APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 523–529

Syntheses of novel silylsubstituted distannanes[†]

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Received 30 August 2004; Revised 8 October 2004; Accepted 10 October 2004

Starting from diorganodichlorostannanes, a series of novel bis(triorganosilyl)-stannanes and -distannanes has been prepared either by one-pot reactions via Wurtz-type coupling reactions with magnesium or lithium and triorganochlorostannanes, or by salt elimination reactions from triorganosilyllithium and diorganodichlorostannanes. A convenient and remarkably straightforward method is the oxidative coupling of potassium stannides with 1,2-dibromoethane. Isolable intermediates and products were characterized by multinuclear magnetic resonance spectroscopy. In order to prove the constitution of a distannane, an X-ray crystal structure analysis was performed. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: silylstannanes; distannanes; preparation; crystal structure; ^{29}Si NMR; ^{119}Sn NMR

INTRODUCTION

Despite their interesting spectroscopic properties and numerous applications in organic and organometallic chemistry, only a limited number of triorganosilyl-substituted stannanes with two or more R_3Si groups has been reported. Synthetic methods yielding bis(triorganosilyl)-substituted stannanes are even less explored, leaving this tin species as a rather exotic class of organometallic compounds.[1] Subtle changes in the reaction conditions strongly affect the result of the synthesis, i.e. coupling reactions of trimethylchlorosilane of tetrachlorostannane with lithium in tetrahydrofuran (THF) afforded $(Me_3Si)_4Sn$,[2] $(Me_3Si)_3SnLi$[3] or $(Me_3Si)_3SnSn(SiMe_3)_3$.[4] However, as recently reported, coupling reactions of various organodichlorostannanes with organodichlorosilanes using magnesium provide a useful method for the syntheses of linear, ring- and cage-shaped silastannanes.[5–10]

One of our special interests is focused on the synthesis of alkali-metal stannides bearing further triorganosilyl groups, because these are versatile building blocks for the generation of novel cyclic, cage-shaped or dendrimeric systems. In this context we became interested in exploring synthetic routes yielding novel starting materials for the generation of alkali-metal stannides such as bis(triorganosilyl)diorganostannanes or 1,2-bis(triorganosilyl)tetraorganodistannanes.

RESULTS AND DISCUSSION

Wurtz-type coupling of diorganodichlorostannanes with triorganochlorosilanes employing lithium or magnesium proves to be a convenient way for the generation of bis(triorganosilyl)-substituted mono- and distannanes. In analogy to the reaction reported earlier by Buerger and Goetze,[2] the reaction of dimethyldichlorostannane and trimethylchlorosilane with lithium in THF at low temperatures affords dimethyl bis(trimethylsilyl)stannane (**1**) as the sole product.

In addition to Wurtz-type syntheses, the salt elimination reactions of two equivalents of phenyldimethylsilyllithium with R_2SnCl_2 (R=Me, Ph) provide a straightforward access to the corresponding disilylated tin derivatives **2** and **3**. However, as a consequence of metal–halogen exchange reactions, the corresponding distannanes **4** and **5** are formed together with $PhMe_2SiSiMe_2Ph$ as minor side products. This is a significant drawback of this

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[†]Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

Contract/grant sponsor: Graz University of Technology.
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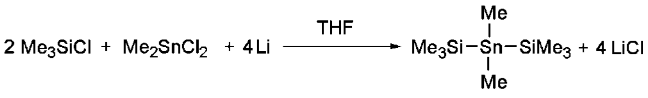
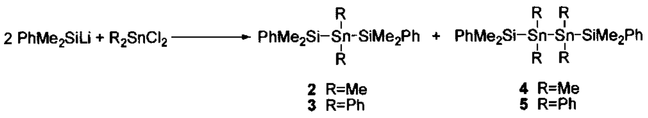
method, because the products were found to be difficult to purify from side products, as both thermal stability and choice of solvents suitable for recrystallization are limited (Scheme 1).



$$2\,Me_3SiCl + Me_2SnCl_2 + 4\,Li \xrightarrow{THF} Me_3Si-\overset{Me}{\underset{Me}{Sn}}-SiMe_3 + 4\,LiCl$$

1

In addition to reactions involving lithium species, coupling reactions of di(*tert*-butyl)dichlorostannanes and triorganochlorosilanes with magnesium in THF allow for a one-pot synthesis of the monostannane (**6**), the distannane (**11**) or mixtures of mono- and distannanes (**7**–**10**). Coupling of trimethylchlorosilane and di(*tert*-butyl)dichlorostannane with magnesium in THF yields the distannane **6** as the single product. This is in sharp contrast to the reaction of triphenylchlorosilane with di(*tert*-butyl)dichlorostannane, which produces only the monostannane **11** in high yield; compound **8** was obtained earlier by Hassler[11] via a different route. Reaction of dimethylphenylchlorosilane and methyldiphenylchlorosilane with di(*tert*-butyl)dichlorostannane, however, gives mixtures of mono- and distannanes in ratios 95% **7**:5% **8** and 5% **9**:95% **10**. Changing the ratio between educts or using stoichiometric amounts of magnesium did not result in different product distribution. An overview is given in Scheme 2.

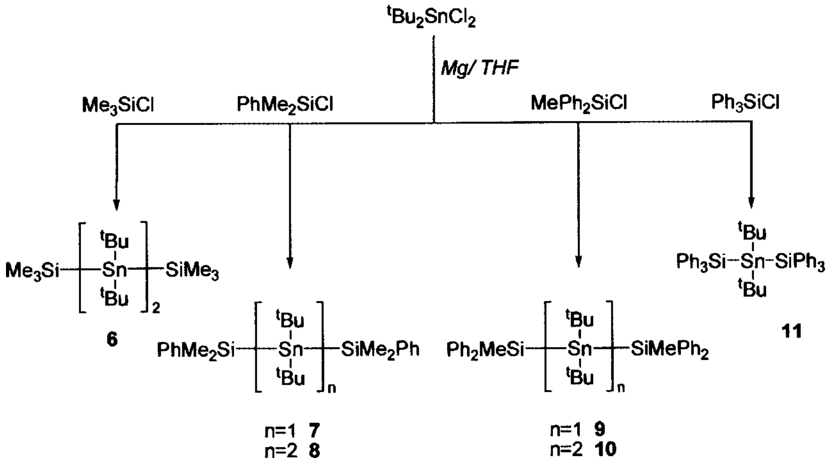


Scheme 1. Reaction of triorganosilyllithiums with R_2SnCl_2 (R=Me, Ph).

Apparently, the number of phenyl groups attached to the silicon moieties determines product composition. This is most probably due to competitive formation of organosilyl and organotin anions and subsequent salt elimination steps. In contrast to phenylated chlorosilanes,[12] trimethylchlorosilane is known not to form Grignard reagents in THF, but Me_3SiMgX (X = Br, I) were only obtained from trimethylbromo- and -iodosilane and activated magnesium in amine solutions.[13]

In contrast to reaction pathways including $PhMe_2SiLi$ leading to compounds **2**–**5**, we were able to separate **7**–**10** by fractional crystallization, yielding, for example, X-ray-quality crystals of **8**. In Fig. 1, the solid-state structure of compound **8** is given. The central tin–tin bond was determined as 2.884(1) Å, which is slightly elongated compared with other compounds with tin–tin bonds.[4,14] This fact is most probably due to the steric demand of the tin-bound *tert*-butyl and the dimethylphenylsilyl groups. Silicon–tin distance is 2.624(2) Å and within the expected range.[4] Bond angles surrounding the tin centres are close to the ideal tetrahedral geometry with the exception of a tin–tin–silicon angle being widened to 118.73(6)°. Again, this is most likely due to the bulkiness of the substituents. The two dimethylphenylsilyl groups acquire an exact trans-configuration.

In contrast to the reactions involving di(*tert*-butyl) dichlorostannane, the outcome of reacting diphenyldichlorostannane with trimethylchlorosilane is surprisingly time dependent, as monitored by means of heteronuclear magnetic resonance spectroscopy. After about 30 min the starting material (Ph_2SnCl_2) has disappeared and dodecaphenylcyclohexastannane is formed as the first product, as can be judged by ^{119}Sn shifts and coupling constants.[15] Within the next 90 min the whole amount of $Ph_{12}Sn_6$ is consumed and bis(trimethylsilyl)tetraphenyldistannane (**13**) is almost exclusively obtained. Removal of excess magnesium and workup at this stage allows for the isolation of **13** in



Scheme 2. Formation of mono- and di-stannanes from $^tBu_2SnCl_2$ and $R'R''_2SiCl$ with magnesium.

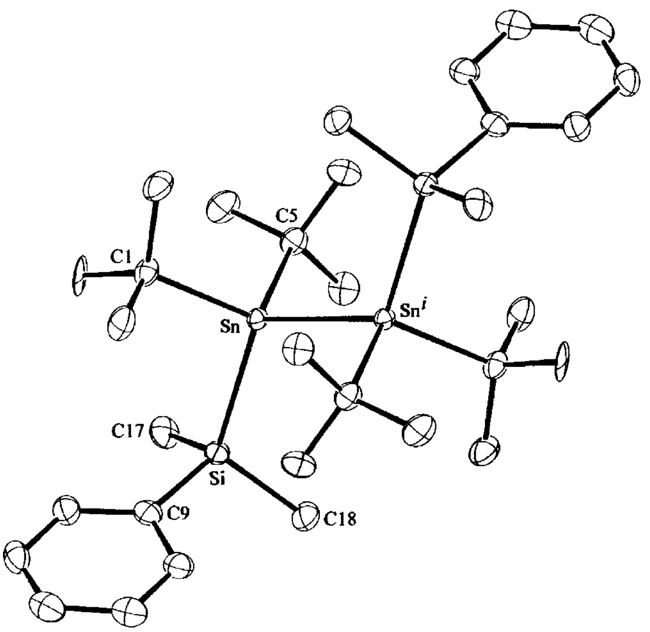


Figure 1. Molecular structure of 1,2-bis(dimethylphenylsilyl)-1,1,2,2-tetra-*tert*-butyldistannane (**8**). ORTEP drawing with 30% displacement ellipsoids and hydrogen atoms omitted for clarity. Selected geometric parameters: Sn–Sn^i 2.8840(10), Sn–Si–C9 112.8(3), Sn–Si 2.642(2), Sn–C1 2.216(8), Sn–C5 2.229(9), Si–C9 1.880(9), Si–C15, 1.863(9) Å; Sn^i–Sn–Si 118.73(6), Sn^i–Sn–C1, 111.3(2), Sn^i–Sn–C5 107.7(2), Si–Sn–C1 104.9(2), Si–Sn–C5 104.6(2), C1–Sn–C5 109.1(3), Sn–Si–C15 109.4(3), Sn–Si–C16 112.4(3), C9–Si–C15 107.1(4), C15–Si–C16 107.4(5)°; symmetry operation *i*: 1 − *x*, −*y*, −*z*.

yields of more than 90%. However, if stirring with magnesium in the presence of trimethylchlorosilane is continued for an additional 24 h, then subsequent metallation of the central tin–tin bond followed by silylation finally affords bis(trimethylsilyl)diphenylstannane (**14**) as the only product (Scheme 3, Fig. 2).

Starting from bis(silylated) monostannanes, symmetrical silyl-substituted distannanes may be obtained in high purity and good yields via potassium stannide intermediates. This approach is superior to Wurtz-type coupling reactions, where mixtures of mono- and di-stannanes are obtained. Cleavage of silicon–tin bonds, e.g. with potassium hydride in the presence of crown ether, i.e. 18crown6, is a generally applicable method for the generation of potassium stannides (Scheme 4).[16] Oxidative coupling of such readily obtainable metallated stannanes, e.g. with 1,2-dibromoethane, selectively yields the corresponding distannanes **4, 5, 13** and **15** in excellent yields. However, distannanes are sensitive towards potassium bromide formed during the course of the reaction. Hence, a fast workup, including evaporation of the solvent and extraction of the distannane from the residue with pentane, proved necessary to prevent decomposition under formation of elemental tin.

The ^{29}Si and ^{119}Sn NMR data of all reported compounds are summarized in Table 1. Upon comparison of shifts and coupling constants, the sharp contrast between methyl- or phenyl- and the *tert*-butyl-substituted stannanes becomes obvious. Di(*tert*-butyl)-substituted distannanes **6–11** not only share a larger chemical shift difference between mono- and distannanes compared with methylated and phenylated tin derivatives **1–5, 13** and **14**, but they also have much smaller

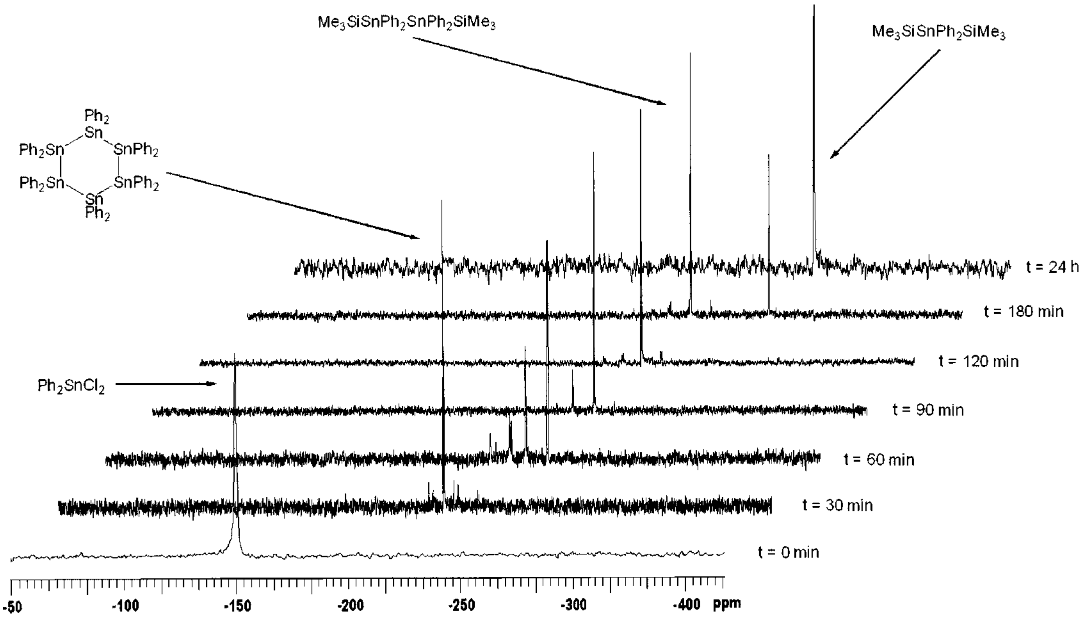
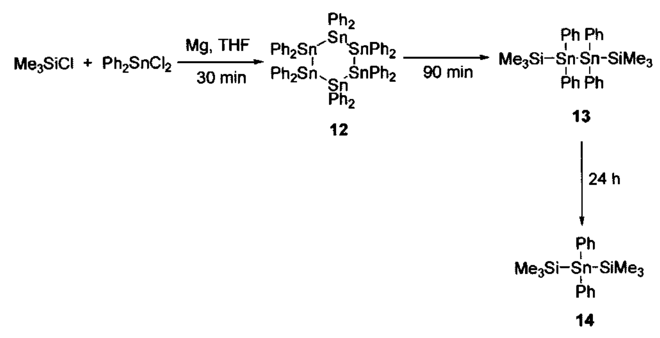
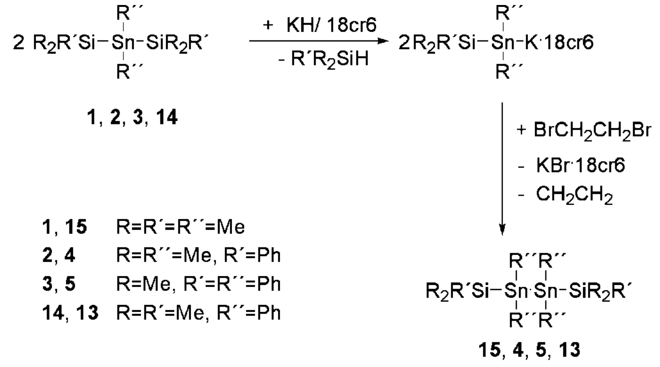


Figure 2. Time-dependent NMR spectroscopy for the reaction of Ph_2SnCl_2 and Me_3SiCl with magnesium.



Scheme 3. Reaction of Ph_2SnCl_2 and Me_3SiCl with magnesium in THF.



Scheme 4. Formation of distannanes from potassium stannides.

$^1J_{^{119}Sn-^{29}Si}$ and $^1J_{^{117}Sn-^{119}Sn}$ coupling constants in common, as indicated in Table 1. It is also interesting to note that $^{119}Sn-^{29}Si$ coupling constants decrease from monostannanes to distannanes, with compounds **9** and **10** as the only exceptions.

EXPERIMENTAL

General

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of inert gas (nitrogen or argon) using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. Dimethylphenylsilyllithium was prepared according to literature procedures and directly used for the next step.[17] The ^{29}Si (59.587 MHz) and ^{119}Sn (111.817 MHz) spectra were recorded on a Varian Unity INOVA 300 spectrometer. To compensate for the low abundance of ^{29}Si, the INEPT pulse sequence was used for amplification of the signals.[18,19] NMR samples were either prepared in deuterated solvents to provide an internal lock frequency signal or a D_2O capillary was used to provide an external lock signal. The silicon and tin signals are referenced to Me_4Si and Me_4Sn respectively.

Dimethylbis(trimethylsilyl)stannane (1)

To a suspension of 3.47 g (0.5 mol) finely grated lithium in 250 ml THF cooled to −40 °C, a solution of 25.0 g (0.114 mol) dimethyldichlorostannane and 29.2 ml (25.0 g, 0.23 mol) trimethylchlorosilane in 100 ml THF was added dropwise over a period of 3 h. After complete addition, the reaction mixture was kept at −40 °C for an additional 2 h and was then allowed to warm up slowly to room temperature. During the warming up the colour changed to a dark red–brown. Stirring was continued for a further 12 h. Afterwards the solvent and all volatiles were removed *in vacuo*. The residue was extracted with 3 × 100 ml portions of *n*-pentane. After removal of the salts, *n*-pentane was evaporated to leave 29.8 g (0.101 mol, 88.6% yield) of **1** as a pale yellow liquid. $\delta_{^{29}Si}$ (59.587 MHz, C_6D_6): −10.4 ppm; $^1J_{^{119}Sn-^{29}Si}$: 525 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −274.4 ppm. Elemental analysis: $C_8H_{24}Si_2Sn$ M_w: 295.14. Calc.: Found: C, 32.31; H, 8.34. C, 32.56; H, 8.20%.

Table 1. ^{119}Sn and ^{29}Si coupling constants for compounds **1**–**15**

				$(R_2R'Si)SnR''_2(SiR_2R')$				$(R_2R'Si)SnR''_2SnR''_2(SiR_2R')$			
	R	R′	R″	$\delta^{29}Si$	$\delta^{119}Sn$	$^1J_{^{119}Sn-^{29}Si}$		$\delta^{29}Si$	$\delta^{119}Sn$	$^1J_{^{119}Sn-^{29}Si}$	$^1J_{^{117}Sn-^{119}Sn}$
1[a]	Me	Me	Me	−10.4	−274.4	525	**15**[a]	−8.3	−261.5	513	1751
2[a]	Me	Ph	Me	−10.4	−269.9	525	**4**[a]	−10.5	−256.1	509	1820
3[a]	Me	Ph	Ph	−10.5	−258.9	519	**5**[a]	−10.6	−229.4	511	1560
14[b]	Me	Me	Ph	−7.0	−255.2	520	**13**[b]	−6.5	−229.4	510	1493
	Me	Me	^tBu				**6**[b]	−7.2	−110.6	342	78
7[b]	Me	Ph	^tBu	−11.8	−188.0	385	**8**[b]	−11.3	−103.9	314	78
9[b]	Ph	Me	^tBu	−10.3	−188.2	379	**10**[b]	−11.1	−100.5	415	<40
11[b]	Ph	Ph	^tBu	−7.2	−169.1	357					

[a] C_6D_6 solution.
[b] Pentane solution/D_2O capillary.

Bis(dimethylphenylsilyl)dimethylstannane (2) and bis(dimethylphenylsilyl)diphenylstannane (3)

To a solution of 7.5 mmol diorganodichlorostannane (1.65 g Me_2SnCl_2, 2.58 g Ph_2SnCl_2) in 30 ml diethyl ether cooled to −30 °C a solution of 15.0 mmol $PhMe_2SiLi$ in 10 ml THF was added at such a rate as to maintain the reaction mixture colourless. After complete addition, the reaction mixture was kept at −30 °C for an additional 30 min and was then allowed to warm up to room temperature. Stirring was continued for a further 12 h. Afterwards, the solvent was removed *in vacuo* and the residue was extracted with 3 × 25 ml portions of *n*-pentane. NMR spectroscopy revealed that **2** contained approximately 10% **4** and 15% **5** for the case of **3**. Contents of **4** and **5** can be reduced to ~3% by repeated freezing from *n*-pentane. Yields: 1.89 g (60.1%) **2** and 2.28 g (55.9%) **3**. **3**: $\delta_{^{29}Si}$ (59.587 MHz, C_6D_6): −10.4 ppm; $^1J_{^{119}Sn-^{29}Si}$: 525 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −269.9 ppm.

3. $\delta_{^{29}Si}$ (59.587 MHz, C_6D_6): −10.5 ppm; $^1J_{^{119}Sn-^{29}Si}$: 519 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −258.9 ppm.

1,2-Bis(dimethylphenylsilyl)-1,1,2,2-tetramethyldistannane (4), 1,2-bis(dimethylphenylsilyl)-1,1,2,2-tetraphenyldistannane (5) and 1,2-bis(trimethylsilyl)-1,1,2,2-tetramethyldistannane (15)

To a cold solution (−30 °C) of 1.88 g (0.85 ml, 10 mmol) 1,2-dibromoethane in 10 ml diethyl ether, a solution of 10 mmol of the corresponding potassium stannide in 5 ml THF was rapidly added at such a rate as to keep the reaction mixture colourless. Gas evolution was observed during the addition. Immediately after the addition was completed the reaction mixture was allowed to warm up to room temperature and all volatiles were removed *in vacuo*. The residue was extracted with 3 × 10 ml portions of *n*-pentane. After removal of the solvent, 2.62 g (4.61 mmol, 92.1% yield) of **4**, 3.72 g (4.56 mmol, 91.1% yield) of **5** and 2.16 g (4.87 mmol, 97.3% yield) of **15** were obtained as slightly yellow oils.

4. $\delta_{^{29}Si}$ (59.587 MHz, C_6D_6): −10.5 ppm; $^1J_{^{119}Sn-^{29}Si}$: 509 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −256.1 ppm; $^1J_{^{119}Sn-^{117}Sn}$: 1820 Hz. $C_{20}H_{34}Si_2Sn_2$ M_w: 568.04. Found: C, 41.89; H, 5.97. Calc.: C, 42.29; H, 6.03%.

5. $\delta_{^{29}Si}$ (59.587 MHz, C_6D_6): −10.6 ppm; $^1J_{^{119}Sn-^{29}Si}$: 511 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −229.4 ppm; $^1J_{^{119}Sn-^{117}Sn}$: 1560 Hz. Elemental analysis: $C_{40}H_{42}Si_2Sn_2$ M_w: 816.32. Found: C, 58.49; H, 5.24. Calc.: C, 58.85; H, 5.19%.

15. $\delta_{^{29}Si}$ (59.587 MHz, C_6D_6): −8.3 ppm; $^1J_{^{119}Sn-^{29}Si}$: 513 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −261.5 ppm; $^1J_{^{119}Sn-^{117}Si}$: 1751 Hz. Elemental analysis: $C_{10}H_{30}Si_2Sn_2$ M_w: 443.90. Found: C, 27.12; H, 6.94. Calc.: C, 27.05; H, 6.81%.

General procedure for compounds 6–11, 13, 14

To a solution of 12.5 mmol di(*tert*-butyl)dichlorostannane and 25 mmol of the corresponding triorganochlorosilane in 120 ml THF cooled to 0 °C, 1.25 g (51.4 mmol) magnesium was added with stirring. The reaction mixture was kept at 0 °C for 15 min, during which a yellow–green suspension was formed. The reaction mixture was allowed to warm up to room temperature and stirring was continued for 48 h, after which all volatiles were removed *in vacuo*. To the residue, 100 ml of *n*-pentane was added. After filtration and washing the residue twice with 25 ml portions of *n*-pentane, the product was obtained upon removal of the solvent.

1,2-Bis(trimethylsilyl)-1,1,2,2-tetra-*tert*-butyldistannane (6)

Starting from 3.80 g $^tBu_2SnCl_2$ and 3.14 ml (2.72 g, 25 mmol) Me_3SiCl, 3.44 g (90.0% yield) of **6** were obtained.

$\delta_{^{29}Si}$ (59.587 MHz, D_2O/*n*-pentane): −7.2 ppm; $^1J_{^{119}Sn-^{29}Si}$: 342 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −110.6 ppm; $^1J_{^{119}Sn-^{117}Si}$: 78 Hz. Elemental analysis: $C_{22}H_{54}Si_2Sn_2$ M_w: 612.22. Found: C, 43.26; H, 8.83. Calc.: C, 43.16; H, 8.89%.

Bis(dimethylphenylsilyl)di(*tert*-butyl)stannane (7) and 1,2-bis(dimethylphenylsilyl)-1,1,2,2-tetra-*tert*-butyldistannane (8)

Starting from 3.80 g $^tBu_2SnCl_2$ and 4.2 ml (4.3 g, 25 mmol) $Me_2PhSiCl$, **7** and **8** were synthesized according to the procedure given above. Crystallization from *n*-pentane at −20 °C yielded 120 mg (2.6%) of **8**. Concentration of the mother liquor and cooling to −60 °C gave 5.32 g (84.6%) of **7**.

7. $\delta_{^{29}Si}$ (59.587 MHz, D_2O/*n*-pentane): −11.8 ppm; $^1J_{^{119}Sn-^{29}Si}$: 385 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −188.0 ppm. Elemental analysis: $C_{24}H_{40}Si_2Sn$ M_w: 503.44. Found: C, 56.94; H, 7.93. Calc.: C, 57.26; H, 8.01%.

8. $\delta_{^{29}Si}$ (59.587 MHz, D_2O/*n*-pentane): −11.3 ppm; $^1J_{^{119}Sn-^{29}Si}$: 314 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −103.9 ppm; $^1J_{^{119}Sn-^{117}Si}$: 78 Hz. Elemental analysis: $C_{32}H_{58}Si_2Sn_2$ M_w: 736.36. Found: C, 52.05; H, 7.88. Calc.: C, 52.20; H, 7.94%.

Bis(methyldiphenylsilyl)di(*tert*-butyl)stannane (9) and 1,2-bis(methyldiphenylsilyl)-1,1,2,2-tetra-*tert*-butyldistannane (10)

Starting from 3.80 g $^tBu_2SnCl_2$ and 5.2 ml (5.82 g, 25 mmol) $MePh_2SiCl$, **9** and **10** were synthesized according to the procedure given above. Crystallization from *n*-pentane at −20 °C yields 6.12 g (78.1%) of **10**. Concentration of the mother liquor and cooling to −60 °C gave 340 mg (7.9%) of **9**.

9. $\delta_{^{29}Si}$ (59.587 MHz, D_2O/*n*-pentane): −10.3 ppm; $^1J_{^{119}Sn-^{29}Si}$: 379 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −188.2 ppm. Elemental analysis: $C_{34}H_{44}Si_2Sn$ M_w: 627.58. Found: C, 64.88; H, 7.12. Calc.: C, 65.07; H, 7.07%.

10. $\delta_{^{29}Si}$ (59.587 MHz, D_2O/*n*-pentane): −11.1 ppm; $^1J_{^{119}Sn-^{29}Si}$: 415 Hz. $\delta_{^{119}Sn}$ (111.817 MHz, C_6D_6): −100.5 ppm; $^1J_{^{119}Sn-^{117}Si}$: <40 Hz. Elemental analysis: $C_{42}H_{62}Si_2Sn_2$ M_w: 860.50. Found: C, 58.51; H, 7.32. Calc.: C, 58.62; H, 7.26%.

Bis(triphenylsilyl)di(*tert*-butyl)stannane (11)

Starting from 3.80 mg $^tBu_2SnCl_2$ and 7.4 g (25 mmol) Ph_3SiCl, 8.33 g (88.7%) of **11** were synthesized according to the procedure given above.

$\delta_{^{29}\mathrm{Si}}$ (59.587 MHz, D_2O/*n*-pentane): −7.2 ppm; $^1J_{^{119}\mathrm{Sn}-^{29}\mathrm{Si}}$: 357 Hz. $\delta_{^{119}\mathrm{Sn}}$ (111.817 MHz, C_6D_6): −169.1 ppm. Elemental analysis: $C_{44}H_{48}Si_2Sn$ M_w: 751.72. Found: C, 69.84; H, 6.53. Calc.: C, 70.30; H, 6.44%.

1,2-Bis(trimethylsilyl)-1,1,2,2-tetraphenyldistannane (13) and bis(trimethylsilyl) diphenylstannane (14)

According to the general procedure given above, starting from 4.30 mg (12.5 mmol) Ph_2SnCl_2 and 3.14 ml (2.72 g, 25 mmol) Me_3SiCl, 4.13 g (95.4%) of **13** were obtained as colourless crystals when magnesium was filtered off after 120 min followed by removal of the solvent and extraction of the residue with 3 × 100 ml portions of *n*-pentane. Recrystallization from *n*-pentane yielded analytically pure **13**. Starting from the same amounts of starting materials given above, but allowing the reaction mixture to stir with magnesium for 24 h, yields 4.89 g (93.3%) of **14** as a colourless oil.

13. $\delta_{^{29}\mathrm{Si}}$ (59.587 MHz, D_2O/*n*-pentane): −7.0 ppm; $^1J_{^{119}\mathrm{Sn}-^{29}\mathrm{Si}}$: 520 Hz. $\delta_{^{119}\mathrm{Sn}}$ (111.817 MHz, C_6D_6): −255.2 ppm. Elemental analysis: $C_{18}H_{28}Si_2Sn$ M_w: 419.28. Found: C, 51.32; H, 6.82. Calc.: C, 51.56; H, 6.73%.

14. $\delta_{^{29}\mathrm{Si}}$ (59.587 MHz, D_2O/*n*-pentane): −6.5 ppm $^1J_{^{119}\mathrm{Sn}-^{29}\mathrm{Si}}$. 510 Hz$\delta_{^{119}\mathrm{Sn}}$ (111.817 MHz, C_6D_6): −229.4 ppm $^1J_{^{119}\mathrm{Sn}-^{112}\mathrm{Si}}$ 1493 Hz. Elemental analysis: $C_{30}H_{38}Si_2Sn_2$ M_w: 692.18. Found: C, 52.13; H, 5.61. Calc.: C, 52.06; H, 5.53%.

Crystallography for 8

The crystallographic data for **8** are summarized in Table 2. $C_{32}H_{58}Si_2Sn_2$, $M = 736.34$, triclinic, $P\bar{1}$, $a = 9.2223(2)$, $b = 9.5596(2)$, $c = 11.1916(3)$ Å, $\alpha = 110.6323(8)$, $\beta = 102.0516(8)$, $\gamma = 96.1171(8)°$, $V = 885.37(4)$ Å^3, $Z = 1$, $D_{\mathrm{calcd}} = 1.381$ Mg m^{-3}, $\mu = 1.496$ mm^{-1}, $F(000) = 378$. The colourless crystal, 0.24 × 0.24 × 0.25 mm^3, was in a sealed Lindemann capillary and mounted on a Nonius Kappa CCD diffractometer fitted with graphite monochromated Mo Kα radiation. The 19 904 data were collected at 293 K to a maximum θ of 27.5°; 3976 data were unique, and of these 3702 satisfied $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS97)[20] and refined by full-matrix least-squares on F^2 (SHELXL97).[21] Non-hydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were included in a riding model with a common isotropic temperature factor (C–H = 0.96 Å, $U_{\mathrm{iso}} = 0.147(10)$ Å^2). Final $R = 0.055$ and $wR = 0.168$ (all data). The largest residual of 3.34 e$^-$ Å^{-3} was located near the C3 atom of one of the *tert*-butyl groups. CCDC deposition no: 252 414.

Acknowledgements

We acknowledge funds from the Graz University of Technology (Austria), the Deutsche Forschungsgemeinschaft (DFG, Germany) and the Fonds der chemischen Industrie (Germany). Wacker GmbH, Burghausen, Germany is gratefully acknowledged for donation of chlorosilanes.

Table 2. Crystallographic data for compound **8**

Empirical formula	$C_{32}H_{58}Si_2Sn_2$
M_w (g mol^{-1})	736.34
Temperature (K)	293(2)
size (mm^3)	0.25 × 0.24 × 0.24
Colour	Colorless
Cryst system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.2223(2)
b (Å)	9.5596(2)
c (Å)	11.1916(3)
α (°)	110.6323(8)
β (°)	102.0516(8)
γ (°)	96.1171(8)
V (Å^3)	885.37(4)
Z	1
D_{calcd} (Mg m^{-3})	1.381
Absorption coefficient (mm^{-1})	1.496
$F(000)$	378
θ range (°)	2.93–27.46
h, k, l range	$0 \le h \le 11$ $-12 \le k \le 12$ $-14 \le l \le 13$
No. reflections collected	19 904
Unique rflns/R_{int}	3976/6.3
GoF (F^2)	1.252
Final R indices ($I > 2\sigma(I)$)	0.0554
R indices (all data)	0.1679
Largest diff peak/hole (e$^-$ Å^{-3})	3.336; −1.427

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