr$_2$Si(H)F, 10 mmol $NaSnMe_3$; yield: 1.7 g (63%); b.p.: 65–70°C (7 mbar); ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 0.15$ (s, 9H, $Sn(CH_3)_3$, $^2J(^1H{-}^{119/117}Sn) = 47$ Hz), 1.05 (d, 12H, $SiCH(C\mathit{H}_3)_2$, $^3J(^1H{-}^1H) = 7$ Hz), 1.25 (m, 2H, $SiC\mathit{H}(CH_3)_2$, $^3J(^1H{-}^1H) = 7$ Hz), 3.75 (m, 1H, SiH, $^1J(^1H{-}^{29}Si) = 174$ Hz, $^2J(^1H{-}^{119/117}Sn) = 94/90$ Hz, $^3J(^1H{-}^1H) = 3$ Hz) ppm; ^{13}C NMR (100.63 MHz, C_6D_6): $\delta = -9.8$ (s, Sn–C, $^1J(^{13}C{-}^{119/117}Sn) = 256/245$ Hz), 12.1 (s, $Si\mathit{C}H(CH_3)_2$, $^1J(^{13}C{-}^{29}Si) = 47$ Hz, $^2J(^{13}C{-}^{119/117}Sn) = 33$ Hz), 20.5 (s, $SiCH(\mathit{C}H_3)_2$, $^3J(^{13}C{-}^{119/117}Sn) = 11$ Hz), 20.7 (s, $SiCH(\mathit{C}H_3)_2$, $^3J(^{13}C{-}^{119/117}Sn) = 16$ Hz) ppm; MS (EI): m/z (%) = 278 (3) [M^+], 265 (33) [$M^+ - Me$], 163 (25) [$SnMe_3^+$], 130 (100) [$SiMe^iPr_2^+$], 101 (23) [$SiMe_2^iPr^+$], 73 (83) [$SiMe_3^+$], 43 (21) [$^iPr^+$].

Trimethylstannyldi-tert-butylsilan (**3**; $C_{11}H_{28}SiSn$)

Starting material: 2.3 g (12.8 mmol) ^{t}Bu$_2$Si(H)Cl, 12.8 mmol Me_3SnLi; yield: 2.3 g (7.68 mmol, 60%); b.p.: 84°C/5 torr; ^{1}H NMR (400.15 MHz, C_6D_6): $\delta = 0.36$ (s, 9H, $(CH_3)_3Sn$–), 1.15 (s, 18H, –$Si(C(CH_3)_3)_2$), 4.07 (s, 1H, –Si^tBu_2–H) ppm; ^{13}C NMR (100.63 MHz, C_6D_6): $\delta = -8.86$ (s, 3C, Me_3Sn–, $^1J(^{13}C{-}^{119/117}Sn) = 255/243$ Hz), 20.9 (s, 2C, –$Si(\mathit{C}(CH_3)_3)_2$–H, $^1J(^{13}C{-}^{29}Si) = 47$ Hz, $^2J(^{13}C{-}^{119/117}Sn) = 35/33$ Hz), 30.1 (s, 6C, –$Si(C(\mathit{C}H_3)_3)_2$–H, $^1J(^{13}C{-}^{119/117}Sn) = 13$ Hz) ppm.

General procedure for the preparation of **4–6**

In a 100 cm^3 *Schlenk* tube, chlorodiisopropylsilane and the adequate amount of chlorostannane were dissolved in 80 cm^3 of *THF*, and Mg turnings were added. The reaction mixture was stirred at room temperature for approximately 120 h. After evaporation of the *THF*, the oily residue was extracted twice with 80 cm^3 of ether:hexane = 80:20. The extracts were filtered (G3) to remove magnesium salts. The products were obtained after evaporation of the solvents *in vacuo* as colourless oils.

Triphenylstannyldiisopropylsilane (**4**; $C_{24}H_{30}SiSn$)

Starting material: 0.66 g (5 mmol) ^{i}Pr$_2$Si(H)F, 1.9 g (5 mmol) Ph_3SnCl, 80 cm^3 *THF*, 0.35 g (15 mmol) Mg; yield: 2.2 g (95%); colourless oil; ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 1.16$ (d, 6H, $CH(C\mathit{H}_3)_2$), 1.18 (d, 6H, $CH(C\mathit{H}_3)_2$), 1.42 (m, 2H, $C\mathit{H}(CH_3)_2$), 4.56 (s, 1H, SiH, $^2J(^1H{-}^{119/117}Sn) = 95/90$ Hz), 7.26–7.32 (m, 9H, *m*-Ph, *p*-Ph), 7.80 (m, 6H, *o*-Ph, $^3J(^1H{-}^{119/117}Sn) = 44$ Hz) ppm; ^{13}C NMR (100.63 MHz, C_6D_6) $\delta = 12.5$ (SiCH, $^2J(^{13}C{-}^{119/117}Sn) = 38$ Hz, $^1J(^{13}C{-}^{29}Si) = 48$ Hz), 20.7 ($SiCH(\mathit{C}H_3)_2$, $^3J(^{13}C{-}^{119/117}Sn) = 15$ Hz), 20.9 ($SiCH(\mathit{C}H_3)_2$, $^3J(^{13}C{-}^{119/117}Sn) = 15$ Hz), 128.7 (*p*-Ph), 128.9 (*m*-Ph, $^3J(^{13}C{-}^{119/117}Sn) = 56/54$ Hz), 137.8 (*o*-Ph, $^2J(^{13}C{-}^{119/117}Sn) = 37$ Hz), 140.5 ($Sn(CH_3)_3$, $^1J(^{13}C{-}^{119/117}Sn) = 390/373$ Hz) ppm; MS (EI): m/z (%) = 466 (10) [M^+], 351 (48) [Ph_3Sn^+], 274 (100) [Ph_2Sn^+], 197 (86) [$PhSn^+$], 183 (16) [$SiPh_2H^+$], 165 (21) [$Si^iPrPhMe^+$], 149 (30) [Si^iPrPhH^+], 121 (56) [$SiPhMeH^+$], 107 (20) [$SiPhH_2^+$], 73 (14) [$SiMe_3^+$], 59 (46) [$SiMe_2H^+$], 43 (33) [$^iPr^+$] ppm.

Bis(diisopropylsilyl)dimethylstannane (**5**; $C_{14}H_{36}Si_2Sn$)

Starting material: 5.4 g (40 mmol) $^{i}Pr_2Si(H)F$, 4.4 g (20 mmol) Me_2SnCl_2, 80 cm^3 *THF*, 2 g (80 mmol) Mg; yield: 2.1 g (28%); colourless oil; b.p.: 65–70°C (0.05 mmHg); ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 0.36$ (s, 6H, $Sn(CH_3)_2$, $^2J(^1H–^{119/117}Sn) = 43$ Hz), 1.01 (d, 12H, $SiCH(CH_3)_2$, $^3J(^1H–^1H) = 7$ Hz), 1.03 (d, 12H, $SiCH(CH_3)_2$, $^3J(^1H–^1H) = 7$ Hz), 1.15 (m, 4H, $SiCH(CH_3)_2$, $^3J(^1H–^1H) = 7$ Hz), 3.78 (m, 2H, SiH, $^1J(^1H–^{29}Si) = 174$ Hz, $^2J(^1H–^{119/117}Sn) = 95/90$ Hz, $^3J(^1H–^1H) = 3$ Hz) ppm; ^{13}C NMR (100.63 MHz, C_6D_6): $\delta = -12.7$ (s, $Sn(CH_3)_2$, $^1J(^{13}C–^{119/117}Sn) = 200/192$ Hz), 12.9 (s, $SiCH(CH_3)_2$, $^1J(^{13}C–^{29}Si) = 46$ Hz, $^2J(^{13}C–^{119/117}Sn) = 28$ Hz), 20.9 (s, $SiCH(CH_3)_2$, $^3J(^{13}C–^{119/117}Sn) = 9$ Hz), 20.8 (s, $SiCH(CH_3)_2$, $^3J(^{13}C–^{119/117}Sn) = 14$ Hz) ppm; MS (EI); m/z (%) = 380 (10) [M^+], 365 (9) [M^+ – Me], 264 (25) [M^+ – Si^iPr_2H], 249 (29) [M^+ – Si^iPr_2H – Me], 235 (27) [M^+ – Si^iPr_2H – 2Me], 207 (30) [M^+ – Si^iPr_2H – Me – Pr], 193 (32) [M^+ – Si^iPr_2H – 2Me – Pr], 163 (17) [$SnMe_3^+$], 151 (9) [$SnMe_2H^+$], 133 (24) [$SnMe^+$], 129 (45) [$Si^iPr_2Me^+$], 101 (12) [$Si^iPrMe_2^+$], 87 (31) [Si^iPrMeH^+], 73 (51) [$SiMe_3^+$], 59 (100) [$SiMe_2H^+$].

Bis(diisopropylsilyl)diphenylstannane (**6**; $C_{24}H_{40}Si_2S_4$)

Starting material: 1.34 g (10 mmol) $^{i}Pr_2Si(H)F$, 1.7 g (5 mmol) Ph_2SnCl_2, 80 cm^3 *THF*, 0.4 g (18 mmol) Mg; yield: 2.4 g; colorless oil; ^{29}Si NMR (59.6 MHz, D_2O-cap./Et_2O): $\delta = -2.3$ (**4**), -10.6 (s, $^1J(^{29}Si–^{119/117}Sn) = 443/425$ Hz) ppm; ^{119}Sn NMR (111.92 MHz, D_2O-cap./Et_2O): $\delta = -167.7$ (**4**, 45%), -265.3 (s, $^1J(^{119}Sn–^{29}Si) = 443$ Hz, 55%) ppm; the conversion rate was determined by ^{119}Sn NMR spectroscopy.

General procedure for the preparation of **7** *and* **8**

Freshly prepared lithium diisopropylamide (*LDA*, 5 mmol) was added dropwise to a cooled (–65°C) solution of di-*tert*-butyltindihydride (1.2 g, 5 mmol) in 50 cm^3 of hexane and 50 cm^3 of *THF*. The reaction mixture was slowly warmed to –50°C, and chlorosilane (5 mmol) was added. After warming the reaction mixture to –30°C, 25 cm^3 of petrol ether (30–60°C) were added, and stirring was continued for 1 h at –10°C. The mixture was hydrolyzed by addition of 20 cm^3 H_2O. The organic layer was separated and dried over $CaCl_3$. After removal of the drying agent the solvents were evaporated. The desired products remain as colourless oils.

Di-tert-butylstannyldiisopropylsilane (**7**; $C_{14}H_{34}SiSn$)

Starting material: 7.5 mmol *LDA*, 1.76 g (7.5 mmol) $^tBu_2SnH_2$, 1.13 g (7.5 mmol) $^iPr_2Si(H)Cl$; yield: 2.41 g (92%); ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 1.12$ (d, 6H, $SiCH(CH_3)_2$, $^3J(^1H–^1H) = 5$ Hz), 1.14 (d, 6H, $SiCH(CH_3)_2$, $^3J(^1H–^1H) = 5$ Hz), 1.26 (m, 2H, $SiCH(CH_3)_2$, $^3J(^1H–^1H) = 5$ Hz), 1.36 (s, 18H, $Sn(C(CH_3)_3)_2H$, $^3J(^1H–^{119/117}Sn) = 62/60$ Hz), 4.06 (s, 1H, $SiCH(CH_3)_2H$, $^2J(^1H–^{119/117}Sn) = 78/75$ Hz), 4.92 (s, 1H, $Sn(C(CH_3)_3)_2H$, $^1J(^1H–^{119/117}Sn) = 1228/1231$ Hz) ppm; ^{13}C NMR (100.63 MHz, C_6D_6): $\delta = 12.1$ ($SiCH(CH_3)_2$, $^1J(^{13}C–^{29}Si) = 47$ Hz, $^2J(^{13}C–^{119/117}Sn) = 27$ Hz), 20.7 ($SiCH(CH_3)_2$, $^3J(^{13}C–^{119/117}Sn) = 13$ Hz), 21.0 ($SiCH(CH_3)_2$), 27.2 ($Sn(C(CH_3)_3)_2$, $^1J(^{13}C–^{119/117}Sn) = 326/312$ Hz), 33.5 ($Sn(C(CH_3)_3)_2$) ppm; IR (nujol): $\tilde{\nu}$ (Sn–H) = 1769 cm^{-1}; MS (EI): m/z (%) = 349 (3) [M^+], 293 (19) [M^+ – ^tBu], 235 (47) [M^+ – 2^tBu], 177 (100) [$^tBuSn^+$], 173 (47) [$^tBu^iPr_2Si^+$], 57 (88) [$^tBu^+$].

Di-tert-butylstannyldi-tert-butylsilane (**8**; $C_{16}H_{38}SiS_4$)

Starting material: 10 mmol *LDA*, 2.35 g (10 mmol) $^tBu_2SnH_2$, 1.79 g (10 mmol) $^tBu_2Si(H)Cl$; yield: 2.62 g (70%); ^{1}H NMR (400.13 MHz, C_6D_6): $\delta = 1.25$ (s, 18H, $Si(C(CH_3)_3)_2H$), 1.42 (s, 18H, $Sn(C(CH_3)_3)_2H$, $^3J(^1H–^{119/117}Sn) = 62/59$ Hz), 4.15 (s, 1H, $Si(C(CH_3)_3)_2H$, $^2J(^1H–^{119/117}Sn) = 66/63$ Hz), 5.06 (s, 1H,

$Sn(C(CH_3)_3)_2\mathit{H}$, $^1J(^1H–^{119/117}Sn) = 1260/1204$ Hz) ppm; ^{13}C NMR (100.63 MHz, C_6D_6): $\delta = 20.9$ ($Si(\mathit{C}(CH_3)_3)_2H$, $^2J(^{13}C–^{119/117}Sn) = 27$ Hz), 27.8 ($Sn(\mathit{C}(CH_3)_3)_2$, $^1J(^{13}C–^{119/117}Sn) = 320/306$ Hz), 31.1 ($Si(C(\mathit{C}H_3)_3)_2$), 33.9 ($Sn(C(\mathit{C}H_3)_3)_2$) ppm; IR (nujol): $\tilde{\nu}$ (Sn–H) = 1767 cm^{-1}; MS (EI): m/z (%) = 377 (2) [M^+], 321 (33) [M^+ – ^{t}Bu], 262 (22) [M^+ – 2^{t}Bu], 234 (23) [$H^tBu_2Sn^+$], 177 (100) [$^tBuSn^+$], 120 (13) [HSn^+], 73 (52) [Me_3Si^+], 57 (29) [$^tBu^+$].

General procedure for the preparation of **9** *and* **10**

5 mmol of the hydridostannasilane was dissolved in 15 cm^3 hexane. 1 cm^3 $CHCl_3$ was added slowly to the cooled solution (0°C). The reaction mixture was stirred for 30 min at 0°C and then slowly warmed to room temperature. After evaporation of the volatiles *in vacuo* the desired products remained as colourless oils.

Di-tert-butylchlorostannyldiisopropylsilane (**9**; $C_{14}H_{33}ClSiSn$)

Starting material: 1.62 g (4.7 mmol) **7**, 1 cm^3 $CHCl_3$; yield: 1.80 g (98%); ^1H NMR (400.13 MHz, C_6D_6): $\delta = 1.15$ (d, 12H, $SiCH(C\mathit{H}_3)_2$, $^3J(^1H–^1H) = 8$ Hz), 1.29 (s, 18H, $Sn(C(C\mathit{H}_3)_3)_2$, $^3J(^1H–^{119/117}Sn) = 75/72$ Hz), 1.39 (m, 2H, $SiC\mathit{H}(CH_3)_2$, $^3J(^1H–^1H) = 8$ Hz), 4.10 (s, 1H, $SiCH(CH_3)_2\mathit{H}$, $^2J(^1H–^{29}Si) = 181$ Hz, $^2J(^1H–^{119/117}Sn) = 97/93$ Hz) ppm; ^{13}C NMR (100.63 MHz, C_6D_6): $\delta = 12.4$ ($Si\mathit{C}H(CH_3)_2$, $^1J(^{13}C–^{29}Si) = 48$ Hz, $^2J(^{13}C–^{119/117}Sn) = 33$ Hz), 20.2 ($SiCH(\mathit{C}H_3)_2$, $^3J(^{13}C–^{119/117}Sn) = 14$ Hz), 20.8 ($SiCH(\mathit{C}H_3)_2$, $^3J(^{13}C–^{119/117}Sn) = 12$ Hz), 30.5 ($Sn(C(\mathit{C}H_3)_3)_2$), 34.8 ($Sn(\mathit{C}(CH_3)_3)_2$, $^1J(^{13}C–^{119/117}Sn) = 279/266$ Hz) ppm; MS (EI): m/z (%) = 383 (1) [M^+], 349 (45) [M^+ – Cl], 327 (7) [M^+ – ^{t}Bu], 271 (15) [$^tBu_2SnCl^+$], 233 (31) [$^tBu_2Sn^+$], 177 (30) [$^tBuSn^+$], 73 (11) [Me_3Si^+], 57 (100) [$^tBu^+$].

Di-tert-butylchlorostannyldi-tert-butylsilane (**10**; $C_{16}H_{37}ClSiS_4$)

Starting material: 0.73 g (1.94 mmol) **8**, 15 cm^3 *n*-hexane, 1 cm^3 $CHCl_3$; yield: 0.78 g (98%); ^1H NMR (400.13 MHz, C_6D_6): $\delta = 1.18$ (s, 18H, $SiC(C\mathit{H}_3)_3$), 1.33 (s, 18H, $Sn(C(C\mathit{H}_3)_3)_2Cl$, $^3J(^1H–^{119/117}Sn) = 74/71$ Hz), 4.14 (s, 1H, $SiC(CH_3)_3\mathit{H}$, $^2J(^1H–^{29}Si) = 180$ Hz, $^2J(^1H–^{119/117}Sn) = 82/79$ Hz) ppm; ^{13}C NMR (100.63 MHz, C_6D_6): $\delta = 21.30$ ($Si\mathit{C}(CH_3)_3$, $^1J(^{13}C–^{29}Si) = 48$ Hz, $^2J(^{13}C–^{119/117}Sn) = 34$ Hz), 30.42 ($SiC(\mathit{C}H_3)_3$, $^3J(^{13}C–^{119/117}Sn) = 12$ Hz), 30.84 ($Sn(C(\mathit{C}H_3)_3)_2$), 35.51 ($Sn(\mathit{C}(CH_3)_3)_2$, $^1J(^{13}C–^{119/117}Sn) = 274/262$ Hz) ppm; MS (EI): m/z (%) = 412 (1) [M^+], 371 (4) [M^+ – Cl], 355 (22) [M^+ – ^{t}Bu], 315 (11) [M^+ – ^{t}Bu – Cl], 299 (46) [M^+ – 2^{t}Bu], 177 (41) [$^tBuSn^+$], 155 (23) [$ClSn^+$], 73 (100) [Me_3Si^+], 57 (96) [$^tBu^+$].

General procedure for the preparation of **11**–**15**

5 mmol of the stannylhydridosilane are dissolved in 25 cm^3 CCl_4. The reaction mixture was stirred at elevated temperature (45–70°C) for 72 h. After evaporation of the CCl_4 the residue was extracted with 30 cm^3 of hexane and filtered. After removing the volatiles *in vacuo* the desired products remain as colourless oils.

Trimethylstannyldiisopropylchlorosilane (**11**; $C_9H_{24}ClSiS_4$)

Starting material: 1.16 g (4.2 mmol) **2**, 30 cm^3 CCl_4; 50°C; yield: 1 g (76%); ^1H NMR (400.13 MHz, C_6D_6): $\delta = 0.23$ (s, 9H, $Sn(CH_3)_3$, $^2J(^1H–^{119/117}Sn) = 50$ Hz), 1.09 (d, 6H, $SiCH(C\mathit{H}_3)_2$, $^3J(^1H–^1H) = 7$ Hz), 1.17 (d, 6H, $SiCH(C\mathit{H}_3)_2$, $^3J(^1H–^1H) = 7$ Hz), 1.45 (m, 2H, $SiC\mathit{H}(CH_3)_2$, $^3J(^1H–^1H) = 7$ Hz) ppm; ^{13}C NMR (100.63 MHz, C_6D_6): $\delta = -10.2$ ($Sn(CH_3)_3$, $^1J(^{13}C–^{119/117}Sn) = 275/261$ Hz), 17.2 (Si*C*H(CH$_3$)$_2$, $^{1}J(^{13}\mathrm{C}{-}^{29}\mathrm{Si})$ = 28 Hz, $^{2}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 14 Hz), 17.7 (SiCH(*C*H$_3$)$_2$), 17.8 (s, SiCH(*C*H$_3$)$_2$) ppm; MS (EI): *m/z* (%) = 313 (19) [M$^+$], 299 (100) [M$^+$ – Me], 161 (17) [SnMe$_3^+$], 133 (26) [SnMe$^+$], 129 (58) [Si^{i}Pr$_2$Me$^+$], 101 (43) [Si^{i}PrMe$_2^+$], 73 (69) [SiMe$_3^+$], 43 (11) [^{i}Pr$^+$].

Triphenylstannyldiisopropylchlorosilane (**12**; $C_{24}H_{29}ClSiS_4$)

Starting material: 1.64 g (3.5 mmol) **4**, 30 cm^3 CCl$_4$; 50°C; yield: 1.67 g (96%); ^{1}H NMR (400.13 MHz, C$_6$D$_6$): δ = 0.55 (m, 2H, C*H*(CH$_3$)$_2$), 1.01 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 7 Hz), 1.02 (d, 6H, CH(C*H*$_3$)$_2$, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 7 Hz), 7.32–7.35 (m, 9H, *m*-Ph, *p*-Ph), 7.56 (*m*, 6H, *o*-Ph) ppm; ^{13}C NMR (100.63 MHz, CDCl$_3$): δ = 17.7 (SiCH(*C*H$_3$)$_2$), 17.8 (SiCH(*C*H$_3$)$_2$), 18.1 (SiCH), 129.7 (*p*-Ph), 129.1 (*m*-Ph, $^{3}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 40 Hz), 137.9 (*o*-Ph, $^{2}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 37 Hz), 139.6 (*i*-Ph, $^{1}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 413/398 Hz) ppm; MS (EI): *m/z* (%) = 500 (8) [M$^+$], 386 (9) [M$^+$ – Ph – Cl], 351 (100) [Ph$_3$Sn$^+$] 310 (54) [PhSnSi^{i}Pr$_2^+$], 274 (56) [Ph$_2$Sn$^+$], 232 (12) [SnSi^{i}Pr$_2^+$], 197 (55) [PhSn$^+$], 154 (80) [SnCl$^+$], 149 (23) [Si^{i}Pr$_2$Cl$^+$], 120 (28) [Sn$^+$], 105 (21) [SiPh$^+$], 77 (50) [Ph$^+$], 43 (43) [^{i}Pr$^+$].

Bis(chlorodiisopropylsilyl)dimethylstannane (**13**; $C_{14}H_{34}Cl_2Si_2S_4$)

Starting material: 2.05 g (5.41 mmol) **5**, 30 cm^3 CCl$_4$; 50°C; yield: 2.4 g (99%); ^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 0.34 (s, 6H, Sn(CH$_3$)$_2$, $^{2}J(^{1}\mathrm{H}{-}^{119/117}\mathrm{Sn})$ = 46 Hz), 1.08 (d, 12H, SiCH(C*H*$_3$)$_2$, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 7 Hz), 1.10 (d, 12H, SiCH(C*H*$_3$)$_2$, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 7 Hz), 1.33 (m, 4H, SiC*H*(CH$_3$)$_2$, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 7 Hz) ppm; ^{13}C NMR (100.63 MHz, CDCl$_3$): δ = – 12.7 (Sn(CH$_3$)$_2$, $^{1}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 218/208 Hz), 17.7 (SiCH(*C*H$_3$)$_2$, $^{3}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 9 Hz), 17.8 (SiCH(*C*H$_3$)$_2$, $^{3}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 9 Hz), 18.0 (Si*C*H(CH$_3$)$_2$, $^{2}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 15 Hz) ppm; MS (EI): *m/z* (%) = 448 (10) [M$^+$], 433 (28) [M$^+$ – Me], 299 (62) [M$^+$ – Si^{i}Pr$_2$Cl], 269 (30) [M$^+$ – Si^{i}Pr$_2$Cl – 2Me], 227 (29) [M$^+$ – Si^{i}Pr$_2$Cl – 2Me – Pr], 129 (100) [Si^{i}Pr$_2$Me$^+$], 93 (81) [SiMe$_2$Cl$^+$], 87 (53) [Si^{i}PrMeH$^+$], 73 (70) [SiMe$_3^+$].

Di-tert-butylchlorostannyldiisopropylchlorosilane (**14**; $C_{14}H_{32}Cl_2SiS_4$)

Starting material: 0.47 g (1.23 mmol) **9**, 20 cm^3 CCl$_4$; 45°C; yield: 0.43 g (83%); ^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 1.15 (m, 2H, SiC*H*(CH$_3$)$_2$, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 8 Hz), 1.17 (d, 12H, SiCH(C*H*$_3$)$_2$, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 8 Hz), 1.33 (s, 18H, Sn(C(C*H*$_3$)$_3$)$_2$, $^{3}J(^{1}\mathrm{H}{-}^{119/117}\mathrm{Sn})$ = 79/76 Hz) ppm; ^{13}C NMR (100.63 MHz, CDCl$_3$): δ = 17.3 (SiCH(*C*H$_3$)$_2$, $^{3}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 30 Hz), 17.9 (SiCH(*C*H$_3$)$_2$, $^{3}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 22 Hz), 18.3 (SiCH(CH$_3$)$_2$, $^{2}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 54/52 Hz), 30.6 (Sn(C(CH$_3$)$_3$)$_2$), 36.8 (Sn(C(CH$_3$)$_3$)$_2$, $^{1}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 294/281 Hz) ppm; MS (EI): *m/z* (%) = 418 (7) [M$^+$], 349 (19) [M$^+$ – 2Cl], 305 (7) [M$^+$ – 2^{t}Bu], 271 (15) [^{t}Bu$_2$SnCl$^+$], 233 (26) [^{t}Bu$_2$Sn$^+$], 177 (13) [^{t}BuSn$^+$], 57 (100) [^{t}Bu$^+$].

Di-tert-butylchlorostannyldi-tert-butylchlorosilane (**15**; $C_{16}H_{36}Cl_2SiS_4$)

Starting material: 0.69 g (1.68 mmol) **10**, 20 cm^3 CCl$_4$; 45°C; yield: 0.51 g (68%); ^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 1.13 (s, 18H, Si(C*H*$_3$)$_3$), 1.33 (s, 18H, Sn(C(C*H*$_3$)$_3$)$_2$, $^{3}J(^{1}\mathrm{H}{-}^{119/117}\mathrm{Sn})$ = 72/68 Hz) ppm; ^{13}C NMR (100.63 MHz, CDCl$_3$): δ = 23.5 (Si*C*(CH$_3$)$_3$, $^{3}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 80/76 Hz), 27.9 (SiC(CH$_3$)$_3$), 30.9 (Sn(C(*C*H$_3$)$_3$)$_2$), 36.3 (Sn(*C*(CH$_3$)$_3$)$_2$, $^{1}J(^{13}\mathrm{C}{-}^{119/117}\mathrm{Sn})$ = 248/238 Hz) ppm; MS (EI): *m/z* (%) = 447 (1) [M$^+$], 412 (43) [M$^+$ – Cl], 389 (5) [M$^+$ – ^{t}Bu], 355 (15) [M$^+$ – Cl – ^{t}Bu], 297 (6) [M$^+$ – Cl – 2^{t}Bu], 275 (9) [M$^+$ – 3^{t}Bu], 177 (11) [Sn^{t}Bu$^+$], 95 (11) [SiMe$_2$Cl$^+$], 73 (21) [SiMe$_3^+$], 57 (100) [^{t}Bu$^+$].

3,3,7,7-Tetra-tert-butyl-1,1,5,5-tetraisopropyl-2,4,6,8-tetraoxa-1,5-disila-3,7-distannacyclooctane (**16**; $C_{28}H_{64}O_4Si_2Sn_2$)

7 (0.32 g, 0.92 mmol) was brought in contact with air moisture for 120 h. The remaining colorless solid was extracted with diethyl ether and filtered. After removing the volatiles *in vacuo* the desired products remained as colorless solid.

Yield: 0.33 g (95%); m.p.: 215°C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.79$ (m, 4H, $SiCH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz), 1.24 (d, 24H, $SiCH(CH_3)_2$, $^3J(^1H-^1H) = 7$ Hz), 1.31 (s, 36H, $Sn(C(CH_3)_3)_2H$, $^3J(^1H-^{119/117}Sn) = 97/93$ Hz) ppm; ^{13}C NMR (100.63 MHz, $CDCl_3$): $\delta = 16.3$ ($SiCH(CH_3)_2$), 18.7 ($SiCH(CH_3)_2$), 29.9 ($Sn(C(CH_3)_3)_2$), 37.9 ($Sn(C(CH_3)_3)_2$) ppm; ^{29}Si NMR (59.63 MHz, D_2O-cap./Et_2O): $\delta = -22.5$ ($^2J(^{29}Si-^{119/117}Sn) = 81/78$ Hz) ppm; ^{119}Sn NMR (111.92 MHz, D_2O-cap./Et_2O): $\delta = -168.2$ ($^2J(^{119}Sn-^{29}Si) = 81$ Hz) ppm; MS (EI): m/z (%) = 715 (64) [$M^+ - {}^i$Pr], 599 (41) [$M^+ - {}^i$Pr – 2^{t}Bu], 487 (21) [$M^+ - {}^i$Pr – 4^{t}Bu], 445 (21) [$M^+ -$ 2^{i}Pr – 4^{t}Bu], 401 (12) [$M^+ -$ 3^{i}Pr – 4^{t}Bu], 459 (6) [$M^+ -$ 4^{i}Pr – 4^{t}Bu], 57 (100) [^{t}Bu$^+$].

X-Ray crystallographic analysis of **16**

The crystal was mounted on the diffractometer as described previously [10]. Intensity data were collected at – 182°C with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) using a Siemens SMART system with 3-circle goniometer and CCD detector operating at – 54°C. For details regarding instrumentation and data treatment, see Ref. [11]. An absorption correction was applied utilizing the program SADABS [12]. The crystal structure was solved by direct methods as included in the SHELXTL-Plus program package [13]. Hydrogen atoms were placed geometrically and refined using a riding model with U_{iso} constrained at $1.5 \times U_{eq}$ of the carrier C atom for methyl groups. The structure was refined by full-matrix least-squares refinement on F^2 (SHELX-93) [14]. Scattering factors were those provided with the SHELX program system. All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically.

Bis(di-tert-butylsiloxy)di-tert-butylstannane (**17**; $C_{24}H_{56}O_2Si_2Sn$)

8 (1.45 g, 2.63 mmol) was brought in contact with air moisture for 120 h. The remaining colorless solid was extracted with diethyl ether and filtered. After removing the volatiles *in vacuo* the desired products remained as colorless solid.

Yield: 1.02 g (75%); m.p.: 99°C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.98$ (s, 36H, $SiC(CH_3)_3H$), 1.36 (s, 18H, $Sn(C(CH_3)_3)_2H$, $^3J(^1H-^{119/117}Sn) = 100/96$ Hz), 4.25 (m, 2H, $SiC(CH_3)_3H$, $^1J(^1H-^{29}Si) = 187$ Hz) ppm; ^{13}C NMR (100.63 MHz, $CDCl_3$): $\delta = 20.7$ ($SiC(CH_3)_3$), 27.7 ($SiCH(CH_3)_2$), 29.8 ($Sn(C(CH_3)_3)_2$), 40.1 ($Sn(C(CH_3)_3)_2$, $^1J(^{13}C-^{119/117}Sn) = 518$ Hz) ppm; ^{29}Si NMR (59.63 MHz, D_2O-cap./Et_2O): $\delta = 8.4$ ($^2J(^{29}Si-^{119/117}Sn) = 73/70$ Hz) ppm; ^{119}Sn NMR (111.92 MHz, D_2O-cap./Et_2O): $\delta = -160.5$ ($^2J(^{119}Sn-^{29}Si) = 73$ Hz) ppm; MS (EI): m/z (%) = 495 (50) [$M^+ - {}^t$Bu], 436 (15) [$M^+ -$ 2^{t}Bu], 380 (41) [$M^+ -$ 3^{t}Bu], 324 (18) [$M^+ -$ 4^{t}Bu], 57 (100) [^{t}Bu$^+$].

Acknowledgements

The authors gratefully acknowledge funding from the *Deutsche Forschungsgemeinschaft* and the *Fonds der chemischen Industrie*. *K. Ruhtandt-Senge* is grateful for support by the Syracuse University, the National Science Foundation (CHE-9702246, CHE-97-02246), and the *W. M. Keck Foundation*. *F. Uhlig* thanks Prof. Dr. *K. Jurkschat* (Dortmund University) for generous support.

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Received November 29, 2001. Accepted (revised) January 16, 2002