ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

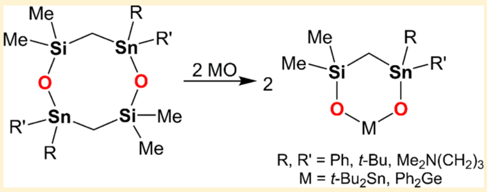
cyclo-Stannasiloxanes Containing both Oxygen Atoms and Methylene Moieties within the Ring and Formation of Related Organotin Oxo Clusters

Samer Baba Haj, Christina Dietz, Michael Lutter, and Klaus Jurkschat*

Lehrstuhl für Anorganische Chemie II, Technische Universität Dortmund, 44221 Dortmund, Germany

Supporting Information

ABSTRACT: The syntheses of the 8-membered stannasiloxanes *cyclo*-$[RR'SnOSi(Me_2)CH_2]_2$ (**5**, R = R′ = Ph; **6**, R = R′ = *t*-Bu; **7**, R = $Me_2N(CH_2)_3$, R′ = Ph) is reported. These react with organoelement oxides, providing the novel metallasiloxanes *cyclo*-$[Me_2SiCH_2(RR')SnOMO]$ (**8**, R = R′ = Ph, M = *t*-Bu_2Sn; **9**, R = R′ = *t*-Bu, M = *t*-Bu_2Sn; **10**, R = $Me_2N(CH_2)_3$, R′ = Ph, M = *t*-Bu_2Sn; **11**, R = $Me_2N(CH_2)_3$, R′ = Ph, M = Ph_2Ge). Among these, compound **11** is the first example of such species being composed of four different group 14 elements in the 6-membered-ring skeleton. On contact with moist air compound **8** surprisingly undergoes Sn−Ph bond cleavage, giving the diorganotinoxo cluster $[PhSn(CH_2Me_2SiO)Sn(\mu_3\text{-}O)(\mu\text{-}OH)t\text{-}Bu_2]_2$ (**12**), which shows a ladder-type structure. The latter reacts with 2 molar equiv of *t*-Bu_2SnO, affording the Sn_6-diorganotin oxo cluster $[t\text{-}Bu_2(\mu\text{-}OH)Sn(\mu_3\text{-}O)SnPh(CH_2Me_2SiO)Sn\text{-}t\text{-}Bu_2(\mu_3\text{-}O)]_2$ (**13**). The compounds have been characterized by NMR spectroscopy, electrospray mass spectrometry, and in the case of compounds **5**−**7**, **12**, and **13** also by single-crystal X-ray diffraction analysis.



INTRODUCTION

Polysiloxanes are the most important inorganic polymers. They show a variety of molecular structures and demonstrate an intimate relationship between structure and properties not easily achievable by other classes of polymers. Consequently, a wide diversity of applications is known. The ring-opening polymerization (ROP) procedure of the *cyclo*-siloxanes has been applied to the production of high-molecular-weight polysiloxanes.[1] This initiated activities regarding the synthesis, characterization, and reactivity of *cyclo*-metallasiloxanes.[2] Such compounds hold potential as single-source precursors for new inorganic polymers.[2a,3] A rich structural diversity of *cyclo*-metallasiloxanes incorporating various heteroatoms, such as B, Al, Ge, Sn, Pb, P, Sb, Bi, Ti, Zr, Hf, Cr, Mo, and W, exists among the *cyclo*-metallasiloxanes.[2b,3a,4] The first tin-containing *cyclo*-metallasiloxane, *cyclo*-*t*-$Bu_2Si(OMe_2SnO)_2Si$-*t*-Bu_2, was prepared in 1986 by Klingebiel et al.[4c] In 1997, we reported the syntheses and molecular structures of the *cyclo*-stannasiloxanes *cyclo*-*t*-$Bu_2Sn[O(t\text{-}Bu_2)Si]_2O$ and *cyclo*-*t*-$Bu_2Si[O(t\text{-}Bu_2)SnO]_2Si$-*t*-$Bu_2$, obtained by the reaction of $(t\text{-}Bu_2SnO)_3$ with *t*-Bu_2SiCl_2.[5] These were followed by the syntheses and reactivity studies of a series of *cyclo*-stannasiloxanes of different ring sizes and variable substituents at both the silicon and tin atoms.[2a]

The studies showed that the reactivity of the *cyclo*-stannasiloxanes differs drastically from that of the parent *cyclo*-siloxanes as a result of the higher kinetic lability of the Sn−O bond in comparison to the Si−O bond. Consequently, reactions involving Sn−O bonds usually proceed rapidly at room temperature on the laboratory time scale.[2a] While the ROP of *cyclo*-$(Ph_2SiO)_3$ occurs at temperatures between 150 and 190 °C in the presence of initiators, the *cyclo*-stannasiloxane *cyclo*-$R_2Sn(OPh_2Si)_2O$ (R = *t*-Bu, *i*-Pr) undergoes ROP upon crystallization, in absence of any initiator, giving the first well-defined polymetallasiloxanes $(R_2SnOPh_2SiOPh_2SiO)_n$.[2a,6] However, the polymers are not stable and they depolymerize upon dissolving in solvent.[6] The release of the ring strain is foreseen to be the thermodynamic driving force for the ROP process.

The ability of *cyclo*-stannasiloxanes to undergo ring-opening polymerization strongly depends on the identity of the exocyclic substituents at the tin and silicon atoms, as the ferrocenyl-substituted 6-membered stannasiloxane *cyclo*-$Fc_2Sn(OPh_2Si)_2O$ (Fc = $CpFeC_5H_4$) dimerizes under crystallization, affording the corresponding 12-membered stannasiloxane *cyclo*-$[(Fc_2Sn(OPh_2SiOPh_2SiO)_2SnFc_2]$.[2a] In contrast, the 6-membered stannasiloxane *cyclo*-$[Me_2N(CH_2)_3]_2Sn(OPh_2Si)_2O$ containing a *built-in* ligand does not polymerize or dimerize upon crystallization.[7] Furthermore, the connectivity of the atoms within the ring plays a major role. Thus, the 5-membered stannasiloxane *cyclo*-$(Ph_2SiO)_2Sn$-*t*-Bu_2 containing a Si−Si bond does not polymerize upon crystallization. It reversibly dimerizes, providing the 10-membered stannasiloxane *cyclo*-*t*-$Bu_2Sn(OPh_2SiPh_2SiO)_2Sn$-*t*-$Bu_2$.[2a]

The reactions of *cyclo*-stannasiloxanes with organoelement oxides allowed the isolation of new interesting *cyclo*-metallasiloxanes of different ring sizes thanks to the kinetically labile Sn−OSi bond. Thus, the reaction of the 8-membered stannasiloxanes *cyclo*-$R_2Sn(OPh_2SiO)_2SnR_2$ (R = $Me_2N(CH_2)_3$) with $(t\text{-}Bu_2SnO)_3$, *t*-$Bu_2Ge(OH)_2$. and $PhB(OH)_2$ gave the 6-membered metallasiloxanes *cyclo*-(R_2SnOPh_2SiOMO) (M = *t*-Bu_2Sn, *t*-Bu_2Ge, PhB),[8] and the

Received: September 8, 2015

reaction of $LPhSn(OPh_2SiO)_2SnLPh$ (L = C_6H_3-2,6-$(CH_2NMe_2)_2$) with $Ph_2Si(OH)_2$ afforded the 6-membered stannasiloxane *cyclo*-$LPhSn(OPh_2Si)_2O$.[2b]

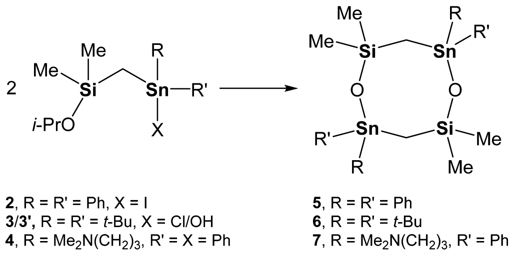
Furthermore, the reactions of the 5-membered stannasiloxane *cyclo*-*t*-$Bu_2Sn(OPh_2Si)_2$ and the 6-membered stannasiloxane *cyclo*-*t*-$Bu_2Sn(OPh_2Si)_2O$ with (*t*-$Bu_2SnO)_3$ result in ring enlargement, giving the corresponding 7- and 8-membered stannasiloxanes *cyclo*-O(*t*-$Bu_2SnOPh_2Si)_2$[2a] and *cyclo*-O(*t*-$Bu_2SnOPh_2Si)_2O$, respectively.[4r,6]

To the best of our knowledge, *cyclo*-stannasiloxanes in which the oxygen atoms are partially replaced by CH_2 moieties have been almost unexplored. As systematic studies showed that even very similar compounds can have drastically different chemical reactivities, this raises interest in synthesizing this type of *cyclo*-stannasiloxanes and study their behavior against organoelement oxides.

■ RESULTS AND DISCUSSION

Syntheses and Structures of the 8-Membered Stannasiloxanes *cyclo*-[RR′SnOSi(Me$_2$)CH$_2$]$_2$ (5, R = R′ = Ph; 6, R = R′ = *t*-Bu; 7, R = Me$_2$N(CH$_2$)$_3$, R′ = Ph). The hydrolyses under basic conditions of the Me_2(*i*-PrO)$SiCH_2$-substituted triorganotin halides [Me_2(*i*-PrO)$SiCH_2$]RR′SnX (**2**, R = R′ = Ph, X = I; **3**/**3′**, R = R′ = *t*-Bu, X = Cl/OH) provided the corresponding 8-membered stannasiloxanes *cyclo*-[RR′SnOSi(Me_2)CH_2]$_2$ (**5**, R = R′ = Ph; **6**, R = R′ = *t*-Bu). The subsequent reaction of the tetraorganotin derivative {Me_2(*i*-PrO)$SiCH_2$}{$Me_2N(CH_2)_3$}$SnPh_2$ (**4**) with (i) elemental iodine (I_2) and (ii) aqueous sodium hydroxide (NaOH) gave the *cyclo*-stannasiloxane **7** (Scheme 1). Compounds **5**−**7** were obtained as colorless solid materials in very good yields.

Scheme 1. Syntheses of the Eight-Membered Stannasiloxanes 5−7[a]



[a]For reactions involving **2** and **3**/**3′**: NaOH, H_2O, −NaX, −*i*-PrOH. For the reaction involving **4**: (i) I_2, −PhI; (ii) NaOH, H_2O, −NaI, −*i*-PrOH.

They show good solubility in common organic solvents such as CH_2Cl_2, $CHCl_3$, toluene, and THF.

Compounds **5**−**7** each crystallized in the triclinic space group $P\bar{1}$ with one molecule in the unit cell. The molecular structures are shown in Figures 1−3, respectively, and selected interatomic distances and bond angles are summarized in Table 1.

The 8-membered rings are centrosymmetric, with half of each molecule comprising the crystallographic asymmetric unit and the other half being generated by an inversion center. According to a classification scheme introduced by Puff, Kök, et al.,[4r,9] the 8-membered rings in compounds **5** and **6** are of D type and that in **7** is of J type (Figure 4).

In compounds **5** and **6**, the Sn(1) atoms show a distorted-tetrahedral geometry with angles ranging between 100.41(6) (O(1)−Sn(1)−C(11) in **6**) and 118.33(9)° (C(1A)−Sn(1)−C(21) in **5**). The Sn(1)−O(1)−Si(1) angle in **5** (137.52(8)°) is much smaller than the corresponding angles in **6** (152.29(9)°) and $Ph_3SiOSnPh_3$ (144.2(6)°),[10] while the Sn(1)−C(1A)−Si(1A) angle (113.86(11)°) is close to that in **6** (117.89(9)°). As result of an intramolecular N→Sn interaction, the Sn(1) atom in compound **7** is pentacoordinated and shows a distorted-trigonal-bipyramidal environment (geometrical goodness[11] $\Delta\sum(\theta) = 59.1°$) with C(1A), C(11), and C(21) occupying the equatorial positions and O(1) and N(14) occupying the axial positions. The distortion from ideal geometry is expressed by the O(1)−Sn(1)−N(14) angle of 166.94(17)° being smaller than the ideal value of 180°. The Sn(1)−N(14) interatomic distance of 2.766(6) Å is rather long and indicates only weak interaction between these atoms. Nevertheless, as a consequence of this interaction, the Sn(1)−O(1) distance of 2.020(4) Å is greater than the corresponding distances in compounds **5** (1.9815(14) Å) and **6** (1.9687(13) Å), which in turn are close to those reported for 2,2,6,6-tetra-*tert*-butyl-4,8-dimethyl-1,5,9-trioxa-4,8-disila-2,6-distannabicyclo[3.3.1]nonane.[12]

The ^{119}Sn NMR spectra of solutions of compounds **5** and **6** in $CDCl_3$ showed singlet resonances at δ −31 and 34, respectively. The corresponding ^{29}Si NMR spectra showed singlet resonances with unresolved $^{117/119}Sn$ coupling satellites from two magnetically different tin atoms at δ 8.6 (**5**, $^2J(^{29}Si-^{117/119}Sn)$ = 33 Hz, $^2J(^{29}Si-^{117/119}Sn)$ = 54 Hz) and δ 1.8 (**6**, $^2J(^{29}Si-^{117/119}Sn)$ = 46 Hz, $^2J(^{29}Si-^{117/119}Sn)$ = 56 Hz), respectively. On the other hand, compound **7** adopts chirality at the tin atom. A ^{119}Sn NMR spectrum of a solution of the bulk material in $CDCl_3$ showed two resonances at δ −53 (integral 45) and −55 (integral 55). Furthermore, a ^{29}Si NMR spectrum showed two resonances at δ 1.4 ($^2J(^{29}Si-^{117/119}Sn)$ = 38 Hz, $^2J(^{29}Si-^{117/119}Sn)$ = 47 Hz) and at δ 1.0 ($^2J(^{29}Si-^{117/119}Sn)$ = 42 Hz, $^2J(^{29}Si-^{117/119}Sn)$ = 49 Hz) (Table 2). A ^{119}Sn NMR spectrum of a solution of single crystals of **7** in C_7D_8 at ambient temperature displayed two resonances of almost equal intensity at δ −62.8 and −62.6, respectively. At *T* = 333 K, these signals shifted to δ −54.4 and −54.2, respectively. The data indicate the presence of two diastereomers in solution, with the phenyl groups being either cis or trans. Apparently, epimerization takes place in solution. It is fast on the laboratory time scale but slow on the ^{119}Sn NMR time scale. The mechanism of this epimerization was not investigated in more detail.

ESI MS spectra of compounds **5**−**7** in the positive mode showed major mass clusters centered at *m*/*z* 723.1 ([**5** + H]$^+$), 643.2 ([**6** + H]$^+$), and 741.2 ([**7** + H]$^+$), respectively. In addition, mass clusters for the species [$Me_2(OH)SiCH_2$RR′Sn + *n* H_2O + *m* MeCN]$^+$, (*n*, *m* = natural numbers between 0 and 4) were also observed.

Syntheses of the 6-Membered Metallasiloxanes *cyclo*-[Me$_2$SiCH$_2$(RR′)SnOMO] (8, R = R′ = Ph, M = *t*-Bu$_2$Sn; 9, R = R′ = *t*-Bu, M = *t*-Bu$_2$Sn; 10, R = Me$_2$N(CH$_2$)$_3$, R′ = Ph, M = *t*-Bu$_2$Sn; 11, R = Me$_2$N(CH$_2$)$_3$, R′ = Ph, M = Ph$_2$Ge). The reactions of the 8-membered stannasiloxanes *cyclo*-[RR′SnOSi(Me_2)CH_2]$_2$ (**5**, R = R′ = Ph; **6**, R = R′ = *t*-Bu; **7**, R = $Me_2N(CH_2)_3$, R′ = Ph) with 2 molar equiv of di-*tert*-butyltin oxide (*t*-Bu_2SnO) or diphenylgermanium oxide (Ph_2GeO) in CH_2Cl_2 at room temperature or in $CHCl_3$ at reflux gave the corresponding 6-membered metallasiloxanes *cyclo*-[Me_2SiCH_2(RR′)SnOMO] (**8**, R = R′ = Ph, M = *t*-Bu_2Sn; **9**, R = R′ = *t*-Bu, M = *t*-Bu_2Sn; **10**, R = $Me_2N(CH_2)_3$, R′ = Ph, M

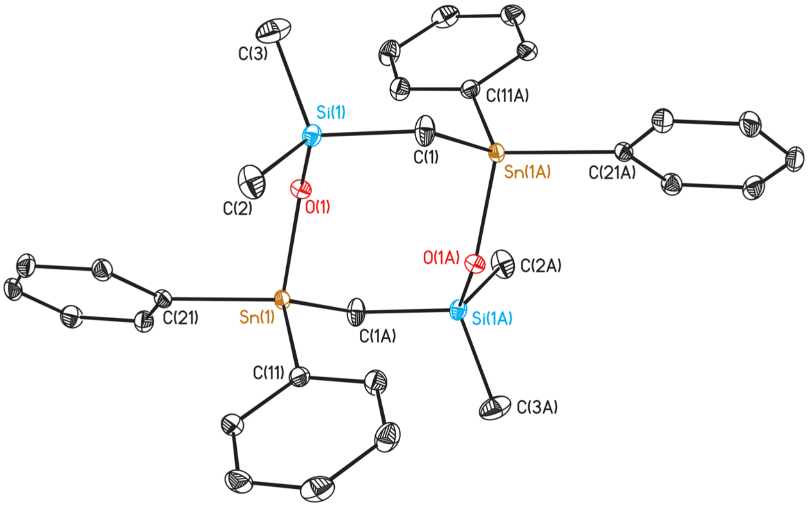


Figure 1. General view (SHELXTL) of a molecule of **5** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

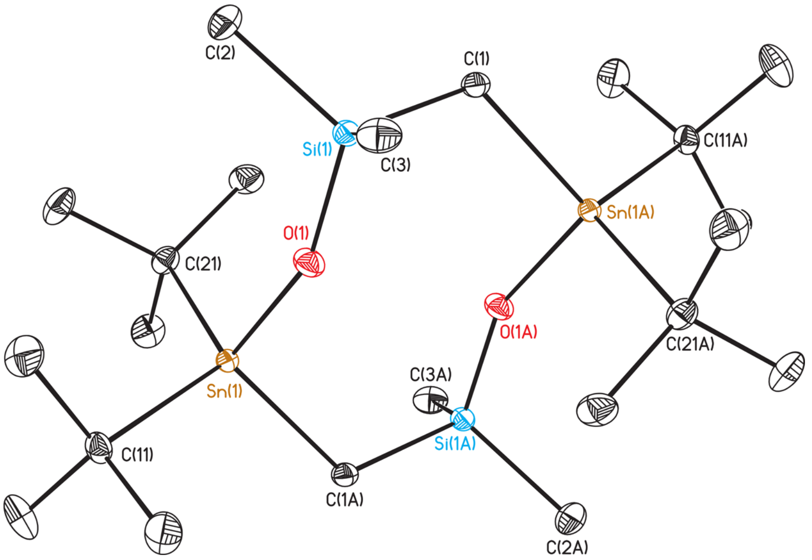


Figure 2. General view (SHELXTL) of a molecule of **6** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

= *t*-Bu$_2$Sn; **11**, R = Me$_2$N(CH$_2$)$_3$, R′ = Ph, M = Ph$_2$Ge) in excellent yields (Scheme 2).

Compounds **8**−**11** show good solubility in common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$, and toluene.

Compounds **8**−**10** contain two differently substituted tin atoms linked to one silicon atom by oxygen or carbon bridges. The first *cyclo*-stannasiloxane with two differently substituted tin atoms, *cyclo*-[Ph$_2$SiO(R$_2$)SnO(*t*-Bu$_2$)SnO] (R = Me$_2$N-(CH$_2$)$_3$), was obtained by the reaction of *cyclo*-(Ph$_2$SiOR$_2$SnO)$_2$ with di-*tert*-butyltin oxide.[8] On the other hand, the compound *cyclo*-[Me$_2$SiCH$_2$(*t*-Bu$_2$)SnOPh$_2$GeO] (**11**) is the first 6-membered *cyclo*-metallasiloxane to be composed of four different group 14 elements in the ring skeleton.

The two chemically and magnetically different tin atoms in compounds **8**−**10** result in two ^{119}Sn NMR singlet resonances, each with $^{117/119}$Sn coupling satellites. The ^{119}Sn NMR spectrum of compound **8** in CDCl$_3$ showed two resonances at δ −13 assigned to OPh$_2$*Sn*CH$_2$ and at δ −93 that corresponds to O-*t*-Bu$_2$*Sn*O with a $^{2}J(^{119}\mathrm{Sn}-^{117/119}\mathrm{Sn})$ coupling constant of 317/335 Hz for each resonance (Figure S36 in the Supporting Information). Similarly, the ^{119}Sn NMR spectra of solutions of compounds **9** and **10** in CDCl$_3$ (Figures S40 and S44 in the Supporting Information) showed two resonances (**9**, δ 49 [O(*t*-Bu$_2$)*Sn*CH$_2$], −98 [O(*t*-Bu$_2$)*Sn*O], $^{2}J(^{119}\mathrm{Sn}-^{117/119}\mathrm{Sn})$ = 351/367 Hz; **10**, δ −23 [O{Me$_2$N-(CH$_2$)$_3$Ph}*Sn*CH$_2$], −89 (O(*t*-Bu$_2$)*Sn*O), $^{2}J(^{119}\mathrm{Sn}-^{117/119}\mathrm{Sn})$ = 293 Hz). A ^{119}Sn NMR spectrum of a solution of compound **11** in CDCl$_3$ (Figure S47 in the Supporting Information) showed one resonance at δ −59 (Table 3).

The ^{29}Si NMR spectra of compounds **8**−**11** each showed a single resonance at δ 5.9, 5.2, 6.5, and 10.7, respectively, with $^{2}J(^{29}\mathrm{Si}-^{117/119}\mathrm{Sn})$ coupling satellites ranging between 40 and 49 Hz (Table 3).

The ESI MS spectra of compounds **10** and **11** in the positive mode showed major mass clusters that are assigned to the protonated compounds centered at m/z 620.1 ([**10** + H]$^+$) and 614.1 ([**11** + H]$^+$). The ESI MS spectrum of compound **8** showed a mass cluster of 12% relative abundance centered at

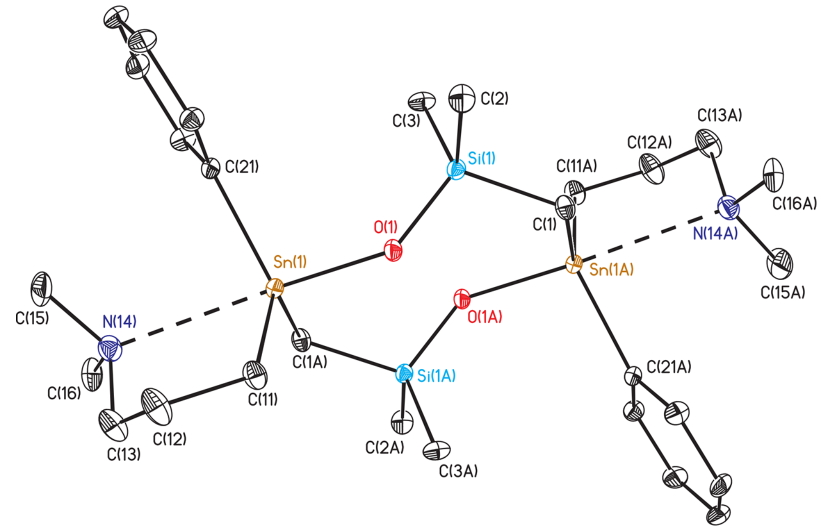
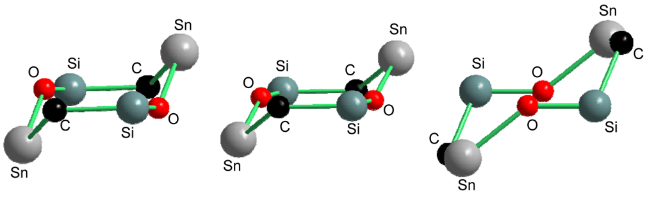


Figure 3. General view (SHELXTL) of a molecule of **7** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1. Selected Interatomic Distances (Å) and Bond Angles (deg) in the Stannasiloxanes ***cyclo*-[RR′SnOSi(Me$_2$)CH$_2$]$_2$ (5, R = R′ = Ph; 6, R = R′ = *t*-Bu; 7, R = Me$_2$N(CH$_2$)$_3$, R′ = Ph)**

	5	6	7
Sn(1)–O(1)	1.9815(14)	1.9687(13)	2.020(4)
Sn(1)–C(1A)	2.125(2)	2.1361(17)	2.135(6)
Si(1)–O(1)	1.6264(15)	1.6072(13)	1.610(4)
Sn(1)–C(11)	2.137(2)	2.1739(18)	2.141(6)
Sn(1)–C(21)	2.137(2)	2.1746(19)	2.136(6)
Sn(1)–N(14)			2.766(6)
O(1)–Sn(1)–C(1A)	103.71(8)	105.84(7)	101.8(2)
O(1)–Sn(1)–C(11)	106.62(7)	100.41(6)	93.2(2)
O(1)–Sn(1)–C(21)	102.84(7)	108.76(7)	99.8(2)
C(1A)–Sn(1)–C(11)	118.33(9)	110.10(7)	119.0(3)
C(1A)–Sn(1)–C(21)	113.91(8)	113.53(7)	116.8(2)
C(11)–Sn(1)–C(21)	109.76(8)	116.81(7)	118.1(3)
Sn(1)–O(1)–Si(1)	137.52(8)	152.29(9)	140.7(2)
Sn(1)–C(1A)–Si(1A)	113.86(11)	117.89(9)	116.1(3)
N(14)–Sn(1)–O(1)			166.94(17)
N(14)–Sn(1)–C(1A)			88.7(2)
N(14)–Sn(1)–C(11)			74.7(2)
N(14)–Sn(1)–C(21)			82.1(2)



0 0 0 + 0 0 0 – 0 0 0 + 0 0 0 – 0 0 + + 0 0 – –

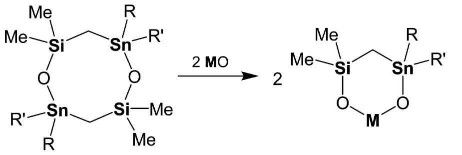
5 (D-type) **6** (D-type) **7** (J-type)

Figure 4. Reduced ball-and-stick molecular structures of compounds **5**–**7**. All exocyclic substituents are omitted for clarity.

Table 2. Selected NMR Data of the Stannasiloxanes ***cyclo*-[RR′SnOSi(Me$_2$)CH$_2$]$_2$ (5, R = R′ = Ph; 6, R = R′ = *t*-Bu; 7, R = Me$_2$N(CH$_2$)$_3$, R′ = Ph)**

	$\delta(^{29}Si)$ (ppm)	$\delta(^{119}Sn)$ (ppm)	$^2J(^{29}Si-^{117/119}Sn)$ (Hz)
5	8.6	−31	33, 54
6	1.8	34	46, 56
7	1.0; 1.4	−53; −55	42, 49; 38, 47

Scheme 2. Syntheses of the 6-Membered Metallasiloxanes 8–11



8; R = R′ = Ph, **M** = *t*-Bu$_2$Sn
9; R = R′ = *t*-Bu, **M** = *t*-Bu$_2$Sn
10; R = Me$_2$N(CH$_2$)$_3$, R′ = Ph, **M** = *t*-Bu$_2$Sn
11; R = Me$_2$N(CH$_2$)$_3$, R′ = Ph, **M** = Ph$_2$Ge

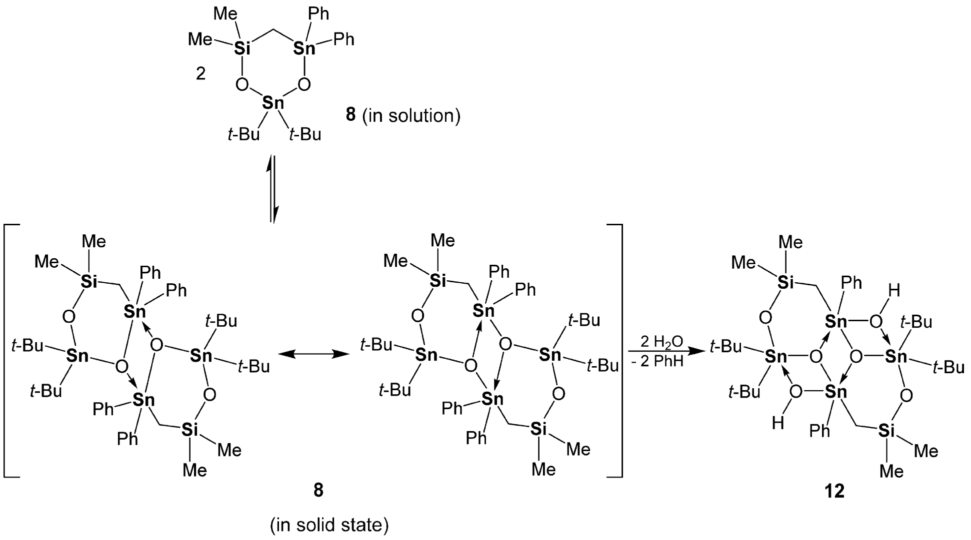
Table 3. Selected NMR Data of Compounds 8–11

	$\delta(^{29}Si)$ (ppm)	$^2J(^{29}Si-^{117/119}Sn)$ (Hz)	$\delta(^{119}Sn)$ (ppm)	$^2J(^{119}Sn-^{117/119}Sn)$ (Hz)
8	5.9	43, 49	−13, −93	317/335
9	5.2	40, 44	49, −98	351/367
10	6.5	40	−23, −89	292
11	10.7	42	−59	

m/*z* 611.1 for [**8** + H]$^+$. An ESI MS spectrum of compound **9** in the negative mode showed a major mass cluster centered at *m*/*z* 587.1 which fits exactly with [**9** + OH]$^-$.

Formation of the Ladderlike Diorganotinoxo Clusters [PhSn(CH$_2$Me$_2$SiO)Sn(μ_3-O)(μ-OH)*t*-Bu$_2$]$_2$ (12) and [*t*-Bu$_2$(μ-OH)Sn(μ_3-O)SnPh(CH$_2$Me$_2$SiO)Sn-*t*-Bu$_2$(μ_3-O)]$_2$ (13). Recrystallization of the stannasiloxane *cyclo*-[Me$_2$SiCH$_2$Ph$_2$SnO(*t*-Bu$_2$)SnO] (**8**) by slow evaporation of a solution of the compound in CH$_2$Cl$_2$/hexane in aerobic conditions gave, as the mixture was dried, a few single crystals suitable for X-ray diffraction analysis of the ladder-type dimeric tetraorganodistannoxane [PhSn(CH$_2$Me$_2$SiO)Sn(μ_3-O)(μ-OH)*t*-Bu$_2$]$_2$ (**12**). This is a result of Sn–C$_{Ph}$ bond cleavage in the presence of moist air (Scheme 3). Chandrasekhar et al. reported before on Sn–C$_{Ph}$ bond cleavage, as the reaction of the diorganotin dichloride Ph$_2$SnCl$_2$ with cycPO$_2$H (1,1,2,3,3-pentamethyltrimethylenephosphinic acid) gave the monoorga-

Scheme 3. Hydrolysis of Compound 8 in Moist Air Giving the Ladder-Type Diorganotinoxo Cluster [PhSn(CH$_2$Me$_2$SiO)Sn(μ_3-O)(μ-OH)*t*-Bu$_2$]$_2$ (12)



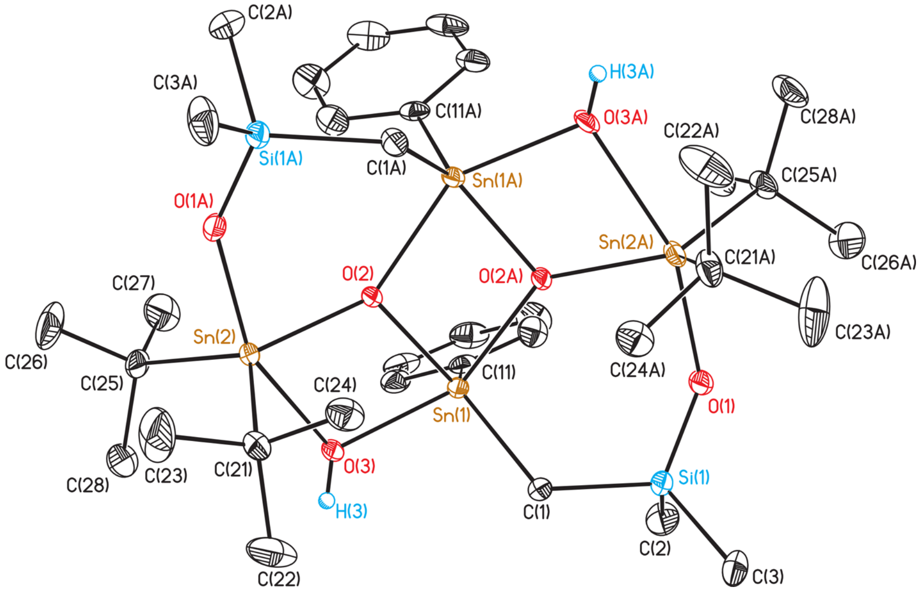


Figure 5. General view (SHELXTL) of a molecule of **12** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Carbon-bound hydrogen atoms are omitted for clarity.

notin oxo cluster [(PhSn)$_3$(μ_3-O)(μ-*cyc*PO$_2$)$_3$(μ-OH)$_3$][cycPO$_2$].[13]

Compound **12** is a high-melting solid material that shows good solubility in CH$_2$Cl$_2$ and CHCl$_3$.

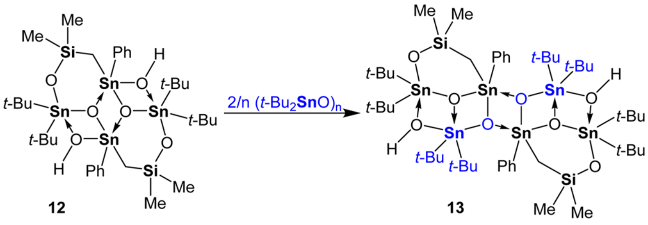
In an attempt to synthesize compound **12**, a solution of **8** in CH$_2$Cl$_2$ to which a few droplets of water had been added was stirred for a few days at room temperature. Surprisingly, no reaction took place. After the solution was evaporated to dryness and the residue kept for a few weeks in moist air, ^{29}Si and ^{119}Sn NMR spectra of the residue in CDCl$_3$ solution were recorded. A ^{29}Si NMR spectrum showed two signals, at δ 8.6 for the 8-membered *cyclo*-stannasiloxane **5** and at δ −2.4 with $^2J(^{29}\mathrm{Si}-^{117/119}\mathrm{Sn})$ coupling constants of 40 and 69 Hz assigned to **12** (Figure S51 in the Supporting Information). The corresponding ^{119}Sn NMR spectrum showed major equally intense resonances at δ −219 and −260 that are characteristic for pentacoordinated tin atoms found in ladder-type diorganotinoxo clusters.[14] The signal at δ −219 ($^2J(^{119}\mathrm{Sn}_{\mathrm{endo}}-^{29}\mathrm{Si})$ = 41 Hz, $^2J(^{119}\mathrm{Sn}_{\mathrm{endo}}-^{117/119}\mathrm{Sn}_{\mathrm{exo}})$ = 228/242 Hz, $^2J(^{119}\mathrm{Sn}_{\mathrm{endo}}-^{117}\mathrm{Sn}_{\mathrm{endo}})$ = 82 Hz) is assigned to the endocyclic tin atom (Sn1, Figure 5) in compound **12**, while the signal at δ −260 ($^2J(^{119}\mathrm{Sn}_{\mathrm{exo}}-^{29}\mathrm{Si})$ = 71 Hz, $^2J(^{119}\mathrm{Sn}_{\mathrm{exo}}-^{117/119}\mathrm{Sn}_{\mathrm{endo}})$ = 228/242 Hz, $^4J(^{119}\mathrm{Sn}_{\mathrm{exo}}-^{117}\mathrm{Sn}_{\mathrm{exo}})$ = 84 Hz) belongs to the exocyclic tin (Sn2, Figure 5) (Figure S50 in the Supporting Information). In addition, resonances at δ −31 (compound **5**, 25%), −38 (11%), and −54 (6%) were observed. The last two signals are likely related to the hydrolysis products that contain the *t*-Bu$_2$Sn moiety, as they do not have corresponding signals in the ^{29}Si NMR spectrum.

We suppose that the cleavage of the Sn−C$_{\mathrm{Ph}}$ bond in **8** by water is facilitated by activation of this bond as a result of an O→Sn donor−acceptor interaction in the solid state, realized by dimerization. The O→Sn interaction vanishes upon dilution (in solution), explaining why stirring a solution of compound **8** in presence of water does not afford compound **12**.

The rearrangement of 6-membered cyclic stannasiloxanes upon recrystallization to give the corresponding 12-membered rings was also described for *cyclo*-$[R_2Sn(OPh_2Si)_2O]_n$ (R = $CpFeC_5H_4$).[2a]

Interestingly, when $CDCl_3$ was allowed to evaporate slowly from a solution containing **8** (93%), **5** (4%), and t-Bu_2SnO (3%), in a not completely closed NMR tube, one single crystal of the ladderlike hydrolysis product $[t\text{-}Bu_2(\mu\text{-}OH)Sn(\mu_3\text{-}O)SnPh(CH_2Me_2SiO)S\text{-}n t\text{-}Bu_2(\mu_3\text{-}O)]_2$ (**13**) suitable for X-ray diffraction analysis was isolated. Compound **13** is formed by insertion of two t-Bu_2SnO moieties into the Sn−OH bonds in **12** (Scheme 4).

Scheme 4. Reaction of Compound 12 with Di-*tert*-butyltin Oxide Providing the Hexanuclear Diorganotinoxo Cluster 13



Molecular Structures of the Ladderlike Diorganotinoxo Clusters 12 and 13. The compounds **12** and **13** crystallized in the monoclinic space groups $P2/n$ and $P2_1/n$, respectively, with two molecules in the unit cell. The molecular structures of compounds **12** and **13** are shown in Figures 5 and 6, respectively, and selected interatomic distances and bond angles are summarized in Tables 4 and 5, respectively.

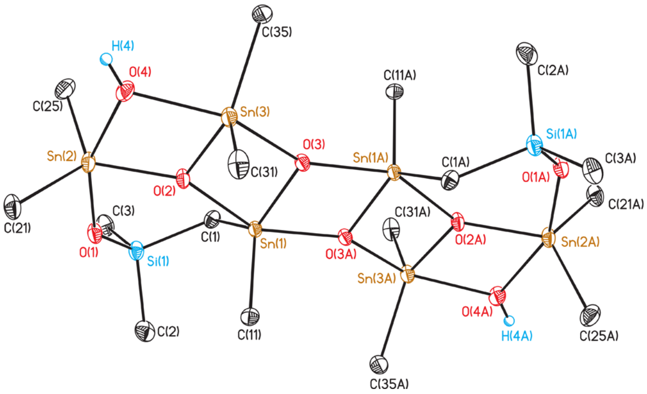


Figure 6. General view (SHELXTL) of a molecule of **13** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. The methyl carbon atoms of the *tert*-butyl substituents are omitted for clarity. Only the C_{ipso} carbon atoms (C11, C11A) of the phenyl substituents are shown. Carbon-bound hydrogen atoms are omitted for clarity.

Both **12** and **13** exist as ladder-type compounds that contain pentacoordinated tin atoms. They can be viewed as symmetric dimers, as one half of the molecules comprises the crystallographic asymmetric unit and the other half is generated by a C_2 proper axis (in compound **12**) or inversion center (in compound **13**). The endocyclic tin atoms have square-pyramidal environments with one carbon atom and three oxygen atoms in the equatorial positions (C(1), O(2), O(2A), and O(3) for Sn(1) in **12**, C(1), O(2), O(3A), and O(3) for Sn(1) in **13**, and C(35), O(2), O(3), and O(4) for Sn(3) in **13**). The axial positions are occupied by one carbon atom (C(11) for Sn(1) in **12** and **13**; and C(31) for Sn(3) in **13**) (geometrical parameter[15] $\tau = 0.32$ for Sn(1) in **12**; $\tau = 0.37$ and 0.12 for Sn(1) and Sn(3), respectively, in **13**). The exocyclic tin atoms Sn(2) exhibit distorted-trigonal-bipyramidal geometry with the equatorial positions being occupied by the C(21), C(25), and O(2) atoms and the axial positions by one silicon-bound oxygen atom (O(1A) in **12** and O(1) in **13**) and one μ_2 oxygen atom (O(3) in **12** and O(4) in **13**) (geometrical goodness[11] $\Delta\sum(\theta) = 72.4°$ for **12** and 75.9° for **13**).

The Sn−O interatomic distances range between 2.0253(18) and 2.301(2) Å for **12** and between 2.035(2) and 2.273(3) for **13**. The Sn_{endo}−μ_2-O−Sn_{exo} bridges are not symmetric (**12**, Sn(1)−O(3) 2.0936(18) Å, Sn(2)−O(3) 2.301(2) Å; **13**, Sn(3)−O(4) 2.149(3) Å, Sn(2)−O(4) 2.273(3) Å). With respect to the central Sn_2O_2 ring being almost (**12**) or perfectly (**13**) planar, the phenyl substituents are cis for **12** but trans for **13**.

On the basis of the different Sn−O interatomic distances, compound **12** can formally and with caution be viewed as a 12-membered ring showing intramolecular O(2)→Sn(1A) (2.1266(16) Å) and O(3)→Sn(2) (2.301(2) Å) interactions. The alternative view of two head-to-tail linked 6-membered rings giving a centrosymmetric dimer is less favored, as the Sn(1)−O(2) distance of 2.0344(17) Å is much shorter. Regardless of this, the formal replacement of a tin-bound phenyl substituent in **8** by a hydroxyl group in **12** enhances the Lewis acidity at the tin atom in the latter, affording a stronger O→Sn interaction. Consequently, a ladderlike structure results. The latter consists of three 4-membered and two 6-membered rings (Figure 7).

Compound **13**, on the other hand, comprises the structural motif $[Me_2SiCH_2(Ph)Sn(\mu_3\text{-}O)O(t\text{-}Bu_2)Sn(\mu\text{-}OH)Sn(t\text{-}Bu_2)]$ that resembles [*cyclo*-$R_2Si(OSnt\text{-}Bu_2)_2O\cdot t\text{-}Bu_2Sn(OH)_2$] (R = Ph,[16] Me[17]) and related compounds,[18] by replacing one oxygen atom with a methylene moiety and one oxygen-bound proton and one *tert*-butyl substituent with a tin and oxygen atom, respectively, belonging to the second half of **13** (Chart 1).

A search in the Cambridge Structural Data Base (CCSD) revealed 12 entries for hexanuclear tin oxo clusters that are ladderlike, as for compound **13**, but show different connectivities. Eight of them represent open-drum structures,[19] two contain both di- and triorganotin moieties,[20] and two show the presence of Sn−O as well as Sn−N bonds.[21]

In conclusion, a series of novel metallasiloxanes *cyclo*-$[RR'SnOSi(Me_2)CH_2]_2$ (**5**, R = R′ = Ph; **6**, R = R′ = t-Bu; **7**, R = $Me_2N(CH_2)_3$, R′ = Ph) and *cyclo*-$[Me_2SiCH_2(RR')SnOMO]$ (**8**, R = R′ = Ph, M = t-Bu_2Sn; **9**, R = R′ = t-Bu, M = t-Bu_2Sn; **10**, R = $Me_2N(CH_2)_3$, R′ = Ph, M = t-Bu_2Sn; **11**, R = $Me_2N(CH_2)_3$, R′ = Ph, M = Ph_2Ge) were synthesized and characterized. On contact with air moisture, compound **8** surprisingly undergoes Sn−C_{Ph} bond cleavage to give the ladderlike diorganotin oxo cluster $[PhSn(CH_2Me_2SiO)(\mu_3\text{-}O)Sn(\mu\text{-}OH)t\text{-}Bu_2]_2$ (**12**). The latter reacts with 2 molar equiv of t-Bu_2SnO, affording the hexanuclear diorganotinoxo cluster $[(t\text{-}Bu_2)(\mu\text{-}OH)Sn(\mu_3\text{-}O)Sn(Ph)(CH_2Me_2SiO)Sn(t\text{-}Bu_2)(\mu_3\text{-}O)]_2$ (**13**). The cyclic metallasiloxanes **5**−**11** hold potential as single-source precursors for new inorganic polymers and structurally modified polysiloxanes by the so-called ring-opening polymerization.[2a]

Table 4. Selected Interatomic Distances (Å) and Bond Angles (deg) in 12

Sn(1)−O(2)	2.0344(17)	Sn(2)−O(2)	2.0329(16)
Sn(1)−O(2A)	2.1266(16)	Sn(2)−O(3)	2.301(2)
Sn(1)−O(3)	2.0936(18)	Sn(2)−O(1A)	2.0253(18)
Sn(1)−C(1)	2.119(3)	Sn(2)−C(21)	2.167(3)
Sn(1)−C(11)	2.123(3)	Sn(2)−C(25)	2.165(3)
Si(1)−O(1)	1.5993(19)		
O(3)−Sn(1)−O(2A)	146.87(7)	O(3)−Sn(2)−O(1A)	155.92(7)
O(3)−Sn(1)−O(2)	73.54(7)	O(3)−Sn(2)−O(2)	69.22(7)
O(3)−Sn(1)−C(1)	99.68(9)	O(3)−Sn(2)−C(21)	94.60(10)
O(3)−Sn(1)−C(11)	99.25(10)	O(3)−Sn(2)−C(25)	90.60(10)
O(2A)−Sn(1)−O(2)	74.30(7)	O(1A)−Sn(2)−O(2)	87.32(7)
O(2A)−Sn(1)−C(1)	93.59(8)	O(1A)−Sn(2)−C(21)	99.80(10)
O(2A)−Sn(1)−C(11)	98.78(9)	O(1A)−Sn(2)−C(25)	98.04(9)
O(2)−Sn(1)−C(1)	127.54(9)	O(2)−Sn(2)−C(21)	113.29(9)
O(2)−Sn(1)−C(11)	109.68(9)	O(2)−Sn(2)−C(25)	122.73(10)
C(1)−Sn(1)−C(11)	122.67(11)	C(21)−Sn(2)−C(25)	121.58(11)
Sn(1)−C(1)−Si(1)	114.29(13)	Sn(2A)−O(1)−Si(1)	143.13(11)

Table 5. Selected Interatomic Distances (Å) and Bond Angles (deg) in 13

Sn(1)−O(2)	2.128(2)	Sn(2)−C(21)	2.191(4)
Sn(1)−O(3A)	2.141(2)	Sn(2)−C(25)	2.200(5)
Sn(1)−O(3)	2.040(3)	Sn(3)−O(4)	2.149(3)
Sn(1)−C(1)	2.119(4)	Sn(3)−O(3)	2.161(2)
Sn(1)−C(11)	2.121(5)	Sn(3)−O(2)	2.049(3)
Sn(2)−O(1)	2.060(3)	Sn(3)−C(31)	2.195(5)
Sn(2)−O(4)	2.273(3)	Sn(3)−C(35)	2.186(5)
Sn(2)−O(2)	2.035(2)	Si(1)−O(1)	1.612(3)
O(2)−Sn(1)−O(3A)	151.44(10)	O(3A)−Sn(1)−C(1)	97.64(12)
O(2)−Sn(1)−O(3)	74.62(10)	O(3A)−Sn(1)−C(11)	98.63(13)
O(2)−Sn(1)−C(1)	93.09(13)	O(3)−Sn(1)−C(1)	129.00(15)
O(2)−Sn(1)−C(11)	98.53(13)	O(3)−Sn(1)−C(11)	110.36(13)
O(3A)−Sn(1)−O(3)	78.07(11)	C(1)−Sn(1)−C(11)	120.45(16)
O(1)−Sn(2)−O(4)	156.15(10)	O(4)−Sn(2)−C(21)	93.28(15)
O(1)−Sn(2)−O(2)	86.92(10)	O(4)−Sn(2)−C(25)	94.14(16)
O(1)−Sn(2)−C(21)	97.42(15)	O(2)−Sn(2)−C(21)	118.06(14)
O(1)−Sn(2)−C(25)	98.14(15)	O(2)−Sn(2)−C(25)	118.41(14)
O(4)−Sn(2)−O(2)	69.24(11)	C(21)−Sn(2)−C(25)	121.88(17)
O(4)−Sn(3)−O(3)	141.87(11)	O(3)−Sn(3)−C(31)	105.52(14)
O(4)−Sn(3)−O(2)	71.54(11)	O(3)−Sn(3)−C(35)	99.52(13)
O(4)−Sn(3)−C(31)	100.78(14)	O(2)−Sn(3)−C(31)	110.09(15)
O(4)−Sn(3)−C(35)	93.83(14)	O(2)−Sn(3)−C(35)	134.66(15)
O(3)−Sn(3)−O(2)	73.74(9)	C(31)−Sn(3)−C(35)	114.81(19)
Sn(1)−O(2)−Sn(2)	137.16(13)	Sn(1)−O(2)−Sn(3)	105.66(10)
Sn(1)−O(3)−Sn(3)	104.75(10)	Sn(1)−O(3)−Sn(1A)	101.93(11)
Sn(2)−O(4)−Sn(3)	103.10(13)	Sn(2)−O(2)−Sn(3)	116.05(13)
Sn(3)−O(3)−Sn(1A)	153.32(14)	Si(1)−O(1)−Sn(2)	138.74(17)
Si(1)−C(1)−Sn(1)	113.8(2)		

■ EXPERIMENTAL SECTION

General Considerations. The solvents used for the Grignard-type reactions were purified by distillation under argon from the appropriate drying agents. $Me_2(i\text{-PrO})SiCH_2Cl$,[22] $Me_2N(CH_2)_3Cl$,[23] and $(t\text{-Bu}_2SnO)_3$[24] were synthesized according to literature methods. Ph_2GeO was synthesized by a procedure modified from that described in the literature.[25] Triphenyltin chloride and diphenylgermanium dichloride were commercially available, and they were used without further purification. Bruker DPX-300, DRX-400, and AVIII-600 spectrometers were used to obtain ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra at ambient temperature. Solution ^1H, ^{13}C, ^{29}Si-INEPT, and ^{119}Sn NMR chemical shifts are given in ppm and were referenced to Me_4Si (^1H, ^{13}C, ^{29}Si), and Me_4Sn (^{119}Sn). Elemental analyses were performed on a LECO-CHNS-932 analyzer. No elemental analyses were performed for compounds that are oils. The electrospray mass spectra were recorded with a Thermoquest-Finnigan instrument, using CH_3CN or CH_2Cl_2 as the mobile phase.

Crystallography. Intensity data for all crystals were collected on a XcaliburS CCD diffractometer (Oxford Diffraction) using Mo Kα radiation at 173 K. The structures were solved with direct methods using SHELXS-2014/7,[26] and refinements were carried out against F^2 by using SHELXL-2014/7.[26] The C−H hydrogen atoms were positioned with idealized geometry and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters. The studied crystal of compound 7 was a nonmerohedral twin. Refinement of the fractional contributions of the two twin components yielded a ratio of 0.55969:0.44031. The twin operation is a 180° rotation about the *c* axis. Both of the compounds exist in the

DOI: 10.1021/acs.organomet.5b00768
Organometallics XXXX, XXX, XXX−XXX

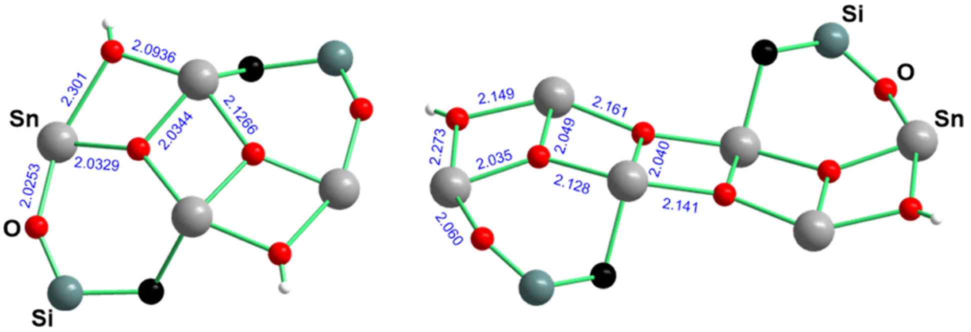
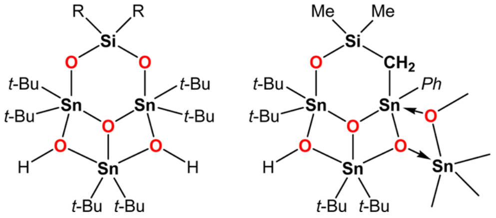


Figure 7. Reduced ball and stick molecular structures of compounds **12** (left) and **13** (right). The organic substituents are omitted for clarity. For simplification, the Sn−O interatomic distances (Å) are given without standard deviations.

Chart 1. Schematic Presentation of the Structural Similarity between [*cyclo*-$R_2Si(OSn$*t*-$Bu_2)_2O$·*t*-$Bu_2Sn(OH)_2$] (Left; R = Ph,[16] Me[17]) and Compound 13 (Right)



trans conformation. In compound **13** one *tert*-butyl group is affected by disorder and was refined by a split model over two positions. Their occupancies were allowed to refine freely until a constant number (0.74627/0.25373) was obtained.

CCDC-1409967 (**5**), CCDC-1409968 (**6**), CCDC-1409969 (**7**), CCDC-1409970 (**12**), and CCDC-1409971 (**13**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

For decimal rounding of numerical parameters and su values the IUCr rules have been employed.[27]

Synthesis of Diphenylgermanium Oxide, Ph_2GeO. A solution of sodium hydroxide (300 mg, 7.5 mmol) in a mixture of water (15 mL) and ethanol (10 mL) was added to a solution of Ph_2GeCl_2 (280 mg, 0.94 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred for 3 days at room temperature before CH_2Cl_2 and ethanol were evaporated. The residue was extracted with CH_2Cl_2. The organic phase was separated, and CH_2Cl_2 was evaporated to give Ph_2GeO (0.21 g, 92%) as a white solid with mp 148 °C.

^{1}H NMR (400.13 MHz, C_6D_6): δ 7.30−7.63 (m, 10H, Ar H). $^{13}C\{^{1}H\}$ NMR (75.48 MHz, C_6D_6): δ 128.2 (C_m), 130.3 (C_p), 133.6 (C_o), 135.9 (C_i). Electrospray MS: *m*/*z* (%), positive mode, calcd for $[(Ph_2GeO)_3 + H]^+$ ($C_{36}H_{31}Ge_3O_3^{+}$) 728.9946, found 729.0. Anal. Calcd for $C_{12}H_{10}OGe$ (242.85 g/mol): C, 59.35; H, 4.15. Found: C, 59.5, H, 4.2.

Synthesis of Me_2(*i*-PrO)$SiCH_2SnPh_3$ (1). A solution of triphenyltin chloride (104.08 g, 270 mmol) in THF (350 mL) was added dropwise to a Grignard reagent prepared from Me_2(*i*-PrO)$SiCH_2Cl$ (50.02 g, 300 mmol) and magnesium turnings (8.02 g, 330 mmol) in THF (230 mL). The reaction mixture was stirred overnight at room temperature and then heated at reflux for 1 h. Then it was cooled to room temperature and the solvent was evaporated in vacuo. The viscous oil obtained was extracted in a Soxhlet extractor using hexane as a solvent. After the solvent was evaporated, compound **1** (121.30 g, 93%) was obtained as a colorless liquid.

^{1}H NMR (300.13 MHz, C_6D_6): δ 0.16 (s, 6H, Me_2Si), 0.55 (s, 2H, $^{2}J(^{1}H-^{117/119}Sn)$ = 75.1/77.2 Hz, $SiCH_2Sn$), 1.08 (d, 6H, $^{3}J(^{1}H-^{1}H)$ = 5.8 Hz, Me_2CH), 3.87 (m, 1H, CHO), 7.27−7.77 (m, 15H, Ar H). $^{13}C\{^{1}H\}$ NMR (75.48 MHz, C_6D_6): δ −3.7 ($^{1}J(^{13}C-^{29}Si)$ = 60 Hz, $^{1}J(^{13}C-^{117/119}Sn)$ = 258/270 Hz, $SiCH_2Sn$), 1.9 ($^{1}J(^{13}C-^{29}Si)$ = 58 Hz, $^{3}J(^{13}C-^{117/119}Sn)$ = 12 Hz, Me_2Si), 26.3 (Me_2CH), 65.51 (CHO), 129.0 (C_m), 129.4 (C_p), 137.8 ($^{2}J(^{13}C-^{117/119}Sn)$ = 38 Hz, C_o), 140.5 ($^{1}J(^{13}C-^{117/119}Sn)$ = 488/512 Hz, C_i). $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, C_6D_6): δ 14.2 ($^{2}J(^{29}Si-^{117/119}Sn)$ = 25 Hz, $^{2}J(^{29}Si-^{13}C)$ = 57 Hz). $^{119}Sn\{^{1}H\}$ NMR (111.92 MHz, C_6D_6): δ −89 ($^{1}J(^{119}Sn-^{13}C_{CH_2})$ = 271 Hz, $^{1}J(^{119}Sn-^{13}C_{Ph})$ = 513 Hz). Electrospray MS: *m*/*z* (%), positive mode, calcd for $[\mathbf{1} - Ph]^+$ ($C_{18}H_{25}OSiSn^{+}$) 405.0699, found 405.1.

Synthesis of $\{Me_2$(*i*-PrO)$SiCH_2\}SnPh_2I$ (2). Elemental iodine (2.64 g, 10.4 mmol) was added in small portions at 0 °C to a solution of **1** (5.00 g, 10.4 mmol) in CH_2Cl_2 (50 mL), and the mixture was warmed to reach room temperature and stirred overnight. Removal of the solvent and iodobenzene in vacuo gave 5.07 g (92%) of compound **2** as a colorless oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.25 (s, 6H, Me_2Si), 1.06 (d, 6H, $^{3}J(^{1}H-^{1}H)$ = 6.0 Hz, Me_2CH), 1.15 (s, 2H, $^{2}J(^{1}H-^{117/119}Sn)$ = 87.4/91.4 Hz, $SiCH_2Sn$), 4.01 (m, 1H, $^{3}J(^{1}H-^{1}H)$ = 6.1 Hz, CHO), 7.43−7.88 (m, 10H, Ar H). $^{13}C\{^{1}H\}$ NMR (100.63 MHz, $CDCl_3$): δ 1.2 ($^{1}J(^{13}C-^{29}Si)$ = 58 Hz, $^{3}J(^{13}C-^{117/119}Sn)$ = 15 Hz, Me_2Si), 4.6 ($^{1}J(^{13}C-^{117/119}Sn)$ = 251/262 Hz, $^{1}J(^{13}C-^{29}Si)$ = 57 Hz, $SiCH_2Sn$), 25.5 (Me_2CH), 65.5 (CHO), 128.5 ($^{3}J(^{13}C-^{117/119}Sn)$ = 61 Hz, C_m), 129.6 ($^{4}J(^{13}C-^{117/119}Sn)$ = 14 Hz, C_p), 136.0 ($^{2}J(^{13}C-^{117/119}Sn)$ = 50 Hz, C_o), 138.4 ($^{1}J(^{13}C-^{117/119}Sn)$ = 536/562 Hz, C_i). $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, $CDCl_3$): δ 15.1 ($^{2}J(^{29}Si-^{117/119}Sn)$ = 30 Hz). $^{119}Sn\{^{1}H\}$ NMR (111.91, $CDCl_3$): δ −67 (92%, $^{1}J(^{119}Sn-^{13}C_{CH_2})$ = 263 Hz, $^{1}J(^{119}Sn-^{13}C_{Ph})$ = 561 Hz), −7 (1%), −60 (3%), −114 (2%, Ph_3SnI), −217 (2%, Me_2(*i*-PrO)$SiCH_2PhSnI_2$). Electrospray MS: *m*/*z* (%), positive mode, calcd for $[O(Me_2SiCH_2SnPh_2)_2 + OH]^+$ ($C_{30}H_{37}O_2Si_2Sn_2^{+}$) 723.0380, found 723.1.

Synthesis of a Mixture Consisting of $\{Me_2$(*i*-PrO)$SiCH_2\}$*t*-Bu_2SnX (3, X = Cl; 3′, X = OH). A Grignard reagent prepared from Me_2(*i*-PrO)$SiCH_2Cl$ (2.19 g, 13.16 mmol) and magnesium turnings (0.35 g, 14.48 mmol) in THF (30 mL) was added dropwise at −50 °C over a period of 1 h to a solution of *t*-Bu_2SnCl_2 (4.00 g, 13.16 mmol) in THF (15 mL), and the mixture was warmed to room temperature and stirred overnight. The solvent was evaporated, hexane (100 mL) was added, and the mixture was stirred for 15 min before it was filtered under inert conditions. Hexane was evaporated, and the residue was distilled at 133−138 °C in vacuo (9 mbar), giving 3.95 g of a mixture of two compounds with a ratio (4:1) according to the ^{119}Sn NMR spectrum that could be related to compounds **3** and **3′** (resulting from hydrolysis of compound **3**). No attempts were made to separate the two compounds, and the mixture was used for the synthesis of compound **7** (see below).

*Compound **3***. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.21 (s, 6H, Me_2Si), 0.29 (s, 2H, $^{2}J(^{1}H-^{117/119}Sn)$ = 64.2/66.8 Hz, $SiCH_2Sn$), 1.15 (d, 6H, $^{3}J(^{1}H-^{1}H)$ = 6.3 Hz, Me_2CH), 1.32 (s, 18H, $^{3}J(^{1}H-^{117/119}Sn)$ = 80.8/84.8 Hz, *t*-Bu_2Sn), 4.01 (m, 1H, $^{3}J(^{1}H-^{1}H)$ = 6.0 Hz, CHO). $^{13}C\{^{1}H\}$ NMR (100.63 MHz, $CDCl_3$): δ −0.1 ($^{1}J(^{13}C-^{117/119}Sn)$ = 111/115 Hz, $^{1}J(^{13}C-^{29}Si)$ = 58 Hz, $SiCH_2Sn$), 1.1 ($^{1}J(^{13}C-^{29}Si)$ = 58 Hz, $^{3}J(^{13}C-^{117/119}Sn)$ = 9 Hz, Me_2Si), 25.8 (Me_2CH), 29.9 (Me_3C), 34.9 ($^{1}J(^{13}C-^{117/119}Sn)$ = 371/389 Hz, Me_3CSn), 65.1 (CHO). $^{29}Si\{^{1}H\}$ NMR (59.63 MHz, $CDCl_3$): δ 14.66 ($^{2}J(^{29}Si-^{117/119}Sn)$ = 16

DOI: 10.1021/acs.organomet.5b00768

Hz, $^{1}J(^{29}\mathrm{Si}{-}^{13}\mathrm{C})$ = 58 Hz). $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (111.92 MHz, $\mathrm{CDCl_3}$): δ 122 (80%).

Compound **3′**. ^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): δ 0.21 (s, 6H, $Me_2\mathrm{Si}$), 0.35 (s, 2H, $^{2}J(^{1}\mathrm{H}{-}^{117/119}\mathrm{Sn})$ = 62.8/65.0 Hz, $\mathrm{Si}CH_2\mathrm{Sn}$), 1.15 (d, 6H, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 6.3 Hz, $Me_2\mathrm{CH}$), 1.33 (s, 18H, $^{3}J(^{1}\mathrm{H}{-}^{117/119}\mathrm{Sn})$ = 81.8/85.3 Hz, $t\text{-}Bu_2\mathrm{Sn}$), 4.01 (m, 1H, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 6.0 Hz, $\mathrm{C}H\mathrm{O}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100.63 MHz, $\mathrm{CDCl_3}$): δ 0.0 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 103/107 Hz, $^{1}J(^{13}\mathrm{C}{-}^{29}\mathrm{Si})$ = 58 Hz, $\mathrm{SiCH_2Sn}$), 1.2 ($^{1}J(^{13}\mathrm{C}{-}^{29}\mathrm{Si})$ = 58 Hz, $^{3}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 9 Hz, $Me_2\mathrm{Si}$), 25.8 ($Me_2\mathrm{CH}$), 30.0 ($Me_3\mathrm{C}$), 34.6 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 361/378 Hz, $\mathrm{Me_3CSn}$), 65.1 (CHO). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (59.63 MHz, $\mathrm{CDCl_3}$): δ 14.71 ($^{1}J(^{29}\mathrm{Si}{-}^{13}\mathrm{C})$ = 58 Hz). $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (111.92 MHz, $\mathrm{CDCl_3}$): δ 128 (20%). Electrospray MS: *m*/*z* (%), positive mode, calcd for $[\mathrm{Me_2}(i\text{-}\mathrm{PrO})\mathrm{SiCH_2}(t\text{-}\mathrm{Bu_2})\mathrm{Sn}]^+$ ($\mathrm{C_{14}H_{33}OSiSn^+}$) 365.1324, found 365.1.

Synthesis of $\{\mathrm{Me_2}(i\text{-}\mathrm{PrO})\mathrm{SiCH_2}\}\{\mathrm{Me_2N(CH_2)_3}\}\mathrm{SnPh_2}$ (4). A Grignard reagent prepared from $\mathrm{Me_2N(CH_2)_3Cl}$ (610 mg, 5.00 mmol) and magnesium turnings (134 mg, 5.50 mmol) in THF (10 mL) was added at room temperature to a solution of **2** (2.12 g, 4.00 mmol) in THF (15 mL), and the mixture was stirred overnight. The solvent was evaporated, and hexane (50 mL) was added. The mixture obtained was filtered under inert conditions. The solvent of the filtrate was evaporated in vacuo to give compound **4** (1.63 g, 83%) as a colorless oil that was not purified further.

^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 0.06 (s, 6H, $Me_2\mathrm{Si}$), 0.32 (s, 2H, $^{2}J(^{1}\mathrm{H}{-}^{117/119}\mathrm{Sn})$ = 73.6 Hz, $\mathrm{Si}CH_2\mathrm{Sn}$), 1.11 (d, 6H, $^{3}J(^{1}\mathrm{H}{-}^{1}\mathrm{H})$ = 5.8 Hz, $Me_2\mathrm{CH}$), 1.31 (t, 2H, $\mathrm{CH_2}CH_2\mathrm{Sn}$), 1.81 (m, 2H, $\mathrm{CH_2}CH_2\mathrm{CH_2}$), 2.17 (s, 6H, $Me_2\mathrm{N}$), 2.28 (t, 2H, $CH_2\mathrm{N}$), 3.98 (m, 1H, $\mathrm{C}H\mathrm{O}$), 7.34–7.63 (m, 10H, Ar H). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (59.63 MHz, $\mathrm{CDCl_3}$): δ 15.1 ($^{2}J(^{29}\mathrm{Si}{-}^{117/119}\mathrm{Sn})$ = 18 Hz). $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (111.92 MHz, $\mathrm{CDCl_3}$): δ −62.

Synthesis of *cyclo*-$[\mathrm{Ph_2SnOSi(Me_2)CH_2}]_2$ (5). A solution of sodium hydroxide (0.90 g, 22.6 mmol) in water (50 mL) and ethanol (10 mL) was added to a solution of **2** (1.50 g, 2.82 mmol) in $\mathrm{CH_2Cl_2}$ (25 mL), and the mixture was stirred for 3 days at room temperature before $\mathrm{CH_2Cl_2}$ and ethanol were evaporated in vacuo. The residue was extracted with $\mathrm{CH_2Cl_2}$. The organic phase was separated, and the solvent was evaporated. The residue was recrystallized from a solution in $\mathrm{CH_2Cl_2}$/hexane to give 0.98 g (96%) of **5** as colorless crystals with mp 167–169 °C suitable for X-ray diffraction analysis.

^{1}H NMR (300.13 MHz, $\mathrm{CDCl_3}$): δ 0.15 (s, 12H, $Me_2\mathrm{Si}$), 0.58 (s, 4H, $^{2}J(^{1}\mathrm{H}{-}^{117/119}\mathrm{Sn})$ = 73.6/76.5 Hz, $\mathrm{Si}CH_2\mathrm{Sn}$), 7.37–7.78 (m, 20H, Ar H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.48 MHz, $\mathrm{CDCl_3}$): δ 3.3 ($^{1}J(^{13}\mathrm{C}{-}^{29}\mathrm{Si})$ = 84 Hz, $^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 326/341 Hz, $\mathrm{SiCH_2Sn}$), 4.5 ($^{1}J(^{13}\mathrm{C}{-}^{29}\mathrm{Si})$ = 59 Hz, $^{3}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 18 Hz, $Me_2\mathrm{Si}$), 128.4 ($^{3}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 58 Hz, C_m), 129.4 ($^{4}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 12 Hz, C_p), 135.9 ($^{2}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 46 Hz, C_o), 142.1 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 572/599 Hz, C_i). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (59.63 MHz, $\mathrm{CDCl_3}$): δ 8.6 ($^{2}J(^{29}\mathrm{Si}{-}^{117/119}\mathrm{Sn})$ = 33 Hz, $^{2}J(^{29}\mathrm{Si}{-}^{117/119}\mathrm{Sn})$ = 54 Hz, $^{1}J(^{29}\mathrm{Si}{-}^{13}\mathrm{C})$ = 87 Hz). $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (111.92 MHz, $\mathrm{CDCl_3}$): δ −31 ($^{1}J(^{119}\mathrm{Sn}{-}^{13}\mathrm{CH_2})$ = 341 Hz, $^{1}J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C}i)$ = 598 Hz). Electrospray MS: *m*/*z* (%), positive mode, calcd for $[\mathbf{5} + \mathrm{H}]^+$ ($\mathrm{C_{30}H_{37}O_2Si_2Sn_2^+}$) 723.0380, found 723.1. Anal. Calcd for $\mathrm{C_{30}H_{36}O_2Si_2Sn_2}$ (722.20 g/mol): C, 49.89; H, 5.02. Found: C, 49.8; H, 5.1.

Synthesis of *cyclo*-$[t\text{-}\mathrm{Bu_2SnOSi(Me_2)CH_2}]_2$ (6). A solution of sodium hydroxide (0.32 g, 8.0 mmol) in water (15 mL) and ethanol (10 mL) was added to a solution of the **3**/**3′** mixture (0.396 g, 1.0 mmol based on $[\mathrm{Me_2}(i\text{-}\mathrm{PrO})\mathrm{SiCH_2Sn}(t\text{-}\mathrm{Bu})_2]^+$) in $\mathrm{CH_2Cl_2}$ (15 mL) and the mixture was stirred for 3 days at room temperature before $\mathrm{CH_2Cl_2}$ and ethanol were evaporated. The residue was extracted with $\mathrm{CH_2Cl_2}$. The organic phase was separated, and the solvent was evaporated before the residue was recrystallized from a solution in $\mathrm{CH_2Cl_2}$/hexane to give 0.29 g (90%) of **6** as colorless crystals with mp 100.5–102.5 °C suitable for X-ray diffraction analysis.

^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): δ −0.10 (s, 4H, $^{2}J(^{1}\mathrm{H}{-}^{117/119}\mathrm{Sn})$ = 55.0 Hz, $\mathrm{Si}CH_2\mathrm{Sn}$), 0.12 (s, 12H, $Me_2\mathrm{Si}$), 1.2 (s, 36H, $^{3}J(^{1}\mathrm{H}{-}^{117/119}\mathrm{Sn})$ = 71.8/75.3 Hz, $Me_3\mathrm{CSn}$). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100.63 MHz, $\mathrm{CDCl_3}$): δ −0.8 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 190/198 Hz, $^{1}J(^{13}\mathrm{C}{-}^{29}\mathrm{Si})$ = 54 Hz, $\mathrm{SiCH_2Sn}$), 5.4 ($^{1}J(^{13}\mathrm{C}{-}^{29}\mathrm{Si})$ = 59 Hz, $^{3}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 15 Hz, $Me_2\mathrm{Si}$), 30.0 ($Me_3\mathrm{C}$), 31.5 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 409/428 Hz, $\mathrm{Me_3CSn}$). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (59.63 MHz, $\mathrm{CDCl_3}$): δ 1.8 ($^{2}J(^{29}\mathrm{Si}{-}^{117/119}\mathrm{Sn})$ = 46 Hz, $^{2}J(^{29}\mathrm{Si}{-}^{117/119}\mathrm{Sn})$ = 56/60 Hz). $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (111.92 MHz, $\mathrm{CDCl_3}$): δ 34 ($^{1}J(^{119}\mathrm{Sn}{-}^{13}\mathrm{CCH_2})$ = 198 Hz, $^{1}J(^{119}\mathrm{Sn}{-}^{13}\mathrm{C}t\text{-}\mathrm{Bu})$ = 428 Hz, $^{2}J(^{119}\mathrm{Sn}{-}^{29}\mathrm{Si})$ = 48 Hz, $^{2}J(^{119}\mathrm{Sn}{-}^{29}\mathrm{Si})$ = 60 Hz). Electrospray MS: *m*/*z* (%), positive mode, calcd for $[\mathbf{6} + \mathrm{H}]^+$ ($\mathrm{C_{22}H_{53}O_2Si_2Sn_2^+}$) 643.1630, found 643.2; calcd for $[\mathrm{Me_2(HO)SiCH_2}(t\text{-}\mathrm{Bu_2})\mathrm{Sn}]^+$ ($\mathrm{C_{11}H_{27}OSiSn^+}$) 323.0854, found 323.0. Anal. Calcd for $\mathrm{C_{22}H_{52}O_2Si_2Sn_2}$ (642.20 g/mol): C, 41.14; H, 8.16. Found: C, 41.1; H, 8.2.

Synthesis of *cyclo*-$[\{\mathrm{Me_2N(CH_2)_3}\}\mathrm{PhSnOSi(Me_2)CH_2}]_2$ (7). Elemental iodine (0.76 g, 3.00 mmol) was added in portions at 0 °C to a solution of compound **4** (1.47 g, 3.00 mmol) in $\mathrm{CH_2Cl_2}$ (50 mL). After the addition was complete, the mixture was warmed to room temperature and stirred overnight, before the solvent and iodobenzene were removed in vacuo to give $[\mathrm{Me_2}(i\text{-}\mathrm{PrO})\mathrm{SiCH_2}]$-PhRSnI (R = $\mathrm{Me_2N(CH_2)_3}$, 1.40 g, 86%) as a yellowish viscous oil that was not purified further. Its $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR spectrum (59.63 MHz, $\mathrm{CDCl_3}$) showed a major resonance at δ 9.4 ($^{2}J(^{29}\mathrm{Si}{-}^{117/119}\mathrm{Sn})$ = 20 Hz) and a minor resonance at δ 19.4. A $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR spectrum (111.92 MHz, $\mathrm{CDCl_3}$) of the same solution revealed two signals of different integral ratios at δ 3 (87%) and −4 (13%), respectively.

A solution of sodium hydroxide (0.55 g, 13.75 mmol) in water (40 mL) and ethanol (10 mL) was added to a solution of $[\mathrm{Me_2}(i\text{-}\mathrm{PrO})\mathrm{SiCH_2}]$PhRSnI (1.40 g, 2.60 mmol) in $\mathrm{CH_2Cl_2}$ (25 mL), and the mixture was stirred for 3 days at room temperature before $\mathrm{CH_2Cl_2}$ and ethanol were evaporated in vacuo. The residue was extracted with $\mathrm{CH_2Cl_2}$. The organic phase was separated, and the solvent was evaporated to give compound 7 (0.89 g, 92%) as a light yellowish solid. Recrystallization from $\mathrm{CHCl_3}$ afforded colorless single crystals with mp 142.5–144.5 °C suitable for X-ray diffraction analysis.

^{1}H NMR (400.25 MHz, $\mathrm{C_6D_6}$): δ 0.14 (complex pattern, 4H), 0.29 (s, 3H, $\mathrm{Si}CH_3$), 0.32 (s, 3H, $\mathrm{Si}CH_3$), 0.47 (s, 3H, $\mathrm{Si}CH_3$), 0.51 (s, 3H, $\mathrm{Si}CH_3$), 1.44 (s, 12H, $\mathrm{N}CH_3$) 1.22–2.00 (complex patterns, 12H, $\mathrm{Sn}CH_2CH_2CH_2\mathrm{N}$), 7.21–7.32 (complex pattern, 6H, Ph-$\mathrm{H}_{m\!,p}$), 7.66 (complex pattern, 1H, Ph-H_o), 7.68 (complex pattern, 1H, Ph-H_o), 7.75 (complex pattern, 1H, Ph-H_o), 7.77 (complex pattern, 1H, Ph-H_o). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (150.94 MHz, $\mathrm{C_7D_8}$): δ 3.68 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 361/379 Hz, $\mathrm{SiCH_2Sn}$), 3.89 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 365/382 Hz, $\mathrm{SiCH_2Sn}$), 5.40 ($Me\mathrm{Si}$), 5.70 ($Me\mathrm{Si}$), 5.75 ($Me\mathrm{Si}$), 6.08 ($Me\mathrm{Si}$), 14.83 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 528/554 Hz, $\mathrm{CH_2CH_2Sn}$), 14.97 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 531/567 Hz, $\mathrm{CH_2CH_2Sn}$), 22.65 ($\mathrm{CH_2CH_2CH_2}$), 22.76 ($\mathrm{CH_2CH_2CH_2}$), 46.02 ($Me_2\mathrm{N}$), 46.05 ($Me_2\mathrm{N}$), 61.49 ($\mathrm{CH_2N}$), 61.55 ($\mathrm{CH_2N}$), 128.05 (C_m), 128.20 (C_p), 128.21 (C_p), 135.82 (C_o), 135.94 (C_o), 147.58 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 592/619 Hz, C_i), 146.7 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 586/614 Hz, C_i). $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (79.52, $\mathrm{CDCl_3}$): δ 1.4 ($^{2}J(^{29}\mathrm{Si}{-}^{117/119}\mathrm{Sn})$ = 39/47 Hz), 1.0 ($^{2}J(^{29}\mathrm{Si}{-}^{117/119}\mathrm{Sn})$ = 40/48 Hz), 4.7. $^{29}\mathrm{Si}\{^{1}\mathrm{H}\}$ NMR (79.52 MHz, $\mathrm{C_7D_8}$): δ −0.4, −0.9. $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (149.26 MHz, $\mathrm{C_7D_8}$): T = 298 K, δ −62.6 (45%, $^{2}J(^{119}\mathrm{Sn}{-}^{29}\mathrm{Si})$ = 46 Hz), −62.8 (52%, $^{2}J(^{119}\mathrm{Sn}{-}^{29}\mathrm{Si})$ = 46 Hz), 70.4 (3%); T = 333 K, δ −54.2 (45%), −54.4 (52%), −64.0 (3%). $^{119}\mathrm{Sn}\{^{1}\mathrm{H}\}$ NMR (111.92 MHz, $\mathrm{CDCl_3}$): δ −55 (50%, $^{2}J(^{119}\mathrm{Sn}{-}^{29}\mathrm{Si})$ = 48 Hz), −53 (43%, $^{2}J(^{119}\mathrm{Sn}\ {-}^{29}\mathrm{Si})$ = 48 Hz), −66 (4%), 4 (3%). Electrospray MS: *m*/*z* (%), positive mode, calcd for $[7 + \mathrm{H}]^+$ ($\mathrm{C_{28}H_{51}N_2O_2Si_2Sn_2^+}$) 741.1536, found 741.2; calcd for $[\{\mathrm{Me_2(OH)SiCH_2}\}\{\mathrm{Me_2N(CH_2)_3}\}$-$\mathrm{PhSn} + 4\mathrm{H_2O}]^+$ ($\mathrm{C_{14}H_{34}NO_5SiSn^+}$) 444.1230, found 444.1. Anal. Calcd for $\mathrm{C_{28}H_{50}N_2O_2Si_2Sn_2}$ (740.266 g/mol): C, 45.43; H, 6.81; N, 3.78. Found: C, 45.1; H, 7.2; N, 4.1.

Synthesis of *cyclo*-[Me2SiCH2$\mathrm{(Ph)_2SnO}$-*t*-$\mathrm{Bu_2SnO}$] (8). A mixture of di-*tert*-butyltin oxide (100 mg, 0.40 mmol) and **5** (145 mg, 0.20 mmol) in $\mathrm{CH_2Cl_2}$ (3 mL) was stirred for 10 min at room temperature. Then the solvent was evaporated, giving a white solid with mp 145–149 °C.

^{1}H NMR (400.13 MHz, $\mathrm{CDCl_3}$): δ 0.18 (s, 6H, $Me_2\mathrm{Si}$), 0.56 (s, 2H, $^{2}J(^{1}\mathrm{H}{-}^{117/119}\mathrm{Sn})$ = 71.3/73.8 Hz, $\mathrm{Si}CH_2\mathrm{Sn}$), 1.36 (s, 18H, $^{3}J(^{1}\mathrm{H}{-}^{117/119}\mathrm{Sn})$ = 91.4/95.9 Hz, *Me*3CSn), 7.37–7.73 (m, 10H, Ar H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (100.63 MHz, $\mathrm{CDCl_3}$): δ 3.0 ($^{1}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 282/295 Hz, SiCH2Sn), 4.4 ($^{1}J(^{13}\mathrm{C}{-}^{29}\mathrm{Si})$ = 59 Hz, $^{3}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 17 Hz, $Me_2\mathrm{Si}$), 29.8 (*Me*3C), 38.4 (Me3CSn), 128.4 ($^{3}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 57 Hz, C*m*), 129.3 ($^{4}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 13 Hz, C*p*), 135.7 ($^{2}J(^{13}\mathrm{C}{-}^{117/119}\mathrm{Sn})$ = 47 Hz, C*o*), 142.5 ($^{1}J(^{13}\mathrm{C}{-}^{117}\mathrm{Sn})$ =

DOI: 10.1021/acs.organomet.5b00768

568 Hz, $^1J(^{13}C-^{119}Sn)$ = 595 Hz, C*i*). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$): δ 5.9 ($^2J(^{29}Si-^{117/119}Sn$*t*-Bu) = 43 Hz, $^2J(^{29}Si-^{117/119}SnPh)$ = 49 Hz), 8.5 (**5**). $^{119}Sn\{^1H\}$ NMR (111.91 MHz, $CDCl_3$): δ −13 [$^2J(^{119}Sn-^{117}Sn)$ = 317 Hz, $^2J(^{119}Sn-^{119}Sn)$ = 334 Hz, $^2J(^{119}Sn-^{29}Si)$ = 51 Hz, $CH_2Sn(Ph_2)O$], −93 [$^2J(^{119}Sn-^{117}Sn)$ = 317 Hz, $^2J(^{119}Sn-^{119}Sn)$ = 337 Hz, $^2J(^{119}Sn-^{29}Si)$ = 44 Hz, OSn(*t*-Bu_2)O], −31 (3%, **5**), −84 (5%, (*t*-Bu2SnO)3). Electrospray MS: *m*/*z* (%), positive mode, calcd for [**8** + H]$^+$ ($C_{23}H_{37}O_2SiSn_2^+$) 611.0609, found 611.1; calcd for $[Me_2(OH)SiCH_2(Ph_2)Sn(OH)_2]^-$ ($C_{15}H_{21}O_3SiSn^-$) 397.0284, found 397.0. Anal. Calcd for $C_{23}H_{36}O_2SiSn_2$ (610.04 g/mol): C, 45.28; H, 5.95. Found: C, 45.3; H, 5.9.

Synthesis of *cyclo*-[Me2SiCH2(*t*-Bu)$_2$SnO-*t*-Bu$_2$SnO] (9). A mixture of di-*tert*-butyltin oxide (60 mg, 0.24 mmol) and **6** (77 mg, 0.12 mmol) in $CHCl_3$ (25 mL) was heated at reflux for 5 h. The mixture was cooled to room temperature, and the solvent was evaporated in vacuo to give a white solid.

^1H NMR (300.13 MHz, $CDCl_3$): δ −0.00 (s, 2H, $^2J(^1H-^{117/119}Sn)$ = 57.0 Hz, SiC*H*$_2$Sn), 0.17 (s, 6H, *Me*$_2$Si), 1.27 (s, 18H, $^3J(^1H-^{117/119}Sn)$ = 72.7/74.6 Hz, *Me*$_3$CSn), 1.33 (s, 18H, $^3J(^1H-^{117/119}Sn)$ = 89.3/93.7 Hz, *Me*$_3$CSn). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ −1.4 ($SnCH_2Si$), 5.0 ($^3J(^{13}C-^{117/119}Sn)$ = 9 Hz, *Me*$_2$Si), 30.1 (*Me*$_3$C), 30.4 (*Me*$_3$C), 32.3 (Me_3CSn), 38.0 (Me_3CSn). $^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$): δ 5.2 ($^2J(^{29}Si-^{117/119}Sn)$ = 42 Hz), 1.8 (**6**). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −98 ($^2J(^{119}Sn-^{117/119}Sn)$ = 351/367 Hz, $^2J(^{119}Sn-^{29}Si)$ = 44 Hz), 49 ($^2J(^{119}Sn-^{117/119}Sn)$ = 351/367 Hz, $^2J(^{119}Sn-^{29}Si)$ = 41 Hz), −83 (5%, (*t*-$Bu_2SnO)_3$), 34 (5% of the major resonances, **6**). Electrospray MS: *m*/*z* (%), negative mode, calcd for [**9** + OH]$^-$ ($C_{19}H_{45}O_3SiSn_2^-$) 587.1183, found 587.1. Anal. Calcd for $C_{19}H_{44}O_2SiSn_2$ (570.06 g/mol): C, 40.03; H, 7.78. Found: C, 39.7; H, 7.7.

Synthesis of *cyclo*-[Me2SiCH2{Me$_2$N(CH$_2$)$_3$}PhSnO-*t*-Bu$_2$SnO] (10). A mixture of di-*tert*-butyltin oxide (60 mg, 0.240 mmol) and **7** (100 mg, 0.135 mmol) in $CHCl_3$ (25 mL) was heated at reflux for 5 h. The mixture was cooled to room temperature, and the solvent was evaporated in vacuo, giving a white yellowish solid.

$^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$): δ 6.5 ($^2J(^{29}Si-^{117/119}Sn)$ = 40 Hz), 4.5, 1.3, 1.3, 0.9, 3.3. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −23 (45%, $^2J(^{119}Sn-^{117/119}Sn)$ = 292 Hz), −89 (45%, $^2J(^{119}Sn-^{117/119}Sn)$ = 292 Hz), −55 (4%, **7**), −54 (3%, **7**), −66 (3%). Electrospray MS: *m*/*z* (%), positive mode, calcd for [**10** + H]$^+$ ($C_{22}H_{44}NO_2SiSn_2^+$) 620.1187, found 620.1. Anal. Calcd for $C_{22}H_{43}NO_2SiSn_2$ (619.00 g/mol): C, 42.68; H, 7.00; N, 2.26. Found: C, 42.0; H, 7.0; N, 2.2. As evidenced by ^{119}Sn NMR spectroscopy (additional resonance at δ −66 (3%)), the compound measured contained a second species, the identity of which could not be established. This is the origin for the discrepancy between calculated and measured elemental analyses.

Synthesis of *cyclo*-[Me2SiCH2{Me$_2$N(CH$_2$)$_3$}PhSnOPh$_2$GeO] (11). A mixture of Ph_2GeO (56 mg, 0.230 mmol) and **7** (85 mg, 0.115 mmol) in $CHCl_3$ (20 mL) was heated at reflux for 5 h. The mixture was cooled to room temperature, and the solvent was evaporated in vacuo to give a yellowish oil.

$^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$): δ 10.7 ($^2J(^{29}Si-^{117/119}Sn)$ = 41 Hz), 4.6, 1.4. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −59 (95%, $^2J(^{119}Sn-^{29}Si)$ = 43 Hz), −66 (5%). Electrospray MS: *m*/*z* (%), positive mode, calcd for [**11** + H]$^+$ ($C_{26}H_{36}GeNO_2SiSn^+$) 614.0760, found 614.0. Anal. Calcd for $C_{26}H_{35}GeNO_2SiSn$ (613.00 g/mol): C, 50.94; H, 5.76; N, 2.29. Found: C, 49.8; H, 5.7; N, 2.0. As evidenced by ^{119}Sn NMR spectroscopy (additional resonance at δ −66 (3%)), the compound measured contained a second species, the identity of which could not be established. This is the origin for the discrepancy between calculated and measured elemental analyses.

Synthesis of [PhSn(CH$_2$Me$_2$SiO)Sn(μ_3-O)(μ-OH)*t*-Bu$_2$]$_2$ (12). Compound **8** was kept in moist air for a few weeks before ^{29}Si and ^{119}Sn NMR spectra were recorded. A few colorless single crystals of compound **12** with mp 266−270 °C suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of compound **8** in CH_2Cl_2/hexane under aerobic conditions.

$^{29}Si\{^1H\}$ NMR (59.63 MHz, $CDCl_3$): δ 8.5 ($^2J(^{29}Si-^{117/119}Sn)$ = 33/54 Hz, **5**), −2.4 ($^2J(^{29}Si-^{117/119}Sn)$ = 40/69 Hz). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −219 [29%, $^2J(^{119}Sn_{endo}-^{29}Si)$ = 41 Hz, $^2J(^{119}Sn_{endo}-^{117/119}Sn_{exo})$ = 228/242 Hz, $^2J(^{119}Sn_{endo}-^{117}Sn_{endo})$ = 82 Hz], −260 [29%, $^2J(^{119}Sn_{exo}-^{29}Si)$ = 71 Hz, $^2J(^{119}Sn_{exo}-^{117/119}Sn_{endo})$ = 228/242 Hz, $^4J(^{119}Sn_{exo}-^{117}Sn_{exo})$ = 84 Hz], −31 [25%, $^2J(^{119}Sn-^{29}Si)$ = 34, 55 Hz, **5**], −38 (11%), −54 (6%). Electrospray MS: *m*/*z* (%), positive mode, calcd for [**12** − OH]$^+$ ($C_{34}H_{63}O_5Si_2Sn_4^+$) 1083.0314, found 1083.1. There was not a sufficient amount of these crystals to perform elemental analyses.

Formation of the Ladder-Type Cluster [*t*-Bu$_2$(μ-OH)Sn(μ_3-O)SnPh(CH$_2$Me$_2$SiO)Sn-*t*-Bu$_2$(μ_3-O)]$_2$ (13). A solution containing the compounds **8** (93%), **6** (4%), and (*t*-$Bu_2SnO)_3$ (3%) in $CDCl_3$ in a not completely closed NMR tube was allowed to evaporate slowly, providing a single crystal of **13**. The identity of **13** was established by single-crystal X-ray diffraction analysis. No further analytical methods were applied.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00768.

NMR spectra and crystallographic data (PDF)
Crystallographic data for **5**−**7**, **12**, and **13** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for K.J.: klaus.jurkschat@tu-dortmund.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.B.H. is grateful to Damascus University for a scholarship. Thomas Zöller is acknowledged for recording the X-ray diffraction data for compound **13**.

■ REFERENCES

(1) (a) Chojnowski, J. *J. Inorg. Organomet. Polym.* **1991**, *1*, 299−323. (b) Priegert, A. M.; Rawe, B. W.; Serin, S. C.; Gates, D. P. *Chem. Soc. Rev.* **2016**, DOI: 10.1039/C5CS00725A.

(2) (a) Beckmann, J.; Jurkschat, K. *Coord. Chem. Rev.* **2001**, *215*, 267−300 and references cited therein. (b) Fridrichova, A.; Mairychova, B.; Padelkova, Z.; Lycka, A.; Jurkschat, K.; Jambor, R.; Dostal, L. *Dalton Trans.* **2013**, *42*, 16403−16411.

(3) (a) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205−2236. (b) Gates, D. P.; Manners, I. *J. Chem. Soc., Dalton Trans.* **1997**, 2525−2532.

(4) (a) Graalmann, O.; Klingebiel, U.; Clegg, W.; Haase, M.; Sheldrick, G. M. *Z. Anorg. Allg. Chem.* **1984**, *519*, 87−95. (b) Puff, H.; Boeckmann, M. P.; Kök, T. R.; Schuh, W. *J. Organomet. Chem.* **1984**, *268*, 197−206. (c) Graalmann, O.; Meyer, M.; Klingebiel, U. *Z. Anorg. Allg. Chem.* **1986**, *534*, 109−114. (d) Haoudi-Mazzah, A.; Mazzah, A.; Schmidt, H. G.; Noltemeyer, M.; Roesky, H. W. *Z. Naturforsch., B: J. Chem. Sci.* **1991**, *46*, 587−592. (e) Mazzah, A.; Haoudi-Mazzah, A.; Noltemeyer, M.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1991**, *604*, 93−103. (f) Brisdon, B. J.; Mahon, M. F.; Molloy, K. C.; Schofield, P. J. *J. Organomet. Chem.* **1992**, *436*, 11−22. (g) Foucher, D. A.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1992**, *31*, 3034−3043. (h) Liu, F. Q.; Schmidt, H. G.; Noltemeyer, M.; Freire-Erdbrügger, C.; Sheldrick, G. M.; Roesky, H. W. *Z. Naturforsch., B: J. Chem. Sci.* **1992**, *47*, 1085−1090. (i) Liu, F. Q.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M. *Organometallics* **1992**, *11*, 2965−2967. (j) Gosink, H. J.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H. G.; Freire-Erdbrügger, C.; Sheldrick, G. M. *Chem. Ber.* **1993**, *126*, 279−283. (k) Akkurt, M.; Kök, T. R.; Faleschini, P.; Randaccio, L.; Puff, H.; Schuh, W. *J. Organomet. Chem.*

1994, *470*, 59−66. (l) Gosink, H. J.; Roesky, H. W.; Schmidt, H. G.; Noltemeyer, M.; Irmer, E.; Herbst-Irmer, R. *Organometallics* **1994**, *13*, 3420−3426. (m) Montero, M. L.; Uson, I.; Roesky, H. W. *Angew. Chem.* **1994**, *106*, 2198−2200. (n) Samuel, E.; Harrod, J. F.; McGlinchey, M. J.; Cabestaing, C.; Robert, F. *Inorg. Chem.* **1994**, *33*, 1292−1296. (o) Liu, F. Q.; Uson, I.; Roesky, H. W. *J. Chem. Soc., Dalton Trans.* **1995**, 2453−2458. (p) Haoudi-Mazzah, A.; Mazzah, A.; Gnado, J.; Dhamelincourt, P. *J. Raman Spectrosc.* **1996**, *27*, 451−455. (q) Liu, F. Q.; Uson, I.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 819−822. (r) Beckmann, J.; Mahieu, B.; Nigge, W.; Schollmeyer, D.; Schürmann, M.; Jurkschat, K. *Organometallics* **1998**, *17*, 5697−5712. (s) Hoebbel, D.; Nacken, M.; Schmidt, H.; Huch, V.; Veith, M. *J. Mater. Chem.* **1998**, *8*, 171−178. (t) Vaugeois, Y.; De Jaeger, R.; Levalois-Mitjaville, J.; Mazzah, A.; Worle, M.; Grützmacher, H. *New J. Chem.* **1998**, *22*, 783−785. (u) Beckett, M. A.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. A.; Owen, P.; Varma, K. S. *J. Organomet. Chem.* **2000**, *595*, 241−247. (v) Gun'ko, Y. K.; Reilly, R.; Kessler, V. G. *New J. Chem.* **2001**, *25*, 528−530. (w) Li, Y.; Wang, J.; Wu, Y.; Zhu, H.; Samuel, P. P.; Roesky, H. W. *Dalton Trans.* **2013**, *42*, 13715−13722. (x) Padělková, Z.; Švec, P.; Kampová, H.; Sýkora, J.; Semler, M.; Štěpnička, P.; Bakardjieva, S.; Willem, R.; Růžička, A. *Organometallics* **2013**, *32*, 2398−2405. (y) Carbó, J. J.; González-del Moral, O.; Martín, A.; Mena, M.; Poblet, J.-M.; Santamaría, C. *Chem. - Eur. J.* **2008**, *14*, 7930−7938. (z) Levitsky, M. M.; Zavin, B. G.; Bilyachenko, A. N. *Russ. Chem. Rev.* **2007**, *76*, 847−866. (aa) Postigo, L.; Vázquez, A. B.; Sánchez-Nieves, J.; Royo, P.; Herdtweck, E. *Organometallics* **2008**, *27*, 5588−5597. (ab) Kung, M. C.; Riofski, M. V.; Missaghi, M. N.; Kung, H. H. *Chem. Commun.* **2014**, *50*, 3262−3276. (ac) Nehete, U. N.; Chandrasekhar, V.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Organometallics* **2004**, *23*, 5372−5374. (ad) Abbenhuis, H. C. L.; Vorstenbosch, M. L. W.; van Santen, R. A.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1997**, *36*, 6431−6433.

(5) Beckmann, J.; Jurkschat, K.; Schollmeyer, D., On the Reaction of (t-$Bu_2SnO)_3$ with Organochlorosilanes. Simple Formation of $[(t$-$Bu_2SnO)_2(t$-$Bu_2SiO)]$. In *Organosilicon Chemistry III*; Wiley: New York, 1997; pp 403−406.

(6) Beckmann, J.; Jurkschat, K.; Schollmeyer, D.; Schürmann, M. *J. Organomet. Chem.* **1997**, *543*, 229−232.

(7) Beckmann, J.; Jurkschat, K.; Kaltenbrunner, U.; Pieper, N.; Schürmann, M. *Organometallics* **1999**, *18*, 1586−1595.

(8) Beckmann, J.; Jurkschat, K.; Pieper, N.; Schürmann, M. *Chem. Commun.* **1999**, 1095−1096.

(9) Akkurt, M.; Kök, T. R.; Faleschini, P.; Randaccio, L.; Puff, H.; Schuh, H. *J. Organomet. Chem.* **1994**, *470*, 59−66.

(10) Morosin, B.; Harrah, L. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *37*, 579−586.

(11) (a) Dräger, M. *J. Organomet. Chem.* **1983**, *251*, 209−214. (b) Kolb, U.; Beuter, M.; Dräger, M. *Inorg. Chem.* **1994**, *33*, 4522−4530. (c) Dräger, M. *Z. Anorg. Allg. Chem.* **1976**, *423*, 53−66. (d) Beuter, M.; Kolb, U.; Zickgraf, A.; Bräu, E.; Bletz, M.; Dräger, M. *Polyhedron* **1997**, *16*, 4005−4015.

(12) Jurkschat, K.; Rosche, F.; Schürmann, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, *115*, 161−167.

(13) Chandrasekhar, V.; Thirumoorthi, R. *Inorg. Chem.* **2009**, *48*, 10330−10337.

(14) Jurkschat, K., Tetraorganodistannoxanes: Simple Chemistry From a Personal Perspective. In *Tin Chemistry: Fundamentals, Frontiers, and Applications*, Davies, A. G., Gielen, M., Pannell, K. H., Tiekink, E. R. T., Eds.; Wiley: Hoboken, NJ, 2008, and references cited therein.

(15) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, *0*, 1349−1356.

(16) Beckmann, J.; Jurkschat, K. *Main Group Met. Chem.* **1998**, *21*, 113−122.

(17) Cervantes-Lee, F.; Sharma, H. K.; Haiduc, I.; Pannell, K. H. *J. Chem. Soc., Dalton Trans.* **1998**, 1−2.

(18) (a) Beckmann, J.; Dakternieks, D.; Duthie, A.; Jurkschat, K.; Mehring, M.; Mitchell, C.; Schürmann, M. *Eur. J. Inorg. Chem.* **2003**, 4356−4360. (b) Beckmann, J.; Jurkschat, K.; Schürmann, M.; Suter, D.; Willem, R. *Organometallics* **2002**, *21*, 3819−3822.

(19) (a) Holmes, R. R.; Schmid, C. G.; Chandrasekhar, V.; Day, R. O.; Holmes, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 1408−1414. (b) Chandrasekhar, V.; Schmid, C. G.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 1050−1056. (c) Swamy, K. C. K.; Said, M. A.; Nagabrahmanandachari, S.; Poojary, D. M.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1998**, 1645−1652. (d) Alcock, N. W.; Roe, S. M. *J. Chem. Soc., Dalton Trans.* **1989**, 1589−1598. (e) Nagabrahmanandachari, S.; Hemavathi, C.; Swamy, K. C. K.; Damodara, D. M.; Clearfield, A. *Main Group Met. Chem.* **1998**, *21*, 789−802.

(20) (a) Li, Q.; Wang, F.; Zhang, R.; Cui, J.; Ma, C. *Polyhedron* **2015**, *85*, 361−368. (b) Mitzel, N.; Lustig, C.; Scharfe, S. *Z. Naturforsch., B* **2001**, *56*, 440−442.

(21) (a) Hill, M.; Mahon, M. F.; Molloy, K. C. *Main Group Chem.* **1996**, *1*, 309−315. (b) Veith, M.; Recktenwald, O. *Z. Anorg. Allg. Chem.* **1979**, *459*, 208−216.

(22) Andrianov, K. A.; Golubenko, A. *J. Gen. Chem. USSR* **1975**, *45*, 2614.

(23) Zickgraf, A.; Beuter, M.; Kolb, U.; Dräger, M.; Tozer, R.; Dakternieks, D.; Jurkschat, K. *Inorg. Chim. Acta* **1998**, *275−276*, 203−214.

(24) Puff, H.; Schuh, W.; Sievers, R.; Wald, W.; Zimmer, R. *J. Organomet. Chem.* **1984**, *260*, 271−280.

(25) Ross, L.; Dräger, M. *Z. Naturforsch. B* **1984**, *39*, 868.

(26) (a) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. C* **2015**, *71*, 3−8.

(27) Clegg, W. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *59*, e2.