Reaction of $(t\text{-}Bu_2SnO)_3$ with Organohalosilanes. Simple Formation of Open-Chain and Cyclic Stannasiloxanes†

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The synthesis or *in situ* formation of the new stannasiloxanes $R^1R^2Si(OSn\text{-}t\text{-}Bu_2)_2E$ (**2**, $R^1 = R^2 = t$-Bu, E = O; **22**, $R^1 = t$-Bu, R^2 = F, E = O; **23**, $R^1 = R^2$ = Ph, E = O; **24**, $R^1 = R^2 = t$-Bu, E = S; **25**, $R^1 = t$-Bu, R^2 = F, E = S; **26**, $R^1 = R^2$ = Ph, E = S), $t\text{-}Bu_2Si[OSn(Cl)\text{-}t\text{-}Bu_2]_2$ (**3**), $t\text{-}Bu_2(Cl)SnOSi(X)\text{-}t\text{-}Bu_2$ (**4**, X = Cl; **12**, X = H), $t\text{-}Bu_2Sn(OSiR^1R^2O)_2M$ (**5**, $R^1 = R^2 = t$-Bu, M = Sn-*t*-Bu_2; **7**, $R^1 = R^2$ = Ph, M = Sn-*t*-Bu_2; **9**, $R^1 = R^2$ = Ph, M = $SiPh_2$; **18**, $R^1 = t$-Bu, R^2 = Cl, M = Sn-*t*-Bu_2; **21**, $R^1 = t$-Bu, R^2 = F, M = Sn-*t*-Bu_2), $t\text{-}Bu_2Sn(OSiXR_2)_2$ (**10**, X = H, R = *t*-Bu; **11**, X = F, R = *t*-Bu; **13**, X = F, R = Et; **14**, X = F, R = *i*-Pr; **15**, X = F, R = Ph), $t\text{-}Bu_2Sn(OSiX_2\text{-}t\text{-}Bu)_2$ (**16**, X = Cl; **19**, X = F), $t\text{-}Bu_2ClSnOSiCl_2\text{-}t\text{-}Bu$ (**17**), $[R^1R^2Si(OSn\text{-}t\text{-}Bu_2)_2O.t\text{-}Bu_2SnX_2]$ (**20**, $R^1 = t$-Bu, R^2 = F, X = F; **27**, $R^1 = t$-Bu, R^2 = F, X = OH; **28**, $R^1 = R^2$ = Ph, X = OH), $O(t\text{-}Bu_2SnOSiPh_2)_2O$ (**29**), $t\text{-}Bu_2Sn(OSiMe_2CH_2)_2$ (**30**), and $t\text{-}Bu_2SnOSiF\text{-}t\text{-}BuOSn\text{-}t\text{-}Bu_2OSit\text{-}Bu_2O$ (**31**) is described. The compounds were characterized by means of multinuclear NMR spectroscopy and Mössbauer spectroscopy. The molecular structures of the eight-membered stannasiloxane rings **5**, **7**, **9**, **21**, and **29** were determined by X-ray analysis. On the basis of NMR and electrospray mass spectrometry a mechanism is proposed involving protonated species for the redistribution reaction between **5** and **21**.

Introduction

The chemistry of metallasiloxanes containing Si−O−M linkages (M = main-group elements as well as transition metals) has been extensively investigated over the last two decades and has been reviewed recently.[1] In contrast, much less attention has been paid to the systematic development of the chemistry of stannasiloxanes,[1c,2,3] although a number of such compounds has been described over the years. Even less is known on metallastannoxanes.[4] Such compounds are of increasing interest as models for catalytically active metal oxide surfaces[5] or might serve as molecular precursors for well-defined inorganic polymers.[3r,6] Furthermore, stannasiloxanes are thought to be intermediates in polycondensation of silanols[2h,n,7] and, therefore, a better understanding of their chemistry is welcome.

So far, stannasiloxanes have been prepared by the reaction of organosilanols with organochlorostannanes in the presence of a base,[3f,l,n,r,s] by the reaction of organosilanols with organotin oxides,[2e,h,3k,u] or by lithium halide elimination from organosilanolates and organohalostannanes.[1c,2a,b,l−n,3b,c,e,h−k,m,t] The formation of Si−O−Sn linkages was also achieved by making use of the high Bronsted acidity of silica surfaces, which allows the cleavage of Sn−C and Sn−H bonds.[5a,c,h,k,l]

The idea of reacting polymeric diorganotin oxides $(R_2SnO)_n$ (R = Me, *n*-Bu) with organohalosilanes R_2SiCl_2 to provide stannasiloxanes dates back to 1967, but the products obtained were characterized only by elemental analyses and infrared spectroscopy.[2j,k]

In this paper we report on the reaction of di-*tert*-butyltin oxide $(t\text{-}Bu_2SnO)_3$[8a] with organohalosilanes such as R_2SiX_2 (R = Et, *i*-Pr, *t*-Bu, Ph; X = Cl, F), $t\text{-}Bu_2SiHCl$, and $t\text{-}BuSiX_3$ (X = Cl, F). Depending on the identity of R and X, either the reaction provided a number of new well-defined stannasiloxanes or it pro-

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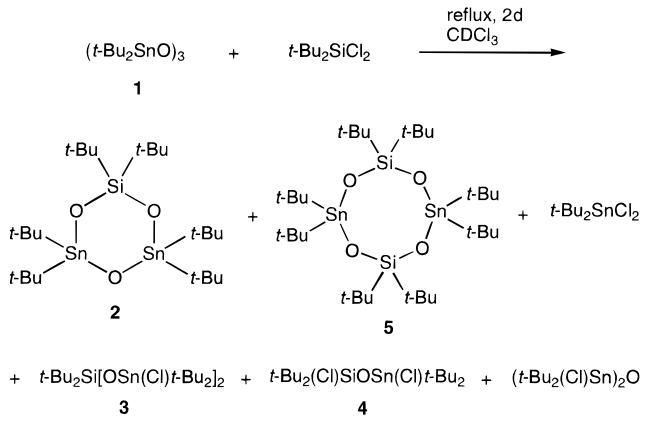
Scheme 1



ceeded under complete oxygen transfer to give siloxanes and t-Bu_2SnCl_2.

Also reported are redistribution reactions of several cyclic model compounds as well as their reactions with 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane.

Most of the reactions described here are equilibria similar to those reported by Van Wazer and Moedritzer for silicon- and germanium-containing systems.[8b,c] However, no efforts were made to determine the equilibrium constants for these equilibria.

Results and Discussion

Synthetic Aspects. The reaction of equimolar quantities of di-*tert*-butyltin oxide, $(t\text{-}Bu_2SnO)_3$ (**1**), and di-*tert*-butyldichlorosilane, t-Bu_2SiCl_2, resulted in formation of a clear solution. Its ^{119}Sn and ^{29}Si NMR spectra showed the presence of the cyclic and open-chain stannasiloxanes **2**−**5** (Scheme 1, Table 1).

When the ratio of di-*tert*-butyltin oxide (**1**) to t-Bu_2SiCl_2 was changed to 2:3, the ^{119}Sn NMR signal assigned to bis(di-*tert*-butylchlorostannoxy)di-*tert*-butylsilane (**3**) showed the highest integral (1.00) followed by the signals assigned to (di-*tert*-butylchlorostannoxy)di-*tert*-butylchlorosilane (**4**; integral 0.58), t-$Bu_2ClSnOSnCl$-t-Bu_2[9] (δ −28.3 ppm, integral 0.44), 1,1,3,3,5,5-hexa-*tert*-butyl-2,4,6-trioxa-5-sila-1,3-distannacyclohexane (**2**; integral 0.17), and 1,1,3,3,5,5,7,7-octa-*tert*-butyl-2,4,6,8-tetraoxa-3,7-disila-1,5-distannacyclooctane (**5**; integral 0.08). Also present was a broad signal at 53.1 ppm (integral ratio 0.22), which was assigned to t-Bu_2SnCl_2. The identification of **2**−**5** followed from chemical shifts, coupling patterns, and signal-to-satellite integral ratios[10] of both the ^{119}Sn and ^{29}Si NMR spectra (Scheme 1, Table 1). Reactions were performed in toluene at 100 °C and after cooling to room temperature and recrystallization of the precipitate resulted in the isolation of t-$Bu_2Si(OSn$-t-$Bu_2)_2O$[3u] (**2**) and $(t$-Bu_2SiOSn-t-$Bu_2O)_2$ (**5**) as colorless crystals. The complete NMR data for **2** and **5** (Table 1, Experimental Section) as well as molecular weight determinations and mass spectra (Experimental Section) are in agreement with their six- and eight-membered ring structures, respectively.

The formation of the six-membered stannasiloxane ring **2** can formally be rationalized as nucleophilic attack of the Si−Cl function at a tin atom in di-*tert*-butyltin oxide (**1**) followed by ring opening under formation of a

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Table 1. Selected NMR Data for 1−31 (Chemical Shifts δ in ppm, Coupling Constants J in Hz)

	δ (^{119}Sn)	^2J(^{119}Sn−X−^{117}Sn)	δ(MAS ^{119}Sn)	δ(^{29}Si)[h]	^2J(^{29}Si−O−^{119}Sn)	^1J(^{29}Si−^{19}F)
1	−83.5[3u]	365	−84.3			
2[i 10c]	−107.2	293	−106.6	−17.9	50[a]	
3	−67.9			−23.5	105	
4	−58.5			6.7	105	
5[i 10c]	−178.5		−178.1[b]	−25.7	98	
6	−56.8			−14.7	85	
7[i]	−149.5		−145.6	−42.7	65	
8[i]	−119.5[3r]		−167.1	−35.9	34[a]	
9[i]	−153.1		−150.2	−43.2, −45.8	70	
10[i]	−161.4		−160.2	7.5	77	
11[i]	−164.7		−162.1	−15.0 (d)	84	312
12	−58.4			9.4	85	
13	−161.9			−11.2 (d)	73	302
14	−159.4			−7.1 (d)	65	290
15	−152.6			−35.3 (d)	67	282
16	−160.1			−14.6	87	
17	−53.2			−14.0	94	
18	−166.6 (*trans*)			−38.9	95	
	−167.7 (*cis*)			−39.1	95	
19	−164.7			−58.4 (*t*)	73	293
20	−228.3 (d)[c]	n.o.		−52.3	57	278
	−279.5 (t)[d]					
21[i]	−161.5 (*trans*)		−161.2[e]	−55.7 (d)	81	282
	−163.1 (*cis*)		−164.9	−56.0 (d)	82	278
22	−100.8[f]	323		−52.5 (d)	43[a]	290
23	−98.6	298		−38.3	36[a]	
24	−3.6	35.0		−19.7	60	
25	8.8[g])	47.8		−53.1 (d)	50	308
26	10.7	36.4		−39.9	41	
27	−268.5 (1)	n.o.		−55.3	n.o.	282
	−270.6 (2)					
28[i]	−267.2 (2)[3u]	n.o.	−265.7[3u]	−42.7	59	
	−269.0 (1)		−273.7			
29[i]	−125.7	688	−123.0	−45.3	67	
			−132.3			
30[i]	−135.7			10.6	58	
31	−169.2			−25.9 *t*-Bu	97	282
				−56.5 F (d)	82	

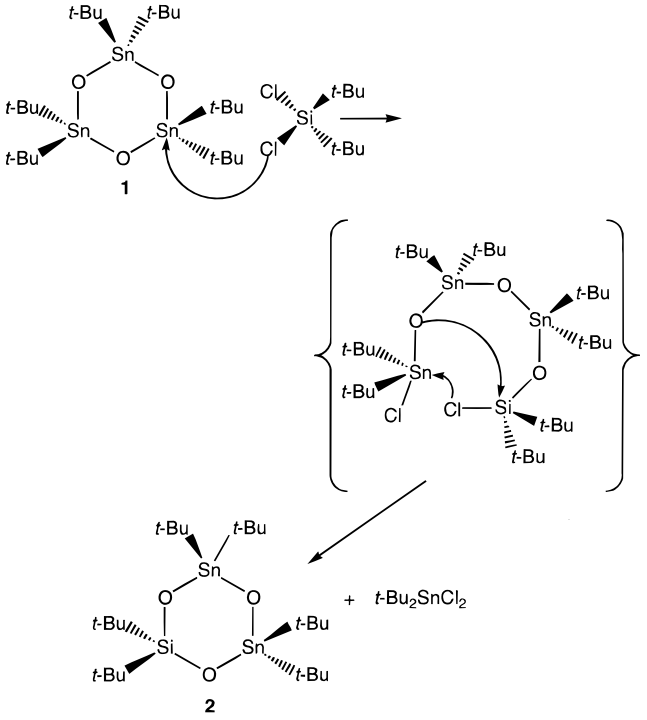
[a] Unresolved ^1J(^{29}Si−O−$^{119/117}$Sn). [b] The value reported in ref 10c is not correct. [c] ^1J(^{119}Sn−^{19}F) = 1250 Hz. [d] ^1J(^{119}Sn−^{19}F) = 2450 Hz. [e] Disordered Sn sites; ratio 60:40. [f] ^3J(^{119}Sn−OSi−^{19}F) = 9.1 Hz). [g] ^3J(^{119}Sn−OSi−^{19}F) = 6.8 Hz. [h] d = doublet, t = triplet. [i] Isolated species.

silicon−oxygen bond. The six-membered ring is then closed by release of *t*-Bu_2SnCl_2 (Scheme 2). The latter accounts for formation of 1,3-dichloro-tetra-*tert*-butyldistannoxane, *t*-$Bu_2ClSnOSnCl$-*t*-Bu_2, as it reacts with di-*tert*-butyltin oxide (**1**), which is still present in the reaction mixture.

Interestingly, there was formation neither of (*t*-$Bu_2SiO)_3$[11] nor of *t*-$Bu_2Sn(OSi$-*t*-$Bu_2)_2O$ (**3b**); i.e., in no case was formation of a Si−O−Si linkage achieved. In fact, the latter compound should be formed by reaction of *t*-Bu_2SiCl_2 with the six-membered stannasiloxane ring **2**, but it seems that steric crowding prevents the Sn−O−Si oxygen in **3a** from attacking the Si−Cl function (Scheme 3). Instead, **3a** reacts with *t*-Bu_2SnCl_2, which was generated according to Scheme 2, to form the open-chain stannasiloxanes **3** and **4**. Compound **3** is in equilibrium with *t*-Bu_2SnCl_2 and the eight-membered stannasiloxane ring **5**.

Compounds **3**, **4**, and *t*-$Bu_2ClSnOSnCl$-*t*-Bu_2[9] are moisture-sensitive, as was shown by formation of *t*-$Bu_2Sn(OH)Cl$[12a] and *t*-$Bu_2Si(OH)_2$[12b] upon treatment with water of the solution obtained according to Scheme 1.

Scheme 2



The last two compounds were isolated and found to be

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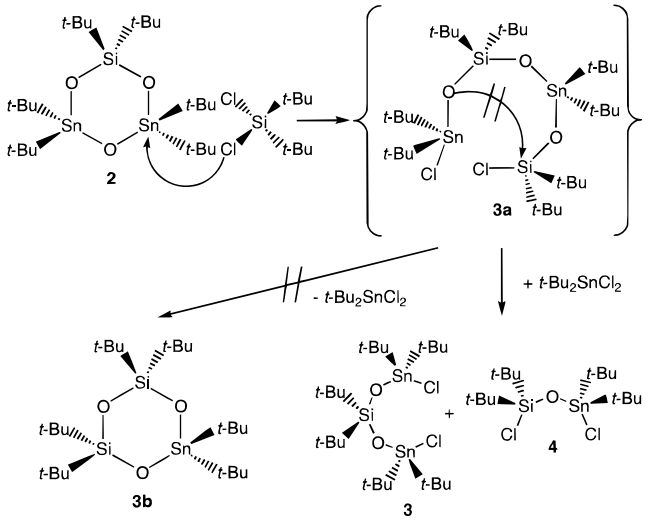
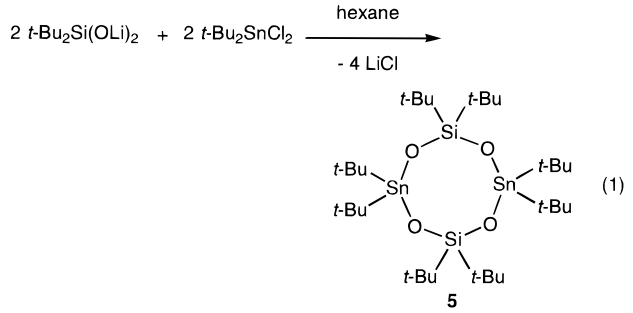
Scheme 3



identical with the compounds described in the literature.[12] The hydrolysis of stannasiloxane **3** proceeds via formation of *t*-$Bu_2ClSnOSi(OH)$-*t*-Bu_2 (**6**), which was identified *in situ* by its ^{29}Si and ^{119}Sn NMR spectra (Table 1).

The eight-membered stannasiloxane ring **5** was also prepared by reaction of *t*-$Bu_2Si(OLi)_2$[3i] with *t*-Bu_2SnCl_2 (eq 1). On exposure to atmospheric moisture compound

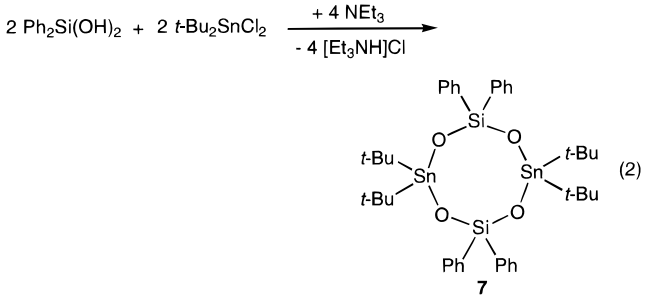


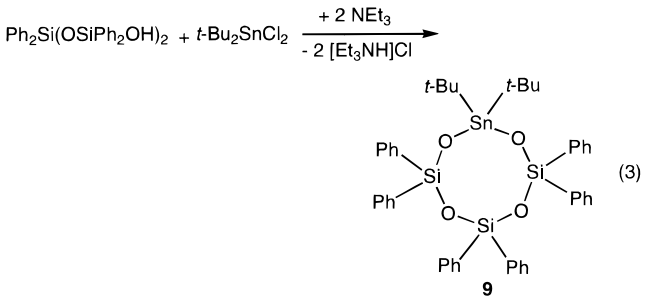
5 hydrolyzes, with formation of the six-membered stannasiloxane ring **2** and *t*-$Bu_2Si(OH)_2$.

The molecular structure of the eight-membered stannasiloxane ring **5** is discussed below. X-ray measurements were also performed on single crystals of stannasiloxane **2** and its related stannagermoxane *t*-$Bu_2Ge(OSn\text{-}t\text{-}Bu_2)_2O$. However, these compounds show a statistical disorder of silicon and tin and of germanium and tin, respectively, and their structures will be discussed in a forthcoming paper.

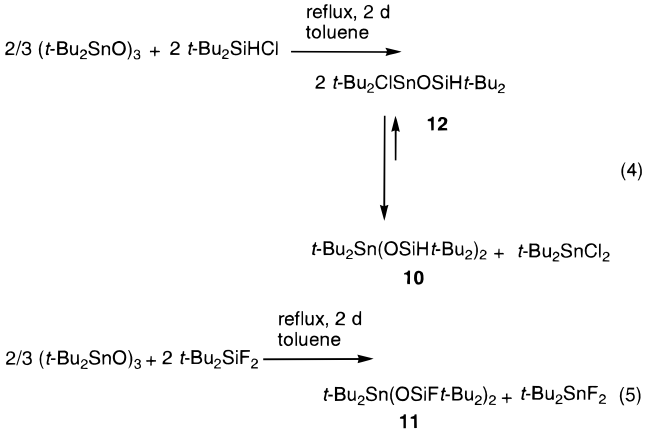
When the reaction according to Scheme 1 was performed with Ph_2SiCl_2 instead of *t*-Bu_2SiCl_2, complete oxygen transfer and formation of *t*-Bu_2SnCl_2 and $(Ph_2SiO)_n$ ($n = 3$, δ (^{29}Si) $-$ 33.3 ppm,[13a] integral 2.0; $n = 4$, δ (^{29}Si) $-$ 42.4 ppm,[6c] integral 4.1) was observed. In addition, there were signals of low intensity at $-$ 42.7, $-$ 43.9, $-$ 45.2, and $-$45.9 ppm (total integral 0.6) which are likely to represent higher siloxane oligomers. However, during the reaction the cyclic stannasiloxanes $(Ph_2SiOSn\text{-}t\text{-}Bu_2O)_2$ (**7**), *t*-$Bu_2Sn(OSiPh_2)_2O$ (**8**),[3r] and *t*-$Bu_2Sn(OSiPh_2O)_2SiPh_2$ (**9**) were formed as intermediates, as was evidenced by ^{29}Si and ^{119}Sn NMR studies (see Table 1) of the reaction mixture after 1.5 h at 57 °C.

The eight-membered stannasiloxane rings **7** and **9** were prepared by reaction of $Ph_2Si(OH)_2$[14] and $Ph_2Si(OSiPh_2OH)_2$,[14] respectively, with *t*-Bu_2SnCl_2 in the presence of triethylamine (eqs 2 and 3). Compounds **7** and **9** are stable to moisture. Their molecular structures are discussed below.





In contrast to the complex reaction shown in Scheme 1, both di-*tert*-butylchlorosilane, *t*-Bu_2SiHCl, and di-*tert*-butyldifluorosilane, *t*-Bu_2SiF_2, react almost quantitatively with **1** to provide bis(di-*tert*-butylsiloxy)di-*tert*-butylstannane, *t*-$Bu_2Sn(OSiHt\text{-}Bu_2)_2$ (**10**), and bis(di-*tert*-butylfluorosiloxy)di-*tert*-butylstannane, *t*-$Bu_2Sn(OSiFt\text{-}Bu_2)_2$ (**11**), respectively (eqs 4 and 5). In the presence

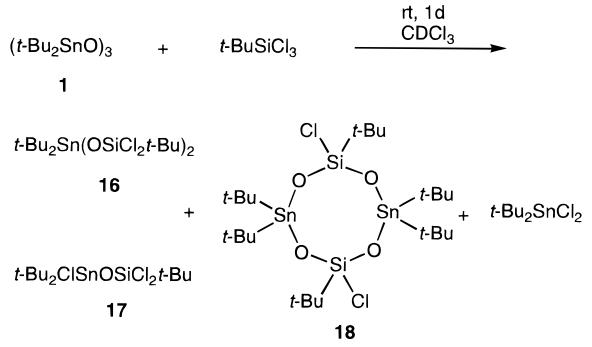


of *t*-Bu_2SnCl_2, stannasiloxane **10** is in equilibrium with (di-*tert*-butylsiloxy)di-*tert*-butylchlorostannane, *t*-$Bu_2ClSnOSi(H)$-*t*-Bu_2 (**12**). During the reactions according to eqs 4 and 5, there was no formation of the six- and eight-membered stannasiloxane rings **2** and **5**, which is attributed to the low reactivity of the Si$-$H and Si$-$F bonds in **10** and **11**, respectively. Sterically less crowded organohydridosiloxanes such as $(MeSiHO)_x$ even trans-

(13) Engelhardt, G.; Mägi, M.; Lippmaa, E. *J. Organomet. Chem.* **1973**, *54*, 115.

(14) Behbehani, H.; Brisdon, B. J.; Mahon, M. F.; Molloy, K. C.; Mazhar, M. *J. Organomet. Chem.* **1993**, *463*, 41.

Scheme 4



fer their hydrogen to stannoxanes.[2i] Compounds **10** and **11** are low-melting colorless solids which show low sensitivity toward moisture.

The identity of *t*-Bu_2SnF_2 formed along the reaction according to eq 5 was confirmed by elemental analysis and by the ^{119}Sn NMR spectrum of its fluoride adduct $[t\text{-}Bu_2SnF_3]^-$,[15] which showed a quartet at −363.4 ppm ($^1J(^{119}Sn-^{19}F) = 2752$ Hz).

The reaction according to eq 5 can be extended to the *in situ* synthesis of the stannasiloxanes *t*-$Bu_2Sn(OSiFR_2)_2$ (**13**, R = Et; **14**, R = *i*-Pr; **15**, R = Ph), as was evidenced by ^{29}Si and ^{119}Sn NMR studies of the reaction mixtures of **1** and the corresponding diorganodifluorosilanes R_2SiF_2 (R = Et, *i*-Pr, Ph) (Table 1). However, no attempts were made to isolate these species.

The reaction of di-*tert*-butyltin oxide (**1**) with *t*-$BuSiCl_3$ in $CDCl_3$ at room temperature was studied in the molar ratios 1:6 (case A), 1:3 (case B), and 1:2 (case C), by monitoring ^{29}Si and ^{119}Sn NMR spectra and considering the signal-to-satellite integral ratios and coupling patterns (Scheme 4, Table 1).

In case A formation of *t*-Bu_2SnCl_2 ($\delta(^{119}Sn)$ 53.7 ppm, 35%), *t*-$Bu_2Sn(OSiCl_2\text{-}t\text{-}Bu)_2$ (**16**; 21%), and *t*-$Bu_2ClSnOSiCl_2\text{-}t\text{-}Bu$ (**17**; 44%) was observed. In case B the product distribution was more complex. In addition to *t*-Bu_2SnCl_2 (35%), **16** (11%), and **17** (15%) the ^{29}Si and ^{119}Sn NMR spectra showed signals which were assigned with caution to the eight-membered ring **18** (*cis*−*trans* mixture, 40:60; 18%) (Scheme 4, Table 1). Furthermore, there were ^{119}Sn NMR signals of low intensity at − 63.0 and − 161.2 ppm that have not been assigned yet.

In case C the reaction mixture contained again *t*-Bu_2SnCl_2 (29%), **18** (*cis*−*trans* mixture, 40:60; 35%), and traces of **16** (6%), but no **17**. Also present in the ^{119}Sn NMR spectrum were minor signals at −61.2 and −63.0 ppm, for which no assignments were made. After this reaction mixture was heated for 2 days at 57 °C the ^{119}Sn NMR spectrum shows quantitative formation of *t*-Bu_2SnCl_2 ($\delta(^{119}Sn)$ 54.0 ppm), indicating complete oxygen transfer from **1** to silicon. Removing the *t*-Bu_2SnCl_2 in vacuo by Kugelrohr distillation resulted in a residue which was soluble in THF but not in $CDCl_3$. Its ^{29}Si NMR spectrum displayed nine resonances at δ (integral) −40.9 (26), −49.0 (5), −49.2 (9), −49.6 (8), −49.8 (8), −49.9 (8), −57.6 (3), −58.4 (4), and −58.6 (5) ppm. The signal at −49.8 ppm was assigned to (*t*-$BuSiO_{1.5})_4$, as could be demonstrated by adding an authentic sample of this compound, which was prepared according to the procedure reported by Wiberg.[16a] The other signals have not been assigned yet, although one of these signals may belong to (*t*-$BuSiO_{1.5})_6$, for which a $\delta(^{29}Si)$ (C_6D_6) value of −53.3 ppm was reported recently.[16b]

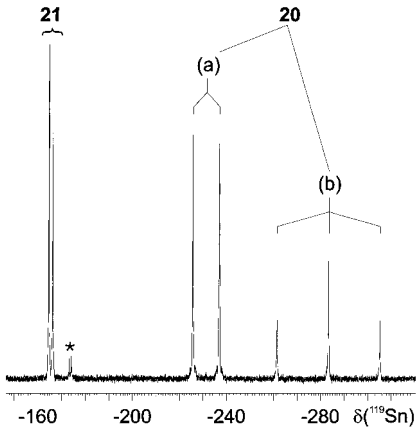
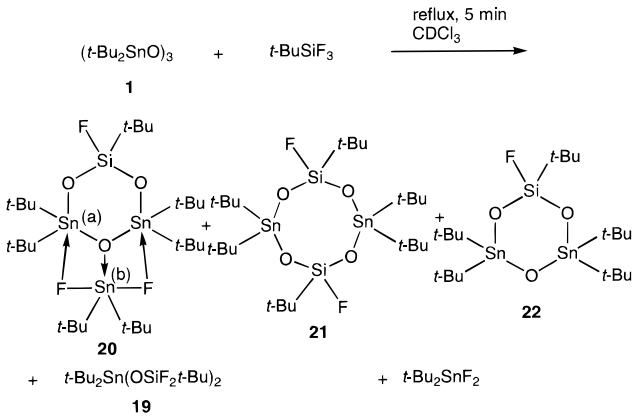


Figure 1. ^{119}Sn NMR spectrum in $CDCl_3$ of the reaction mixture of $(t\text{-}Bu_2SnO)_3$ (**1**) and *t*-$BuSiF_3$ in the molar ratio 1:1.5 (case B, Scheme 5). (a) and (b) refer to the labels given for **20** in Scheme 5. The signals with an asterisk could not be assigned.

Scheme 5



The reaction of **1** with *tert*-butyltrifluorosilane, *t*-$BuSiF_3$, was studied in the molar ratios 1:3 (case A), 1:1.5 (case B), and 1:1 (case C) (Scheme 5, Table 1).

For case A ^{1}H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectroscopy of the reaction mixture (see Table 1 and Experimental Section) revealed exclusive *in situ* formation of *t*-$Bu_2Sn(OSiF_2\text{-}t\text{-}Bu)_2$ (**19**). In case B the ^{29}Si and ^{119}Sn NMR spectra (Table 1, Figure 1) indicate formation of the stannasiloxane complex **20** and of the eight-membered stannasiloxane ring **21** (*cis*−*trans* mixture, ∼41:59) in a ratio of about 1:0.83. The identity of **20** is further confirmed by the observation that as a result of their relative position with regard to the silicon-bonded fluorine the ^{13}C NMR signals of the *tert*-butyl groups bound to Sn(a) as well as to Sn(b) are each split into two resonances of equal integral ratio.

Compound **20** could not be isolated, but recently we succeeded in the synthesis and determination of the molecular structure of $\{[Ph_2Si(OSn\text{-}t\text{-}Bu_2)_2O]\cdot t\text{-}Bu_2$-

(15) Dakternieks, D.; Zhu, H. *Organometallics* **1992**, *11*, 3820.

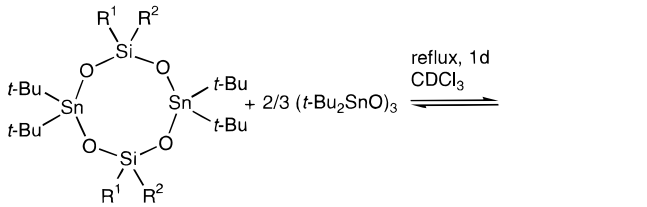
(16) (a) Wiberg, E.; Simmler, W. *Z. Allg. Anorg. Chem.* **1955**, *282*, 331. (b) Unno, M.; Alias, S. B.; Saito, H.; Matsumoto, H. *Organometallics* **1996**, *15*, 2413.

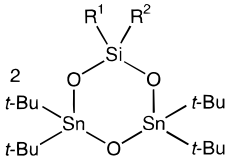
SnF_2} (**20a**),[17] an analogue of **20**. Compounds **20** and **20a** are structurally related to the hydroxy-substituted compounds {[E(OSn-*t*-Bu_2)$_2$O]·*t*-$Bu_2Sn(OH)_2$} (E = CO,[18] MesB,[4a] Me_2Si,[3v] Ph_2Si[3u]).

Compound **21** was isolated as the *trans* isomer, and its crystal structure was determined (see below). The *cis*−*trans* equilibrium observed for **21** is slow on the NMR time scale but fast on the laboratory time scale, and hence, the *cis* isomer was not observed in the solid state.

The solution of case C contained, according to its ^{119}Sn and ^{29}Si NMR spectra (see Table 1), in addition to compounds **20** (integral of the ^{119}Sn resonances ∼2.0) and **21** (integral of the ^{119}Sn resonance ∼1.0) the six-membered ring **22** (integral of the ^{119}Sn resonance 0.5) (Scheme 5).

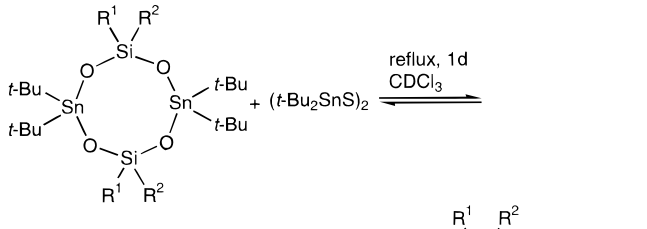
Redistribution Reactions. The *in situ* reaction of the eight-membered stannasiloxane rings **5**, **7**, and **21** with either di-*tert*-butyltin oxide (*t*-$Bu_2SnO)_3$ (**1**), or di-*tert*-butyltin sulfide, (*t*-$Bu_2SnS)_2$,[19] provided the six-membered rings **2**, **23**, and **22** and **24**−**26**, respectively (eqs 6 and 7), as was evidenced by the corresponding signals in the ^{29}Si and ^{119}Sn NMR spectra (Table 1).

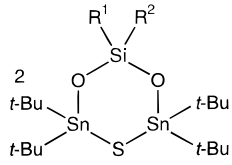




(6)

2, $R^1 = R^2$ = *t*-Bu
22, R^1 = *t*-Bu, R^2 = F
23, $R^1 = R^2$ = Ph





(7)

24, $R^1 = R^2$ = *t*-Bu
25, R^1 = *t*-Bu, R^2 = F
26, $R^1 = R^2$ = Ph

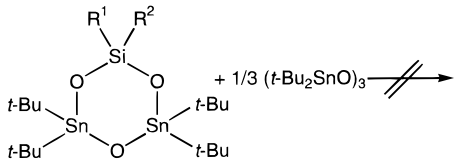
The reaction is quantitative for **2**, **23**, and **24**, but only compound **2** could be isolated. Attempts to isolate **23** and **24** by evaporation of the solvent provided exclusively di-*tert*-butyltin oxide, (*t*-$Bu_2SnO)_3$ (**1**), and (Ph_2-SiOSn-*t*-$Bu_2O)_2$ (**7**) and di-*tert*-butyltin sulfide, (*t*-Bu_2-$SnS)_2$, and (*t*-Bu_2SiOSn-*t*-$Bu_2O)_2$ (**5**), respectively, as was unambiguously evidenced by ^{119}Sn MAS NMR spectroscopy. The signals observed for the corresponding residues were identical with the signals recorded for the authentic compounds **1**, **7,** (*t*-$Bu_2SnS)_2$,[19b] and **5**, respectively (Table 1).

In the case of *t*-BuFSi(OSn-*t*-$Bu_2)_2O$ (**22**) (eq 6) and of *t*-BuFSi(OSn-*t*-$Bu_2)_2S$ (**25**) and Ph_2Si(OSn-*t*-$Bu_2)_2S$ (**26**) (eq 7) the ^{119}Sn NMR spectra indicate equilibria between di-*tert*-butyltin oxide, (*t*-$Bu_2SnO)_3$ (**1**; 13.0%), (*t*-BuFSiOSn-*t*-$Bu_2O)_2$ (**21**; 19.5%), and *t*-BuFSi(OSn-*t*-$Bu_2)_2O$ (**22**; 67.5%), between (*t*-BuFSiOSn-*t*-$Bu_2O)_2$ (**21**; 40%), (*t*-$Bu_2SnS)_2$ (40%), and *t*-BuFSi(OSn-*t*-$Bu_2)_2S$ (**25**; 20%), and between (Ph_2SiOSn-*t*-$Bu_2O)_2$ (**7**; 7%), (*t*-Bu_2-$SnS)_2$ (7%), and Ph_2Si(OSn-*t*-$Bu_2)_2S$ (**26**; 86%), respectively.

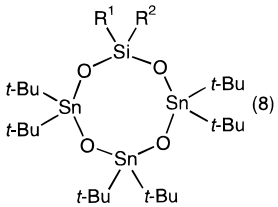
The results for these redistribution reactions demonstrate that the R groups at silicon and the heteroatoms E control the kinetic and thermodynamic stability of R^1R^2Si(OSn-*t*-$Bu_2)_2$E (E = O, S).

The strength of the Si−O bonds in the eight-membered stannasiloxane rings **5**, **7**, and **21** prevents formal extrusion of both [R^1R^2SiO] and [*t*-Bu_2SnO]. Consequently in solutions of **5**, **7**, and **21** no formation of the respective six-membered stannasiloxane rings **2**, **23**, and **22** was observed, even though they should be favored entropically and in the case of **2** also energetically. This view is further supported by the fact that we never observed formation of the single tin-containing eight-membered stannasiloxane ring *t*-$Bu_2Sn(OSiPh_2O)_2$-$SiPh_2$ (**9**) in a solution of the eight-membered stannasiloxane ring (Ph_2SiOSn-*t*-$Bu_2O)_2$ (**7**). This means that there was in no case formation of species containing R_2-Si−O−SiR_2 linkages.

On the other hand, the polarity as well as the kinetic lability of the Sn−O bond in the eight-membered stannasiloxane rings **5**, **7**, and **21** allows formal insertion of [*t*-Bu_2SnX] (X = O, S) followed by formation of the entropy-favored six-membered rings **2** and **22**−**26** (eqs 6 and 7). Furthermore, this high kinetic lability of the Sn−O bond prevents formation of any 2,4,6,8-tetraoxa-3-sila-1,5,7-tristannacyclooctane derivatives R^1R^2Si-(OSn-*t*-$Bu_2O)_2$Sn-*t*-Bu_2 by reaction of the six-membered rings **2**, **22**, and **23** with (*t*-$Bu_2SnO)_3$ (eq 8).



2, $R^1 = R^2$ = *t*-Bu
22, R^1 = *t*-Bu, R^2 = F
23, $R^1 = R^2$ = Ph

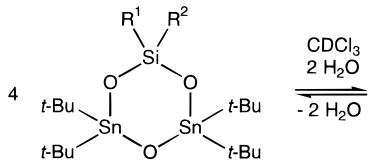


(8)

The *in situ* generated six-membered stannasiloxane rings **22** and **23** (eq 6) are very sensitive toward

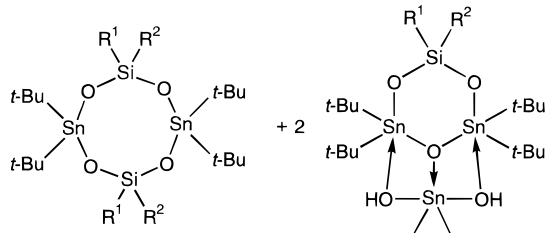
(17) Beckmann, J.; Costisella, B.; Jurkschat, K.; Schürmann, M. Manuscript in preparation.
(18) Reuter, H. Thesis, University of Bonn, 1987.
(19) (a) Puff, H.; Bertram, G.; Ebeling, B.; Franken, M.; Gattermeyer, R.; Hundt, R.; Schuh, W.; Zimmer, R. *J. Organmet. Chem*. **1989**, *379*, 235. (b) Harris, R. K.; Sebald, A. *Magn. Reson. Chem*. **1989**, *27*, 81.

moisture. Thus, the ^{29}Si and ^{119}Sn NMR spectra of $CDCl_3$ solutions of **22** and **23** to which had been added a droplet of water showed formation of the eight-membered stannasiloxane ring **21** and the stannasiloxane complex **27** and of the eight-membered stannasiloxane ring **7** and the stannasiloxane complex **28**,[3u] respectively (eq 9).



22, R^1 = *t*-Bu, R^2 = F (19.2%)
23, R^1 = R^2= Ph (75.7%)

(9)



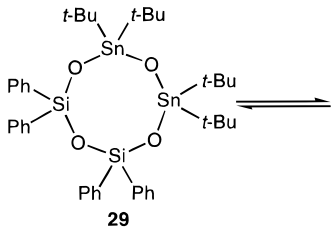
21, R^1 = *t*-Bu, R^2 = F (27.2%)
7, R^1 = R^2= Ph (8.1%)

27, R^1 = *t*-Bu, R^2 = F (53.6%)
28, R^1 = R^2 = Ph (15.9%)

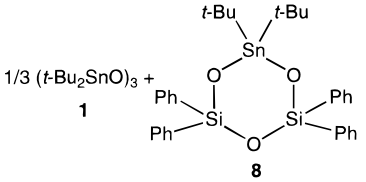
Remarkably, the line width of the ^{119}Sn NMR signal of **23** being in equilibrium with **7** and **28** (eq 9) is about 56 Hz compared to a $W_{1/2}$ value of 3 Hz for the signal of pure **23** in $CDCl_3$[3u] generated according to eq 6. It is worth noting that the reaction according to eq 9 does not proceed for the six-membered stannasiloxane ring *t*-$Bu_2Si(OSn$-*t*-$Bu_2)_2O$ (**2**).

The fine balance between six- and eight-membered stannasiloxane rings in dependence of Si−O and Sn−O bond energies and entropy gain is nicely demonstrated by the behavior of the eight-membered stannasiloxane ring [(*t*-$Bu_2SnO)_2(Ph_2SiO)_2$] (**29**), the *in situ* formation of which we have reported recently[3r] and the molecular structure of which is described below. Compound **29** is a structural isomer of the eight-membered stannasiloxane ring **7**.

In $CDCl_3$ solution, **29** (75%) is in equilibrium with di-*tert*-butyltin oxide, (*t*-$Bu_2SnO)_3$ (**1**), and the six-membered stannasiloxane ring [(*t*-$Bu_2SnO)(Ph_2SiO)_2$] (**8**)[3r] (25%) (eq 10). The entropy gain by formation of six-membered stannasiloxane ring **8** is almost compensated by its high ring strain due to the Ph_2Si−O−$SiPh_2$ fragment. The latter accounts for the polymeric structure of **8** in the solid state.[3r]

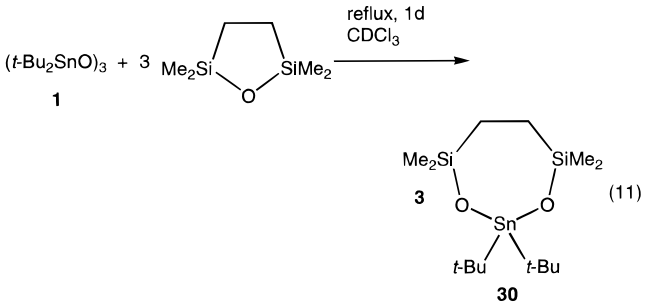


29

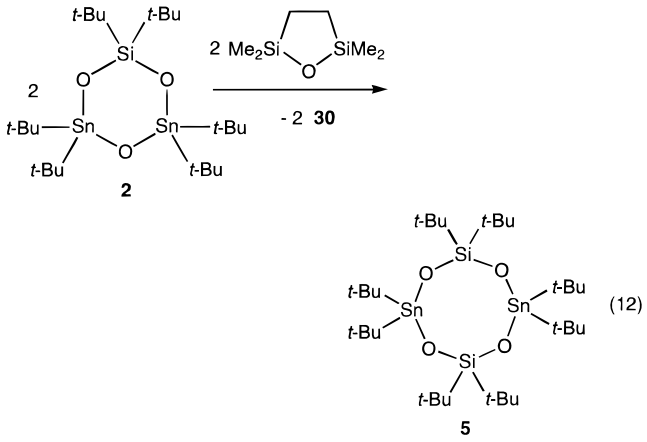


1 **8** (10)

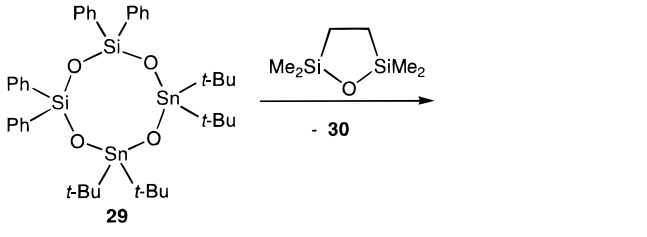
1,1,3,3-Tetramethyl-2-oxa-1,3-disilacyclopentane, $(CH_2SiMe_2)_2O$, is known to be an efficient trap reagent for reactive intermediates in organosilicon chemistry.[20] ^{29}Si and ^{119}Sn NMR studies show that species containing a Sn−O−Sn bridge such as (*t*-$Bu_2SnO)_3$ (**1**), *t*-$Bu_2Si(OSn$-*t*-$Bu_2)_2O$ (**2**), and [(*t*-$Bu_2SnO)_2(Ph_2SiO)_2$] (**29**) react quantitatively with this reagent to provide 1,1-di-*tert*-butyl-3,3,6,6-tetramethyl-2,7-dioxa-3,6-disila-1-stannacycloheptane (**30**) and the stannasiloxanes **5** and **8**, respectively (eqs 11−13). To the best of our knowledge,



1 **3** **30** (11)



2 **5** (12)



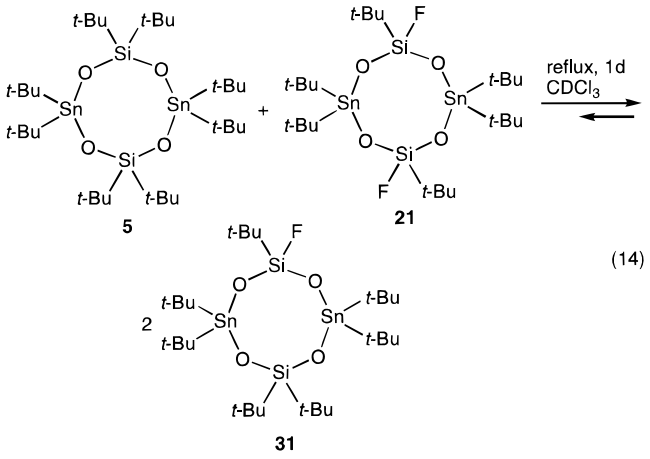
29 **8** (13)

these are the first examples where a Si−O−Si bridge is cleaved in favor of formation of a Si−O−Sn bridge.

Interestingly, under the same reaction conditions the cyclosiloxanes $(Ph_2SiO)_n$ (n = 3, 4) do not react with 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane.[20]

(20) Lu, P.; Paulasaari, J. K.; Weber, W. P. *Organometallics* **1996**, *15*, 4649.

Mixing equimolar quantities of **5** and **21** (*cis*−*trans* mixture) resulted in quantitative *in situ* formation of **31** (eq 14), as was evidenced by ^{29}Si and ^{119}Sn NMR spectroscopy.



(14)

Redistribution reactions of organosilicon chalcogenides have been interpreted in terms of participation of reactive [R_2Si═X] (X = O,[20,21] X = S, Se[21]) species, but this interpretation was questioned recently by Mori *et al.*[22a] and Brook *et al.*[22b] In the case of organotin and organolead chalcogenides, redistribution reactions have been interpreted in terms of participation of ladder-type structures.[23]

The result obtained according to eq 14 demonstrates that species such as [*t*-Bu_2Si═O], [*t*-Bu(F)Si═O], and [*t*-Bu_2Sn═O] are unlikely to be involved in the redistribution reactions discussed in this paper, at least not under the experimental conditions employed: i.e., in the presence of traces of water or protons, respectively. This view is supported by the fact that there was formation neither of eight-membered rings containing Si−O−Si bonds nor of rings containing Sn−O−Sn bonds, although the synthetic availability of such species was demonstrated by isolation of compounds **9** and **29** (see eqs 3 and 10). Recent calculations on H_2M═O (M = Si, Ge, Sn, Pb)[24] show these species to be extremely reactive and hence support our conclusion. One model to rationalize the redistribution reaction according to eq 14 is shown in Scheme 6.

Water-induced ring opening of **5** and **21** is followed by release of *t*-$Bu_2Si(OH)_2$ and *t*-Bu(F)$Si(OH)_2$ and formation of six-membered stannasiloxane rings **2** and **22**, which then recombine crosswise with elimination of water to give the eight-membered stannasiloxane **31**. This mechanism gets support from an electrospray mass spectrum of **21**. The spectrum (positive mode) shows mass clusters for [**21**·H]$^+$ (*m*/*e* 739.5), [**21**·Na]$^+$ (*m*/*e* 761.4), [**21**·K]$^+$ (*m*/*e* 777.4), and [**22**·H]$^+$ (*m*/*e* 619.3) (Chart 1). Interestingly, there are also clusters at *m*/*e* 807.4 and 867.5, which are assigned to [(*t*-$Bu_2SnO)_3$·*i*-$PrOH_2$]$^+$ and [**22**·*t*-Bu_2SnOH]$^+$ (Chart 1). The spectrum showed no evidence for formation of protonated dimers of **21** or of [*t*-Bu(F)SiO_2Sn-*t*-Bu_2·H]$^+$, and hence, alternative mechanisms via 4- or 16-membered rings are less likely.

Scheme 6

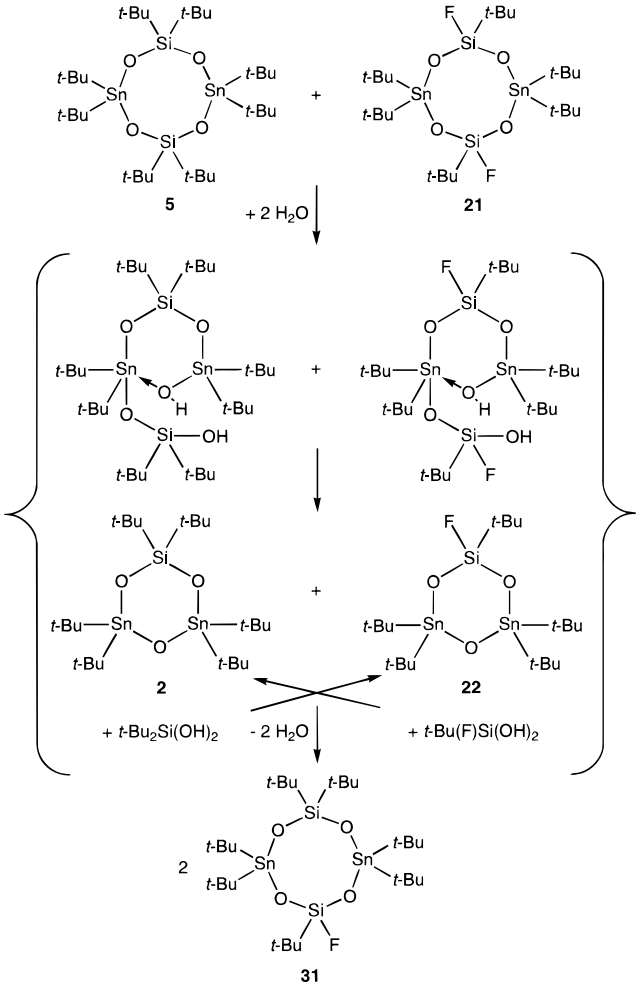
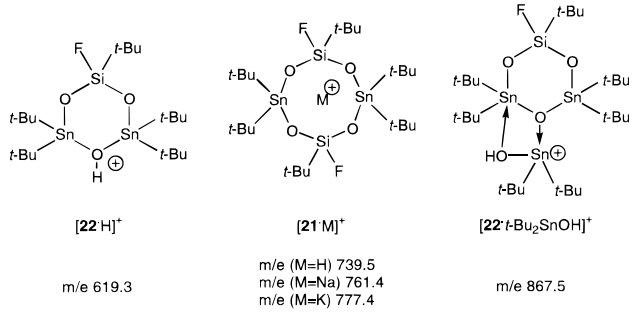


Chart 1



NMR Spectroscopic Trends. From an inspection of the NMR data listed in Table 1, some general trends become apparent concerning the chemical shifts and coupling constants to be expected for different types of stannasiloxanes. These trends resemble those reported for stannacycloalkanes.[25a]

(21) (a) Boudjouk, P.; Bahr, S. R.; Thompson, D. P. *Organometallics* **1991**, *10*, 778. (b) Boudjouk, P. *Polyhedron* **1991**, *10*, 1231. (c) Davies, A. G.; Neville, A. G. *J. Organomet. Chem.* **1992**, *436*, 255. (d) Voronkov, M. G.; Basenko, S. V. *J. Organomet. Chem.* **1995**, *500*, 325.

(22) (a) Mori, S.; Okada, F.; Sekiguchi, O.; Fujishige, M.; Koitabashi, R.; Tajima, S. *J. Organomet. Chem.* **1997**, *527*, 277. (b) Le Roux, C.; Yang, H.; Wenzel, S. Grigoras, S.; Brook, M. A. *Organometallics* **1998**, *17*, 556.

(23) (a) Schmidt, B. M.; Dräger, M. *J. Organomet. Chem.* **1990**, *399*, 63. (b) Flöck, O. R.; Dräger, M. *Organometallics* **1993**, *12*, 4623.

(24) (a) Olah, G. A.; Li, X. Y.; Wang, Q.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 8962. (b) Kapp, J.; Remko, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *118*, 5745. (c) Kapp, J.; Remko, M.; Schleyer, P. v. R. *Inorg. Chem.* **1997**, *36*, 4241.

(25) (a) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73. (b) Kerschl, S.; Wrackmeyer, B. *Z. Naturforsch.* **1987**, *42B*, 387.

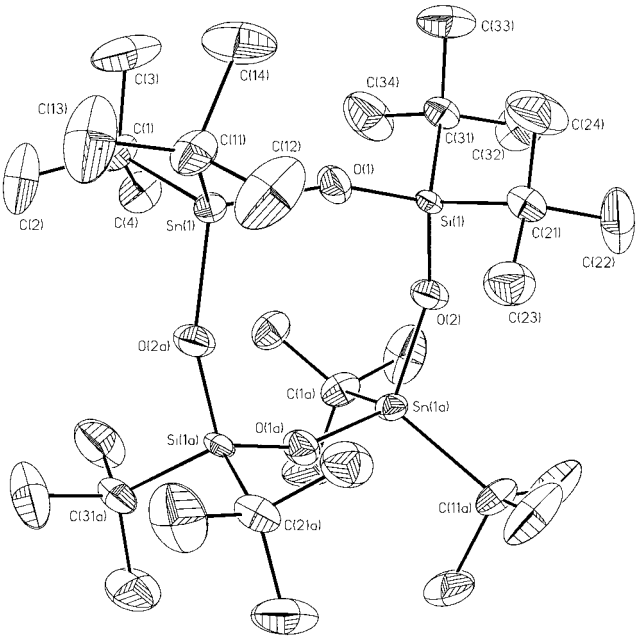


Figure 2. General view (SHELXTL-PLUS) of a molecule of **5** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformation used to generate equivalent atoms: a = $-x$, y, $-z + 0.5$).

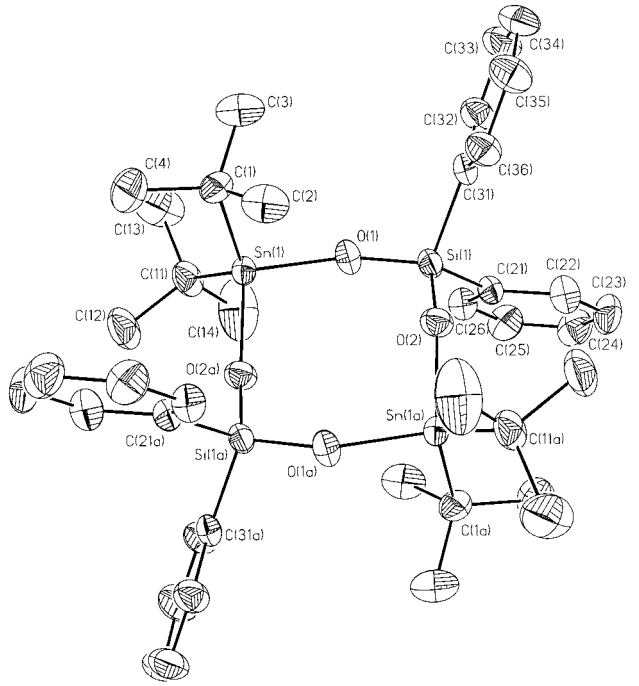


Figure 3. General view (SHELXTL-PLUS) of a molecule of **7** showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformation used to generate equivalent atoms: a = $-x + 1$, $-y + 1$, $-z + 1$).

(i) The ^{119}Sn chemical shift moves to higher frequency as the ring size of the stannasiloxanes increases, provided that compounds with identical substituent patterns at tin are compared. Thus, within the stannasiloxane family containing the *t*-$Bu_2Sn(OSiR_2O-)_2$ fragment, the six-membered stannasiloxane ring **8** shows a chemical shift of −119.5 ppm, whereas the corresponding eight-membered rings **5**, **7**, **9**, **18**, **21**, and **31** show chemical shifts between −149.5 and −178.5 ppm.

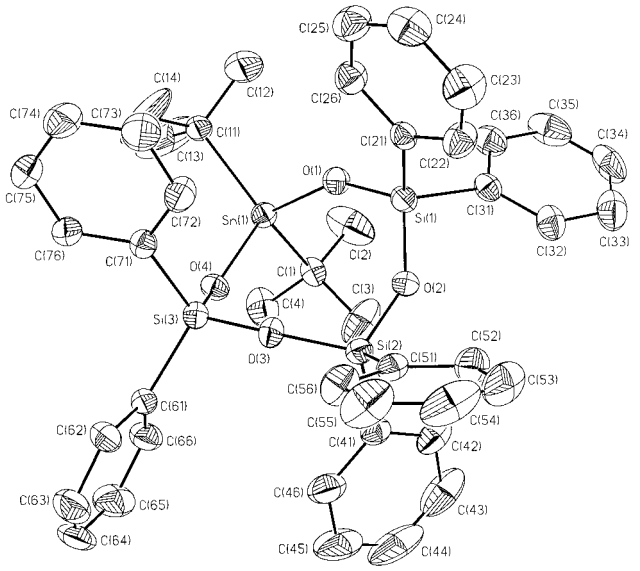


Figure 4. General view (SHELXTL-PLUS) of a molecule of **9** showing 30% probability displacement ellipsoids and the atom numbering.

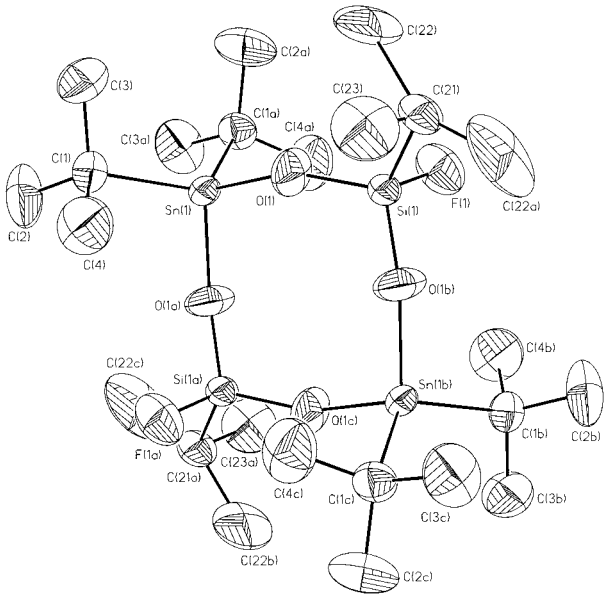


Figure 5. General view (SHELXTL-PLUS) of a molecule of **21** (*trans* isomer) showing 30% probability displacement ellipsoids and the atom numbering (symmetry transformations used to generate equivalent atoms: a = $-x$, y, $-z + 1$; b = x, $-y$, z; c = $-x$, $-y$, $-z + 1$).

(ii) The same trend holds for the ^{29}Si chemical shifts, although it is less pronounced because of the smaller chemical shift range of this nucleus. The six-membered rings **8**, **23**, and **26**, containing the $(Ph_2SiO)_2$ fragment, show chemical shifts between −35.9 and −39.9 ppm, which are close to the value of −33.3 ppm reported for $(Ph_2SiO)_3$.[13] The eight-membered rings **7**, **9**, and **29** exhibit chemical shifts between −42.7 and −45.8 ppm, which are close to the −42.4 ppm measured for $(Ph_2SiO)_4$.[6c] With respect to these values we predict that [Cr(=O)$_2${(OSiPh$_2$)$_2$}] (δ(^{29}Si) 31.9 ppm), which was recently reported by Abbenhuis et al.,[26] is a 6-membered rather than a 12-membered ring in solution.

(26) Abbenhuis, H. C. L.; Vorstenbosch, M. L. W.; van Santen, R. A.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem*. **1997**, *36*, 6431.

Table 2. Crystallographic Data for 5, 7, 9, 21, and 29

	5	7	9	21	29
formula	$C_{32}H_{72}O_4Si_2Sn_2$	$C_{40}H_{56}O_4Si_2Sn_2$	$C_{44}H_{48}O_4Si_3Sn$	$C_{24}H_{54}F_2O_4Si_2Sn_2$	$C_{40}H_{56}O_4Si_2Sn_2$
fw	814.46	894.41	843.78	738.23	894.41
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
cryst size, mm	1.02 × 0.19 × 0.16	0.51 × 0.19 × 0.13	0.20 × 0.20 × 0.20	0.30 × 0.20 × 0.20	0.50 × 0.35 × 0.30
space group	*C*2/*c*	*I*2/*a*	$P2_1/n$	*C*2/*m*	$P2_1/c$
a, Å	21.793(2)	18.848(5)	15.921(1)	17.180(2)	9.993(1)
b, Å	9.3839(5)	12.2214(6)	12.948(1)	12.8535(3)	35.321(1)
c, Å	21.9572(6)	20.526(3)	22.831(1)	8.7915(9)	12.764(1)
α, deg	90	90	90	90	90
β, deg	108.268(4)	112.71(1)	92.986(1)	113.353(5)	102.435(1)
γ, deg	90	90	90	90	90
V, Å^3	4264.0(5)	4362(1)	4688.4(5)	1782.3(3)	4399.5 (6)
Z	4	4	4	2	4
ρ_{calcd}, Mg/m^3	1.269	1.362	1.307	1.376	1.350
ρ_{measd}, Mg/m^3	1.34(1)	1.36(1)	1.19(1)	1.38(3)	1.35(1)
μ, mm^{-1}	10.064	9.904	0.719	12.068	1.224
F(000)	1696	1824	1744	752	1824
θ range, deg	4.24−69.61	4.30−69.57	3.01−26.67	4.44−74.93	2.62−23.24
index ranges	$0 \le h \le 26$	$-22 \le h \le 0$	$-19 \le h \le 19$	$-19 \le h \le 21$	$-10 \le h \le 10$
	$-11 \le k \le 0$	$0 \le k \le 14$	$-16 \le k \le 16$	$-16 \le k \le 16$	$-39 \le k \le 39$
	$26 \le l \le 25$	$-22 \le l \le 24$	$-22 \le l \le 22$	$-11 \le l \le 0$	$-14 \le l \le 13$
no. of rflns collcd	4032	4112	59 088	3913	44 633
completeness to θ_{max}	100.0	100.0	100.0	100.0	94.6
no. of indep rflns/R_{int}	4032/0.0	4112/0.0	8117/0.069	1921/0.0641	5955/0.036
no. of rflns obsd with ($I > 2\sigma(I)$)	3590	3488	3856	1800	3892
abs cor	ψ scan	ψ scan	n.m.[a]	ψ scan	n.m.[a]
T_{max}/T_{min}	1.00/0.64	1.00/0.66		1.00/0.54	
no. of refined params	200	225	477	113	453
GOF(F^2)	1.055	1.044	0.784	1.097	0.904
R1(F) ($I > 2\sigma(I)$)	0.0456	0.0534	0.0363	0.0324	0.0299
wR2(F^2) (all data)	0.1278	0.1452	0.0608	0.0856	0.068
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001	0.001	< 0.001	0.001
largest diff peak/hole, e/Å^3	0.830/−1.615	1.156/−1.433	0.386/−0.360	0.580/−0.865	0.334/−0.396

[a] n.m. = not measured.

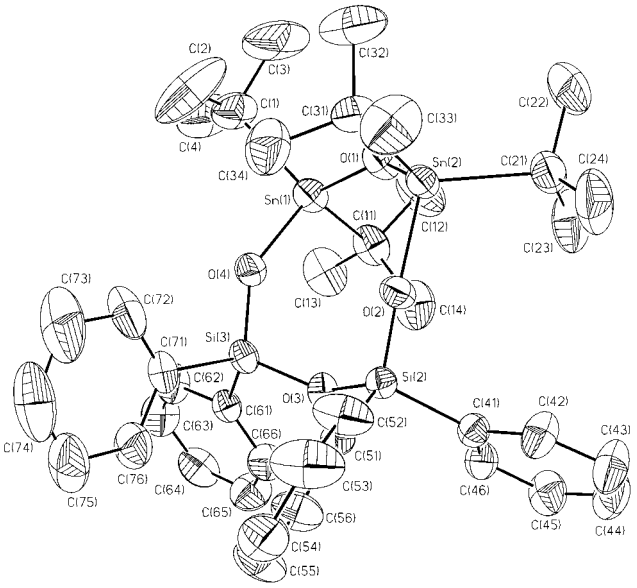


Figure 6. General view (SHELXTL-PLUS) of a molecule of **29** showing 30% probability displacement ellipsoids and the atom numbering.

(iii) The $^2J(^{29}Si-O-^{119}Sn)$ and $^2J(^{117}Sn-O-^{119}Sn)$[25b] coupling constants depend on the corresponding bond angle and are therefore indicative of different ring sizes. The six-membered stannasiloxane rings **2**, **8**, and **22**−**26** show $^2J(^{29}Si-O-^{119}Sn)$ couplings between 34 and 60 Hz, whereas the eight-membered stannasiloxane rings **5**, **7**, **9**, **18**, **21**, and **31** exhibit $^2J(^{29}Si-O-^{119}Sn)$ couplings between 65 and 98 Hz. $^2J(^{117}Sn-O-^{119}Sn)$ couplings are observed in the range between 297 Hz (six-membered stannasiloxane ring **2**) and 688 Hz (eight-membered stannasiloxane ring **29**).

Molecular Structures of the Eight-Membered Stannasiloxane Rings 5, 7, 9, 21, and 29. The molecular structures of **5**, **7**, **9**, **21**, and **29** are shown in Figures 2−6, respectively. Crystal data are given in Table 2. Selected bond lengths and bond angles are listed in Tables 3 and 4, respectively.

The conclusions drawn from NMR, molecular weight determinations, and mass spectra concerning the ring sizes and Si−O−Sn connectivities are confirmed by X-ray analyses. All compounds are eight-membered rings which can be regarded as formal derivatives of $(Ph_2SiO)_4$[27a] in which one or more Ph_2Si units are replaced by *t*-Bu_2Si, *t*-Bu(F)Si, and/or *t*-Bu_2Sn.

The Si−O, Si−C, Si−F, Sn−O, and Sn−C bond lengths are all as expected and are comparable with those of related compounds.[6a−c,8,27] The bond angles at silicon and tin are tetrahedral, with the largest deviation from the ideal value found for the C−Sn−C angles (115.7(2)−124.9(2)°). The intracyclic Si−O−Sn angles vary between 138.9(2) (**6**) and 159.4(3)° (**5**), and the Si−O−Si angles vary between 140.3(2)° (**29**) and 150.6(2)° (**9**). The latter angles are smaller than those reported for the parent compound $(Ph_2SiO)_4$ (152.8(4)−167.8(5)°).[27a] The molecules of **5**, **7**, and **21** lie about a center of inversion.

In **29** both tin atoms are not equivalent, which is confirmed by observation of two ^{119}Sn MAS NMR signals

(27) (a) Braga, D.; Zanotti, G. *Acta Crystallogr.* **1980**, *B36*, 950. (b) Puff, H.; Böckmann, M. P.; Kök, T. R.; Schuh, W. *J. Organomet. Chem.* **1984**, *268*, 197. (c) Akkurt, M.; Kök, T. R.; Faleschini, P.; Randaccio, L.; Puff, H.; Schuh, H. *J. Organomet. Chem.* **1994**, *470*, 59.

Table 3. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for 5, 7, and 21

	5	7	21
Sn(1)−O(1)	1.946(4)	1.970(4)	1.944(3)
Sn(1)−O(2a)	1.948(4)	1.969(4)	
Sn(1)−C(1)	2.179(6)	2.182(6)	2.157(3)
Sn(1)−C(11)	2.166(6)	2.171(6)	1.584(3)
Si(1)−O(1)	1.634(4)	1.611(4)	
Si(1)−O(2)	1.628(4)	1.610(4)	
Si(1)−F(1)			1.583(6)
Si(1)−C(21)	1.922(7)	1.874(6)	
Si(1)−C(31)	1.914(6)	1.873(5)	
O(1)−Sn(1)−O(2a)	106.5(2)	103.0(2)	
O(1)−Sn(1)−O(1a)			105.9(2)
O(1)−Sn(1)−C(1)	110.1(2)	107.1(2)	105.9(2)
O(1)−Sn(1)−C(1a)			106.7(2)
O(1)−Sn(1)−C(11)	107.1(2)	106.0(2)	
O(2a)−Sn(1)−C(1)	107.6(2)	112.3(2)	
O(2a)−Sn(1)−C(11)	109.4(2)	102.0(2)	
C(1)−Sn(1)−C(11)	115.7(2)	124.3(3)	
C(1)−Sn(1)−C(1a)			124.4(3)
O(1)−Si(1)−O(2)	112.2(2)	113.1(2)	
O(1)−Si(1)−O(1b)			112.7(3)
O(1)−Si(1)−C(21)	107.7(3)	107.2(2)	110.2(2)
O(1)−Si(1)−C(31)	107.9(3)	111.1(2)	
O(1)−Si(1)−F(1)			109.3(2)
O(2)−Si(1)−C(21)	107.4(3)	111.7(2)	
O(2)−Si(1)−C(31)	108.5(3)	106.9(2)	
C(31)−Si(1)−C(21)	113.2(3)	106.6(2)	
F(1)−Si(1)−C(21)			104.9(3)
Sn(1)−O(1)−Si(1)	159.4(3)	138.9(2)	149.5(5)
Si(1)−O(2)−Sn(1a)	157.6(3)	149.1(3)	
Sn(1)−O(1)−Si(1)−O(2)	3.8(9)	25.7(5)	
Sn(1)−O(1)−Si(1)−O(1b)			−65.9(6)
Sn(1a)−O(1a)−Si(1a)−O(2a)	3.8(9)	−25.7(5)	
Sn(1b)−O(1c)−Si(1a)−O(1a)			65.9(6)
Si(1)−O(2)−Sn(1a)−O(1a)	−11.4(8)	−96.4(5)	
Si(1)−O(1b)−Sn(1b)−O(1c)			−39.4(4)
Si(1a)−O(2a)−Sn(1)−O(1)	−11.4(8)	96.4(5)	
Si(1a)−O(1a)−Sn(1)−O(1)			39.4(4)
O(1)−Si(1)−O(2)−Sn(1a)	−12.2(8)	71.5(6)	
O(1)−Si(1)−O(1b)−Sn(1b)			65.9(6)
O(1a)−Si(1a)−O(2a)−Sn(1)	−12.2(8)	−71.5(6)	
O(1c)−Si(1a)−O(1a)−Sn(1)			−65.9(6)
O(2)−Sn(1a)−O(1a)−Si(1a)	20.3(9)	56.2(4)	
O(1a)−Sn(1)−O(1)−Si(1)			39.4(4)
O(1b)−Sn(1b)−O(1c)−Si(1a)			−39.4(4)
O(2a)−Sn(1)−O(1)−Si(1)	20.3(9)	−56.2(4)	
symmetry transformation	a = $-x, y, -z + 0.5$	a = $-x + 1, y + 1, -z + 1$	a = $-x, y, -z$; b = $x, -y, z$; c = $-x, -y, -z + 1$

of equal integral ratio at δ −123.0 and −132.3 ppm. In **21** there is a crystallographic disorder of the *t*-Bu(F)Si fragment (Figure 7) with occupancy factors of 0.676(4) and 0.324(4), which is also reflected by observation of two ^{119}Sn MAS signals at δ −161.2 (integral 0.65) and −164.9 (integral 0.35). As a result of the formal replacement of one or more Ph_2Si units in $(Ph_2SiO)_4$ by *t*-Bu_2Si, *t*-Bu(F)Si, and/or *t*-Bu_2Sn a loss of planarity of the eight-membered rings is observed for **5**, **7**, **9**, **21**, and **29** (Figure 8). According to a classification scheme recently introduced for eight-membered rings[27c] **21** adopts a D-type and **9** and **29** a G-type conformation. From the above-mentioned classification scheme, compounds **5** and **7** represent new types of conformations, i.e., I- and J-types, respectively.

Experimental Section

General Considerations. All manipulations were performed under an inert atmosphere of nitrogen using standard Schlenk and vacuum line techniques. Solvents were distilled from the appropriate desiccants prior to use.

Literature procedures were used to prepare (*t*-$Bu_2SnO)_3$,[8] (*t*-$Bu_2SnS)_2$,[19] *t*-Bu_2SnCl_2,[28] Ph_3SnF,[29] $Ph_2Si(OH)_2$,[14] $Ph_2Si(OSiPh_2OH)_2$,[14] *t*-$Bu_2Si(OH)_2$,[12b] [$(Ph_2SiO)_2$(*t*-Bu_2SnO)],[3r] and 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane.[20] The organochlorosilanes employed were commercial products of Gelest (Et_2SiCl_2, *i*-Pr_2SiCl_2, *t*-Bu_2SiCl_2), Aldrich (*t*-$BuSiCl_3$), and Fluka (*t*-Bu_2SiHCl, Ph_2SiCl_2). The purity of all starting compounds was checked by NMR spectroscopy. (*t*-$Bu_2SnO)_3$ (**1**) was stored under exclusion of moisture; otherwise it slowly turns into *t*-$Bu_2Sn(OH)_2$.[3u]

IR spectra were obtained with a Bruker FTIR IFS 113v spectrometer. NMR spectra were recorded on Bruker DRX 400 (^{119}Sn, ^{29}Si, ^{13}C, ^{1}H) and DPX 300 (^{19}F) spectrometers, respectively. Chemical shifts δ are given in ppm and were referenced against Me_4Sn (^{119}Sn), TMS (^{1}H, ^{13}C, ^{29}Si), and $CFCl_3$ (^{19}F), respectively.

^{119}Sn MAS NMR spectra were obtained with a Bruker MSL 400 spectrometer using cross-polarization and high-power proton decoupling (conditions: recycle delay 4.0−6.0 s, 90° pulse 5.0 μs, contact time 3.5 ms). Spinning rates of 4−8 kHz were employed. Each sample was measured with two inde-

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Table 4. Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) for 9 and 29

	9 (M = Si(1))	**29** (M = Sn(2))
Sn(1)−O(1)	1.978(2)	1.942(3)
Sn(1)−O(4)	1.966(2)	1.968(3)
Sn(1)−C(1)	2.161(3)	2.161(6)
Sn(1)−C(11)	2.156(3)	2.170(5)
M−O(1)	1.594(2)	1.944(3)
M−O(2)	1.630(2)	1.961(3)
M−C(21)	1.854(4)	2.155(5)
M−C(31)	1.861(3)	2.157(5)
Si(2)−O(2)	1.617(2)	1.600(3)
Si(2)−O(3)	1.612(2)	1.633(3)
Si(2)−C(41)	1.847(4)	1.863(4)
Si(2)−C(51)	1.854(4)	1.862(4)
Si(3)−O(3)	1.631(2)	1.637(3)
Si(3)−O(4)	1.610(2)	1.598(3)
Si(3)−C(61)	1.850(4)	1.851(4)
Si(3)−C(71)	1.858(3)	1.845(4)
O(1)−Sn(1)−O(4)	101.84(9)	103.3(1)
O(1)−Sn(1)−C(1)	108.3(1)	109.0(2)
O(1)−Sn(1)−C(11)	105.1(1)	106.7(2)
O(4)−Sn(1)−C(1)	103.2(1)	102.9(2)
O(4)−Sn(1)−C(11)	111.4(1)	110.3(2)
C(1)−Sn(1)−C(11)	124.9(2)	122.8(2)
O(1)−M−O(2)	113.6(1)	108.3(1)
O(1)−M−C(21)	108.1(2)	105.9(2)
O(1)−M−C(31)	111.5(2)	109.2(2)
O(2)−M−C(21)	108.8(2)	107.5(2)
O(2)−M−C(31)	105.0(2)	102.4(2)
C(21)−M−C(31)	109.8(2)	122.9(2)
O(2)−Si(2)−O(3)	111.2(1)	113.2(2)
O(2)−Si(2)−C(41)	107.2(2)	110.4(2)
O(2)−Si(2)−C(51)	109.1(2)	109.0(2)
O(3)−Si(2)−C(41)	110.1(2)	106.2(2)
O(3)−Si(2)−C(51)	107.2(1)	108.4(2)
C(41)−Si(2)−C(51)	112.1(2)	109.5(2)
O(3)−Si(3)−O(4)	111.3(1)	111.6(2)
O(3)−Si(3)−C(61)	108.3(1)	106.9(2)
O(3)−Si(3)−C(71)	105.1(1)	109.8(2)
O(4)−Si(3)−C(61)	107.4(2)	110.8(2)
O(4)−Si(3)−C(71)	112.1(1)	107.7(2)
C(61)−Si(3)−C(71)	112.6(2)	110.0(2)
M−O(1)−Sn(1)	148.0(1)	142.4(2)
M−O(2)−Si(2)	145.7(1)	156.4(2)
Si(2)−O(3)−Si(3)	150.6(2)	140.3(2)
Si(3)−O(4)−Sn(1)	142.7(1)	144.3(2)
Sn(1)−O(1)−M−O(2)	−23.1(3)	20.6(3)
M−O(2)−Si(2)−O(3)	16.1(3)	−47.5(5)
Si(2)−O(3)−Si(3)−O(4)	−21.7(4)	61.9(3)
Si(3)−O(4)−Sn(1)−O(1)	23.6(2)	−89.0(3)
O(1)−M−O(2)−Si(2)	−51.7(3)	31.7(5)
O(2)−Si(2)−O(3)−Si(3)	64.1(4)	−44.1(3)
O(3)−Si(3)−O(4)−Sn(1)	−58.3(2)	49.8(3)
O(4)−Sn(1)−O(1)−M	55.0(3)	9.7(3)

pendent spinning rates in order to identify the isotropic chemical shift. Cy_4Sn served as a second reference (−97.35 ppm against Me_4Sn). The Mössbauer spectra were recorded in constant-acceleration mode on a homemade instrument, designed and built by the Institut voor Kernen Stralingsfysica (IKS), Leuven, Belgium. The isomer shifts refer to a source of $Ca^{119m}SnO_3$ from Amersham, U.K., samples being maintained at 90 ± 2 K. The data were treated with a least-squares iterative program that deconvoluted the spectrum into a sum of Lorentzians. Electron ionization mass spectra were recorded on a Finnigan MAT 8230 spectrometer. The electrospray mass spectrum was acquired on a Finnigan MAT 90 spectrometer equipped with an ESI II electrospray ion source. The acceleration voltage was approximately 5 kV. The electrospray operates with a voltage of +3.5 kV. The temperature of the desolvation capillary was held at 250 °C. The source and most interface parameters were tuned once and kept unaltered during this study. A make up solution consisting of 2-propanol and water (3:1) was delivered using a Harvard syringe pump.

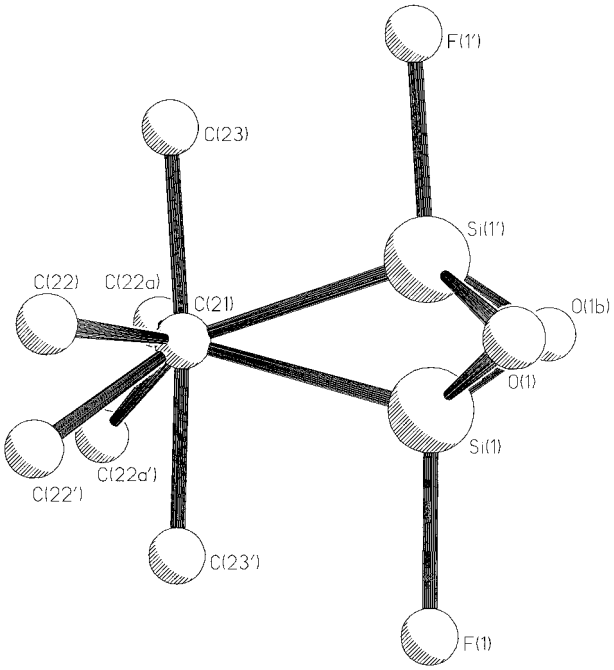

Figure 7. General view (SHELXTL-PLUS) of a disordered *t*-Bu(F)Si fragment of **21** in which C(22) and C(22a) lie 0.13(2) Å above and C(22′) and C(22a′) lie 0.72(3) Å below the plane defined by Sn(1), O(1), O(1b), Sn(1b), O(1c), and O(1a).

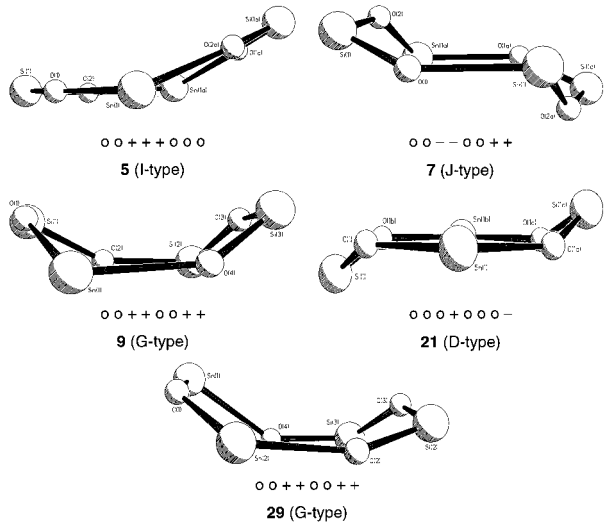

Figure 8. Classification scheme for eight-membered stannasiloxane rings (**5**, **7**, **9**, **21**, **29**).

Acquisition of mass spectra and selected ion monitoring were done in the profile mode. The ions showed the expected isotope pattern. The elemental analyses were performed on an instrument from Carlo Erba Strumentazione (Model 1106). The densities of single crystals were determined using a Micromeritics Accu Pyc 1330. The molecular weight measurements were performed on a Knaur osmometer.

The organofluorosilanes[30] were prepared according to the following modified procedure.[31] The corresponding organochlorosilane (typically 10 g) was added dropwise to a slight excess of Ph_3SnF (ZnF_2 was used for *t*-$BuSiCl_3$). The reaction mixture

(30) *Gmelin Handbook of Inorganic and Organometallic Chemistry*; Springer-Verlag: Berlin, 1992; Silicon, Vol. B7.

(31) (a) Roesky, H. W.; Herzog, A.; Keller, K. *Z. Naturforsch.* **1994**, *49B*, 981. (b) Roesky, H. W.; Keller, K. *J. Fluorine Chem.* **1998**, *89*, 3. (c) Hummeltenberg, R.; Jurkschat, K.; Uhlig, F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1997**, *123*, 255.

was heated at reflux for at least 10 h, after which the corresponding organofluorosilane is distilled off (for *t*-$BuSiF_3$ a cooling trap is recommended). The organofluorosilanes were freshly distilled prior to use, and their purity was checked by ^{29}Si NMR spectroscopy. Yields were in a range between 50 and 85%.

Et_2SiF_2: bp 60 °C; $^{29}Si\{^1H\}$ NMR δ 1.7 (t, [$^1J(^{29}Si-^{19}F)$ 303 Hz]).

i-Pr_2SiF_2: bp 100 °C; $^{29}Si\{^1H\}$ NMR δ −3.0 (t, [$^1J(^{29}Si-^{19}F)$ 316 Hz]).

t-Bu_2SiF_2: bp 130 °C; $^{29}Si\{^1H\}$ NMR δ −8.5 (t, [$^1J(^{29}Si-^{19}F)$ 325 Hz]).

Ph_2SiF_2: bp 250 °C; $^{29}Si\{^1H\}$ NMR δ −29.7 (t, [$^1J(^{29}Si-^{19}F)$ 292 Hz]).

t-$BuSiF_3$: bp 32 °C; $^{29}Si\{^1H\}$ NMR δ −61.8 (q, [$^1J(^{29}Si-^{19}F)$ 302 Hz]).

NMR-Scale Reactions of *t*-Bu_2SiCl_2 with (*t*-$Bu_2SnO)_3$ (1). A mixture of *t*-Bu_2SiCl_2 (21.3 mg, 0.1 mmol) and the appropriate amount of **1** (74.8 mg, 0.1 mmol; 49.8 mg, 0.067 mmol; or 24.9 mg, 0.033 mmol) in $CDCl_3$ (250 μL) was heated at reflux for 2 days to give a clear solution. From this solution NMR measurements were performed as described in the text.

Synthesis of 1,1,3,3,5,5-Hexa-*tert*-butyl-2,4,6-trioxa-5-sila-1,3-distannacyclohexane (2). A mixture of *t*-Bu_2SiCl_2 (2.13 g, 10.0 mmol) and **1** (7.47 g, 10.0 mmol) was heated at reflux in 30 mL of toluene for 2 days. After the mixture was cooled, the colorless precipitate (3.8 g) was filtered off. Recrystallization from toluene gave **2** as colorless crystals (2.3 g, 3.5 mmol, 35%) with mp 242 °C.

IR (KBr): 2969 s, 2850 s, 1469 s, 1366 m, 1168 m, 909 s, 825 m, 731 s, 637 m, 450 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.49 (s, $^3J(^1H-CC-^{119}Sn)$ = 94.7 Hz, 36H, SnCMe_3), 1.16 (s, 18H, SiCMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 39.7 ($^1J(^{13}C-^{119}Sn)$ = 497 Hz, SnCMe_3), 30.6 (SnCMe_3), 29.2 (SiCMe_3), 22.2 (SiCMe_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −17.9 ($^2J(^{29}Si-O-^{119/117}Sn)$ = 50 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −107.2 ($^2J(^{119}Sn-O-^{117}Sn)$ = 293 Hz, $^2J(^{119}Sn-O-^{29}Si)$ = 51 Hz). ^{119}Sn MAS NMR: δ −106.6. Mössbauer spectroscopy: QS = 2.10 mm s^{-1}, IS = 1.25 mm s^{-1}. MS (*m*/*z* (%)): 599 (86) [$M^+ - C_4H_9$], 485 (53) [$M^+ - C_{12}H_{16}$], 371 (30) [$M^+ - C_{20}H_{44}$], 57 (100) ($C_4H_9^+$). Anal. Calcd for $C_{24}H_{54}O_3SiSn_2$ (656.25): C, 43.93; H, 8.29. Found: C, 43.85; H, 8.61. MW (20 mg mL^{-1} $CHCl_3$): 565.

Synthesis of 1,1,3,3,5,5,7,7-Octa-*tert*-butyl-2,4,6,8-tetraoxa-3,7-disila-1,5-distannacyclooctane (5). Method A. A mixture of *t*-Bu_2SiCl_2 (2.13 g, 10.0 mmol) and **1** (5.48 g, 7.3 mmol) in 30 mL of toluene was heated at reflux for 2 days. When this mixture was cooled, a colorless precipitate (1.34 g) crystallized, which was filtered off. Recrystallization from toluene gave **5** as colorless crystals (600 mg, 0.74 mmol, 15%) with mp 250 °C dec.

IR (KBr): 2968 vs, 2850 vs, 1458 s, 1377 s, 1161 s, 1015 m, 965 m, 802 m, 723 m, 524 m, 488 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.37 (s, $^3J(^1H-CC-^{119}Sn)$ = 98.9 Hz, 36H, SnCMe_3), 1.02 (s, 36H, SiCMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 39.3 ($^1J(^{13}C-^{119}Sn)$ = 540 Hz, SnCMe_3), 30.4 (SnCMe_3), 29.6 (Si−CMe_3), 22.2 (SiCMe_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −25.7 ($^2J(^{29}Si-O-^{119}Sn)$ = 98 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −178.5 ($^2J(^{119}Sn-O-^{29}Si)$ = 98 Hz). ^{119}Sn MAS NMR: δ −178.1. MS (*m*/*z* (%)): 758 (48) [$M^+ - C_4H_8$], 642 (30%) [$M^+ - C_{12}H_{28}$], 528 (27) [$M^+ - C_{20}H_{45}$], 472 (20) [$M^+ - C_{24}H_{53}$], 57 (100) ($C_4H_9^+$). Anal. Calcd for $C_{32}H_{72}O_4Si_2Sn_2$ (814.56): C, 47.19; H, 8.91. Found: C, 46.94; H, 8.97. MW (20 mg mL^{-1} $CHCl_3$): 780.

The mother liquid was allowed to slowly evaporate in air to give *t*-$Bu_2Sn(OH)Cl$[12a] and *t*-$Bu_2Si(OH)_2$.[12b] Both compounds were shown to be identical with those described in the literature.

t-$Bu_2Sn(OH)Cl$[12a] is a crystalline solid with mp 135 °C.

IR (KBr): 3448 mb, 2947 vs, 2853 vs, 1459 s, 1377 m, 1162 m, 1016 m, 967 m, 526 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.41 (s, $^3J(^1H-CC-^{117/119}Sn)$ = 116.0 Hz). Anal. Calcd for $C_8H_{19}ClOSn$ (285.43): C, 33.67; H, 6.71. Found: C, 33.64; H, 6.98.

t-$Bu_2Si(OH)_2$[12b] is a crystalline solid with mp 148 °C.

IR (KBr): 3400 vs, 2948 vs, 2860 vs, 1467 vs, 1364 s, 1013 s, 827 s, 655 s, 438 s cm^{-1}. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −6.5. Anal. Calcd for $C_8H_{20}O_2Si$ (285.4): C, 54.49; H, 11.43. Found: C, 54.70; H 12.10.

Method B. A solution of BuLi (2 M) in hexane (10 mL, 20 mmol) was added dropwise to a suspension of *t*-$Bu_2Si(OH)_2$ (1.76 g, 10.0 mmol) in hexane (50 mL) with magnetic stirring. After 2 h, a solution of *t*-Bu_2SnCl_2 (3.04 g, 10 mmol) in hexane (10 mL) was added. The mixture was heated at reflux for 10 h, and the colorless precipitate of LiCl was removed by filtration. The solvent was evaporated to approximately 10 mL. Cooling to −10 °C gave **5** (2.4 g, 2.9 mmol, 59%) as colorless crystals with mp 250 °C dec.

***In Situ* Reaction of Ph_2SiCl_2 with (*t*-$Bu_2SnO)_3$ (1).** A mixture of Ph_2SiCl_2 (76.0 mg, 0.3 mmol) and **1** (74.7 mg, 0.1 mmol) in $CDCl_3$ (250 μL) was heated at reflux for 1.5 h. ^{119}Sn and $^{29}Si\{^1H\}$ NMR spectra of the clear solution were recorded in order to identify intermediate stannasiloxanes (see discussion). After 5 days at 57 °C the $^{119}Sn\{^1H\}$ NMR spectrum of the reaction mixture showed exclusively *t*-Bu_2SnCl_2.

The same reaction was repeated on a preparative scale (Ph_2SiCl_2, 2.53 g, 10.0 mmol; **1**, 2.49 g, 3.33 mmol in $CHCl_3$ (40 mL)). After the solvent was evaporated *in vacuo*, the *t*-Bu_2SnCl_2 was removed by Kugelrohr distillation to provide a solid residue (1.81 g). A $^{29}Si\{^1H\}$ NMR spectrum was recorded which is discussed in the text.

Anal. Calcd for $C_{12}H_{10}OSi$ (198.30): C, 71.69; H, 5.08. Found: C, 71.29; H, 5.13.

Synthesis of 1,1,5,5-Tetra-*tert*-butyl-3,3,7,7-tetraphenyl-2,4,6,8-tetraoxa-3,7-disila-1,5-distannacyclooctane (7). A solution of *t*-Bu_2SnCl_2 (3.04 g, 10 mmol) in acetone (30 mL) was added dropwise to a magnetically stirred mixture of $Ph_2Si(OH)_2$ (2.16 g, 10.0 mmol) and triethylamine (2.02 g, 20.0 mmol) in acetone (30 mL). Immediate precipitation of triethylammonium chloride took place, which after 15 h was removed by filtration. The solvent was evaporated *in vacuo* to give a solid residue that was recrystallized from hexane to afford **7** as colorless crystals (3.30 g, 3.60 mmol, 74%) with mp 198 °C.

IR (KBr): 2960 vs, 2847 vs, 1465 s, 1377 s, 1166 m, 1112 s, 1025 s, 1009 s, 945 s, 806 w, 735 s, 710 s, 511 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.8−7.1 (m, 20H, SiPh), 1.11 (s, $^3J(^1H-^{119}Sn)$ = 100.9 Hz, 36H; SnCMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.4, 134.6, 128.6, 127.1 (i, o, p, m SiPh), 38.9 ($^1J(^{13}C-^{119}Sn)$ = 511 Hz, SnCMe_3), 29.3 (SnCMe_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −42.7 ($^2J(^{29}Si-O-^{119}Sn)$ = 65 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −149.5 ($^2J(^{119}Sn-O-^{29}Si)$ = 64 Hz). ^{119}Sn MAS NMR: δ −145.6. Mössbauer spectroscopy: QS = 2.32 mm s^{-1}, IS = 1.33 mm s^{-1}. MS (*m*/*z* (%)): 839 (59) [$M^+ - C_4H_7$], 591 (70) [$M^+ - C_{22}H_{39}$], 511 (18) [$M^+ - C_{28}H_{46}$], 57 (100) ($C_4H_9^+$). Anal. Calcd for $C_{40}H_{56}O_4Si_2Sn_2$ (894.53): C, 53.71; H, 6.31. Found: C, 53.56; H, 6.50. MW (20 mg mL^{-1} $CHCl_3$): 726.

Synthesis of 1,1-Di-*tert*-butyl-3,3,5,5,7,7-hexaphenyl-2,4,6,8-tetraoxa-3,5,7-trisilastannacyclooctane (9). A solution of *t*-Bu_2SnCl_2 (1.52 g, 5.0 mmol) in acetone (30 mL) was slowly added to a magnetically stirred solution of $Ph_2Si(OSiPh_2OH)_2$ (3.06 g, 5.0 mmol) and triethylamine (1.01 g, 10.0 mmol) in acetone (30 mL). Immediate precipitation of triethylammonium chloride took place, which after 10 h was removed by filtration. The solvent was removed *in vacuo* to give a solid residue that was recrystallized from CH_2Cl_2 to give **9** (3.4 g, 4.0 mmol, 81%) as colorless crystals with mp 210 °C.

IR (KBr): 2958 vs, 1590 m, 1463 vs, 1428 s, 1377 s, 1118 vs, 1077 vs, 966 s, 698 s, 527 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.7−7.1 (m, 30H, SiPh), 1.10 (18H, $^3J(^1H-CC-^{119}Sn)$ = 103.9 Hz, SnCMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.7, 135.8, 134.4, 134.2, 129.4, 129.2, 127.3, 127.2 (i, o, p, m SiPh), 39.8 ($^1J(^{13}C-^{119}Sn)$ = 495 Hz, SnCMe_3), 29.1 (SnCMe_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −43.2 (s, $^2J(^{29}Si-O-^{119}Sn)$ = 70 Hz, 2Si), −45.8 (s, 1Si). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −153.1 ($^2J(^{119}Sn-O-^{29}Si)$ = 70 Hz). ^{119}Sn MAS NMR (149.2 MHz): δ −150.2. Mössbauer spectros-

copy: QS = 2.52 mm s^{-1}, IS = 1.39 mm s^{-1}. MS (*m*/*z* (%)): 786 (18) [$M^+ - C_4H_9$], 652 (70) [$M^+ - C_{14}H_{23}$], 593 (20) [$(Ph_2SiO)_3^+$], 574 (21) [$M^+ - C_{20}H_{29}$], 515 (16) [$(Ph_2SiO)_3^+ - C_6H_5$], 438 (70) [$(Ph_2SiO)_3^+ - C_{12}H_{10}$], 57 (100) ($C_4H_9^+$). Anal. Calcd for $C_{44}H_{48}O_4Si_3Sn$ (843.86): C, 62.63; H, 5.73. Found: C, 63.27; H 6.11. MW (20 mg mL^{-1} $CHCl_3$): 731.

Synthesis of Bis(di-*tert*-butylsiloxy)di-*tert*-butylstannane (10). A mixture of *t*-Bu_2SiHCl (1.79 g, 10.0 mmol) and **1** (2.49 g, 3.33 mmol) in $CHCl_3$ (50 mL) was heated at reflux for 10 h. The solvent was evaporated *in vacuo*, and the *t*-Bu_2SnCl_2 was removed by Kugelrohr distillation. The residue was recrystallized from pentane to give **10** (2.2 g, 4.0 mmol, 80%) as colorless crystals with mp 109 °C.

IR (KBr): 2953 s, 2914 vs, 2066 m, 1466 m, 1387 m, 1363 m, 944 s, 825 s, 622 w, 515 w cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.25 ($^1J(^1H-^{29}Si)$ = 187.2 Hz, 1H, Si*H*), 1.36 ($^3J(^1H-CC-^{119}Sn)$ = 100.4 Hz, 18H, SnC*Me*$_3$), 0.98 (36H, SiC*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 40.1 ($^1J(^{13}C-^{119}Sn)$ = 518 Hz, Sn*C*Me$_3$), 29.8 (SnC*Me*$_3$), 27.7 (SiC*Me*$_3$), 20.7 (Si−*C*Me$_3$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 7.5 ($^2J(^{29}Si-O-^{119}Sn)$ = 77 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −161.4 ($^2J(^{119}Sn-O-^{29}Si)$ = 76 Hz). ^{119}Sn MAS NMR: δ 160.2. Mössbauer spectroscopy: QS = 2.27 mm s^{-1}, IS = 1.31 mm s^{-1}. MS (*m*/*z* (%)): 495 (50) [$M^+ - C_4H_7$], 436 (15%) [$M^+ - C_8H_{19}$], 380 (41) [$M^+ - C_{12}H_{28}$], 324 (18) [$M^+ - C_{16}H_{36}$], 57 (100) ($C_4H_9^+$). Anal. Calcd for $C_{24}H_{56}O_2Si_2Sn$ (551.62): C, 52.26; H, 10.23. Found: C, 52.50; H, 11.01.

Synthesis of Bis(di-*tert*-butylfluorosiloxy)di-*tert*-butylstannane (11). *t*-Bu_2SiF_2 (1.80 g, 10 mmol) and **1** (2.49 g, 33.3 mmol) were dissolved in toluene (10 mL) and were heated at reflux for 2 days. The precipitate of *t*-Bu_2SnF_2 (1.02 g) was filtered and the solvent evaporated in vacuo. Hexane (5 mL) was added, and the resulting mixture was magnetically stirred for 5 min. The mixture was then filtered in order to remove residual traces of *t*-Bu_2SnF_2. **11** crystallizes from the clear filtrate as a colorless solid (2.75 g, 4.68 mmol, 93%) of mp 96 °C.

IR (KBr): 2969 vs, 2855 vs, 1465 s, 1377 m, 1010 m, 975 s, 830 m, 812 m, 655 m, 446 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.39 (s, $^3J(^1H-CC-^{119}Sn)$ = 104.4 Hz, 18H, SnC*Me*$_3$), 1.03 (s, 36H, SiC*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 42.5 (s, $^1J(^{13}C-^{119}Sn)$ = 477 Hz, Sn*C*Me$_3$), 32.0 (s, SnC*Me*$_3$), 30.1 (s, SiC*Me*$_3$), 23.5 (d, $^2J(^{13}C-C-^{19}F)$ = 23 Hz, Si*C*Me$_3$). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −150.1 ($^1J(^{19}F-^{29}Si)$ = 312 Hz). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −15.0 (d, $^1J(^{29}Si-^{19}F)$ = 312 Hz, $^2J(^{29}Si-O-^{119}Sn)$ = 84 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −164.7 (s, $^2J(^{119}Sn-^{29}Si)$ = 83 Hz. ^{119}Sn MAS NMR: δ −162.1. Mössbauer spectroscopy: QS = 2.47 mm s^{-1}, IS = 1.32 mm s^{-1}. MS (*m*/*z* (%)): 531 (9) [$M^+ - C_4H_8$], 475 (52%) [$M^+ - C_8H_{16}$], 415 (23) [$M^+ - C_{12}H_{28}$], 297 (49) [$M^+ - C_{20}H_{47}$], 57 (100) ($C_4H_9^+$). Anal. Calcd for $C_{24}H_{54}F_2O_2Si_2Sn$ (587.60): C, 49.06; H, 9.26. Found: C, 49.13; H, 9.64.

t-Bu_2SnF_2 is an amorphous colorless solid with mp 250 °C dec which is insoluble in common organic solvents. Mössbauer: QS = 2.81 mm s^{-1}, IS = 1.31 mm s^{-1}. Anal. Calcd for $C_8H_{18}F_2Sn$ (270.96): C, 35.46; H, 6.70. Found: C, 36.50; H, 7.20.

***In Situ* Synthesis of [TAS]$^+$[*t*-Bu_2SnF_3]$^-$.** Equimolar amounts of tris(dimethylamino)sulfur (trimethylsilyl)difluoride (TASF) (55.1 mg, 0.20 mmol) and *t*-Bu_2SnF_2 (54.2 mg, 0.20 mmol) were heated at reflux in $CDCl_3$ (300 μL) until the solution became almost clear.

$^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −362.9 (q, $^1J(^{119}Sn-^{19}F)$ = 2752 Hz).

***In Situ* Preparation of *t*-$Bu_2Sn(OSiFR_2)_2$ (13, R = Et; 14, R = *i*-Pr; 15, R = Ph) by Reaction of R_2SiF_2 (R = Et, *i*-Pr, Ph) with (*t*-$Bu_2SnO)_3$ (1).** A mixture of **1** (74.7 mg, 0.1 mmol) and R_2SnF_2 (0.3 mmol: R = Et, 37.3 mg; R = *i*-Pr, 45.7 mg; R = Ph, 66.1 mg) in $CDCl_3$ (250 μL) was heated at reflux for 5 h. In each case a colorless precipitate that was very likely *t*-Bu_2SnF_2 (see above) was formed, which was not filtered. According to ^{119}Sn and ^{29}Si NMR spectra (Table 1) the reaction mixture contained almost exclusively species **13**, **14**, and **15**, respectively.

***In Situ* Reactions of *t*-$BuSiCl_3$ with (*t*-$Bu_2SnO)_3$ (1).** Mixtures of *t*-$BuSiCl_3$ (57.5 mg, 0.30 mmol) and the appropriate amounts of **1** (case A, 37.3 mg, 0.05 mmol; case B, 74.7 mg, 0.10 mmol; case C, 112.0 mg, 0.15 mmol) in $CDCl_3$ (250 μL) were prepared and kept at room temperature for 2 h to give a clear solution. ^{119}Sn and ^{29}Si NMR spectra (see Table 1) were recorded. The mixture of case C was heated at reflux for 2 days, and $^{29}Si\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR measurements were repeated. The latter revealed exclusive formation of *t*-Bu_2SnCl_2.

The reaction according to case C was repeated on a preparative scale (*t*-$BuSiCl_3$, 192 mg, 1.0 mmol; **1**, 373 mg, 0.50 mmol in $CHCl_3$ (5 mL)). After evaporation of the solvent the *t*-Bu_2SnCl_2 was removed by Kugelrohr distillation to leave a solid residue, the $^{29}Si\{^1H\}$ NMR (d_8-thf) spectrum of which is discussed in the text.

Anal. Calcd for $C_4H_9O_{1.5}Si$ (109.20): C, 44.00; H, 8.31. Found: C, 43.59; H, 9.03.

***In Situ* Preparation of *t*-$Bu_2Sn(OSiF_2t$-$Bu)_2$ (19), [*t*-BuFSi(OSn-*t*-$Bu_2)_2O$•*t*-Bu_2SnF_2] (20), (*t*-BuFSiOSn-*t*-$Bu_2O)_2$ (21), and *t*-BuFSi(OSn-*t*-$Bu_2)_2O$ (22) by Reaction of *t*-$BuSiF_3$ with (*t*-$Bu_2SnO)_3$ (1). Case A.** A mixture of *t*-$BuSiF_3$ (20.4 mg, 0.20 mmol) and **1** (49.8 mg, 0.067 mmol) in $CDCl_3$ (250 μL) was heated at reflux for 2 h.

Case B. A mixture of *t*-$BuSiF_3$ (20.4 mg, 0.20 mmol) and **1** (99.6 mg, 0.133 mmol) in $CDCl_3$ (250 μL) was refluxed for 2 h.

Case C. A mixture of *t*-$BuSiF_3$ (10.2 mg, 0.10 mmol) and **1** (74,7 mg, 0.100 mmol) in $CDCl_3$ (250 μL) was heated at reflux for 2 h. In all cases precipitation of *t*-Bu_2SnF_2 was observed, and it was not removed by filtration. NMR spectra were recorded of the reaction mixtures (see Scheme 5, Table 1, and below).

***t*-$Bu_2Sn(OSiF_2$-*t*-$Bu)_2$ (19).** ^1H NMR ($CDCl_3$): δ 1.38 (s, 18H, SnC*Me*$_3$) [$^3J(^1H-CC-^{119/117}Sn)$ = 108.2 Hz], 1.04 (s, 18H, SiC*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 41.7 (Sn*C*Me$_3$), 29.0 (SnC*Me*$_3$), 25.7 (SiC*Me*$_3$), 16.4 (t, Si*C*Me$_3$) [$^2J(^{19}F-Si-^{13}C)$ = 23 Hz]. $^{29}Si\{^1H\}$ ($CDCl_3$): δ −52.3 (t) [$^1J(^{29}Si-^{19}F)$ 293 Hz] [$^2J(^{29}Si-O-^{119/117}Sn)$ = 70 Hz]. $^{119}Sn\{^1H\}$ ($CDCl_3$): δ −164.7 [$^2J(^{119}Sn-O-^{29}Si)$ = 71 Hz].

[*t*-BuFSi(OSn-*t*-$Bu_2)_2O$·*t*-Bu_2SnF_2] (20). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 43.6 (t, Sn*C*Me$_3$) [$^2J(^{13}C-Sn-^{19}F)$ = 4.8 Hz], 43.2 (t, Sn*C*Me$_3$) [$^2J(^{13}C-Sn-^{19}F)$ = 5 Hz], 42.4 (t, Sn*C*Me$_3$) [$^2J(^{13}C-Sn-^{19}F)$ = 10 Hz], 42.0 (t, Sn*C*Me$_3$) [$^2J(^{13}C-Sn-^{19}F)$ = 10 Hz], 30.8, 30.6, 30.4, 30.3 (SnC*Me*$_3$), 27.2 (SiC*Me*$_3$), 17.9 (d, Si*C*Me$_3$) [$^2J(^{13}C-Si-^{19}F)$ = 29 Hz]. $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −133.9 (s, 1F, Si*F*) [$^1J(^{19}F-^{29}Si)$ = 276 Hz], −137.5 (s, 2F, Sn*F*) [$^1J(^{19}F-^{119}Sn)$ = 2451, 1182 Hz]. $^{29}Si\{^1H\}$ ($CDCl_3$): δ −52.3 [$^1J(^{29}Si-^{19}F)$ = 278 Hz] [$^2J(^{29}Si-O-^{119/117}Sn)$ = 56 Hz]. $^{119}Sn\{^1H\}$ ($CDCl_3$) (2:1): δ −228.3 (d, 2Sn) [$^1J(^{119}Sn-^{19}F)$ = 1250 Hz], −279.5 (t, 1Sn) [$^1J(^{119}Sn-^{19}F)$ = 2450 Hz].

Synthesis of 1,1,3,5,5,7-Hexa-*tert*-butyl-3,7-difluoro-2,4,6,8-tetraoxa-3,7-disila-1,5-distannacyclooctane (21). (*t*-$Bu_2SnO)_3$ (**1**; 4.98 g, 6.67 mmol) was added in small portions to a magnetically stirred solution of *t*-$BuSiF_3$ (1.02 g, 10.0 mmol) in toluene (20 mL) at 0 °C. The mixture was stirred for 24 h at room temperature and for 24 h at 60 °C. After the mixture was cooled to room temperature, the colorless precipitate of *t*-Bu_2SnF_2 (500 mg, 1.85 mmol, 9%) was filtered and identified as [TAS]$^+$[*t*-Bu_2SnF_3]$^-$ by ^{119}Sn NMR spectroscopy after adding 1 mol equiv of TASF. The clear filtrate was evaporated to approximately 5 mL. When the filtrate was cooled to −10 °C, colorless crystals (3.5 g, mixture of **20** and **21**) precipitated. These crystals were kept at atmospheric moisture for 5 h in order to convert **20** into **21** and *t*-$Bu_2Sn(OH)F$. The resulting crystal mass was extracted several times with hexane to leave *t*-$Bu_2Sn(OH)F$ (1.3 g, 4.83 mmol, 24%) as an insoluble solid. The combined hexane layers were evaporated to dryness to provide **21** (2.2 g, 2.98 mmol, 60%) as colorless crystals with mp 208 °C.

IR (KBr): 2956 s, 2929 s, 2854 s, 1473 s, 1387 m, 1370 m, 1171 m, 1053 s, 988 m, 838 m, 817 m, 632.5 m, 442 m cm^{-1}. 1H NMR ($CDCl_3$): δ 1.38 (s, $^3J(^1H-CC-^{119}Sn)$ = 104.6 Hz, SnC*Me*$_3$, *cis*), 1.37 (s, $^3J(^1H-CC-^{119}Sn)$ = 101.8 Hz, SnC*Me*$_3$, *trans*), 1.35 (s, $^3J(^1H-CC-^{119}Sn)$ = 103.3 Hz, SnC*Me*$_3$, *cis*), 1.02 (s, SiC*Me*$_3$, *cis*, *trans*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 39.9 ($^1J(^{13}C-^{119}Sn)$ = 507 Hz, Sn*C*Me$_3$, *cis*), 39.0 ($^1J(^{13}C-^{119}Sn)$ = 510 Hz, Sn*C*Me$_3$, *trans*), 38.3 ($^1J(^{13}C-^{119}Sn)$ = 516 Hz, Sn*C*Me$_3$, *cis*), 29.3, 29.2 (SnC*Me*$_3$, *cis*, *trans*), 27.0, 26.9 (SiC*Me*$_3$, *cis*, *trans*), 18.1 (d, $^2J(^{13}C-Si-^{19}F)$ = 27 Hz, Si*C*Me$_3$, *cis*, *trans*). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −135.0 (s, $^1J(^{19}F-^{29}Si)$ = 282 Hz, *trans*), −135.7 (s, $^1J(^{19}F-^{29}Si)$ = 285 Hz, *cis*). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −55.7 (d, $^1J(^{29}Si-^{19}F)$ = 283 Hz, $^2J(^{29}Si-^{119}Sn)$ = 80.5 Hz, *trans*), −56.0 (d, $^1J(^{29}Si-^{19}F)$ = 282 Hz, $^2J(^{29}Si-O-^{119}Sn)$ = 82 Hz, *cis*). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −161.5 ($^2J(^{119}Sn-O-^{29}Si)$ = 81 Hz, *trans*), −163.1 ($^2J(^{119}Sn-O-^{29}Si)$ = 78 Hz, *cis*). ^{119}Sn MAS NMR: δ −161.2 (65%), −164.9 (35%). Mössbauer: QS = 2.41 mm s^{-1}, IS = 1.34 mm s^{-1}. MS (*m*/*z* (%)): 681 (28) [$M^+ - C_4H_9$], 625 (42%) [$M^+ - C_8H_{17}$], 569 (19) [$M^+ - C_{12}H_{25}$], 511 (13) [$M^+ - C_{16}H_{35}$], 491 [$M^+ - C_{16}H_{34}F$], (20), 453 (20) [$M^+ - C_{20}H_{44}$], 57 (100) ($C_4H_9^+$). Anal. Calcd for $C_{24}H_{54}F_2O_4Si_2Sn_2$ (738.33): C, 39.04; H, 7.37. Found: C, 38.78; H, 7.71.

t-$Bu_2Sn(OH)F$[11] is an amorphous colorless solid, which decomposes at 250 °C without melting.

IR (KBr): 3150 b, 2972 vs, 2838 vs, 1468 vs, 1364 s, 1172 s, 1096 s, 1014 m, 940 m, 810 m, 787 m, 723 m, 550 s, 470 s, 366 s cm^{-1}. ^{119}Sn MAS NMR: δ 303.2 ($^1J(^{119}Sn-^{19}F)$ = 2716 Hz). Anal. Calcd for $C_8H_{19}FOSn$ (269.0): C, 35.72; H, 7.12. Found: C, 35.90; H, 7.33.

***In Situ* Preparation of $R^1R^2Si(OSn$-*t*-$Bu_2)_2O$ (2, R^1 = R^2 = *t*-Bu; 22, R^1 = *t*-Bu, R^2 = F; 26, R^1 = R^2 = Ph) by Reaction of 5, 7, and 21, Respectively, with (*t*-$Bu_2SnO)_3$ (1).** A mixture of **1** (49.8 mg, 0.067 mmol) and the appropriate amount (0.1 mmol) of cyclostannasiloxane (**5**, 81.4 mg; **7**, 89.5 mg; **21**, 73.8 mg) in $CDCl_3$ (250 μL) was heated at reflux for 2 days. NMR spectra recorded from these solutions showed the formation of **2**, **23**, and **22**, respectively (see Table 1).

A droplet of water was added to each sample, and after 15 min ^{29}Si and ^{119}Sn NMR spectra were recorded, which indicated formation of **7**, **21**, **27**, and **28**, respectively (see discussion including eq 9 and Table 1).

Attempt To Isolate $Ph_2Si(OSn$-*t*-$Bu_2)_2O$ (23). The reaction of **7** with **1** was repeated on a preparative scale (**7**, 894.5 mg, 1.0 mmol; **1**, 497.8 mg, 0.67 mmol) in $CHCl_3$ (5 mL) under the same reaction conditions. Solution NMR data (see below) revealed *in situ* formation of **23**.

^1H NMR ($CDCl_3$): δ 7.8−7.3 (m, 10H, Ph), 1.41 (s, $^3J(^1H-CC-^{119}Sn)$ = 96.6 Hz, 36H, SnC*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.2, 134.3, 128.5, 127.1 (i, o, p, m SiPh), 39.4 ($^1J(^{13}C-^{119}Sn)$ = 487 Hz, Sn*C*Me$_3$), 30.1 (SnC*Me*$_3$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −38.3 ($^2J(^{29}Si-O-^{119/117}Sn)$ = 36 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −98.6 ($^2J(^{119}Sn-O-^{117}Sn)$ = 298 Hz, $^2J(^{119}Sn-O-^{29}Si)$ = 36 Hz).

However, slow evaporation of the solvent did not provide **23** but 1.39 g of a mixture of **1** and **7**, as was evidenced by ^{119}Sn MAS NMR of this mixture.

^{119}Sn MAS NMR: δ −84.5 (**1**), −145.6 (**7**).

***In Situ* Preparation of $R^1R^2Si(OSn$-*t*-$Bu_2)_2S$ (24, R^1 = R^2 = *t*-Bu; 25, R^1 = F, R^2 = *t*-Bu; 26, R^1 = R^2 = Ph) by Reaction of 5, 7, and 21, Respectively, with (*t*-$Bu_2SnS)_2$.** A mixture of (*t*-$Bu_2SnS)_2$ (53.0 mg, 0.1 mmol) and the appropriate amount (0.1 mmol) of the cyclostannasiloxane (**5**, 81.4 mg, **7**, 89.5 mg, **21**, 73.8 mg) in $CDCl_3$ (250 μL) was heated at reflux for 2 days. $^{29}Si\{^1H\}$ and $^{119}Sn\{^1H\}$ NMR spectra were recorded from the reaction mixtures and showed the formation of **24**, **25**, and **26**, respectively (see Table 1).

Attempt to Isolate *t*-$Bu_2Si(OSn$-*t*-$Bu_2)_2S$ (24). The reaction of **5** with (*t*-$Bu_2SnS)_2$ was repeated on a preparative scale (**5**, 814.5 mg, 1.00 mmol; (*t*-$Bu_2SnS)_2$, 530.0 mg, 1.00 mmol) in $CHCl_3$ (5 mL) under the same reaction conditions. The solution NMR data (see below) revealed *in situ* formation of **24**.

^1H NMR ($CDCl_3$): δ 1.35 (s, $^3J(^1H-CC-^{119}Sn)$ = 96.9 Hz, 36H, SnC*Me*$_3$), 1.01 (s, 18H, SiC*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 39.5 ($^1J(^{13}C-^{119}Sn)$ = 442 Hz, Sn*C*Me$_3$), 30.2 (SnC*Me*$_3$), 29.2 (SiC*Me*$_3$), 21.9 (Si*C*Me$_3$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −19.7 ($^2J(^{29}Si-O-^{119/117}Sn)$ = 59 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −3.6 ($^2J(^{119}Sn-S-^{117}Sn)$ = 35 Hz, $^2J(^{119}Sn-O-^{29}Si)$ = 60 Hz).

However, slow evaporation of the solvent did not provide **24** but 1.34 g of a mixture of (*t*-$Bu_2SnS)_2$ and **5**, as was evidenced by ^{119}Sn MAS NMR of this mixture.

^{119}Sn MAS NMR: δ −119.5 ((*t*-$Bu_2SnS)_2$), −178.5 (**5**).

Synthesis of 1,1,3,3-Tetra-*tert*-butyl-5,5,7,7-tetraphenyl-2,4,6,8-tetraoxa-5,7-disila-1,3-distannacyclooctane (29). A mixture of **1** (249 mg, 0.33 mmol) and **8** (646 mg, 1.00 mmol) in hexane (10 mL) was heated at reflux for 1 h. Cooling of the reaction mixture at −10 °C provided **29** (870 mg, 0.97 mmol, 97%) as colorless crystals with mp 176 °C.

IR (KBr): 2847 vs, 1559 s, 1540 s, 1336 vs, 1115 vs, 724 s, 700 s, 483 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.8−7.1 (m, 20H, SiPh), 1.27 (s, $^3J(^1H-CC-^{119}Sn)$ = 96.6 Hz, 36H, SnC*Me*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 139.4, 134.5, 128.9, 127.3 (i, o, p, m SiPh), 38.7 ($^1J(^{13}C-^{119}Sn)$ = 507 Hz, Sn*C*Me$_3$), 29.8 (SnC*Me*$_3$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ −45.3 ($^2J(^{29}Si-O-^{119/117}Sn)$ = 67 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −125.7 ($^2J(^{119}Sn-O-^{117}Sn)$ = 688 Hz, $^2J(^{119}Sn-O-^{29}Si)$ = 67 Hz). ^{119}Sn MAS NMR: δ −123.0, −132.3. Mössbauer spectroscopy: QS = 2.31 mm s^{-1}, IS = 1.27 mm s^{-1}. MS (*m*/*z* (%)): 815 (72) [$M^+ - C_6H_7$], 702 (10) [$M^+ - C_{14}H_{25}$], 588 (60) [$M^+ - C_{22}H_{41}$], 510 (18) [$M^+ - C_{28}H_{47}$], 454 (11) [$M^+ - C_{32}H_{56}$], 57 (100) ($C_4H_9^+$). Anal. Calcd for $C_{40}H_{56}O_4Si_2Sn_2$ (894.53): C,53.71; H, 6.31. Found: C, 54.30; H, 7.51.

***In Situ* Reactions of 1, 2, and 29, Respectively, with 1,1,3,3-Tetramethyl-2-oxa-1,3-disilacyclopentane.** A mixture of $(CH_2SiMe_2)_2O$ (16.0 mg, 0.1 mmol) and the appropriate amount of the stannoxane (**1**, 24.9 mg, 0.033 mmol; **2**, 32.8 mg, 0.05 mmol; **29**, 44.8 mg, 0.05 mmol) in $CDCl_3$ (250 μL) was heated at reflux for 1 day. ^{119}Sn and ^{29}Si NMR spectra were recorded from the reaction mixtures and revealed *in situ* formation of **5**, **8**, and **30** (see Table 1).

Synthesis of 1,1-Di-*tert*-butyl-3,3,6,6-tetramethyl-2,7-dioxa-3,6-disila-1-stannacycloheptane (30). A mixture of of $(CH_2SiMe_2)_2O$ (802 mg, 5.00 mmol) and **1** (1.24 g, 1.67 mmol) in $CHCl_3$ (30 mL) was heated at reflux for 1 day. The solvent was removed *in vacuo* to provide **30** as a colorless oil.

^1H NMR ($CDCl_3$): δ 1.26 (s, $^3J(^1H-CC-^{119}Sn)$ = 98.6 Hz, 18H, SnC*Me*$_3$), 0.58 (s, 4H, Si(CH_2)$_2$Si), 0.00 (s, 12H, $SiMe_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 36.9 ($^1J(^{13}C-^{119}Sn)$ = 513 Hz, Sn*C*Me$_3$), 28.5 (SnC*Me*$_3$), 10.4 ($^1J(^{13}C-^{29}Si)$ = 57.4 Hz, Si-(CH_2)$_2$Si), 0.0 ($^1J(^{13}C-^{29}Si)$ = 58 Hz, Si*Me*). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 10.6 ($^2J(^{29}Si-O-^{119}Sn)$ = 58 Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ −135.7 ($^1J(^{119}Sn-O-^{13}C)$ = 515 Hz, $^2J(^{119}Sn-O-^{29}Si)$ = 58 Hz). MS (*m*/*z* (%)): 353 (6) [$M^+ - C_4H_9$], 297 (14) [$M^+ - C_8H_{17}$], 281 (7) [$M^+ - C_9H_{21}$], 269 (15) [$M^+ - C_{10}H_{21}$], 57 (100) [C_4H_9]. Anal. Calcd for $C_{14}H_{34}O_2Si_2Sn$ (409.33): C, 41.08; H, 8.37. Found: C, 40.71; H, 8.83.

***In Situ* Preparation of *t*-BuFSi(OSn-*t*-$Bu_2O)_2Si$-*t*-Bu_2 (31) by Reaction of 5 with 21.** A mixture of **5** (44.7 mg, 0.05 mmol) and **21** (36.9 mg, 0.05 mmol) in $CDCl_3$ (250 μL) was heated at reflux for 2 days to give a clear solution. $^{119}Sn\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra (see Table 1) of this solution showed exclusive formation of **31**.

Crystallography. Intensity data for the colorless crystals were collected on Nonius CAD4 (**5**, **7**, **21**) and Kappa CCD (**9**, **29**) diffractometers with graphite-monochromated Cu Kα (**5**, **7**, **21**) and Mo Kα (**9**, **29**) radiation at 291 K. Three standard reflections were recorded every 60 min (**5**, **7**, **21**), and anisotropic intensity losses up to 22.7% (**5**), 13.3% (**7**), and 35.1% (**21**) were detected during X-ray exposure. The data collections for **9** and **29** covered the sphere of reciprocal space with 360 frames via ω-rotation (Δ/ω = 1°) at 2 × 10 s per frame. The

crystal-to-detector distance was 2.7 cm (**9**) and 3.0 cm (**29**). Crystal decay was monitored by repeating the initial frames at the end of data collection. An analysis of the duplicate reflections showed that there was no indication for any decay (**9**, **29**). The structures were solved by direct methods (SHELXS86[32a]) and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods (SHELXL93[32b]).

The H atoms were placed in geometrically calculated positions using the riding model and refined with common isotropic temperature factors for different C−H types (C_{prim}−H = 0.96 Å, U_{iso} = 0.124(7) (**5**), 0.122(8) (**7**), 0.160(5) (**9**), 0.148(7) (**21**), 0.177(5) (**29**) Å^2; C_{aryl}−H = 0.93 Å, U_{iso} = 0.079(7) (**7**), 0.073(2) (**9**), 0.101(4) (**29**) Å^2).

Disordered *tert*-butyl groups were found for **5** (C(13), C(14), C(13′), C(14′)) and **29** (C(3), C(4), C(3′), C(4′)) with an occupancy of 0.5, whereas the occupancy of the disordered fragment *t*-Bu(F)Si was refined at 0.676(4) (Si(1), F(1), C(22), C(23)) and 0.324(4) (Si(1′), F(1′), C(22′), C(23′)), respectively.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 32c. Figures were created by SHELXTL-Plus.[32d] Crystallographic data are given in Table 2, and selected bond lengths (Å), angles (deg), and torsion angles (deg) are listed in Table 3 (**5**, **7**, and **21**) and Table 4 (**9**, **29**).

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Supporting Information Available: Tables giving atomic coordinates, thermal parameters, bond distances and angles, and least-squares planes for **5**, **7**, **9**, **21**, and **29** (27 pages). Ordering information is given on any current masthead page.

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