Syntheses and Reactivity of Stannyloligosilanes. 2.[†] Branched Stannyloligosilanes

Burkhard Costisella,[‡] Ulrich Englich,[§] Ingo Prass,[‡] Markus Schürmann,[‡]
Karin Ruhlandt-Senge,[§] and Frank Uhlig*,[‡]

*Fachbereich Chemie der Universität Dortmund, Anorganische Chemie II, Otto-Hahn-Strasse 6,
D-44221 Dortmund, Germany, and Department of Chemistry and the W.M. Keck Center for
Molecular Electronics, 1-014 Center for Science and Technology,
Syracuse University, New York 13244-4100*

Received January 7, 2000

Branched tri(stannyl)tetrasilanes $MeSi[SiMe_2SnR_2R']_3$ (**2**, R = R′ = Ph; **3**, R = R′ = Me; **5**, R = *t*-Bu, R′ = H) were synthesized by the reaction of alkali metal tri- or diorganostannides with methyltris(fluorodimethylsilyl)silane (**1**) or methyltris(chlorodimethylsilyl)silane (**4**) or by reacting triphenylchlorostannane with **1** in the presence of magnesium. Methyltris[(hydridodi-*tert*-butylstannyl)dimethylsilyl]silane (**5**) was halogenated at the tin atom by treatment with $CHCl_3$ or $CHBr_3$. Surprisingly, the reaction of **5** with 3 equiv of lithium diisopropylamide (LDA) resulted in the formation of the five-membered ring **10** (2-dimethylsilyl-1,1,2,3,3-pentamethyl-4,4,5,5-tetra-*tert*-butyl-1,2,3-trisila-4,5-distannacyclopentane) with a bridging Sn−Sn unit. Reacting **5** with triethylamine or aminostannanes resulted in the formation of 2-dimethylsilyl-1,1,2,3,3-pentamethyl-4,4,5,6,6-penta-*tert*-butyl-1,2,3-trisila-4,5,6-tristannacyclohexane (**14**). The solid-state structures of **5** and **14b** were determined by X-ray crystallography.

Introduction

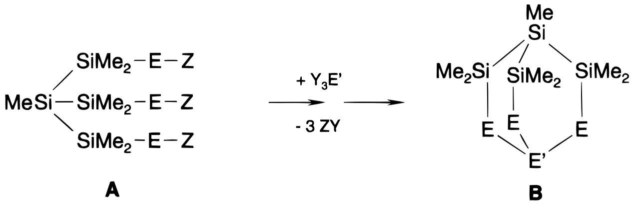
Branched heptameric silanes of type **A** (E = $SiMe_2$,[2] NR,[3] Z = Cl,[2] H[3]) are important building blocks for the synthesis of tetrasila- or heptasilabicyclo[2.2.2]octane derivatives of type **B** (Scheme 1). Hassler et al. reported the synthesis of cage-like compounds with capping pnicogen atoms (E = $SiMe_2$; E′ = P, As);[2] Gade et al. described a methyltris(aminodimethylsilyl)silane with group 4 metals in identical positions (E = NR; E′ = TiCl, ZrCl, HfCl).[3]

As far as we are aware, no reports describe the synthesis of type **A** compounds in which E is an organostannyl group. Previous work in our group was concerned with the exploration of synthetic routes, structural features, and reactivity of linear stannyloligosilanes (t-$Bu_2Sn(Z)(SiMe_2)_nSn(Z)$-t-Bu_2; Z = H, Cl, Br; $n = 1-6$).[1] As a continuation of this work, we are now reporting on the synthesis, structure, and reactivity of the first heptameric stannasilanes (type **A**), in which E is a di- or triorganostannyl group (E = t-Bu_2Sn; R_3Sn). First attempts toward cage-like compounds of type **B** are also discussed.

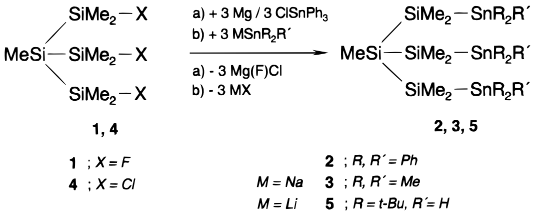
Results and Discussion

The reaction of methyltris(fluorodimethylsilyl)silane (**1**) with triphenylchlorostannane and magnesium in THF served well in the preparation of methyltris[(triphenylstannyl)dimethylsilyl]silane (**2**), producing yields of 80−90% (path a, eq 1). The trimethylstannyl-substituted derivative **3** was obtained in 20% yield[4] by the reaction of sodium or potassium trimethylstannide with **1**. Treatment of methyltris(chlorodimethylsilyl)silane (**4**) with 3 equiv of lithium di-*tert*-butylstannide gave methyltris[(di-*tert*-butylhydridostannyl)dimethylsilyl]silane (**5**) in 90% yield (path b, eq 1).

Scheme 1



E = $SiMe_2$; Z = Cl; E′ = P, As[2]
E = NR; Z = H; E′ = TiCl, ZrCl, HfCl[3]



(1)

1 ; *X = F*
4 ; *X = Cl*
2 ; *R, R′ = Ph*
M = Na **3** ; *R, R′ = Me*
M = Li **5** ; *R = t-Bu, R′ = H*

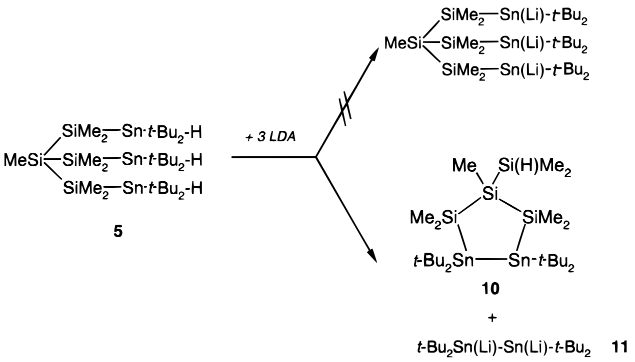
Triorgano-substituted derivatives **2** and **3** cannot be functionalized at the tin atoms without cleavage of the

---

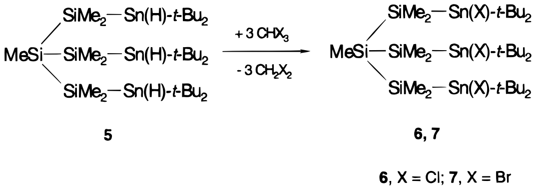
[†] Part 1, see ref 1.
[‡] Fachbereich Chemie der Universität Dortmund.
[§] Syracuse University.
(1) Uhlig, F.; Kayser, C.; Klassen, R.; Hermann, U.; Brecker, L.; Schürmann, M.; Ruhlandt-Senge, K.; Englich, U. *Z. Naturforsch.* **1998**, *54b*, 278.
(2) Hassler, K.; Kollegger, G.; Siegl, H.; Klintschar, G. *J. Organomet. Chem.* **1997**, *533*, 51.
(3) (a) Gade, L. H.; Schubart, M.; Findeis, B.; Li, W.-S.; McPartlin, M. *Chem. Ber.* **1995**, *128*, 329. (b) Gade, L. H.; Schubart, M.; Findeis, B.; Platzek, C.; Scowen, I.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1996**, 219.
(4) After “Kugelrohr“ distillation. The crude product was investigated by NMR spectroscopy (^{119}Sn and ^{29}Si NMR). Integration of the signals of the ^{119}Sn NMR spectra showed more than 85% of **3**.

10.1021/om000024e CCC: $19.00

Scheme 2. Unexpected Formation of the Five-Membered Ring 10



silicon–tin bonds. For example, when **3** was treated with $HgCl_2$, a mixture of **4**, elemental mercury, and Me_3SnCl was obtained. The reaction of **3** with $SnCl_4$ resulted in a mixture of **4**, $MeSnCl_3$, Me_2SnCl_2, and Me_3SnCl. Halogen-functionalized stannylsilanes are accessible by treatment of **5** with bromoform or chloroform (eq 2).



(2)

6, X = Cl; **7**, X = Br

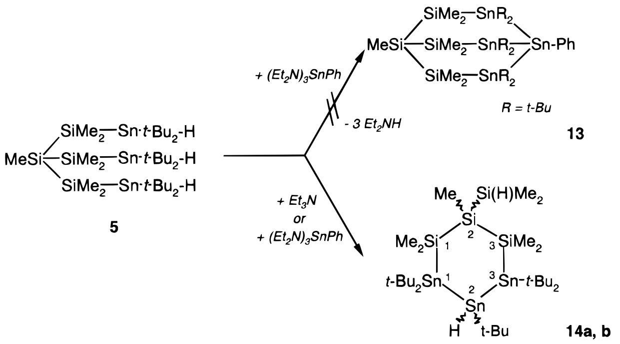
The reactions of the branched oligomeric stannylsilanes **2**, **3**, and **5** are similar to those of linear stannyloligosilanes described previously.[1] However, if a linear monohydrido-substituted compound containing a Si–Sn chain is treated with lithium diisopropylamide (LDA), metalation of the tin atom, under formation of substituted LiSn-*t*-$Bu_2SiMePh_2$ **8**, and diisopropylamine (eq 3) is observed. Disilylstannane **9**, bearing of two different silyl groups, was obtained by reacting **8** with dimethylphenylchlorosilane (eq 4).

$$\mathrm{HSn}\text{-}t\text{-}\mathrm{Bu_2SiMePh_2} \xrightarrow[-\ \mathrm{HN}\text{-}i\text{-}\mathrm{Pr_2}]{+\ \mathrm{LDA}} \underset{\mathbf{8}}{\mathrm{LiSn}\text{-}t\text{-}\mathrm{Bu_2SiMePh_2}} \quad (3)$$

$$\underset{\mathbf{8}}{\mathrm{LiSn}\text{-}t\text{-}\mathrm{Bu_2SiMePh_2}} \xrightarrow[-\ \mathrm{LiCl}]{+\ \mathrm{PhMe_2SiCl}} \underset{\mathbf{9}}{\mathrm{PhMe_2Si}\text{-}\mathrm{Sn}\text{-}t\text{-}\mathrm{Bu_2SiMePh_2}} \quad (4)$$

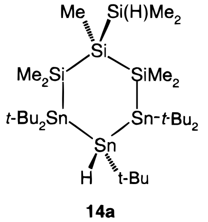
In contrast, reaction of the branched derivative **5** with 3 equiv of LDA did not result in the expected compound with three metalated terminal tin atoms. At temperatures below −10 °C no reaction was observed, whereas above −10 °C a five-membered ring with a bridging tin–tin unit and one exocyclic dimethylsilyl group (**10**) was obtained (Scheme 2). The structure of **10** was confirmed by NMR and MS experiments. Coupling constants for ^1J(Si–H) at 172 Hz and $^1J(^{119}Sn-^{117}Sn)$ at 54 Hz were observed. The latter agrees well with $^1J(^{119}Sn-^{117}Sn)$ for a previously reported stannasilacyclopentane without an exocyclic silyl group, synthesized in a stepwise reaction pathway.[5] Only one tin-containing byproduct, 1,2-dilithio-1,1,2,2-tetra-*tert*-butyldistannide (**11**), was identified by ^{119}Sn NMR spectroscopy.

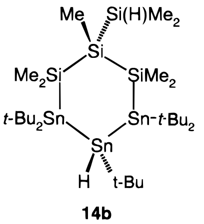
Scheme 3. Amine Catalyzed Formation of 14a,b



Treatment of the product mixture containing **10** and **11** with HCl or H_2O, necessary for the isolation of **10**, converted **11** to *t*-$Bu_2Sn(H)Sn(H)$-*t*-Bu_2 (**12**).[6] Reacting **5** with 1 or 2 equiv of LDA resulted in a mixture of the starting material **5** and products **10** and **11**. Although we have little experimental support to suggest a mechanism for the formation of **10**, we suggest that the first step is the lithiation of one of the tin atoms in the starting material, followed by tin–silicon bond cleavage and amine-catalyzed intramolecular tin–tin coupling. Amine-catalyzed ring closure and rearrangement reactions of the stannasilane **5** have been observed when reacting **5** with triethylamine or phenyltris(diethylamino)stannane. However, heating a solution of **5** and phenyltris(diethylamino)stannane in toluene at 80 °C for 1 week did not yield the expected cage compound 1**3** (Scheme 3);[7] rather, the six-membered ring **14** with a Sn_3 and a Si_3 units was isolated. Similar results were obtained using triethylamine instead of phenyltris(diethylamino)stannane.

The central tin atom of **14** carries a *tert*-butyl group and a hydrido function as a result of a silicon–tin and, more surprising, tin–carbon bond cleavage. In addition, two tin–tin bonds have been formed. Compound **14** contains two ring atoms (Si_2 and Sn_2) with different substitution pattern. Accordingly, two sets of NMR signals were observed for the four resulting equatorial–axial isomers in a molar ratio of 3:1 (**14a**:**14b**).


14a


14b

The assignment of NMR chemical shifts in the isomer mixture of **14a** and **14b** was achieved by a series of $^{119}Sn-^1H$, $^1H-^1H$, and $^{13}C-^1H$ COSY NMR experiments. Compound **14** was isolated as a colorless oil, which crystallized as a mixture of **14a** and **14b** at 0 °C.

---

(5) Uhlig, F.; Hermann, U.; Schürmann, M. *J. Organomet. Chem.* **1999**, *585*, 211.

(6) ^{119}Sn NMR data for **12**: δ −83.7 ($^1J(^{119}Sn-^1H)$ = 1285 Hz; $^3J(^{119}Sn-^{117}Sn)$ = 168 Hz).

(7) For formation of Sn–Sn bonds from the reaction of Sn–H with R_2N–Sn see: (a) Neumann, W. P. *The Organic Chemistry of Tin*; Wiley: London, 1970. (b) Mitchell, T. N.; El-Bahairy, M. *J. Organomet. Chem.* **1977**, *141*, 43.

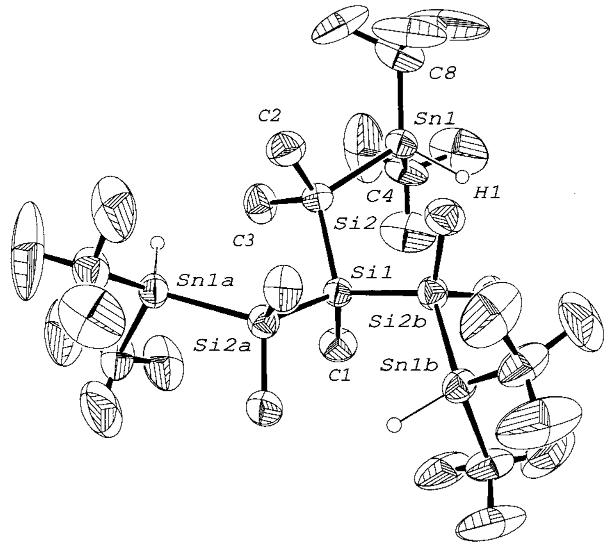


Figure 1. View of a molecule of **5** showing 30% probability displacement ellipsoids and the atom numbering. Hydrogen atoms bonded to carbon have been removed for clarity.

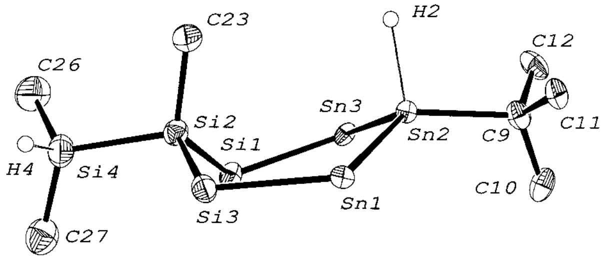


Figure 2. View (SHELXTL-PLUS) of a molecule of **14b** showing 50% probability displacement ellipsoids and the atom numbering. Substituents at Si$_1$, Si$_3$, Sn$_1$, Sn$_3$ and hydrogen atoms bonded to carbon were omitted for clarity. Only one of the two independent molecules is shown.

We were able to isolate one of these isomers by fractional crystallization from *n*-hexane. The NMR spectra of a solution of these crystals showed that isomer **14b** had been isolated. The molecular structures of **5** and **14b** are presented in Figures 1−3. Unit cell data, refinement details, and selected interatomic details are summerized in Tables 1 and 2.

Molecular Structure of 5. Compound **5** contains a tetrahedrally coordinated central silicon atom (Si(1)) connected to three Si(Me)$_2$Sn(H)(*t*-Bu)$_2$ arms in addition to a methyl group. The hydrogen atom at Sn was located in a difference map and refined. Bond distances are 2.346(2) Å for Si−Si, 2.599(2) Å for Sn−Sn, and 1.65(7) Å for Sn−H. Silicon and tin atoms in the appendages are of almost tetrahedral geometry; slight deviations may be rationalized by steric effects. Similar deviations from ideal tetrahedral geometry have been observed for *t*-Bu$_2$Sn(H)SiMe$_2$SiMe$_2$Sn(H)-*t*-Bu$_2$, the only other structurally characterized hydridostannyloligosilane,[1] or other methyl- or phenyl-substituted stannyloligosilanes.[5,8]

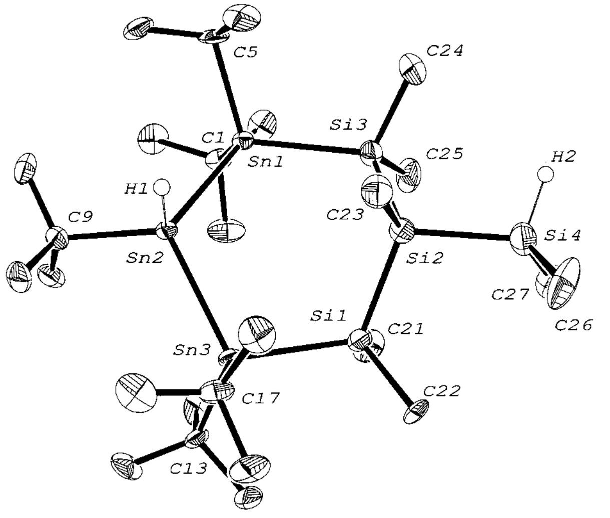


Figure 3. View of a molecule of **14b** showing 50% probability displacement ellipsoids and the atom numbering. Hydrogen atoms bonded to carbon have been removed for clarity. Only one of the two independent molecules is shown.

Table 1. Crystal Data and Structure Refinement for 5 and 14b

	5	14b
formula	$C_{31}H_{78}Si_4Sn_3$	$C_{27}H_{68}Si_4Sn_3$
fw, g/Mol	919.36	860.40
cryst syst	hexagonal	monoclinic
cryst size, mm	0.30 × 0.30 × 0.30	0.34 × 0.10 × 0.06
space group	*P*6(3)	*P*2(1)/*c*
a, Å	13.066(1)	9.1358(5)
b, Å	13.066(1)	18.879(1)
c, Å	16.238(1)	46.986(3)
β, deg		93.669(1)
V, Å^3	2400.8(3)	8087.2(8)
Z	2	4
ρ_{calcd}, Mg/m^3	1.272	1.415
μ, mm^{-1}	1.664	1.971
F(000)	940	3488
θ range, deg	3.09 to 25.67	1.16 to 25.00
index ranges	$-15 \le h \le 15$ $-13 \le k \le 13$ $-19 \le l \le 19$	$-10 \le h \le 10$ $-22 \le k \le 22$ $-55 \le l \le 43$
no. of reflns collected	29 104	43 398
no. of indep reflns/R_{int}	3045/0.025	14219/0.0991
no. of refined params	129	616
GooF (F^2)	0.981	1.001
R1[a] (*F*) ($I > 2\sigma(I)$)	0.0403	0.0582
wR2[b] (F^2) (all data)	0.1015	0.1305
largest diff peak/hole, e/Å^3	1.534/−0.650	0.906/−1.065

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

Molecular Structure of 14b. Compound **14b** crystallizes with two independent molecules in each asymmetric unit. The compound displays a six-membered ring comprised of three neighboring silicon and tin atoms. Figure 2 displays a detailed view of the ring system, while Figure 3 shows the entire molecule (in both figures only one of the two independent molecules is shown). The ring conformation is that of a distorted boat, resulting from the approximate tetrahedral geometry of the ring atoms. Slight distortions from ideal geometry are due to the different steric demands of the ligands. Sn−Sn distances range from 2.8122(8) to 2.8157(8) Å, Sn−Si distances from 2.570(6) to 2.633(5) Å. Si−Si contacts are observed between 2.326(4) and 2.373(7) Å. The hydrogen atoms at Si and Sn were located in the difference Fourier maps and included in the refinement. Sn−H distances were found at 1.55(8) and 1.78(7) Å. Si−H contacts were observed at 1.34(10)

---

(8) Uhlig, F.; Kayser, C.; Klassen, R., Schürmann, M. *J. Organomet. Chem.* **1998**, *556*, 165.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5 and 14b[a]

5		**14b**	
	Bond Lengths		
Sn(1)−Si(2)	2.599(2)	Sn(1)−Si(3)	2.624(3)
Sn(1)−H(1)	1.65(7)	Sn(3)−Si(1)	2.604(3)
Si(1)−Si(2)	2.346(2)	Sn(1)−Sn(2)	2.816(1)
		Sn(2)−Sn(3)	2.814(1)
		Si(1)−Si(2)	2.340(4)
		Si(2)−Si(3)	2.326(4)
		Si(2)−Si(4)	2.352(4)
		Sn(2)−H(2)	1.78(7)
		Si(4)−H(4)	1.34(10)
	Bond Angles		
C(8)−Sn(1)−C(4)	113.1(4)	C(1)−Sn(1)−C(5)	110.6(3)
C(8)−Sn(1)−Si(2)	114.6(3)	C(1)−Sn(1)−Si(3)	110.1(3)
C(4)−Sn(1)−Si(2)	110.3(3)	C(1)−Sn(1)−Sn(2)	108.1(2)
C(8)−Sn(1)−H(1)	117(3)	C(5)−Sn(1)−Si(3)	108.3(3)
C(4)−Sn(1)−H(1)	89(3)	C(5)−Sn(1)−Sn(2)	106.7(2)
Si(2)−Sn(1)−H(1)	109(2)	C(9)−Sn(2)−Sn(3)	114.0(2)
C(1)−Si(1)−Si(2)	109.8(1)	C(9)−Sn(2)−Sn(1)	117.1(2)
Si(2)−Si(1)−Si(2a)	109.1(1)	Si(1)−Sn(3)−Sn(2)	106.73(6)
C(3)−Si(2)−C(2)	106.9(4)	Sn(3)−Sn(2)−Sn(1)	115.04(3)
C(3)−Si(2)−Si(1)	109.0(3)	Si(3)−Sn(1)−Sn(2)	113.01(6)
C(2)−Si(2)−Si(1)	108.5(3)	Si(2)−Si(1)−Sn(3)	114.0(1)
C(3)−Si(2)−Sn(1)	106.6(2)	Si(3)−Si(2)−Si(1)	112.9(1)
C(2)−Si(2)−Sn(1)	108.7(3)	Si(2)−Si(3)−Sn(1)	111.6(1)
Si(1)−Si(2)−Sn(1)	116.8(1)	C(27)−Si(4)−C(26)	110.0(5)
		C(27)−Si(4)−Si(2)	113.9(4)
		C(26)−Si(4)−Si(2)	111.1(4)

[a] $a = -y + 1, x - y, z$; $b = -x + y + 1, -x + 1, z$.

and 1.48(9) Å. These distances are in ranges observed previously in related compounds.

Experimental Section

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. Di-*tert*-butylstannane was prepared by reduction of the corresponding dichloride with lithium aluminum hydride. The alkali metal stannides[9,10] and the isotetrasilanes **1** and **4**[11,12] 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 DRX 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 DRX 400 spectrometer (solvents $CDCl_3$ or C_6D_6, internal reference Me_4Si or Me_4Sn, respectively) or a Bruker DPX 300 spectrometer (solvents hexane or THF with D_2O-capillary, internal reference Me_4Si or Me_4Sn, respectively). Mass spectral analyses were recorded using a MAT 8200. Elemental analyses were performed on a LECO-CHNS-932 analyzer. IR spectra were recorded on a Bruker IFS 28 spectrometer.

General Procedures for 2, 3, 5−7, and 9. The stannylsilanes **2**, **3**, **5**−**7**, and **9** were prepared according to the procedures described in ref 1.

Methyltris[(triphenylstannyl)dimethylsilyl]silane, MeSi(SiMe$_2$SnPh$_3$)$_3$ (2). Starting materials: 1.1 g (4 mmol) of **1**, 4.6 g (12 mmol) of Ph_3SnCl, 80 mL of THF, 0.9 g (37 mmol) of Mg. Recrystallization from diethyl ether gave 4.9 g (97%) of **2** as a colorless solid, mp 127 °C. $^{29}Si\{^1H\}$ NMR (79.49 MHz, $CDCl_3$): δ −64.4 (SiCH$_3$, $^2J(^{29}Si-^{119}Sn) = 56$ Hz), −26.9 (Si(CH$_3$)$_2$, $^1J(^{29}Si-^{119/117}Sn) = 500/479$ Hz, $^3J(^{29}Si-^{119}Sn) = 23$ Hz). $^{119}Sn\{^1H\}$ NMR (149.19 MHz, $CDCl_3$): δ −160.9. Anal. Calcd for $C_{61}H_{66}Si_4Sn_3$ (1267.64): C, 57.80; H, 5.24. Found: C, 58.1; H, 5.4.

Methyltris[(trimethylstannyl)dimethylsilyl]silane, MeSi(SiMe$_2$SnMe$_3$)$_3$ (3). Starting materials: 60 mmol of $NaSnMe_3$ in 80 mL of THF, 5.5 g (20 mmol) of **1** in 30 mL of THF. The crude product was distilled to give 2.9 g (20%) of **3** as a colorless liquid, bp 153 °C (0.001 mmHg). $^{29}Si\{^1H\}$ NMR (79.49 MHz, C_6D_6): δ −68.7 (SiCH$_3$, $^2J(^{29}Si-^{119/117}Sn) = 56/53$ Hz), −33,56 (Si(CH$_3$)$_2$, $^1J(^{29}Si-^{119/117}Sn) = 511/488$ Hz, $^3J(^{29}Si-^{119}Sn) = 19$ Hz). $^{119}Sn\{^1H\}$ NMR (149.19 MHz, C_6D_6): δ −102.7. Anal. Calcd for $C_{16}H_{48}Si_4Sn_3$ (709.02): C, 27.1; H, 6.80. Found: C, 28.0; H, 7.0.

Methyltris[(hydridodi-*tert*-butylstannyl)dimethylsilyl]silane, MeSi(SiMe$_2$Sn-*t*-Bu$_2$H)$_3$ (5). Starting materials: 11 mmol of LiSn(H)-*t*-Bu$_2$,[8] 1.2 g (3.7 mmol) of **4**. Recrystallization from hexane gave 3.1 g (91%) of **5** as a colorless solid, mp 128 °C. $^{29}Si\{^1H\}$ NMR (79.49 MHz, C_6D_6): δ −68.1 (SiCH$_3$, $^2J(^{29}Si-^{119}Sn) = 30$ Hz), −27.4 (Si(CH$_3$)$_2$, $^1J(^{29}Si-^{119/117}Sn) = 349/334$ Hz, $^3J(^{29}Si-^{119}Sn) = 16$ Hz). $^{119}Sn\{^1H\}$ NMR (149.19 MHz, C_6D_6): δ −126.5. IR (Nujol): ν(Sn−H) = 1777 cm^{-1}. Anal. Calcd for $C_{31}H_{78}Si_4Sn_3$ (919.42): C, 40.49; H, 8.55. Found: C, 40.2; H, 8.40.

Methyltris[(chlorodi-*tert*-butylstannyl)dimethylsilyl]silane, MeSi(SiMe$_2$Sn-*t*-Bu$_2$Cl)$_3$ (6). Starting materials: 2.0 g (2.2 mmol) of **5**, 1 mL of $CHCl_3$, 15 mL of *n*-hexane. Recrystallization from $CHCl_3$ gave 0.8 g (35%) of **6** as a colorless solid, mp 129−130 °C. ^{29}Si NMR $\{^1H\}$ NMR (79.49 MHz, $CDCl_3$): δ −62.2 (SiCH$_3$, $^2J(^{29}Si-^{119}Sn) = 25$ Hz), −15.5 (Si(CH$_3$)$_2$, $^1J(^{29}Si\text{-}^{119/117}Sn) = 247/236$ Hz, $^3J(^{29}Si-^{119}Sn) = 18$ Hz). $^{119}Sn\{^1H\}$ NMR (111.91 MHz, D_2O-capillary/hexane): δ 70.0. Anal. Calcd for $C_{31}H_{75}Cl_3Si_4Sn_3$ (1022.75): C, 36.40; H, 7.39. Found: C, 35.9; H, 7.2.

Methyltris[(bromodi-*tert*-butylstannyl)dimethylsilyl]silane, MeSi(SiMe$_2$Sn-*t*-Bu$_2$Br)$_3$ (7). Starting materials: 2.0 g (2.2 mmol) of **5**, 0.1 mL of $CHBr_3$, 15 mL of *n*-hexane. Recrystallization from CH_2Cl_2 gave 1.0 g (86%) of **7** as a colorless solid, mp 149−150 °C. ^{29}Si NMR $\{^1H\}$ NMR (79.49 MHz, $CDCl_3$): δ −61.6 (SiCH$_3$, $^2J(^{29}Si-^{119}Sn) = 26$ Hz), −15.7 (Si(CH$_3$)$_2$, $^1J(^{29}Si-^{119/117}Sn) = 234/223$ Hz, $^3J(^{29}Si-^{119}Sn) = 18$ Hz). ^{119}Sn NMR $\{^1H\}$ NMR (149.19 MHz, $CDCl_3$) δ 79.9. Anal. Calcd for $C_{31}H_{75}Br_3Si_4Sn_3$ (1156.11): C, 32.21; H, 6.54. Found: C, 31.7; H, 6.6.

Lithium Methyldiphenylsilyldi-*tert*-butylstannane, Li Sn-*t*-Bu$_2$-SiPh$_2$Me (8). A solution of LDA (5.4 mmol in 15 mL of hexane and 15 mL of THF) was added dropwise to a cooled (0 °C) solution of MePh$_2$SiSn(H)-*tert*-Bu$_2$ (1.25 g, 1.8 mmol) in 50 mL of hexane and 50 mL of THF. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was examined by ^{29}Si and ^{119}Sn NMR spectroscopy. $^{29}Si\{^1H\}$ NMR (79.49 MHz, C_6D_6): δ −12.0 ($^1J(^{29}Si-^{119/117}Sn)$ = not detected). $^{119}Sn\{^1H\}$ NMR (149.19 MHz, C_6D_6): δ −193.0. **Dimethylphenylsilyl(diphenylmethylsilyl)di-*tert*-butylstannane, Me$_2$PhSiSn-*t*-Bu$_2$SiPh$_2$Me (9).** An LDA solution (2.9 mmol) was added dropwise to a cooled solution (−30 °C) of **8** (1.25 g, 2.9 mmol) in 50 mL of hexane and 50 mL of THF. The reaction mixture was stirred for 1 h, and dimethylphenylchlorosilane (0.49 g, 2.9 mmol) was added. The solution was slowly warmed to room temperature, 20 mL of petrolether (30−60) was added, and the reaction mixture was hydrolyzed by addition of 10 mL of water. The organic layer was separated and dried over calcium chloride. After filtration (G3) and evaporation of the solvents the resulting crude product was purified by column chromatography (silica gel 60, hexane) to give 0.6 g (37%) of **2** as a colorless solid, mp 66−68 °C. $^{29}Si\{^1H\}$ NMR (59.63 MHz, D_2O/hexane): δ −11.4 (SiPhMe$_2$, $^1J(^{29}Si-^{119/117}Sn) = 388/371$ Hz), −10.0 (SiPh$_2$Me, $^1J(^{29}Si-^{119/117}Sn) = 379/362$ Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, D_2O/*n*-hexane): δ −185.1. Anal. Calcd for $C_{29}H_{42}Si_2Sn$ (565.52): C, 61.59; H, 7.43. Found: C, 61.7; H, 7.7.

---

(9) Quintard, J.-P.; Perèyre, M. *Rev. Silicon, Germanium, Tin Lead Compd.* **1980**, *4*, 151.

(10) Jousseaume, B.; Connil, M.-F.; Pereyre, M. *Organometallics* **1996**, *15*, 4469.

(11) Suzuki, H.; Kimata, Y.; Satoh, S.; Kuriyama, A. *Chem. Lett.* **1995**, 293.

(12) Kolleger, G.; Hassler, K. *J. Organomet. Chem.* **1995**, *485*, 233.

2-Dimethylsilyl-1,1,2,3,3-pentamethyl-4,4,5,5-tetra-*tert*-butyl-1,2,3-trisila-4,5-distannacyclopentane, MeSi(SiMe$_2$H)(SiMe$_2$Sn-*t*-Bu$_2$)$_2$ (10). A solution of LDA (5.4 mmol in 15 mL of hexane and 15 mL of THF) was added dropwise to a cooled (0 °C) solution of **5** (1.65 g, 1.8 mmol) in 50 mL of hexane and 50 mL of THF. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was examined by ^{29}Si and ^{119}Sn NMR spectroscopy. ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6): identical with data found for isolated **10**. ^{119}Sn{^{1}H} NMR (149.19 MHz, C_6D_6): δ −98.1 (**10**), −8.6 (**11**).[6]

Subsequently, the reaction mixture was warmed to room temperature, and 0.5 mL of H_2O or dilute HCl (excess) was added. The solvents were evaporated, and the resulting residue was extracted twice with 80 mL of a diethyl ether/*n*-hexane mixture (80:20). The extracts were filtered (G3), and after evaporation of the solvents the resulting crude product was purified by chromatography on silica gel using hexane as eluent to give 0.44 g (35%) of **10** as a colorless solid, mp 40−42 °C. ^{29}Si NMR (79.49 MHz, C_6D_6): δ −75.0 (*Si*CH$_3$, $^2J(^{29}\text{Si}-^{119}\text{Sn}) = 52$ Hz), -33.0 (*Si*(CH$_3$)$_2$H, $^1J(^{29}\text{Si}-^1\text{H}) = 172$ Hz, $^2J(^{29}\text{Si}-^{119}\text{Sn}) = 21$ Hz), −28.1 (*Si*(CH$_3$)$_2$, $^1J(^{29}\text{Si}-^{119/117}\text{Sn}) = 208/200$ Hz, $^2J(^{29}\text{Si}-^{119}\text{Sn}) = 76$ Hz). ^{119}Sn{^{1}H} NMR (149.19 MHz, C_6D_6): δ −98.1 ($^1J(^{119}\text{Sn}-^{117}\text{Sn}) = 54$ Hz). Anal. Calcd for $C_{23}H_{58}Si_4Sn_2$ (684.46): C, 40.36; H, 8.54. Found: C, 40.8; H, 8.6.

2-Dimethylsilyl-4,4,5,6,6-penta-*tert*-butyl -1,1,2,3,3-pentamethyl-1,2,3-trisila-4,5,6-tristannacyclohexane, MeSi(SiMe$_2$H)(SiMe$_2$Sn^{t}Bu$_2$)$_2$Sn^{t}BuH (14). Method A: Reactions of 5 with Phenyltris(diethylamino)stannane. A solution of **5** (6.34 g, 6.9 mmol) and phenyltris(diethylamino)stannane (2.84 g, 6.9 mmol) in 200 mL of toluene was heated and stirred for 16 h at 75 °C. The reaction mixture was then examined by ^{119}Sn NMR spectroscopy. ^{119}Sn{^{1}H} NMR (111.92 MHz, D$_2$O-capillary/hexane): δ −94.6 [PhSn(NEt$_2$)$_3$], −126.5 [**5**]. Subsequently, the reaction mixture was heated for a further 24 h at 95−100 °C. The solvents were evaporated, and the resulting residue was examined by ^{119}Sn NMR spectroscopy. ^{119}Sn{^{1}H} NMR (111.92 MHz, D$_2$O-capillary/hexane): δ -37.9, −72.1, −83.8, −120.1, −121.6, −131.9, −335.1, −335.6.

Method B: Reaction of 5 with Triethylamine. A solution of **5** (0.46 g, 0.5 mmol) and 1 mL of triethylamine in 3 mL of toluene was heated and stirred for 16 h at 90 °C. The reaction mixture was then examined by ^{119}Sn and ^{29}Si NMR spectroscopy. ^{29}Si{^{1}H} NMR (59.62 MHz, D$_2$O-capillary/toluene): δ −74.3, −70.8, −33.5, −33.1, −28.9, −27.7. ^{119}Sn NMR (111.92 MHz, D$_2$O-capillary/toluene): δ −335.5, −334.8, −83.9, −72.2. The crude product was purified by column chromatography on silica gel using *n*-hexane as eluent to give 2.16 g of a yellow oil. Storage of the yellow oil in a refrigerator (0 °C) gave 2.02 g (75%) of **14** as a colorless solid, mp 185 °C (decomp). IR (Nujol): ν(Sn−H) = 1765 cm^{-1}. Anal. Calcd for $C_{27}H_{68}Si_4Sn_3$ (860.40): C, 37.7; H, 7.90. Found: C, 37.7; H, 8.5. Molecular weight determination (osmometric in hexane, 60 °C): calcd 860.40 g/mol; found 863.5 g/mol.

Isomer 14a: ^{29}Si NMR (59.62 MHz, D$_2$O-capillary/hexane): δ −33.5 [d, *Si*(CH$_3$)$_2$H, $^1J(^{29}\text{Si}-^1\text{H}) = 176$ Hz]. ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6): δ −74.3 [*Si*CH$_3$, $^2J(^{29}\text{Si}-^{119}\text{Sn}) = 39$ Hz, $^3J(^{29}\text{Si}-^{119}\text{Sn}) = 11$ Hz], −33.5 [*Si*(CH$_3$)$_2$H], −27.7 [*Si*(CH$_3$)$_2$, $^1J(^{29}\text{Si}-^{119/117}\text{Sn}) = 219/211$ Hz, $^2J(^{29}\text{Si}-^{119}\text{Sn}) = 63$ Hz, $^3J(^{29}\text{Si}-^{119}\text{Sn}) = 10$ Hz]. ^{119}Sn NMR (111.92 MHz, D$_2$O-capillary/hexane): δ −335.5 [d, *Sn*(H)C(CH$_3$)$_3$, $^1J(^{119}\text{Sn}-^1\text{H}) = 1026$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 77$ Hz]. ^{119}Sn{^{1}H} NMR (149.19 MHz, C_6D_6): δ −335.5 [*Sn*(H)C(CH$_3$)$_3$, $^1J(^{119}\text{Sn}-^{119/117}\text{Sn}) = 254/242$ Hz], −83.9 [*Sn*(C(CH$_3$)$_3$)$_2$, $^1J(^{119}\text{Sn}-^{119/117}\text{Sn}) = 254/242$ Hz, $^1J(^{119}\text{Sn}-^{29}\text{Si}) = 221$ Hz, $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 37$ Hz].

Isomer 14b: ^{29}Si NMR (59.62 MHz, D$_2$O-capillary/hexane): δ −34.5 [d, *Si*(CH$_3$)$_2$H, $^1J(^{29}\text{Si}-^1\text{H}) = 177$ Hz]. ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6): δ −70.8 [*Si*CH$_3$, $^2J(^{29}\text{Si}-^{119}\text{Sn}) = 37$ Hz, $^3J(^{29}\text{Si}-^{119}\text{Sn}) = 11$ Hz], −34.5 [*Si*(CH$_3$)$_2$H], −28.9 [*Si*(CH$_3$)$_2$, $^1J(^{29}\text{Si}-^{119/117}\text{Sn}) = 229/219$ Hz, $^2J(^{29}\text{Si}-^{119}\text{Sn}) = 62$ Hz, $^3J(^{29}\text{Si}-^{119}\text{Sn}) = 10$ Hz]. ^{119}Sn NMR (111.92 MHz, D$_2$O-capillary/hexane): δ −334.8 [d, *Sn*(H)C(CH$_3$)$_3$, $^1J(^{119}\text{Sn}-^1\text{H}) = 1025$ Hz, $^3J(^{119}\text{Sn}-^1\text{H}) = 75$ Hz]. ^{119}Sn{^{1}H} NMR (149.19 MHz, C_6D_6): δ −334.8 [*Sn*(H)C(CH$_3$)$_3$, $^1J(^{119}\text{Sn}-^{119/117}\text{Sn}) = 289/276$ Hz], −72.2 [*Sn*(C(CH$_3$)$_3$)$_2$, $^1J(^{119}\text{Sn}-^{119/117}\text{Sn}) = 289/276$ Hz, $^1J(^{119}\text{Sn}-^{29}\text{Si}) = 236$ Hz, $^2J(^{119}\text{Sn}-^{117}\text{Sn}) = 41$ Hz].

Crystallography of 5. The crystals were mounted on the diffractometer in a sealed Lindemann capillary. The data were collected at room temperature to a maximum θ of 25.67° with 360 frames via ω-rotation ($\Delta/\omega = 1°$) twice at 10 s per frame on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXS97),[13] Missing atoms, including the hydrogen atom bound to Sn(1), were located in subsequent difference Fourier cycles and refined by full-matrix least-squares of F^2 (SHELXL97).[14] All other hydrogen atoms were placed geometrically and refined using a riding model with a common isotropic temperature factor (C−H$_{\text{prim.}}$ 0.96 Å, U_{iso} 0.147(10) Å^2). All non-hydrogen atoms were refined using anisotropic displacement parameters.

Crystallography of 14b. The crystals were mounted on the diffractometer as described previously.[15] Intensity data were collected at −182 °C with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), using a Siemens SMART system, complete with a three-circle goniometer and CCD detector operating at −54 °C. Details regarding instrumentation and data treatment have been reported previously.[16] An absorption correction was applied utilizing the program SADABS.[17] The crystal structure was solved by direct methods, as included in the SHELXTL-Plus program package.[18] Missing atoms, including the hydrogen atoms on Si and Sn, were located in subsequent difference Fourier maps and included in the refinement. Remaining hydrogen atoms were placed geometrically and refined using a riding model with U_{iso} constrained at 1.2 for nonmethyl groups and 1.5 for methyl groups times U_{eq} of the carrier C atom. The structure was refined by full-matrix least-squares refinement on F^2 (SHELXL-93).[19] Scattering factors were those provided with the SHELXL program system. All non-hydrogen atoms, with the exception of some disordered or restrained positions, were refined anisotropically. Disorder was handled by including split positions for the affected groups and included in the refinement of the respective occupancies. A set of restraints was applied to aid in modeling the disorder.

Acknowledgment. The authors thank the Deutsche Forschungsgemeinschaft (DFG) and the state Northrhine Westfalia for financial support. We thank also the ASV-innovative Chemie GmbH (Germany) and the Degussa-Huels AG for gifts of silanes. F.U. is grateful to Prof. Dr. K. Jurkschat for support. K.R.S. is grateful for support by Syracuse University, the National Science Foundation (CHE-9702246, CHE-97-02246), and the W. M. Keck Foundation.

Supporting Information Available: The ^{13}C and ^{1}H NMR data of all compounds, tables of all coordinates, anisotropic displacement parameters, and geometric data for compounds **5** and **14b** are available free of charge via the Internet at http://pubs.acs.org.

OM000024E

---

[13] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[14] Sheldrick, G. M. *SHELXL-97*; University of Göttingen, 1997.

[15] Chadwick, S.; Englich, U.; Noll, B.; Ruhlandt-Senge, K. *Inorg. Chem.* **1998**, *37*, 4718.

[16] Hope, H. *Progr. Inorg. Chem.* **1994**, *41*, 1.

[17] Sheldrick, G. M. *SADABS, Program for Absorption Correction Using Area Detector Data*; University of Göttingen, Germany, 1996.

[18] Siemens *SHELXTL-Plus;* Siemens: Madison, WI, 1996.

[19] Sheldrick, G. M. *SHELXL-93;* University of Göttingen, Germany, 1993.